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Oxidative Aromatic Coupling of *meso*-Arylamino-porphyrins

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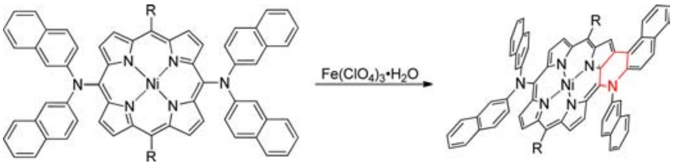
ABSTRACT



Strategic placement of the bis-arylamino group at the *meso*-position of porphyrins allowed fusion of these two moieties *via* aromatic dehydrogenation. By placing two di(naphthalene-2-yl)amine or bis(3,5-dimethoxyphenyl)amine groups at positions 5 and 15 of the porphyrin, the oxidative aromatic coupling was directed toward closing one six-membered ring. The extension of the porphyrin chromophore leads to significant change in linear optical properties, such as a bathochromic shift of absorption and broadening of the Q-band.

Porphyrins[1] are widespread both in nature and in chemical laboratories, as they provide a basis for the design of new materials with specified electronic properties. The combination of suitable optical properties such as strong light absorption and fine-tunability of optoelectronic properties,[2] and the mature state of their synthetic methodology[3] have attracted considerable attention in various photonics applications. π-Expanded[4] and π-extended porphyrins[5] offer several further advantages such as strong absorption in the red and NIR parts of the electromagnetic spectrum. They attract much attention because of the opportunities they offer in technology and medicine that arise from their linear and nonlinear optical properties. Ring extension of a porphyrin leads to a significant modification of the compound's optical features, redox characteristics, and the HOMO−LUMO energy gap. Not surprisingly in both dye-sensitized solar cells and bulk-heterojunction organic solar cells, π-extended porphyrins are top performers.[6]

A subtle relationship exists between the output of an intramolecular oxidative coupling reaction of a porphyrin and the nature of the second aromatic moiety, the cation in the porphyrin cavity, the oxidant, and the type of remaining *meso*-substituents. Various π-extended porphyrins have been prepared *via* oxidative aromatic coupling, including a large number of analogs possessing tetrapyrrolic macrocycle, naphthalene, higher hydrocarbon, and heterocyclic compounds as an additional unit.[7−9] On the other hand, the synthesis and photophysical properties of analogous systems derived from corresponding *meso*-arylamino

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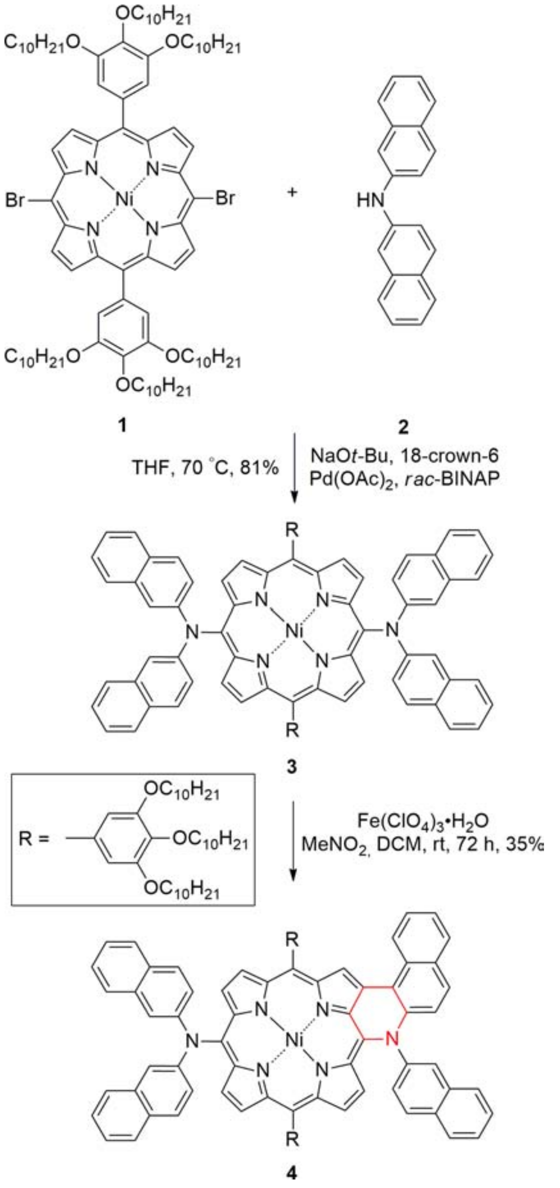
porphyrins have not been studied yet. Such aryl-amino π-extended porphyrins are the missing link in this area. Their synthesis would broaden our understanding of the structure–optical property relationship in the porphyrin family. Herein, we report the first example of the synthesis of porphyrins fused with another aromatic unit *via* nitrogen atom at a *meso*-position.[10]

Previous studies and general knowledge of aromatic oxidative coupling[11] both indicate that the planned concept can only be realized if the additional aromatic moiety bears an electron-donating substituent at a suitable position. We envisioned that the presence of an amine-type nitrogen atom can serve as an activating unit, without the need to add additional functional groups. On the other hand, to minimize the number of side reactions we resolved to initially employ di(naphthalen-2-yl)amine rather than diphenylamine. To provide reasonable solubility of the final fused compound, we equipped our molecule with long alkyl chains. Our strategy toward the synthesis of a fused amino-porphyrin was based on the assumption that the porphyrin molecule containing di(naphthalen-2-yl)amine at the *meso*-positions could be oxidatively coupled at the β-position.

The Buchwald–Hartwig reaction, under conditions developed by Suda and co-workers,[12] of Ni-dibromoporphyrin **1**[13] with di(naphthalen-2-yl)amine (**2**) led to the formation of product **3** (Scheme 1).

Scheme 1. Synthesis of Fused Porphyrin **4**



The coupling reaction was initially attempted under typical oxidative coupling conditions[14] (FeCl$_3$, CH$_2$Cl$_2$/MeNO$_2$), but this led to a complex mixture of products including chlorinated porphyrins. On the other hand the use of DDQ/Sc(OTf)$_3$ resulted only in the decomposition of starting material. Consequently, we decided to employ an alternative protocol for oxidative coupling leading to a *meso*,β-naphthalene-fused porphyrinoid in high yield without contamination from chlorinated side products using Fe(ClO$_4$)$_3$·H$_2$O.[15]

Subjecting porphyrin **3** to 10 equiv of Fe(ClO$_4$)$_3$·H$_2$O at 25 °C afforded a green product in 35% yield (Scheme 1). The reaction carried out at 10 mmol scale required 72 h for completion, but full conversion of substrate allowed for easy isolation of the product.

^{1}H NMR spectra confirmed that single dehydrogenation had occurred. The ^{1}H NMR spectrum consisted of 6 β protons as doublets with a *J* constant of 4.9–5.1 Hz and a characteristic singlet at low frequency corresponding to

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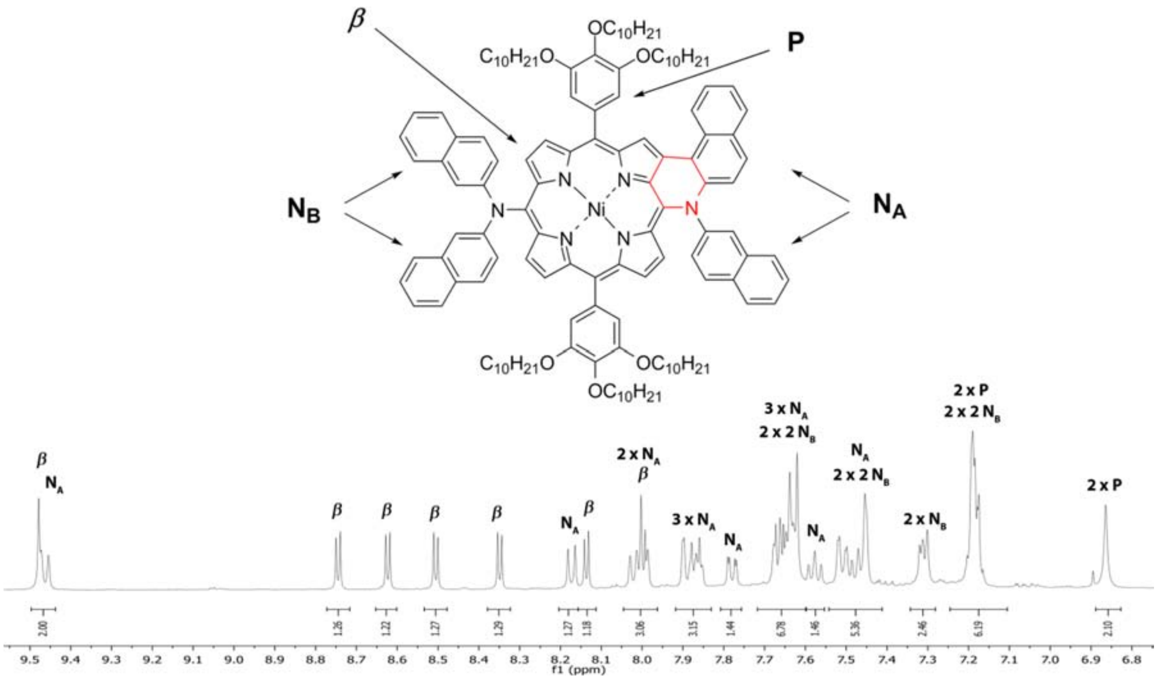

Figure 1. Aromatic part of ^{1}H NMR spectrum of porphyrin **4** in CD_2Cl_2.

proton β, being close to carbon which underwent C–C oxidation. The latter one overlaps with a doublet corresponding to naphthalene. The aromatic part of the ^{1}H NMR spectrum is presented in Figure 1. This structural assignment was further confirmed by analysis of ^{13}C NMR, COSY, HSQC, HMBC, and MS. The HSQC spectrum confirmed the presence of 29 types of carbon atoms, correlated to aromatic protons.

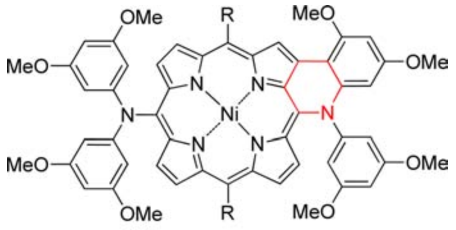

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Figure 2. Structure of fused-porphyrin **5**.

In order to investigate the versatility of this approach bis(3,5-dimethoxyphenyl)amine was designed as a second coupling unit. Porphyrin **1** was smoothly transformed into the corresponding *trans*-A_2B_2-porphyrin **S2** bearing two such units. Compound **S2** underwent oxidation into product **5** (Figure 2) under milder conditions (reaction time = 3 min), which can be rationalized when considering the significantly higher electron density of the amine counterpart.

Recent spectroelectrochemical studies performed for the Ni(II)-complex of electron-rich porphyrin have proven that the radical cation is initially formed on the macrocyclic ring, following its reaction with the linked dimethoxynaphthalene moiety.[16] We are inclined to think that the same order of steps occurs in the case of the formation of compounds **4** and **5**.

Table 1. Redox Potentials for Compounds **3**, **4**, and **S2**[a]

compd	$E^{1/2}{}_{ox1}$ [V]	$E^{1/2}{}_{ox2}$ [V]	$E^{1/2}{}_{red}$ [V]	HOMO–LUMO gap [eV]
3	0.28		−1.80	2.08
4	−0.02	0.19	−1.92	1.90
S2	0.20		−1.91	2.11

[a] The redox potentials were measured by CV in deoxygenated, anhydrous solutions in CH_2Cl_2 using a glassy carbon working electrode. All reported values of *E*[V] are with respect to Fc/Fc$^+$ redox potential.

The electrochemical properties of **3**, **4**, and **S2** were studied by cyclic voltammetry (Table 1). According to predictions, the first oxidation potentials of **4** are lower than that of **3** and **S2**, which originates from enhanced electron donation imparted by the fixed amino group. The electrochemical HOMO–LUMO gap of **4** is 1.90 eV, which is slightly smaller than those for **3** and **S2** (2.08 and 2.11 eV, respectively).

DFT calculations have proven that the HOMO of **3** is well distributed over both the porphyrin core and diarylamino group (Figure 3), which allows the *meso*-diarylamino group to fuse oxidatively by the nucleophilic attack of that

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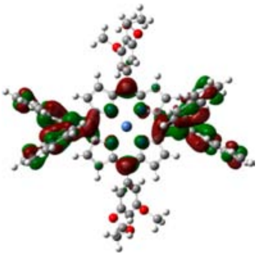

Figure 3. Kohn–Sham orbital representations for HOMO of **3**, obtained by DFT calculations at the B3LYP/6-31* (C,H,N,O) + LANL2DZ (Ni) level. Decyloxy groups were replaced by MeO to simplify calculations.

group at the porphyrin radical cation. The structural novelty of π-extended porphyrins **4** and **5** prompted us to study its optical properties. These photophysical properties of dyes **3**–**5** and **S2** were studied in methylene chloride, which was chosen due to its ability to dissolve both compounds and thus allow the direct comparison and assessment of the effect of the architecture on the photophysical properties of the chromophore (Figure 3). The spectra of both **3** and **4** did not resemble the absorption spectrum of simple *meso*-substituted Ni(II)-porphyrins. In the case of compound **3** an intense split of the Soret band is observed in analogy to the behavior of zinc complexes 5,15-bis(dianisylamino)porphyrins described earlier.[17] The bathochromic shift of the lowest energy absorption band resulting from the fusion of porphyrin and naphthylamino moieties is ∼35 nm. At the same time for compound **4** both the Soret band and Q-bands are exceptionally broad (Figure 4). The λ_{max} and ratio of the Soret band to Q-band resembles that measured for Ni-*meso*,β-fused naphthalene porphyrins.[13] A split of the Soret band, however, with significantly lower intensity of the Q bands has previously been observed for quinolinoporphyrins (bearing nitrogen atom at β-position) by Cavaleiro and co-workers.[18] Similar optical features were observed for porphyrins **S2** and **5** (Figure S3).

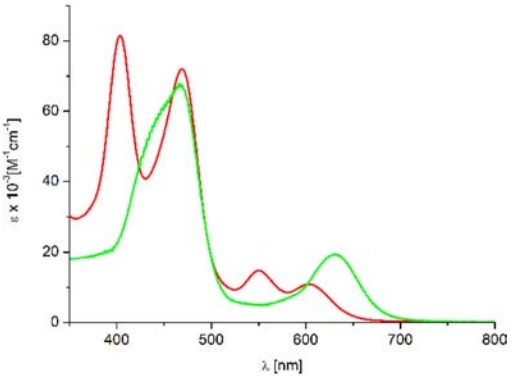

Figure 4. Absorption spectra of porphyrins **3** (red) and **4** (green) measured in CH_2Cl_2.

In summary, we report the discovery of a new pathway toward electron-rich π-extended porphyrins. The proposed synthetic method is operationally simple and leads to the expected porphyrins in a few steps. We disclosed that aromatic intramolecular dehydrogenation can also take place when the second aromatic moiety is linked with a porphyrin *via* nitrogen at a *meso*-position. This synthesis of a π-extended porphyrin represents the successful example of an oxidative aromatic coupling reaction leading to the formation of a new heterocyclic ring. Optical spectra are of significance in that they provide the first insight into factors influencing the optical properties of fused arylamino-porphyrins.

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Supporting Information Available. Full experimental procedures for the synthesis of compounds **1**, **3**–**5**, **S1**–**S2** as well as ^{1}H and ^{13}C NMR and 2D NMR spectra for these compounds, absorption of **S2** and **5**, details of DFT calculations and electrochemistry. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.