

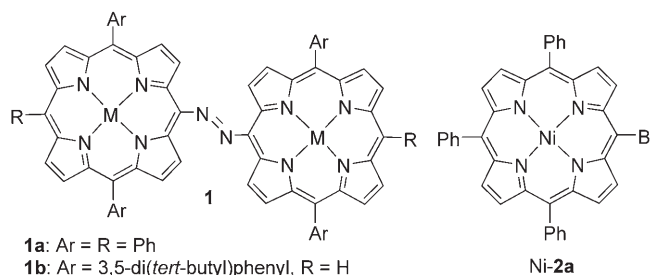
## Azoporphyrin: The Porphyrin Analogue of Azobenzene\*\*

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Azobenzenes (1,2-diaryldiazenes) are very important organic pigments and have a unique place in the field of photo-responsive conjugated molecules because of their (usually) reversible *E/Z* photoisomerization.<sup>[1]</sup> The current intense interest in molecular analogues of mechanical components and information storage and processing elements has stimulated research into conjugated molecules whose shape and/or optical properties can be switched electro- or photochemically.<sup>[2]</sup> Among the classes of conjugated pigments being explored in these contexts are the porphyrinoids, which offer advantages of intense light absorption, a variety of accessible oxidation states, and synthetic control of properties through peripheral or central substitution.<sup>[3]</sup> Extension of porphyrinoid conjugation can be achieved by linking the peripheral carbon atoms either by three direct bonds (as in the porphyrin tapes of Osuka and co-workers)<sup>[4]</sup> or through potentially conjugating bridges such as alkenes<sup>[5]</sup> or, even better, alkynes.<sup>[6]</sup>

Anderson and co-workers compared both experimentally and theoretically the strength of porphyrin–aryl electronic coupling through alkene, alkyne, imino, and azo (diazene) bridges, and found the last of these to be the most efficient, in that good orbital matching through continuous  $sp^2$  conjugation was combined with less steric interference than observed with the alkene linker.<sup>[7]</sup> Thus, 1,2-di(porphyrinyl)diazenes (or azoporphyrins; for example, **1**, Scheme 1) are desirable synthetic targets, in that they combine the extended porphyrinoid conjugation with the potential photoreactivity of the azo linkage.<sup>[8]</sup> Herein, we describe the convenient synthesis and crystallographic and spectroscopic characterizations of the first (*E*)-azoporphyrins.

Azobenzenes can be prepared by a variety of well-known reactions,<sup>[9]</sup> such as the partial reduction of nitro-, nitroso-, or azoxyarenes, coupling of aryl amines with nitrosoarenes, azo coupling of aryl diazonium salts with electron-rich arenes, and one-pot  $Cu^I$ -mediated coupling/oxidation reactions of bis-*tert*-



**Scheme 1.** An example of an azoporphyrin **1** and bromoporphyrin Ni-2a.

butoxycarbonyl-protected aryl hydrazines and aryl halides.<sup>[10]</sup> Anderson and co-workers reported that the azo coupling route was unsuccessful for the formation of Zn<sub>2</sub>-**1b**.<sup>[7]</sup> Our initial approach involved the Pd-catalyzed coupling of monoprotected hydrazines (carbazates) with bromoporphyrins, but this approach generated a variety of products which included the novel diiminoporphodimethenes.<sup>[11]</sup> When unsubstituted hydrazine was used with bromoporphyrin Ni-2a, we isolated the primary amine Ni-3a and the Ni<sup>II</sup> complexes of the corresponding bis(porphyrinyl) secondary amine and 5-hydroxyporphyrin, in proportions that varied with the initial stoichiometry.<sup>[12]</sup>

While trying to improve the yield of the secondary amine from the coupling reaction of Ni-2a with Ni-3a using the catalyst/base system Pd(OAc)<sub>2</sub>/*rac*-binap/Cs<sub>2</sub>CO<sub>3</sub> (binap = 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl) in toluene, we found that a very small amount of a golden brown product was always apparent on TLC plates. The visible absorption spectrum of this compound corresponded with that expected for the elusive target Ni<sub>2</sub>-1a. This product could arise simply from oxidative dimerization of the primary amine induced by the metal salt, so we omitted Ni-2a and changed the oxidant system to copper(II) acetate/pyridine in air. We were pleased to find that this proved to be a very clean method of coupling Ni-3a to form Ni<sub>2</sub>-1a in high yield, with no side products (Scheme 2). Indeed, with longer heating, even 2 mol % Cu catalyst was suitable, but for convenient reaction times, we chose the conditions given in the Supporting Information.

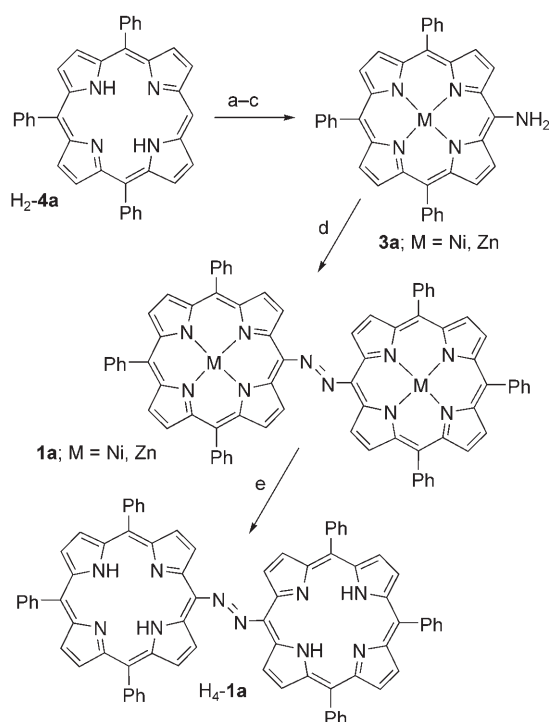
The copper-promoted formation of azoarenes from aryl amines has been largely neglected since the earliest investigations in the 1950s.<sup>[13]</sup> The reaction was extended to the corresponding zinc(II) complexes, which are favored by many research groups because of their emissivity and ease of demetalation. The preparation of the precursor amines Ni-3a and Zn-3a from the free base triphenylporphyrin (H<sub>2</sub>-4a) has been streamlined to give respective yields of 68 and 58 % for the sequence nitration, metalation, and reduction, with purification only after the final step (see the Supporting Information). Alternatively, Ni-3a can be obtained by the

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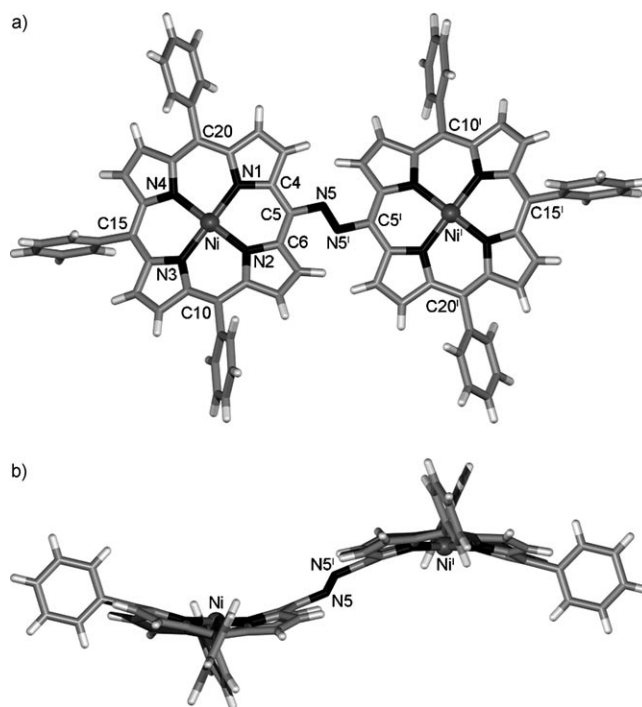
Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.



**Scheme 2.** Synthesis of azoporphyrins **1a**. a) Nitration: I<sub>2</sub>, AgNO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, MeCN, argon, RT; b) metalation: M = Ni: [Ni(acac)<sub>2</sub>], toluene, reflux; M = Zn: Zn(OAc)<sub>2</sub>, CHCl<sub>3</sub>, MeOH, reflux; c) reduction: 10% Pd/C, NaBH<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, MeOH, argon, RT; d) Cu(OAc)<sub>2</sub>, Py, toluene, 2.5–3.5 h, 80 °C; e) TFA, toluene, 20 min, RT. TFA = trifluoroacetic acid, acac = acetylacetonate, Py = pyridine.

hydrazine route.<sup>[12]</sup> Demetallation of Zn<sub>2</sub>-**1a** with TFA in toluene gave the free base azoporphyrin **H<sub>4</sub>-1a**. All three examples are very insoluble in common solvents, although the metal complexes are more soluble in the presence of pyridine.

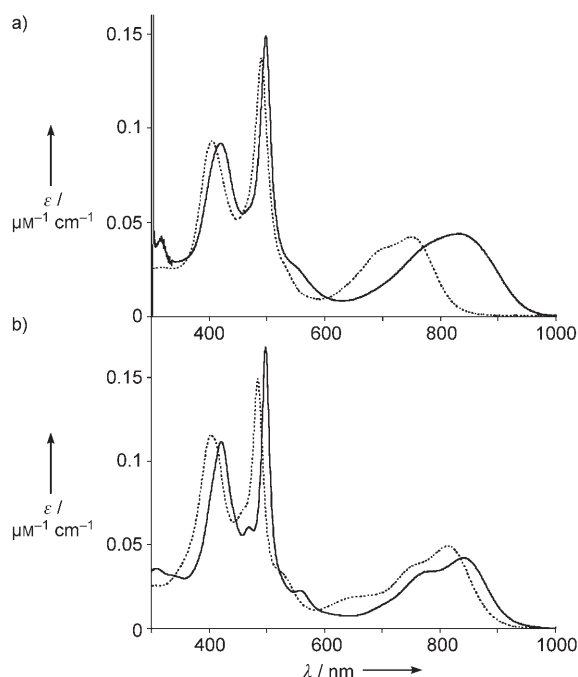
Single crystals of Ni<sub>2</sub>-**1a**·Py were grown by diffusion of methanol into a pyridine solution, and the crystal structure was determined by X-ray analysis.<sup>[14]</sup> The molecule (Figure 1) has crystallographic inversion symmetry with the inversion center on the N5–N5' bridge. The pyridine solvent has twofold symmetry, with the N atom disordered equally across the six pyridyl atom positions. The asymmetric porphyrin ring is considerably distorted from planarity, as is typical for Ni<sup>II</sup>-bound porphyrins. The maximum deviations of atoms from the mean plane of the C<sub>20</sub>N<sub>4</sub>Ni porphyrin component occur for the *meso* carbon atoms C5 and C15 (0.682 Å and 0.546 Å, respectively) and C10 and C20 (0.555 Å and 0.609 Å, respectively). The ring distortion projects C5 and C15 on one side of the mean plane of the ring and C10 and C20 on the other, in the manner described in the literature as ruffled.<sup>[15]</sup> The mean plane of the N<sub>4</sub>Ni coordination sphere is almost coplanar with that of the mean plane of the porphyrin ring (dihedral angle 0.55° with a perpendicular distance for the Ni...C<sub>20</sub>N<sub>4</sub>Ni plane of 0.010 Å). The mean C<sub>20</sub>N<sub>4</sub>Ni planes of the porphyrin rings are exactly parallel and offset by a perpendicular distance of 3.189 Å. This displacement is a consequence of the ring distortion (which projects C5, and therefore the azo-bridging nitrogen atom N5, away from the plane of the ring) and the twisted conformation of the



**Figure 1.** The crystal structure of Ni<sub>2</sub>-**1a** shown from two different perspectives: a) orthogonal to the mean planes of the porphyrin rings; b) parallel to the mean planes. The side view in (b) illustrates the extent of the distortion of the porphyrin rings and the perpendicular displacement of the planes of the rings with respect to each other (3.189 Å). The pyridine solvent molecule has been omitted for clarity.

azobridge. The dihedral angles between the C5–N5–N5'–C5' mean plane and the mean porphyrin planes are 37°. This out-of-plane twist of the azo bridge is significantly smaller than those of the alkene bridges in (*E*)-ethenediyl-linked Ni<sub>2</sub> (50°)<sup>[6c]</sup> and Zn<sub>2</sub> (47°)<sup>[5c]</sup> dimers.

The extension of the porphyrin conjugation and electronic interaction with unsaturated substituents give rise to well-known features in the electronic spectra, namely red-shifting of the absorption and emission bands, increase in the relative intensity of the Q bands against the B (Soret) bands, and splitting of the Soret band. These features have been intensively studied.<sup>[6,7]</sup> The visible absorption spectra of azoporphyrins possess all these characteristics, as shown in Figure 2. The Ni<sup>II</sup> complex displays a large complexation shift (Q-band shift from 749 to 830 nm) when excess pyridine is present—presumably the Ni<sup>II</sup> centers are then six coordinate (Figure 2a). The extent of interporphyrin communication can be assessed qualitatively by means of the energy gap between the two main components of the Soret band. Splittings resulting from different bridges for similar dinuclear Zn complexes are 2430 cm<sup>−1</sup> for (*E*)-ethenediyl,<sup>[6c]</sup> 3320 cm<sup>−1</sup> for ethynediyl,<sup>[5c]</sup> and 3670 cm<sup>−1</sup> for the azo bridge in Zn<sub>2</sub>-**1a**.<sup>[16]</sup> The HOMO–LUMO gap (lowest-energy Q band) is another measure of the expansion of the porphyrin π system. This comparison between the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub> and the azo linkers is complicated by the effects on the HOMO–LUMO gaps of the differences in the electronegativity of the carbon and nitrogen groups as substituents, as well as by the steric demands of the ethene linker. As there is no simple way to separate these



**Figure 2.** Electronic absorption spectra of azoporphyrins: a)  $\text{Ni}_2\text{-1a}$  in  $\text{CH}_2\text{Cl}_2$  (dotted line) and pyridine (solid line); b)  $\text{Zn}_2\text{-1a}$  in  $\text{CH}_2\text{Cl}_2$ /pyridine 99:1 (solid line),  $\text{H}_4\text{-1a}$  in  $\text{CHCl}_3$  (dotted line).

factors, we state that the azo dimer has significantly more red-shifted Q bands than the  $\text{C}_2\text{H}_2/\text{C}_2$ -linked dimers, that is, 841 nm for  $\text{Zn}_2\text{-1a}$ , 713 nm for the ethynediyl dimer,<sup>[5c]</sup> and 661 nm for the (*E*)-ethenediyl dimer.<sup>[6e,16]</sup> This strong red shift is reflected also in the HOMO–LUMO gap of  $\text{Zn}_2\text{-1a}$  measured by cyclic voltammetry,  $E_1^{\text{ox}} - E_1^{\text{red}} = 1.34 \text{ V}$ ,<sup>[17]</sup> which is markedly smaller than those for the ethynediyl (1.98 V) and (*E*)-ethenediyl (1.92 V) dimers.<sup>[5c,17]</sup>

The photoisomerization of many (*E*)-azoarenes is normally readily achievable. However, for azo linkers in porphyrin/phthalocyanine-containing constructs, results are variable. In some cases, the photoexcited states are quenched so rapidly that no isomerization can be observed,<sup>[8a,d]</sup> whereas in others, the isomerization is successful.<sup>[3a,c,8b,c]</sup> We irradiated solutions of both  $\text{Zn}_2\text{-1a}$  and  $\text{Ni}_2\text{-1a}$  (see the Supporting Information), but have not seen evidence for isomerization to the (*Z*)-azoporphyrin. Evidently, the extended conjugation promotes deactivation of the photoexcited states.

We have tried to extend this chemistry to prepare longer azo-linked oligoporphyrin arrays, using 5,15-bis(3,5-di-*tert*-

butylphenyl)porphyrin instead of 5,10,15-triphenylporphyrin, to leave an open meso position for further coupling (Scheme 3). However, treatment of amine  $\text{Ni}_2\text{-3b}$  under our coupling conditions gave less than 10% yield of the desired azoporphyrin  $\text{Ni}_2\text{-1b}$ , the major product being the remarkable head-to-tail dimer  $\text{Ni}_2\text{-5}$ , which contained one iminoporphodimethene ring.<sup>[18]</sup> A second similar product  $\text{Ni}_2\text{-6}$ , the corresponding oxo species, was also isolated. Clearly, another strategy will be required to prepare larger arrays, as we have so far been unable to prepare the required 5,15-diaminoporphyrins.

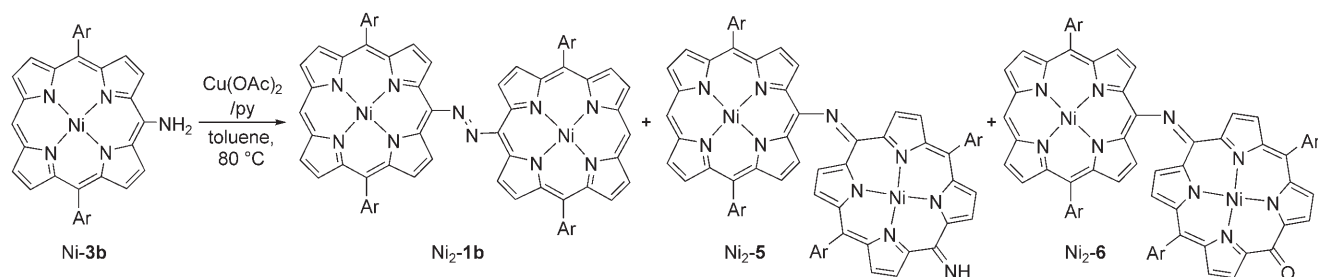
The properties of the azoporphyrins imply a stronger interaction between the porphyrin rings across the azo bridge than across ethene and ethyne linkers. In the solid state, the lone pairs of electrons on the bridging nitrogen atoms still have an effect which results in a 37° out-of-plane rotation of the linker. Nevertheless, the prediction<sup>[7]</sup> that the azo linker would be an attractive molecular wire for connecting porphyrins has been fulfilled. Our recent studies into the coupling of nitrogen nucleophiles with porphyrins,<sup>[11,12]</sup> and our preparation of the first azoporphyrins reported herein, indicate that further studies in this field will be rewarding. In particular, photophysical and nonlinear optical studies of azoporphyrins should prove interesting.

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**Scheme 3.** Attempted preparation of azoporphyrin  $\text{Ni}_2\text{-1b}$ .

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- [14] Crystal data for Ni<sub>2</sub>-**1a**·Py: C<sub>81</sub>H<sub>51</sub>N<sub>11</sub>Ni<sub>2</sub>, *M<sub>r</sub>* = 1295.75, monoclinic, *P2<sub>1</sub>/c*, *a* = 13.0693(3), *b* = 9.7304(2), *c* = 24.1344(5) Å, β = 104.2410(10)°, *V* = 2974.45(11) Å<sup>3</sup>, ρ<sub>calcd</sub> = 1.447 g cm<sup>-3</sup>, *Z* = 2, crystal size 0.20 × 0.13 × 0.09 mm, blue prism, *T* 150(2) K, λ(MoKα) = 0.71073, μ(MoKα) 0.0694 mm<sup>-1</sup>, *T<sub>min</sub>*/*T<sub>max</sub>* = 0.885/0.944 (Gaussian absorption correction), 2θ<sub>max</sub> = 59.96, *hkl* range -18 to 18, -13 to 13, -33 to 33, *N* = 44909, *N<sub>ind</sub>* = 8570 (*R<sub>merge</sub>* = 0.0266), *N<sub>obs</sub>* = 6976 (*I* > 2σ(*I*)), *N<sub>var</sub>* = 424, residuals *R1*(*F*, 2σ) = 0.0423, *wR2*(*F<sup>2</sup>*, all) = 0.0958, *GoF*(all) = 1.023, Δρ<sub>min</sub>/Δρ<sub>max</sub> = -0.434/0.450 e Å<sup>-3</sup>. CCDC-627200 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
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- [17] These data were measured by cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub>/0.1M Bu<sub>4</sub>NPF<sub>6</sub>, Pt working and counter electrodes, Ag/AgCl solid reference electrode, ferrocene at +0.55 V; *E*<sub>1</sub><sup>ox</sup> = +0.63 V, *E*<sub>2</sub><sup>ox</sup> = +0.77 V, *E*<sub>1</sub><sup>red</sup> = -0.71 V, *E*<sub>2</sub><sup>red</sup> = -0.81 V.
- [18] Compound Ni<sub>2</sub>-**5** was isolated in 26% yield from reaction of Ni-**3b** with 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrinatonicel(II) and *tert*-butyl nitrite/BF<sub>3</sub>·Et<sub>2</sub>O in THF at RT; see: M. J. Smith, DPhil thesis, University of Oxford (UK), **2004** and H. L. Anderson, private communication.