

Porphyrinoids

International Edition: DOI: 10.1002/anie.201510734
German Edition: DOI: 10.1002/ange.201510734Redox-Switchable 20 π -, 19 π -, and 18 π -Electron 5,10,15,20-Tetraaryl-5,15-diazaporphyrinoid Nickel(II) Complexes

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Abstract: The first examples of air-stable 20 π -electron 5,10,15,20-tetraaryl-5,15-diaza-5,15-dihydroporphyrins, their 18 π -electron dications, and the 19 π -electron radical cation were prepared through metal-templated annulation of nickel(II) bis(5-arylamino-3-chloro-8-mesityldipyrin) complexes followed by oxidation. The neutral 20 π -electron derivatives are antiaromatic and the cationic 18 π -electron derivatives are aromatic in terms of the magnetic criterion of aromaticity. The meso N atoms in these diazaporphyrinoids give rise to characteristic redox and optical properties for the compounds that are not typical of isoelectronic 5,10,15,20-tetraarylporphyrins.

Porphyrins are redox-active, 18 π -electron aromatic macrocycles. The redox properties of porphyrins have been widely investigated, as have the aromatic and optical properties of the resulting oxidized/reduced macrocyclic π systems.^[1–3] The two-electron reduction of a porphyrin ring produces a dianion, which shows antiaromatic character resulting from its 20 π -electron circuit.^[2] This kind of porphyrin dianion is highly reactive because of its high-energy HOMOs, and thus elaborate molecular designs to prepare and isolate 20 π -electron porphyrinoids in the neutral form have been reported. Vogel and co-workers used core modification for this purpose; they obtained *N,N',N'',N'''*-tetramethylisophlorin and tetraoxaisophlorin as [20]annulenes.^[4] Core modification has also been used to synthesize other N-alkyl-,^[5] S-,^[6] and P,S-containing^[7] isophlorins. Meanwhile, Vaid et al. and Leznoff et al. used the characteristic coordination properties of silicon(IV), germanium(IV), and niobium(V) to obtain metal complexes of 20 π -electron 5,10,15,20-tetraphenylporphyrin (TPP)^[8] and phthalocya-

nine,^[9] and Chen et al. isolated a free base of isophlorin by appending electron-withdrawing trifluoromethyl substituents on its periphery.^[10] However, the number of air-stable 20 π -electron porphyrinoids is still quite limited, so it is therefore important for both basic and applied research to develop a conceptually new approach to precisely tune the redox properties of porphyrin-based 20 π -electron systems.

The redox and optical properties of 5,15-diazaporphyrins (DAP) have been shown to differ substantially from those of their porphyrin counterparts.^[11–14] The characteristic properties of DAP arise from the electronic effects of the two meso N atoms, which not only stabilize the HOMO and LUMO levels but also split both the HOMO/HOMO-1 and LUMO/LUMO + 1 energy levels. We envisioned that replacement of two of the meso C atoms of TPP with two N atoms would be a promising strategy to obtain a new DAP-based 20 π -electron system because unshared electron pairs on the meso N atoms should be involved in the π circuit. This type of meso modification should also alter the net charge of the π circuit; 5,10,15,20-tetraaryl-5,15-diaza-5,15-dihydroporphyrins (TADAP), their radical cation (TADAP^{•+}), and dications (TADAP²⁺)^[15] are isoelectronic forms of the 20 π -electron TPP dianion, 19 π -electron TPP radical anion, and neutral 18 π -electron TPP, respectively (Scheme 1). Herein, we report the first examples of 20 π -, 19 π -, and 18 π -electron TADAP derivatives, which were all isolated as air-stable solids. The structures, aromaticity, and optical/electrochemical properties of these diazaporphyrinoids were investigated.

Scheme 2 shows the syntheses of nickel(II) complexes of TADAP and TADAP²⁺. Treatment of nickel(II) acetate with two equivalents of 3-chloro-5-phenylamino-8-mesityldipyrin **1a** (for the synthesis of **1a,b**, see the Supporting Information; mesityl = 2,4,6-trimethylphenyl) gave nickel(II) bis(dipyrin) complex **2a**. In the presence of K₂CO₃, **2a** underwent intramolecular double nucleophilic substitution at 110°C in DMF to afford 10,20-dimesityl-5,15-diphenyl-5,15-diaza-5,15-dihydroporphyrinato nickel(II) ([Ni(TADAP)]) **3a** as an air-stable reddish-brown solid. Oxidation of **3a** with two equivalents of tris(4-bromophenyl)ammoniumyl hexachloroantim-

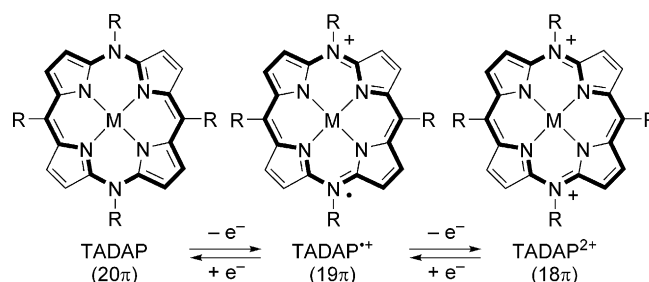
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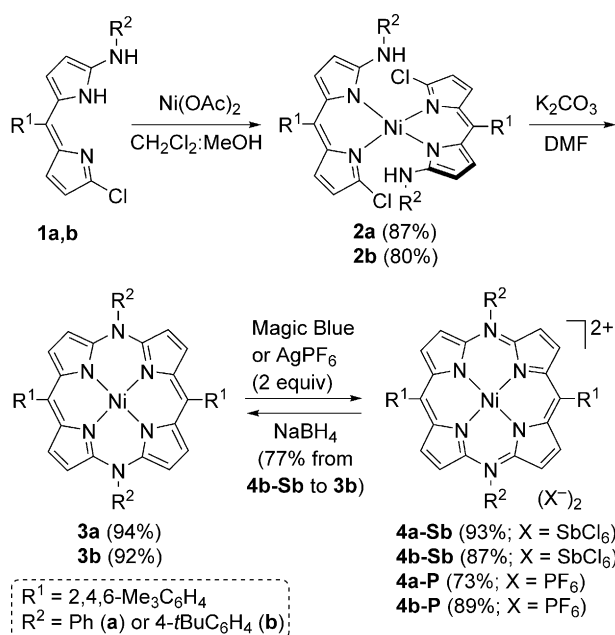
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Scheme 1. Interconversion between TADAP and TADAP²⁺.



Scheme 2. Synthesis of [Ni(TADAP)] and [Ni(TADAP)]²⁺.

onate (Magic Blue) in CH₂Cl₂ gave dication ([Ni(TADAP)]²⁺) **4a-Sb** as an air-stable green solid. Because **3a** was sparingly soluble in common organic solvents, more soluble derivatives **3b** and **4b-Sb** bearing 4-(*tert*-butyl)phenyl groups were prepared from **1b** according to similar procedures. When AgPF₆ was used instead of Magic Blue in the oxidation of **3a,b**, dications **4a-Sb** and **4b-P** were obtained. Conversely, treatment of **4b-Sb** with excess NaBH₄ in THF regenerated **3b**. Therefore, the chemical redox reactions between **3** and **4** are reversible. To discuss the electronic effects of the *meso* N atoms on the redox properties of the TPP-type π system, porphyrin **5** (Figure 1) was prepared as a reference.

Compounds **3** and **4** were characterized by NMR spectroscopy and high-resolution mass spectrometry (HRMS). In the HRMS data for **4**, intense signals consistent with $m/z = [\text{Ni}(\text{TADAP})]^{2+}$ ($z = 1, 2$) were clearly detected. In the ³¹P NMR spectra of **4a,b-P**, a septet attributable to the PF₆[−] counterion was detected (coupling constant $J_{\text{PF}} = 711\text{--}713$ Hz). The structures of **3b** and **4a-Sb** were unambiguously elucidated by X-ray crystallography (Figure 2; Figure S1 and Table S1 in the Supporting Information).^[16] In the crystalline state, these complexes have almost planar DAP π planes; the calculated root-mean-square deviations of the π -planes of **3b**

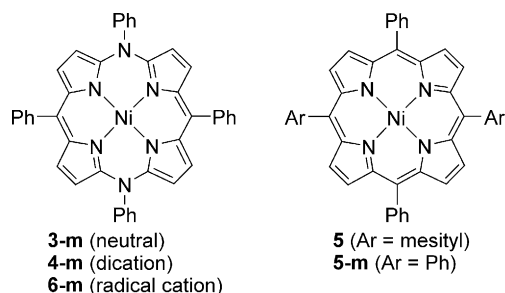


Figure 1. Porphyrin **5** and model compounds **3-m**, **4-m**, **5-m**, and **6-m**.

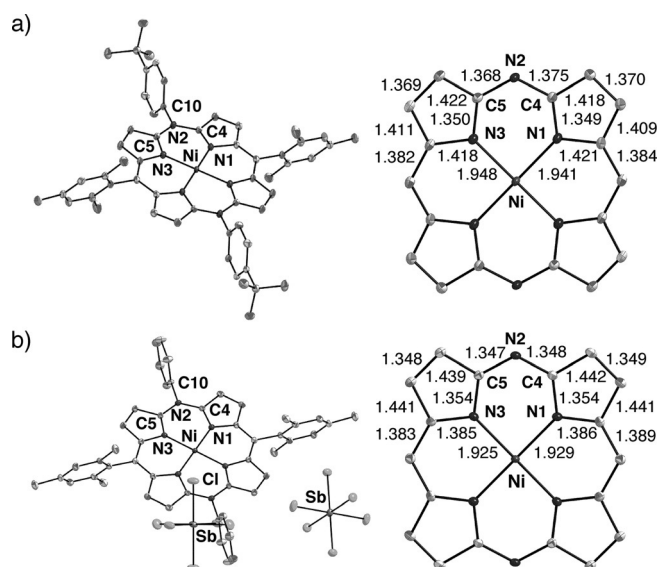


Figure 2. Perspective views of molecules (left) and top views of DAP rings (right) for a) **3b** and b) **4a-Sb**. Thermal ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. Bond lengths [Å] except the standard deviations (0.002–0.003 Å) are shown.

and **4a-Sb** were 0.035 and 0.012 Å, respectively. In **4a-Sb**, two of the chlorine atoms of one counter anion (SbCl₆[−]) coordinate to the nickel center with a Ni–Cl distance of 3.18 Å, which is within the sum of their van der Waals radii (3.4 Å). It is therefore likely that the counter anion interacts with the nickel center. The *meso* N-aryl groups of **3b** and **4a-Sb** are almost perpendicular to the DAP ring (dihedral angles = 85.3–86.1°), suggesting that resonance effects of these aryl groups on the DAP π system would be small. The C4–N2 and C5–N2 bonds (1.368(2) and 1.375(2) Å for **3b**, 1.347(3) and 1.348(3) Å for **4a-Sb**) are much shorter than the C10–N2 bond (1.445(2) Å for **3b**, 1.465(2) Å for **4a-Sb**). These data imply that unshared electron pairs in the p orbitals of the *meso* N atoms effectively conjugate with the π orbitals in the adjacent pyrrole rings. It should be noted that the C4/C5–N2 bonds in **4a-Sb** are appreciably shorter than those in **3b**; removing two π electrons from the TADAP ring strengthens the π conjugation between the pyrrolic β carbon and *meso*-N atoms, which increases the double-bond character of the C4/C5–N2 bonds. The change of the C4/C5–N2 bond lengths is reflected in the shortening of the Ni–N bonds; the central N₄ coordination sphere of **4a-Sb** is smaller than that of **3b**. Furthermore, the difference in some bond lengths between **3** and **4** (labelled *b/d* and *e/f* in Table S1) can be explained by the resonance structures of these π systems.

Considering that the two unshared electron pairs on the *meso* N atoms are involved in their π circuits, **3** and **4** are isoelectronic with 20 π -electron TPP^{2−} and 18 π -electron TPP, respectively. Therefore, **3** and **4** are appropriate model compounds for discussing the aromaticity of diazaporphyrinoids. The ¹H NMR spectra of **3a** and **4a-Sb** are shown in Figure 3. The peripheral β and *meso*-aryl protons were assigned by ¹H–¹H COSY and NOESY experiments. Resonance signals for the β protons (*d* and *e*) of **3a** were detected

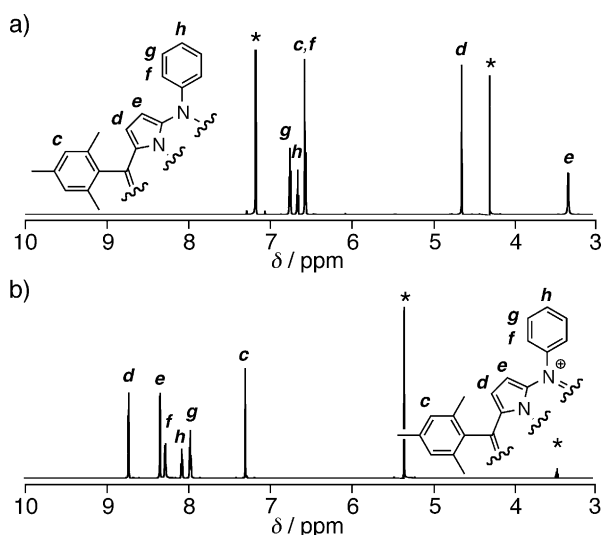


Figure 3. ^1H NMR spectra (700 MHz) of a) **3a** in C_6D_6 and b) **4a-Sb** in CD_2Cl_2 . Asterisks indicate residual solvent signals.

at $\delta = 4.61$ and 3.30 ppm (both doublets, 4H), whereas those for the β protons of **4a-Sb** were detected at $\delta = 8.72$ and 8.33 ppm (both d, 4H), respectively. These upfield and downfield shifts of the peripheral protons indicate paratropic (20π -electron) and diatropic (18π -electron) properties of **3a** and **4a-Sb**, respectively. The chemical shifts of the β protons of **4a-Sb** are close to the corresponding values of reference 18π -electron porphyrin **5** ($\delta = 8.58$ and 8.71 ppm in CD_2Cl_2). The β protons of **3a** are detected downfield compared with those of a $[\text{Zn}(\text{TPP})]$ dianion ($\delta = -0.9$ ppm in $[\text{D}_8]\text{THF}$),^[2d] which may be partly caused by the different number of electrons of their entire π systems. The *ortho*, *meta*, and *para*-protons of the *meso*-aryl groups (*c*, *f*, *g*, and *h*) of **3a** and **4a-Sb** also receive the opposite ring-current effects from each other. The spectral features of **3b** and other dications **4** (see the Supporting Information) are similar to those of **3a** and **4a-Sb**, respectively. Based on these observations, it can be concluded that $[\text{Ni}(\text{TADAP})]$ **3** and $[\text{Ni}(\text{TADAP})]^{2+}$ **4** have antiaromatic and aromatic characters, respectively, according to the magnetic criterion of aromaticity.

To compare the optical properties of the newly prepared diazaporphyrinoids with those of reference porphyrin **5**, UV/Vis absorption spectra of **3** and **4** were measured. As shown in Figure 4a, **3b** displayed two intense absorption bands at $\lambda_{\text{max}} = 446$ and 532 nm, whereas **4b-P** exhibited two bands at $\lambda_{\text{max}} = 393$ and 627 nm in CH_2Cl_2 . The spectral features of **3a** and other dications **4a-Sb**, **4b-Sb**, and **4a-P** (Figure S3) are similar to those of **3b** and **4b-P**, respectively. The Q bands of **4** ($\lambda_{\text{max}} = 626$ – 630 nm) are considerably red-shifted compared with those of isoelectronic porphyrin **5** ($\lambda_{\text{max}} = 526$ nm; Figure S3a) and 10,20-dimesityl-5,15-diazaporphyrinato nickel(II) ($\lambda_{\text{max}} = 571$ nm).^[12]

To obtain deeper insight into the nature of these optical properties, we performed time-dependent density functional theory (TD-DFT) calculations on models **3-m**, **4-m**, and **5-m** (Figure 1). The results are summarized in Table S1–S3 and Figure S4. Both **3-m** and **4-m** possess C_s symmetry and nondegenerate HOMO/HOMO-1 and LUMO/LUMO + 1

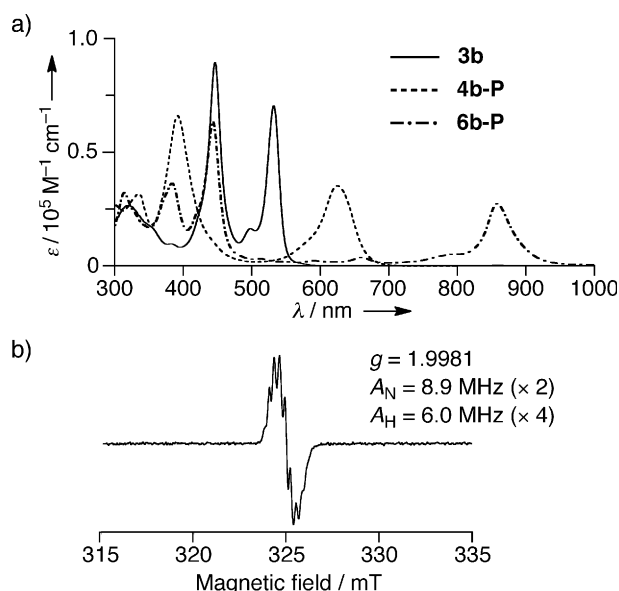
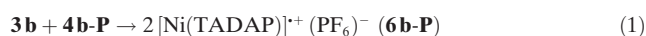


Figure 4. a) UV/Vis/NIR absorption spectra of **3b**, **4b-P**, and **6b-P** in CH_2Cl_2 . b) EPR spectrum of **6b-P** in toluene. The simulated EPR spectrum is shown in Figure S6.

orbitals because of the electronic effect of the two *meso*-N atoms. It is clear that both the HOMO and LUMO levels of **4-m** are appreciably stabilized compared with those of isoelectronic **5-m**. By comparison of the experimental and theoretical results, the long-wavelength absorption bands around $\lambda = 530$ nm detected for **3** were assigned to a combination of the HOMO to LUMO + 1 and HOMO-1 to LUMO transitions. The TD-DFT calculations also indicated that the HOMO to LUMO transition of **3-m** is symmetrically forbidden (oscillator strength (f) = 0). In contrast, the intense, long-wavelength absorption bands around $\lambda = 630$ nm detected for **4** were assigned to the HOMO to LUMO transition ($f = 0.356$ for **4-m**).

Redox potentials of **3b**, **4b-P**, and **5** were measured in CH_2Cl_2 or THF with Bu_4NPF_6 as the supporting electrolyte (Figure S5). $[\text{Ni}(\text{TADAP})]$ **3b** was oxidized reversibly in one-electron steps with separated potentials of -0.39 ($20\pi/19\pi$ electrons) and $+0.30$ V ($19\pi/18\pi$ -electrons), whereas $[\text{Ni}(\text{TADAP})]^{2+}$ **4b-P** was reduced reversibly with potentials of $+0.29$ ($18\pi/19\pi$ -electrons) and -0.39 V ($19\pi/20\pi$ electrons) versus the Ag/Ag^+ redox couple (in CH_2Cl_2). As expected, the redox potentials detected for **3b** and **4b-P** are identical, within experimental error. The $20\pi/19\pi$ -electron redox process of **3b** occurs at a much more positive potential than that of isoelectronic porphyrin **5** ($E < -2$ V versus Ag/Ag^+), which explains the remarkably high air stability of $[\text{Ni}(\text{TADAP})]$ compared with that of the TPP-type porphyrin dianion.^[2d] The electrochemical HOMO–LUMO gap of **3b** was determined to be 1.62 eV (Figure S5e). It should also be noted that the electron-accepting ability of **4b-P** is considerably higher than that of **5** [$E(18\pi/19\pi) = -1.69$ V versus Ag/Ag^+ (in THF)]. The measured redox potentials suggest that single electron transfer (SET) from **3b** to **4b-P** is energetically favorable. Indeed, a greenish-yellow solution with an intense absorption band at $\lambda_{\text{max}} = 860$ nm formed immediately

after mixing equimolar amounts of **3b** and **4b-P** in CH_2Cl_2 . Reprecipitation of the product of this reaction from a mixture of CH_2Cl_2 :hexane gave an air-stable greenish-yellow solid that showed no ^1H NMR resonance signal for the peripheral protons in CD_2Cl_2 but a ^{31}P resonance signal for the PF_6^- counterion at $\delta = -144.5$ ppm (septet, $J_{\text{PF}} = 711$ Hz). These results imply that SET occurred from **3b** to **4b-P**, as expected, to give the 19π -electron radical cation **6b-P** [Eq. (1)]. The UV/Vis/NIR absorption spectrum of **6b-P** is presented in Figure 4a. The same species was generated by the reaction of **3b** with one equivalent of AgPF_6 in CH_2Cl_2 . In toluene, **6b-P** displayed an EPR signal at $g = 1.9981$ with the fine structure derived from two *meso*- ^{14}N and four β - ^1H atoms (Figure 4b). The spin distribution of its model **6-m** (Figure 1) supported the measured fine structure (Figure S6). Redox processes for **6b-P** in CH_2Cl_2 were measured at -0.39 ($19\pi/20\pi$ electrons) and $+0.28$ V ($19\pi/18\pi$ electrons) versus Ag/Ag^+ (Figure S5c), which are in good agreement with the corresponding redox potentials for **3b** and **4b-P**.



In summary, we have synthesized the first examples of TADAP compounds, their dications, and a radical cation as air-stable solids by metal-templated annulation and subsequent oxidation. The antiaromatic, aromatic, and radical character of TADAP, $[\text{Ni}(\text{TADAP})]^{2+}$, and $[\text{Ni}(\text{TADAP})]^{++}$, respectively, were confirmed by NMR, UV/Vis/NIR absorption, and EPR spectroscopies. As a result of the high electron affinity of nitrogen at the *meso* positions, 20π -electron $[\text{Ni}(\text{TADAP})]$ and 19π -electron $[\text{Ni}(\text{TADAP})]^{++}$ are resistant to oxidation in air, whereas 18π -electron $[\text{Ni}(\text{TADAP})]^{2+}$ is strongly electron accepting. These properties are difficult to obtain with isoelectronic 5,10,15,20-tetraarylporphyrins. It is also noteworthy that both chemical and electrochemical redox processes between the 18π - and 20π -electron systems proceed reversibly in one-electron steps via the 19π -electron system. These newly constructed tetraaryldiazaporphyrinoids can be used not only for a fundamental study of π -conjugated azamacrocycles but also for applied research on redox-active sensitizers.

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