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Antiaromatic Porphyrins

Gram-Scale Synthesis of Nickel(II) Norcorrole: The Smallest Antiaromatic Porphyrinoid**

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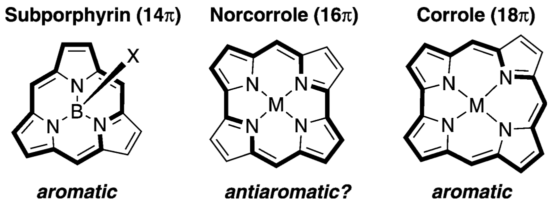
Porphyrins and their related polypyrrolic conjugated macrocycles, porphyrinoids, have been targets of intensive research from basic science to practical applications. Among them, corrole[1] and subporphyrin[2] are the representative ring-contracted porphyrins, both of which exhibit distinct aromatic characters owing to 18 and 14 π-electrons on the conjugation pathway, respectively (Scheme 1). Norcorrole, which lacks two *meso* carbon atoms from a regular porphyrin, would be another attractive ring-contracted porphyrin. In spite of its simple and beautiful structure, the synthesis of norcorrole has been quite challenging owing to structural strain.

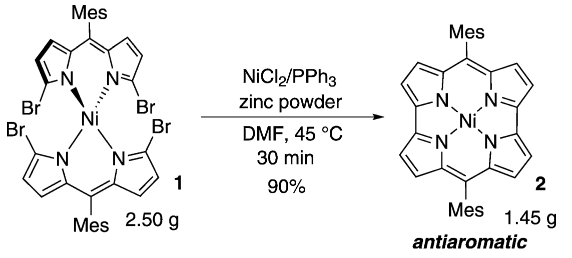


Scheme 1. Structures of subporphyrin, norcorrole, and corrole. The bold lines indicate each conjugation circuit.

On the basis of the Hückel rule, the 16π-electronic system of norcorrole is expected to exhibit antiaromatic character. In 2005, however, the DFT calculations by A. Ghosh et al. predicted a nonaromatic polyenic character rather than antiaromaticity of norcorrole.[3] This intriguing theoretical prediction gave a rise to the necessity for the experimental support. In 2008, Bröring et al. reported the first observation of a norcorrole–iron(III) complex, which was unfortunately not isolable owing to rapid dimerization.[4] The instability of the norcorrole–iron complex prevented further elucidation of the nature of norcorrole. Determination of the structure and possible antiaromaticity of norcorrole have not yet been accomplished.

Herein we present unambiguous characterization of an antiaromatic nickel(II)–norcorrole complex, which can be prepared easily in a gram scale by a metal-templated synthesis. The high efficiency in the preparation of an antiaromatic porphyrinoid is rather remarkable, as the synthesis of antiaromatic compounds is inherently difficult owing to their unstable nature. Furthermore, reactions for the synthesis of porphyrinoids themselves by acid-promoted condensation–oxidation of pyrroles with aldehydes, are generally low-yielding. However, the metal-mediated synthesis offers an efficient route to novel porphyrinoids. Furthermore, the ready availability of antiaromatic norcorroles would lead to practical use of antiaromatic compounds for further applications, such as organic opto-electronic materials.

The synthesis of Ni^{II} norcorrole **2** is depicted in Scheme 2, in which α,α′-dibromodipyrrin Ni^{II} complex **1** was employed as a precursor.[5] We attempted a Ni^0-mediated intramolecular homocoupling[6] of **1** and obtained the formation of Ni^{II} norcorrole **2** in 90% yield as a green solid. Rather unexpectedly, the product **2** is quite stable under air at room temperature and is easily isolatable by silica gel column purification, similar to normal porphyrin complexes. Owing to the facile synthetic procedure, the preparation of compound **2** on a gram scale was easily accomplished. Compound **2** was characterized on the basis of ESI-TOF mass analysis and NMR spectroscopy. The ^{1}H NMR spectrum of **2** proposed a highly symmetric structure, of which sharp signals suggest that the nickel atom takes a low spin state in a square-planar geometry. More importantly, the ^{1}H NMR spectrum of **2** displays two sets of doublet peaks for pyrrole β-protons in the far upfield region from $\delta = 1.45$ to 1.60 ppm, owing to a paratropic ring current effect, which clearly indicates



Scheme 2. Nickel-mediated reductive homocoupling of dipyrrin complex **1** to Ni^{II} norcorrole **2**.

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distinct antiaromaticity of Ni^{II} norcorrole **2**. Recently, antiaromatic porphyrins and expanded porphyrins have been successfully characterized,[7] but this is the first example of isolation of antiaromatic ring-contracted porphyrins.

The structure of Ni^{II} norcorrole **2** was unambiguously elucidated by X-ray diffraction analysis (Figure 1 a,b). The main skeleton of **2** is perfectly planar, with the mean plane deviation of 0.041 Å. The flat structure containing 16 π-electrons on the conjugation pathway results in a strong antiaromaticity. The NICS (nucleus-independent chemical shift) value calculated at the point "a" (indicated in Figure 1 a) is $\delta = 39.4$ ppm, supporting the antiaromaticity of **2**.[8] Reflecting its antiaromaticity, compound **2** displays significant bond length alternation (Figure 1 e), which is unusual for aromatic porphyrins such as compound **3**. The C–C bond length between two dipyrrin moieties is measured to be 1.49 Å, which is somewhat longer than a typical C–C bond between two sp^2 carbon atoms.

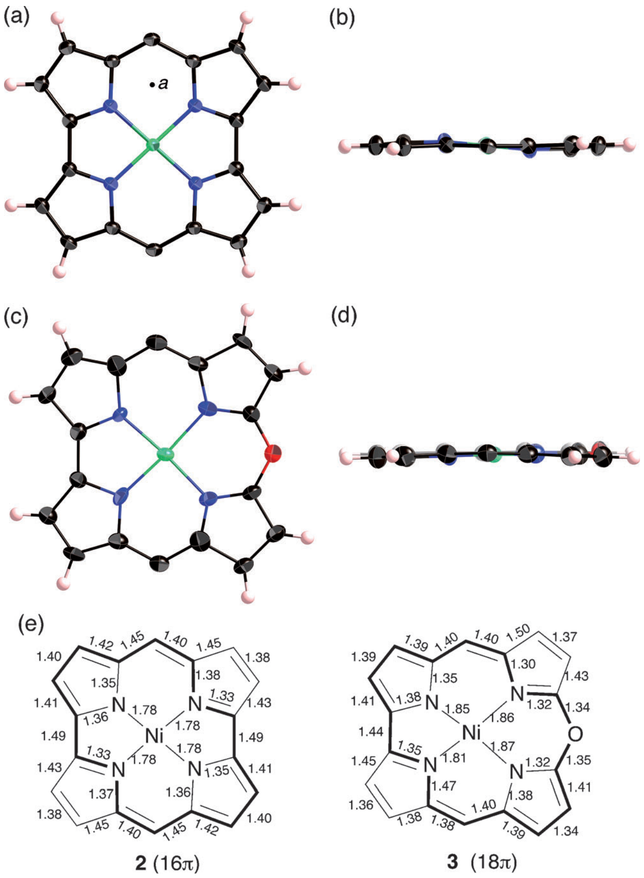
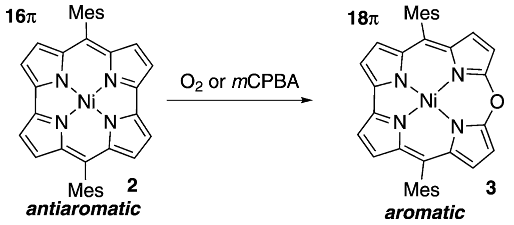


Figure 1. X-ray crystal structures of Ni^{II} norcorrole **2** (a) top view, b) side view) and Ni^{II} 10-oxacorrole **3** (c) top view, d) side view). *meso*-Aryl substituents are omitted for clarity. Ellipsoids are set to 50% probability . e) Bond length alternations for the crystal structures **2** and **3**.

Although Ni^{II} norcorrole **2** is stable at room temperature both in the solution and in the solid state, we found that compound **2** was slowly oxidized under air at high temperatures to afford Ni^{II} 10-oxacorrole **3**.[9] Heating the solution of **3** at 100 °C in anhydrous DMF under an O_2 atmosphere provided **3** in 47% yield in 5 days (Scheme 3). Furthermore, treatment of **2** with *m*-chloroperoxybenzoic acid (mCPBA) at −30 °C also afforded **3** in 51% yield in 3 h. As no formation of **3** was observed in wet DMF in the absence of O_2, we concluded that the oxygen source for the formation of oxacorrole **3** is molecular oxygen, not water. The ^{1}H NMR spectrum of oxacorrole **3** revealed its aromatic character, showing doublet peaks of pyrrole β-protons in the aromatic region from $\delta = 7.5$ to 7.9 ppm. The X-ray diffraction analysis elucidated the structure of Ni^{II} oxacorrole **3** (Figure 1 c,d). The aromaticity of **3** can be explained by 18 π-electrons, including the lone pair on the oxygen atom at the *meso* position.



Scheme 3. Oxidation of Ni^{II} norcorrole **2** to Ni^{II} oxacorrole **3**.

The UV/Vis absorption spectrum of Ni^{II} norcorrole **2** exhibits a substantially different shape from those of typical porphyrins. Characteristically, the spectrum of **2** has a broad absorption band at 431 nm and weak absorption bands ranging from 600 to 1100 nm, which can be considered as diagnostic for antiaromatic porphyrinoids (Figure 2 a).[7c] In contrast, Ni^{II} oxacorrole **3** has a Soret band at 389 nm and Q bands at 680 and 553 nm (Figure 2 b). To elucidate detailed features of these absorption spectra, we further measured magnetic circular dichroism (MCD) spectra of **2** and **3**. Generally, absorption spectra of porphyrinoids with 18π-conjugation systems are interpreted in terms of Gouterman's four-orbital theory,[10] which specifies that the allowed nature of Soret bands and the forbidden nature of Q bands are derived from configuration interactions of four HOMO→LUMO transitions. As these transitions are associated with changes of orbital angular momenta, the Soret and Q bands can be observed as clear CD signals using MCD spectroscopy. Michl et al. successfully predicted MCD signal patterns of aromatic molecules by applying perimeter models of $4n+2$-electron cyclic polyenes.[11] In the MCD spectrum of **3** (Figure 2 b), negative-to-positive MCD signals, which are recognized as Faraday *B* terms in MCD theory,[12] are observed at 677 and 555 nm, assigning the split Q bands of **3** at these wavelengths, whereas similarly intense MCD signals are observed corresponding to the Soret band at 389 nm. The absorption and MCD spectra of **3** are typical of aromatic porphyrinoids with lower molecular symmetries. The perimeter model was further extended to $4n$-electron antiaromatic molecules, in which six frontier orbitals (h_-, h_+, s_-, s_+, l_-, l_+) derived from HOMOs, SOMOs, and LUMOs are involved in the π–π* transitions.[13] In the case of an antiaromatic compound with a closed-shell ground state,[13c] the lowest-

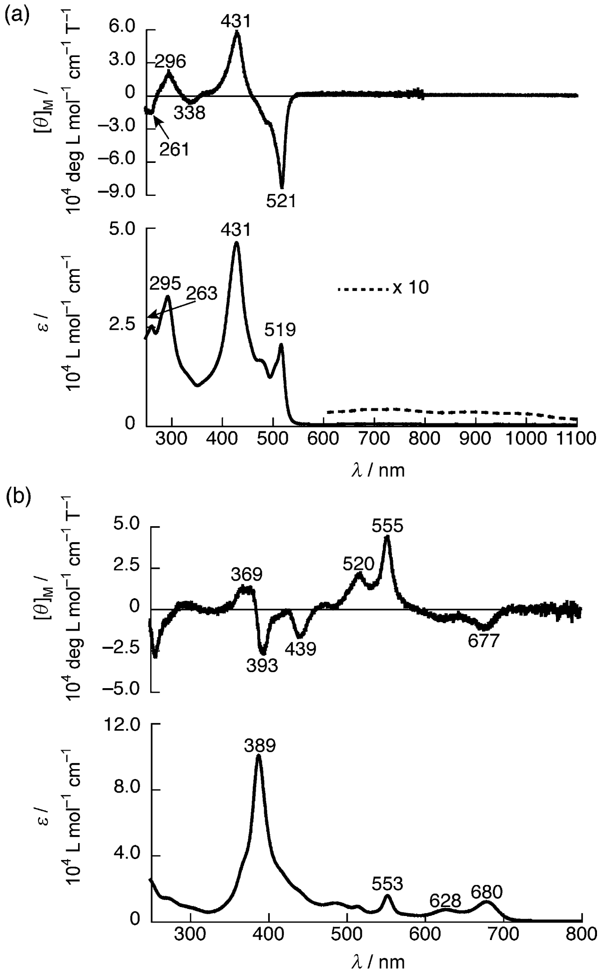


Figure 2. MCD (top) and UV/Vis absorption (bottom) spectra of a) Ni^{II} norcorrole **2** and b) Ni^{II} oxacorrole **3** in CH_2Cl_2.

energy band arises from an $s_{-}\rightarrow s_{+}$ transition, which becomes forbidden owing to an intrashell nature in the perimeter model. Allowed bands of antiaromatic compounds comprise four HOMO→SOMO ($h_{-}\rightarrow s_{+}$ and $h_{+}\rightarrow s_{+}$) and SOMO→LUMO ($s_{-}\rightarrow l_{-}$ and $s_{-}\rightarrow l_{+}$) transitions. Configuration interaction of these four transitions results in two intense bands and two weak bands, which are described as P and N bands, respectively. In the MCD spectra of antiaromatic porphyrinoids, the P bands are generally observed as unequivocal MCD signals, whereas the N bands are quite featureless, being observed as shoulders of P bands.[14] The MCD spectrum of **2** (Figure 2a) exhibits the spectral features of antiaromatic compounds; very weak bands with a forbidden nature in the lower energy region and clear Faraday *B* terms at 521 and 431 nm, indicating that **2** possesses an antiaromatic conjugation system with a closed-shell ground state, as is suggested by NMR spectroscopy.

Electrochemical properties of **2** and **3** were examined by cyclic voltammetry (Supporting Information, Figure S5). Two reversible reduction and two reversible oxidation waves were observed for norcorrole **2**, while oxacorrole **3** exhibited two reversible reduction and one reversible oxidation waves. The electrochemical HOMO–LUMO gaps for **2** and **3** are determined to be 1.08 and 2.05 V, respectively. The substantially narrow HOMO–LUMO gap of **2** well matches with the general trend in antiaromatic compounds.

In conclusion, we have achieved a facile synthesis of Ni^{II} norcorrole **2** through intramolecular reductive homocoupling of a bis(α,α′-dibromodipyrrinato) Ni complex **1**. The highly planar structure and distinct 16π-antiaromaticity of Ni^{II} norcorrole **2** have been unambiguously unveiled for the first time. In spite of the antiaromatic destabilization and the strained core structure, the Ni^{II} norcorrole is unexpectedly stable at room temperature but converted into 18π-aromatic Ni^{II} oxacorrole **3** with molecular oxygen at high temperatures. This interesting reactivity of the oxygen insertion reaction implies that norcorrole could be a prospective precursor for various heteroatom-substituted porphyrinoids. Further investigation into the reactivity of norcorrole is currently underway in our laboratory.

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Communications

Antiaromatic Porphyrins

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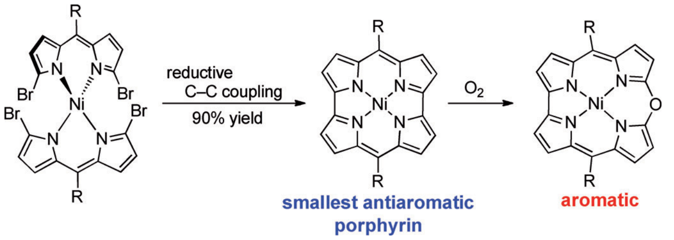
Gram-Scale Synthesis of Nickel(II) Norcorrole: The Smallest Antiaromatic Porphyrinoid



Small is beautiful: A ring-contracted sister of porphyrin, norcorrole, has been synthesized efficiently as a stable molecule by a nickel-templated strategy. The norcorrole complex is stable but exhibits a distinct antiaromatic character according to the Hückel rule. Oxidation of the norcorrole complex provides an aromatic oxacorrole complex.