

Benzonorcorrole Ni^{II} Complexes: Enhancement of Paratropic Ring Current and Singlet Diradical Character by Benzo-Fusion

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Abstract: Fused benzene rings to antiaromatic compounds generally improve their stability but attenuate their antiaromaticity. Here we report the opposite case. We have synthesized Ni^{II} benzenonorcorroles and elucidated the effect of benzo-fusion on the antiaromaticity. The benzo-fusion resulted in significant decrease of the HOMO–LUMO gaps and enhancement of the paratropic ring current effect. Furthermore, the introduction of the benzo groups induced singlet diradical character in the antiaromatic porphyrinoid.

Research on antiaromatic compounds has intensified rapidly in recent years,^[1] mostly motivated by their intriguing properties, which are markedly different from those of conventional aromatic compounds, and by their practical applications in ambipolar semiconductors^[2] and organic secondary batteries.^[3] However, distinctly antiaromatic molecules are inherently unstable, thus hampering deeper understanding of their properties and functions. One of the effective strategies to enhance the stability of antiaromatic molecules is expansion of π -conjugation by benzo-fusion, which has enabled isolation and easy handling of a number of $4n$ π -electron systems. However, the introduction of fused benzo rings usually counterbalances the antiaromatic nature, as the strong local aromaticity of the benzene ring disturbs the contribution of the macrocyclic $4n$ π -conjugation system. For instance, while *s*-indacene is an unstable 12π antiaromatic polycyclic hydrocarbon, indenofluorene is stable due to a significant reduction of antiaromaticity.^[4] Dibenzoborrole also shows attenuated antiaromaticity relative to that of the distinctly antiaromatic pristine borrole.^[5]

While antiaromatic porphyrinoids have been explored extensively,^[6,7] benzo-fused antiaromatic porphyrinoids are still limited to several examples.^[8] Furthermore, the effect of benzo-fusion on their antiaromaticity has not been understood sufficiently. Norcorrole, an antiaromatic porphyrinoid with a 16

π -electron system, was initially reported by Bröring *et al.*^[9] Recently, we have reported a large-scale synthesis of Ni^{II} dimesitylnorcorrole (Nc) (Figure 1), which shows sufficient stability and a distinctly antiaromatic character.^[10] The stability of Nc allowed us to explore the properties and functions of antiaromatic porphyrinoids.^[11] Li and Chmielewski *et al.* have also investigated modification of Nc.^[12]

In this study, we have synthesized benzenonorcorroles (TBNc and DBNc) to reveal the effect of benzo-fusion on the properties of norcorroles (Figure 1). We particularly focused on the change in the ring current effect. A systematic comparison among these Ni^{II} norcorroles allowed us to conclude that benzo-fusion significantly decreases their HOMO–LUMO gaps and increases their paratropic ring current. Moreover, we discovered that benzo-fusion induces singlet diradical character. Since singlet diradical character is associated with nonlinear optical properties and singlet fission processes,^[13] delocalized singlet diradicals have received much attention.^[14]

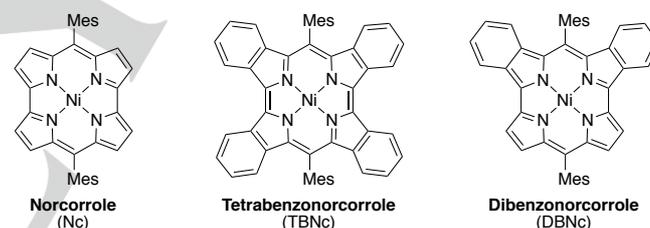
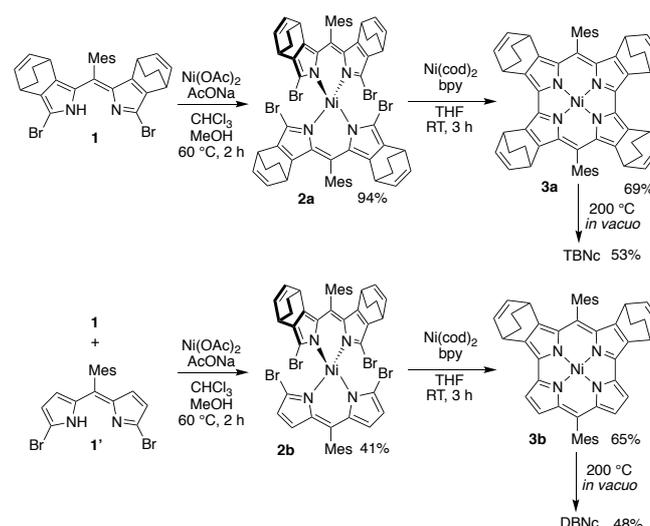


Figure 1. The structures of Ni^{II} dimesitylnorcorrole used in this study.



Scheme 1. Synthesis of TBNc and DBNc.

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The synthesis of benzonorcorroles TBNc and DBNc was conducted on the basis of the preparation of benzoporphyrins,^[15] in which benzo units are formed by the cycloreversion of bicyclo[2.2.2]octadiene moieties (Scheme 1). Treatment of **1** with Ni(OAc)₂ provided Ni^{II} complex **2a**, which was converted to norcorrole **3a**. TBNc was obtained from a retro-Diels–Alder reaction of **3a** at 200 °C under reduced pressure. Complexation of a mixture of **1** and **1'**, followed by chromatographic separation, afforded unsymmetrical Ni^{II} complex **2b**, from which DBNc was prepared. As TBNc and DBNc were gradually oxidized in solution, these complexes were isolated in a glovebox via repeated recrystallization. Since Ni^{II} norcorrole Nc is stable under air at room temperature, the benzo-fusion clearly resulted in destabilization of the π -system.

X-ray diffraction analyses of TBNc and DBNc unambiguously determined their structures (Figure 2). In the crystal, TBNc exhibits a perfectly planer structure. π – π Stacking was not observed in the crystal of TBNc. The crystal structure of DBNc contains two independent stacked molecules per unit cell (structure 1 and structure 2). DBNc maintains rather flat conformation in structure 1, while structure 2 is distorted. TBNc exhibits a different type of the bond length-alternation than Nc and DBNc (Figure S15). The C–C bond lengths between the pyrrole α -carbons in Nc (1.491(2) Å) and DBNc (1.478(7) Å) are relatively long, while the corresponding C _{α} –C _{α} bond in TBNc exhibits a clear double bond character (1.392(2) Å).

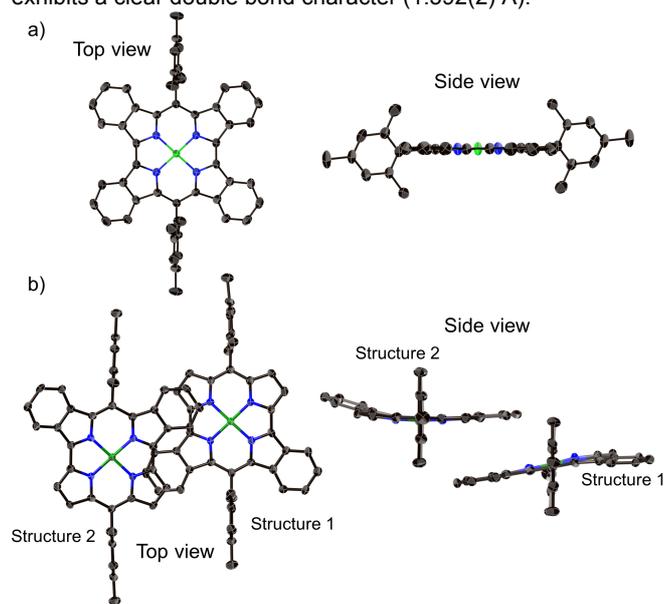


Figure 2. X-ray crystal structures of a) TBNc and b) DBNc; atomic displacement parameters set at 50% probability and hydrogen atoms are omitted for clarity.

Figure 3 shows the ¹H NMR spectra of TBNc and DBNc in toluene-*d*₆. It is remarkable that the protons on the benzene rings of TBNc and DBNc appear at δ = 3.0 and 0.5 ppm, suggesting that the strong paratropic ring current of TBNc and DBNc overrides the inherent diatropic ring current of the benzene rings. Furthermore, DBNc displays significantly high-field shifted pyrrole protons (δ = –2.79 and –3.91 ppm)

compared to those of Nc (δ = 1.44 and 1.22 ppm). These observed chemical shifts verify a dramatic increase in the antiaromatic ring current effect by the benzo-fusion.

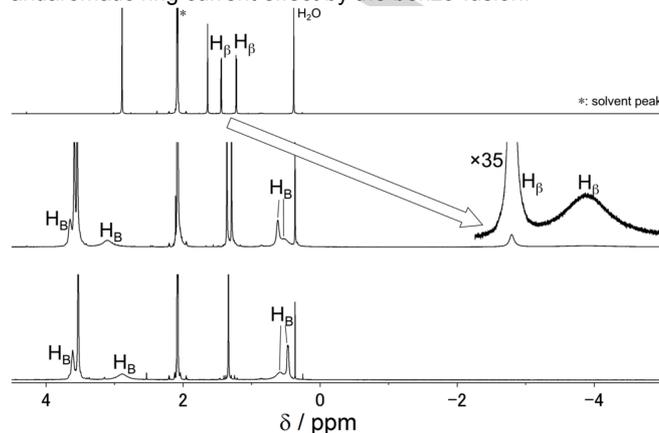


Figure 3. ¹H NMR spectra of Nc (top), DBNc (middle) and TBNc (bottom) in toluene-*d*₆. H _{β} : protons on the pyrrole rings. H _{β} : protons on the benzene rings.

The cyclic voltammograms of Nc, DBNc, and TBNc measured in CH₂Cl₂ exhibited four reversible waves (Figure S17). The first oxidation processes of DBNc (–0.12 V) and TBNc (–0.28 V) are shifted to low potentials in comparison to that of Nc (0.16 V), while their first reduction processes are not affected by the benzo-fusion. The electrochemical HOMO–LUMO gaps (ΔE) for DBNc (0.79 V) and TBNc (0.75 V) are substantially narrow. The UV/Vis/NIR absorption spectra of TBNc, DBNc, and Nc are displayed in Figure S18. Benzonorcorroles TBNc and DBNc show weak and broad absorption bands at 1500–2500 nm. These transition energies are much smaller than that of Nc (~1000 nm). These electrochemical and optical measurements suggest the significantly narrowed HOMO–LUMO gaps in benzonorcorroles.

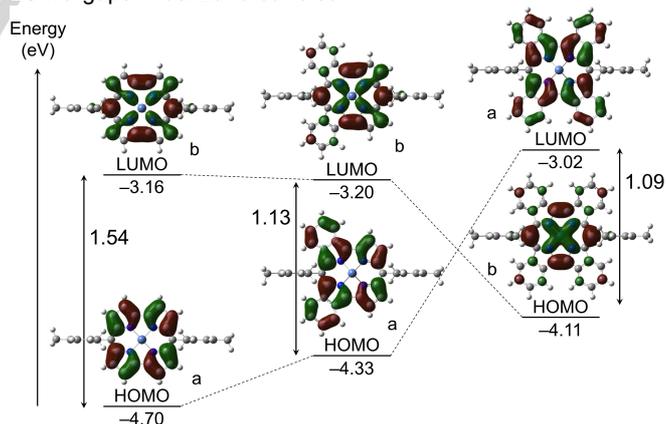


Figure 4. MO diagrams for Nc, DBNc, and TBNc.

To confirm the narrow HOMO–LUMO gaps of TBNc and DBNc, we conducted the DFT calculations at the RB3LYP/6-31G(d)+SDD level (Figure 4). The HOMO and LUMO of Nc can be assigned to *a*-symmetric and *b*-symmetric orbitals, respectively. Comparing the orbitals of DBNc with those of Nc,

the *a*-symmetric HOMO of DBNc is destabilized by interactions between two benzo rings and the norcorrole core. In the case of TBNc, the *a*-symmetric orbital is further destabilized to become the LUMO, while the *b*-symmetric orbital concomitantly becomes the HOMO. The orbital inversion affects the structures of TBNc, which exhibits a much shorter C_α–C_α bond length between the two pyrrole units than Nc or DBNc, as the *b*-symmetric orbital exhibits bonding character between the two C_α carbons.

To reveal the origin of their broad NMR spectra, variable-temperature (VT) ¹H NMR spectra of TBNc and DBNc were recorded from –80 °C to 100 °C in toluene-*d*₆ (Figure S13 and S14). The proton signals were further broadened at higher temperatures. Conversely, the peaks sharpened at lower temperatures. This temperature-dependence led us suspect an open-shell character for TBNc and DBNc. The temperature-dependent magnetic susceptibility ($\chi_p T$) of TBNc was measured by a superconducting quantum-interference device (SQUID) (Figure 5a). In addition, the $\chi_p T$ was also evaluated by the Evans method (Figure 5b). Both measurements provide essentially the same temperature dependence. The magnetic susceptibility gradually increased at *T* > 200 K. This behavior is typical for singlet diradicaloids, whose triplet state is populated by the thermal excitation from the open-shell singlet ground state. The least-square curve fitting of the $\chi_p T$ values using the Bleaney–Bowers equation afforded J_{S-T} values of –1.76 kcal mol^{–1} (SQUID) and –1.40 kcal mol^{–1} (Evans).

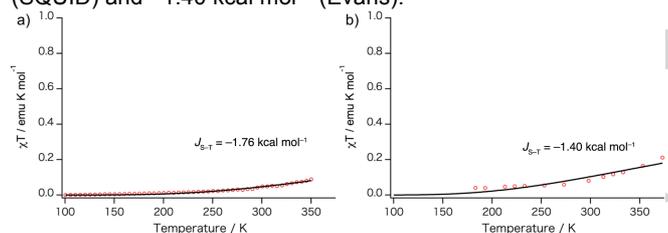


Figure 5. $\chi_p T$ plot of TBNc measured by a) SQUID and b) Evans method.

The energy levels of closed-shell singlet, open-shell singlet, and open-shell triplet configurations of TBNc and DBNc were calculated using the DFT method based on their crystal structures (Table S2). The open-shell singlet state was obtained by the symmetry-broken (BS) method. J_{S-T} values were estimated using Yamaguchi's equation.^[16] The results revealed that the open-shell singlet states are the most stable states for both TBNc and DBNc. The calculated J_{S-T} value was in good agreement with the experimental values. As the diradical characters,^[17] y , of DBNc (0.34) and TBNc (0.39), calculated at the LC-UBLYP(BS)/6-31G(d)+SDD level, are much higher than that of Nc (0.06), we concluded that the benzo-fusion enhances the diradical character (Table S12).

To evaluate the ring current effect, nucleus-independent chemical shift (NICS) values were calculated based on both crystal and DFT optimized structures (Figure S19 and Table S6-11).^[18] To include the influence by the open-shell contribution, the BS method was used for calculations. The NICS(1) values for Nc (~35 ppm) are substantially smaller than those for TBNc and DBNc (52–68 ppm). The anisotropy of the induced current density (ACID) plots^[19] also supported the presence of an

enhanced anticlockwise paratropic ring current in TBNc and DBNc (Figure 6 and S20-22).

In general, fused benzene rings to antiaromatic compounds attenuate their antiaromatic nature. The present observation stands in sharp contrast to common cases of benzo-fused antiaromatic compounds. The ACID plot of Nc suggests that the main ring current flows along the inner periphery involving four nitrogen atoms and fourteen bonds.^[20] If this is the case, the benzo-fusion would not disturb the 16 π -conjugation of the inner circuit and the narrowed HOMO–LUMO gap would increase the paratropic ring current.

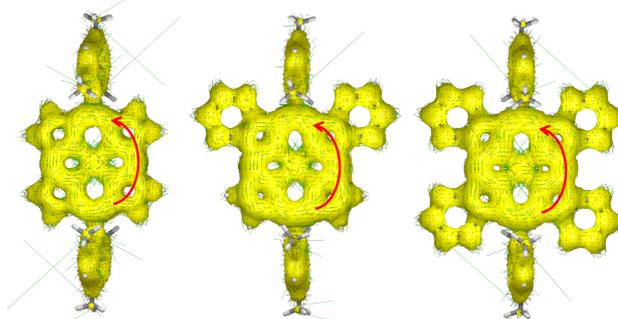


Figure 6. ACID plots for Nc, DBNc, and TBNc calculated at the UB3LYP(BS)/6-31G(d)+SDD level of theory.

In conclusion, we have synthesized Ni^{II} benzonorcorroles TBNc and DBNc through retro-Diels–Alder reactions. The introduction of fused benzene rings resulted in substantial enhancement of the paratropic ring current due to their narrow HOMO–LUMO gaps, which is supported by ¹H NMR spectra and DFT calculations. Moreover, VT-NMR and SQUID experiments revealed the singlet diradical character of TBNc. These results demonstrate that the HOMO–LUMO manipulation by benzo-fusion can induce diradical character and strong antiaromatic ring current in 4*n* π -electron systems.

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Keywords: porphyrinoid • antiaromaticity • ring current • diradical

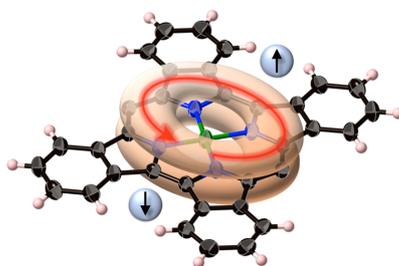
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Entry for the Table of Contents

COMMUNICATION

The effect of benzo-fusion on the antiaromaticity of a 16π porphyrin, Ni^{II} norcorrole, was investigated. The introduction of the benzo groups resulted in significant decrease of the HOMO–LUMO gaps and enhancement of the paratropic ring current effect. Furthermore, Ni^{II} tetrabenzonorcorrole exhibited singlet diradical character.



Strong antiaromaticity with singlet diradical character

Takuya Yoshida, Kohtaro Takahashi, Yuki Ide, Ryohei Kishi, Jun-ya Fujiyoshi, Sangsu Lee, Yuya Hiraoka, Dongho Kim, Masayoshi Nakano, Takahisa Ikeue, Hiroko Yamada, and Hiroshi Shinokubo**

Page No. – Page No.

Benzenorcorrole Ni^{II} complexes: Enhancement of Paratropic Ring Current and Singlet Diradical Character by Benzo-Fusion