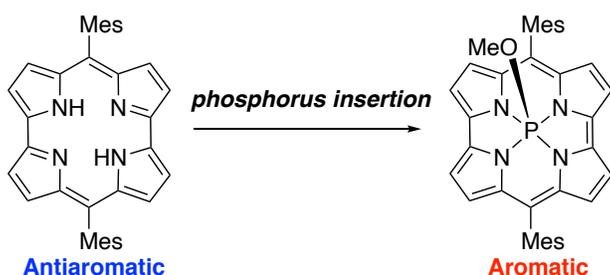


Synthesis and Properties of an 18 π Aromatic Norcorrole P(V) Complex

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Supporting Information Placeholder



ABSTRACT: [16]Norcorrole is an antiaromatic ring contracted porphyrinoid. Here, we unveil that phosphorus insertion of a free-base [16]norcorrole switches its antiaromaticity to aromaticity. Treatment of a free-base *meso*-dimesityl[16]norcorrole with phosphorus tribromide in pyridine afforded a [18]norcorrole P(V) complex, which exhibited porphyrin-like absorption and fluorescence spectra. The phosphorus center adopted distorted tetragonal-pyramidal coordination geometry. The distinct aromatic nature of the [18]norcorrole P(V) complex was corroborated experimentally and theoretically.

[16]Norcorrole is an intriguing 16 π -conjugated macrocyclic ligand, which is the smallest antiaromatic porphyrinoid (Figure 1).¹ [16]Norcorroles exhibit unique properties including distinct paratropic ring current, narrow HOMO–LUMO gap, stable redox performance, and characteristic chemical reactivity.² At the same time, *meso*-substituted [16]norcorrole Ni(II) complexes are considerably stable under ambient conditions in spite of their distinct antiaromaticity.³ Recently, such unique characteristics of [16]norcorrole have enabled the construction of an antiaromatic cyclophane with a three-dimensional aromaticity⁴ and a supramolecular cage with antiaromatic walls.⁵ Because of the two NH protons in its central cavity, a free-base [16]norcorrole²ⁱ serves as a dianionic macrocyclic ligand. As for [16]norcorrole metal complexes, the central metals have been mainly Ni(II), but Fe(III),^{1a} Cu(II),²ⁱ and Pd(II)²ⁱ complexes have also been synthesized.

Because of their low LUMO energy level, norcorroles readily accept electrons to undergo two-electron reduction providing dianionic 18 π aromatic species.^{2b} Li and Chmielewski have confirmed the diatropic ring current of a dianionic tetranitro-substituted [18]norcorrole Ni(II) complex by NMR spectroscopy.^{2e} However, the [18]norcorrole system has not been isolated as a stable molecule probably because its dianionic nature is susceptible to aerobic oxidation. If the two negative charge of the [18]norcorrole ligand is somehow neutralized, the species should exhibit substantial stability.

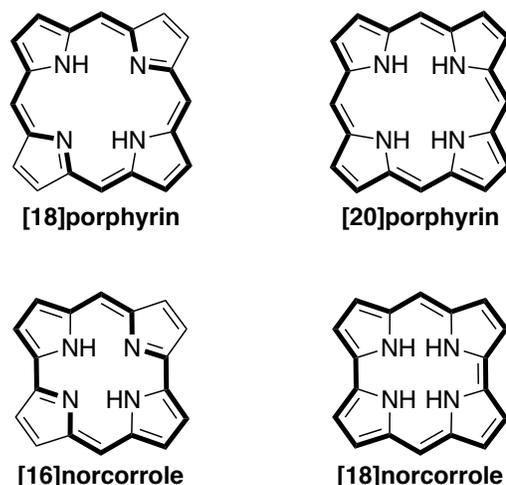


Figure 1. Structures of [18]porphyrin, [20]porphyrin, [16]norcorrole, and [18]norcorrole. The macrocyclic conjugation pathway is shown in bold lines.

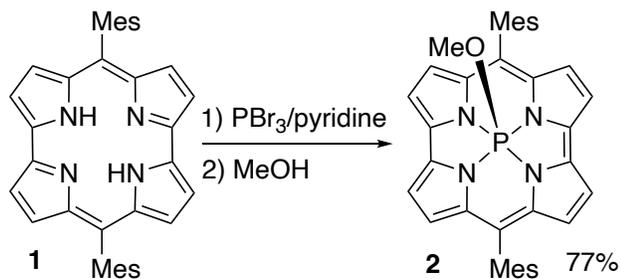
Two electron reduction of aromatic [18]porphyrin provides [20]porphyrin, which has been known as isophlorin (Figure 1).⁶ While free-base isophlorins are nonaromatic due to their highly distorted structures, planarized isophlorins exhibited the distinct antiaromaticity.⁷ Vaid demonstrated that reduction of a Si(IV) [18]porphyrin with sodium amalgam furnished a Si(IV) [20]porphyrin with the antiaromatic character.^{7e} Brothers reported that boron-insertion

is also effective to obtain antiaromatic [20]porphyrin.^{7f} The antiaromaticity of these [20]porphyrins is originated from their peripheral macrocyclic 20 π -conjugation. [18]Norcorrole can be considered as a ring-contracted analogue of isophlorin, which could become aromatic similarly due to its peripheral macrocyclic conjugation.

Here we disclose the characterization of [18]norcorrole P(V) complex **2**, which was prepared through phosphorus insertion into free-base norcorrole **1**. The [16]norcorrole macrocycle in **1** was reduced to an 18 π -conjugation system under the reaction conditions. The P(V) norcorrole complex **2** exhibited similar absorption features to regular porphyrins and rather intense fluorescence with the quantum yield of 0.31. The [18]norcorrole ligand was structurally rigidified owing to the central phosphorus atom, showing considerably small Stokes shift due to restricted dynamics of **2** in its excited state.

Phosphorus insertion was conducted according to the literature procedure for phosphorylation of porphyrinoids (Scheme 1). Treatment of free-base [16]norcorrole **1** with an excess amount (20 equiv) of phosphorus tribromide in pyridine afforded [18]norcorrole P(V) complex **2** in 77% yield. Compound **2** showed no appreciable decomposition under ambient conditions. The parent mass ion peak at $m/z = 580.2389$ and its isotope distribution pattern confirmed the formation of **2** (Figure S5). The ¹H NMR spectrum of **2** exhibited two signals for the pyrrole protons at 8.87 and 8.36 ppm, which are substantially downfield shifted relative to those of **1** (4.58 and 4.54 ppm). These peaks were observed as quasi-triplet and broad singlet owing to coupling with the phosphorus center. Furthermore, the methoxy protons appeared in a substantially upfield-shifted region at -0.55 ppm as a doublet peak ($J_{P-H} = 17$ Hz). These results indicate the presence of a diatropic ring current effect in the macrocyclic conjugation, clearly supporting the aromatic nature of **2**.

Scheme 1. Synthesis of norcorrole P(V) complex **2**.



The structure of [18]norcorrole **2** was unambiguously elucidated by the X-ray diffraction analysis (Figure 2a, b). Compound **2** adopts a shallow bowl-shaped structure, of which bowl depth is 0.624 Å. Characteristically, the framework of **2** shows small bond length alternation (BLA), which is evaluated using the harmonic oscillator model of aromaticity (HOMA) values (Figure 2c).⁸ The HOMA value of **2** is 0.94, confirming the highly delocalized nature of the π -system. The degree of BLA in **2** is contrasting to that in the original norcorrole core of **1**, of which HOMA value is 0.53.

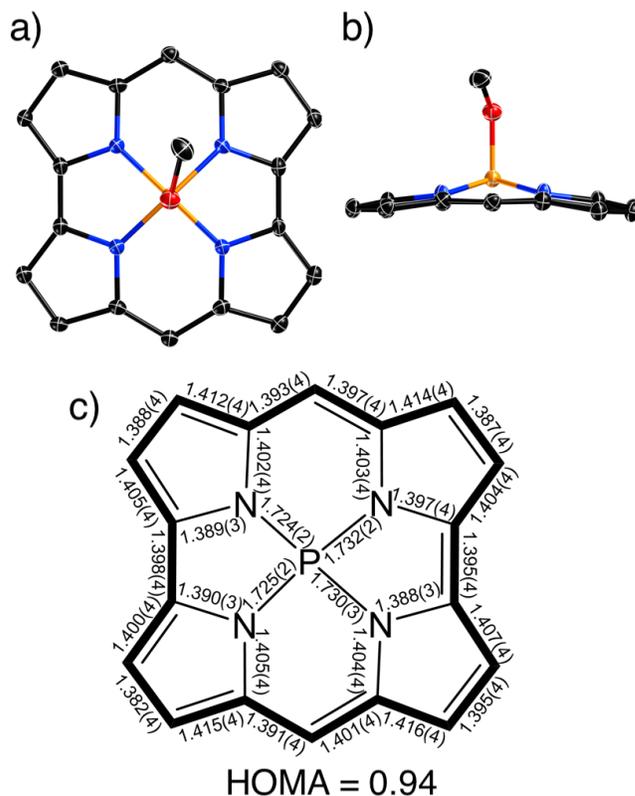


Figure 2. X-ray crystal structure of **2** with thermal ellipsoids at 50% probability; a) top view and b) side view. All hydrogen atoms except for those on the inner nitrogen atoms are omitted for clarity. c) Bond lengths and HOMA value.

The phosphorus center is ligated by the tetraanionic norcorrole ligand, resulting in formation of distorted tetragonal-pyramidal geometry. Such a coordination mode is not typical for a pentacoordinated phosphorus atom, which often takes a trigonal-bipyramidal structure without constraint by the ligand. The decoupled ³¹P NMR spectrum of **2** exhibited a singlet signal due to the central phosphorus atom at -103.9 ppm. Phosphorus(V) porphyrin and corrole complexes have been explored extensively (Figure 3).^{9,10} The phosphorus center in these porphyrinoid complexes often adopted hexacoordinated geometry such as **I** and **II**. Corroles **III**^{10b,d,e} and **IV**^{10f} with pentacoordinated phosphorus(V) center were also reported, in which the phosphorus center exhibited tetragonal-pyramidal geometry. Porphyrinoids with a hexacoordinated phosphorus center typically shows their ³¹P NMR signal at -180 to -260 ppm, while that of pentacoordinated compounds appears at -90 to -110 ppm.¹¹ The chemical shift value of the ³¹P NMR signal of **2** (-103.9 ppm) nicely accords with these previous results.

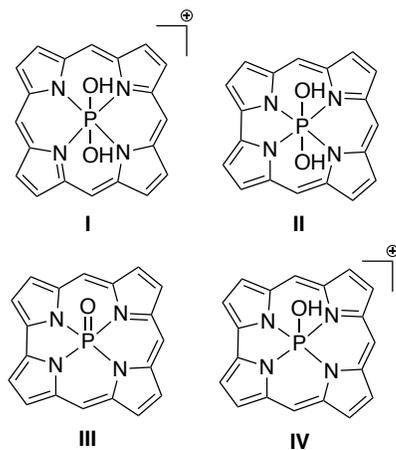


Figure 3. Phosphorus(V) complexes of porphyrin and corrole.

Figure 4 shows the UV/vis absorption and fluorescence spectra of **2**. The absorption spectrum of **2** consists of a sharp Soret band at 356 nm and distinct Q bands at 503 and 579 nm. The sharp and intense Soret band along with Q band with distinct vibronic structures are the diagnostic features of aromatic porphyrinoids. The fluorescence spectra exhibit sharp emission peak at 580 nm upon excitation at 365 nm. The emission quantum yield ($\Phi_F = 0.31$) is substantially higher than those of free-base and Zn(II) complex of 5,10,15,20-tetraphenylporphyrin ($\Phi_F = 0.11$ and 0.033, respectively).¹² The Stokes shift of **2** is only 45 cm^{-1} , while that of Zn(II) 5,10,15,20-tetraphenylporphyrin is 315 cm^{-1} ,¹³ indicating the rigid feature of the 18 π aromatic norcorrole ligand in its excited state.

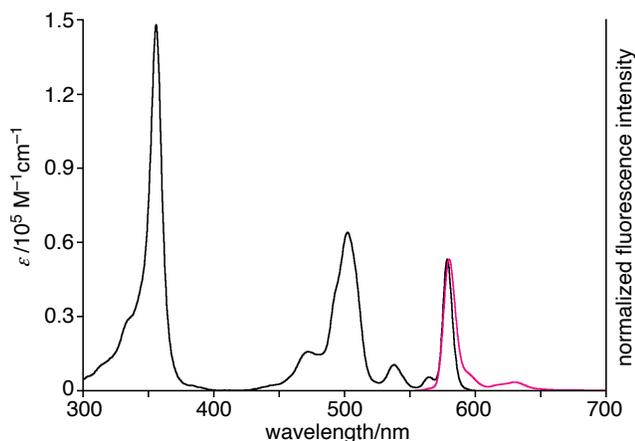


Figure 4. a) UV-vis absorption (black line) and fluorescence (red line; $\lambda_{\text{ex}} = 365$ nm) spectra of **2** in dichloromethane.

The four frontier orbitals (HOMO-1, HOMO, LUMO, and LUMO+1) of **2** were calculated at the B3LYP/6-31G(d) level (Figure 5). The HOMO distribution of **2** is essentially same as the LUMO distribution of [16]norcorrole,¹⁴ which highlights that **2** can be regarded as a (two-electron)-reduced counterpart of [16]norcorrole. The distributions of four frontier orbitals of **2** nicely accord with those expected for an 18 π -annulene.¹⁴ In the case of porphyrin, the LUMO and LUMO+1 are degenerated due to the D_{4h} -symmetric structure. On the other hand, the LUMO of **2** is energetically more stable than LUMO+1 by ca. 1.3 eV, which is attributable to the less-symmetric structure. The absorption features of **2** were reproduced nicely by the TD-DFT calculations, showing nonequivalent Q_x and Q_y transition dipole moments as well as more intensified Q-bands as compared to porphyrins (Figure S7). This spectral feature

can be explained as less effective configuration interaction originated from the less-symmetric structure.^{14,15}

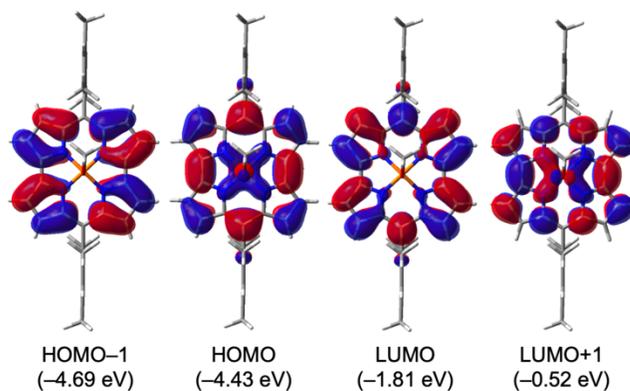


Figure 5. Kohn-Sham orbital distributions of HOMO-1, HOMO, LUMO, and LUMO+1 of **2**. Calculations were conducted at the B3LYP/6-31G(d) level.

The aromatic nature of **2** was further supported by theoretical calculations. The ring current was visualized by the anisotropy of the induced current density (ACID) plot,¹⁶ demonstrating the presence of the diatropic ring current through the periphery of the norcorrole skeleton (Figure 6a). The nucleus-independent chemical shift (NICS) calculation¹⁷ afforded largely negative NICS(1) and NICS(-1) values (from -12 to -18 ppm) (Figure 6b). These results strongly support the distinct aromaticity of P(V) norcorrole **2**.

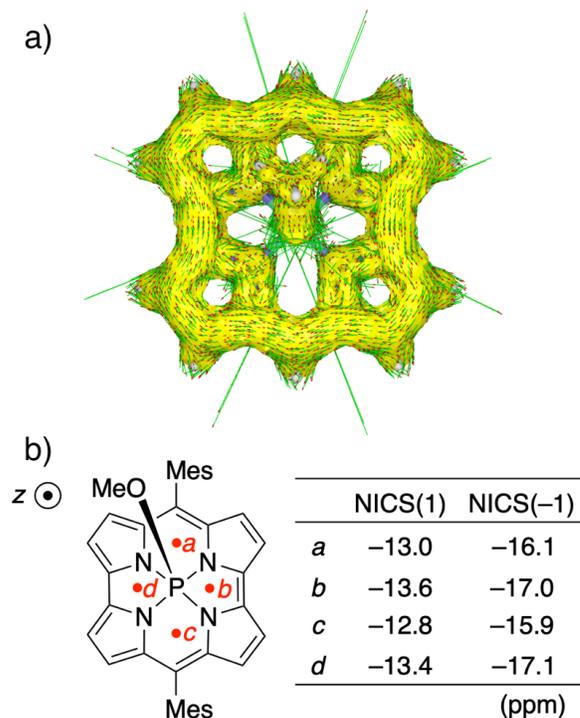


Figure 6. a) ACID plot of **2** (isovalue = 0.04) calculated at the B3LYP/6-31G(d) level. The *meso*-mesityl groups were replaced with hydrogen atoms to reduce the calculation cost. b) NICS(1) and NICS(-1) values calculated at the GIAO-B3LYP/6-31G(d) level.

In summary, we have synthesized aromatic [18]norcorrole **2** as its phosphorus(V) complex through the reaction of free-base *meso*-dimesityl[16]norcorrole **1** with phosphorus(III) tribromide in pyridine. The significantly small bond length alternation supports its

aromaticity in structural criteria. Furthermore, the aromatic nature of **2** was also confirmed both experimentally and theoretically in light of magnetic criteria. The phosphorus center adopted distorted tetragonal-pyramidal coordination geometry to induce the shallow bowl-shaped conformation. As the typical feature of aromatic porphyrinoids, [18]norcorrole **2** exhibited intense Soret band and well-structured Q bands in its absorption spectrum. The fluorescence spectrum of **2** revealed the substantially small Stokes shift of **2**, indicating its restricted dynamics in the excited state. The present findings demonstrate the potential of norcorrole as a tetraanionic aromatic ligand, which would stabilize high oxidation states of transition metals and main group elements.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details and spectral data for all new compounds.

Crystallographic data (CIF files) for **2**

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Notes

The authors declare no competing financial interests.

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