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Synthesis, Structure, and Aromaticity of the Nickel(II) Complex of Pyricorrole, a Molecular Hybrid of Porphyrin and Corrole

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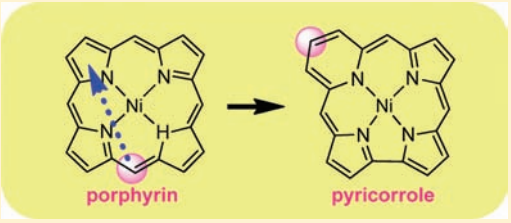
Supporting Information

ABSTRACT: Formal migration of one *meso*-carbon atom in the porphyrin ring into the pyrrole moiety results in an isomer "pyricorrole", a pyridine-containing corrole macrocycle. We prepared the nickel(II) complex of pyricorrole by the nickel(II)-induced cyclization of a linear precursor. Electronic absorption and proton NMR spectra of this compound revealed the presence of an 18π-electron circuit over the macrocycle, suggesting that aromaticity was retained after intensive rearrangement of the porphyrin core. X-ray crystallography of the nickel(II) complex confirmed the planar structure and demonstrated that it possesses hybrid properties of porphyrin and corrole.



INTRODUCTION

Porphyrin is the tetrapyrrole compound found in hemoprotein as the prosthetic group. The four pyrrole rings are arrayed in a square shape. The constitutional isomers such as porphycene, corrphycene, and hemiporphycene bearing various pyrrole arrays have been obtained after *meso*-carbon migration.[1] Corrole is another well-known porphyrin analogue which is one *meso*-carbon smaller than porphyrin.[2] If one *meso*-carbon in porphyrin were formally removed and incorporated into a pyrrole ring, instead of being completely removed as in corrole, the direct pyrrole−pyrrole link is formed and the carbon-incorporated pyrrole is transformed into a six-membered pyridine ring. The total carbon number of porphyrin remains unchanged on manipulation. The resulting molecule is a unique porphyrin isomer bearing a pyridine ring and three *meso*-carbon bridges. We suggest a trivial name of "pyricorrole" for this compound because it is just like a pyridine-embedded corrole. Although porphyrin and corrole represent the two major systems currently being studied, there is no precedent for porphyrin−corrole molecular hybridization. Pyricorrole is the special link between porphyrin and corrole. Preparation of such a macrocycle is challenging, and characterization of the properties will be of significant interest. We attempted the first synthesis of the macrocycle of pyricorrole and obtained the nickel(II) derivative. We demonstrate herein that the macrocycle exhibits hybridized properties of porphyrin and corrole.

RESULTS

Synthesis of the Nickel(II) Macrocycle. There are multiple routes of synthesis for the pyricorrole ring because it is asymmetric. We obtained the nickel(II) complex following the stepwise route outlined in Scheme 1. Several new precursory compounds were prepared during synthesis.

The Friedel−Crafts coupling of pyridine-2,6-dicarbonyl dichloride with 2 equiv of methyl 3,4-diethylpyrrole-2-carboxylate afforded a dicarbonyl compound (**1**) bearing a central pyridine. The carbonyl groups in compound **1** were converted to methylenes by the Clemmensen reduction to afford a tripyrrane-like molecule (**2**). The ester groups in **2** were subsequently hydrolyzed with aqueous sodium hydroxide, and diacid product (**3**) was decarboxylated with trifluoroacetic acid. Coupling of decarboxylated compound **3** with *tert*-butyl 2-acetoxymethyl-3-ethyl-4-methylpyrrole-5-carboxylate furnished a direct precursor (**4**) similar to bilane. Compound **4**, after removal of the *tert*-butyl ester function with trifluoroacetic acid, was cyclized through the nickel-assisted template reaction. In the presence of air at the boiling temperature of dimethylformamide, the saturated macrocycle was spontaneously oxidized into an aromatic system (**5**). Nickel(II) pyricorrole **5**, obtained in a 6% yield, was light green in chloroform; the UV−vis spectrum in Figure 1 showed a strong band at 399 nm and weak peaks in the 500−750 nm region. These absorption peaks were reminiscent of the Soret and Q bands of porphyrin. The appearance of the porphyrin-like electronic spectrum suggested the aromaticity in **5**.

Proton NMR. The proton NMR spectrum of compound **5** was recorded to deduce the structure. The spectrum exhibited only three *meso*-proton signals at δ 8.45, 8.54, and 8.64 (Figure 2). The three *meso*-carbon signals suggested the presence of three *meso*-bridges and formation of a direct pyrrole−pyrrole bond. Appearance of the pyridine signals at δ 8.99, 9.31, and 9.45 indicated incorporation of a pyridine unit into the macrocycle. An additional notable NMR result was that the pyridine resonances were in a δ 9.0−9.5 region while the corresponding signals of free

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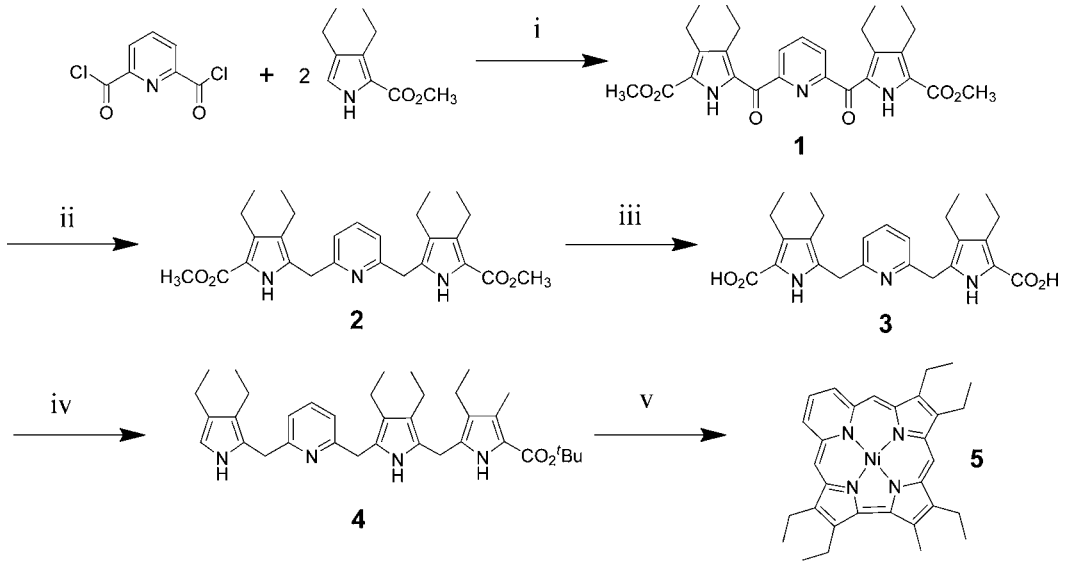
Scheme 1. Synthesis of Nickel(II) Pyricorrole 5



Conditions: i) $AlCl_3/CH_2Cl_2$; ii) Zn + HCl/CH_3OH; iii) aqueous NaOH + CH_3OH/tetrahydrofuran; iv) 1 eq. *t*-butyl 2-acetoxymethyl-3-ethyl-4-methylpyrrole-5-carboxylate, CF_3CO_2H/CH_3OH; v) CF_3CO_2H at 25 °C, $Ni(CH_3CO_2)_2$/*N*,*N*-dimethylformamide at 160 °C.

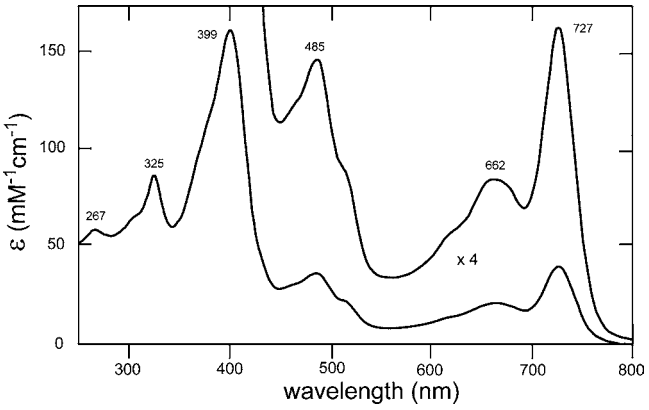


Figure 1. UV–vis absorption spectrum of nickel(II) pyricorrole **5** in $CHCl_3$.

pyridine were found in δ 7.3–8.6.[3] A similar downfield shift was observed for the methyl proton at δ 3.20, which was at δ 2.19 in the free pyrrole.[4] The lower field bias of the NMR peaks from the peripheral protons indicates deshielding with respect to the magnetic effects owing to electron delocalization over the macrocycle. The NMR results and Soret-like band in Figure 1 support the aromaticity of compound **5**.

Single-Crystal Structure. The molecular structure for compound **5** was proved with the single-crystal X-ray diffraction study (Figure 3). The structure confirms formation of the direct pyrrole–pyrrole link and incorporation of a pyridine unit, as suggested by NMR. The mean-plane deviation of the core $C_{20}N_4$ atoms was only ±0.032 Å, indicating that they were essentially coplanar. The central nickel atom was seated within the coordination hole, and the displacement from the N_4 plane was only 0.002 Å. The direct pyrrole–pyrrole bond length of 1.395 Å, an intermediate of those for normal carbon–carbon single (1.54 Å) and double (1.35 Å) bonds,[5] was consistent with the presence of 18π-electron circuit. The three Ni–N(pyrrole) bonds were 1.875, 1.851, and 1.794 Å, and the Ni–N(pyridine) distance was 1.975 Å (Figure 4). The harmonic oscillator model of aromaticity value has been calculated to be 0.745, indicating that it possesses a well-defined macrocycle.[6] The average Ni–N distance (1.873 Å) in complex **5** was shorter than 1.958 Å in nickel(II) porphyrin[7] and close to 1.846 Å in nickel(II) corrole.[8] The two N(pyridine)–Ni–N(pyrrole) bond angles (97.4° and 93.2°) of the nickel(II) compound **5** were larger than the other two N(pyrrole)–Ni–N(pyrrole) angles (88.1° and 81.3°). The bulky pyridine and bipyrrole accordingly deformed the coordination core into an irregular rhombus. The N_4 cavity area of 7.00 Å^2 in compound **5** was smaller than 7.51 Å^2 in nickel porphyrin[7] and comparable with 6.78 Å^2 in nickel corrole.[8]

DISCUSSION

Formation and Acid Stability of Nickel(II) Pyricorrole. At the final stage of the synthesis of compound **5**, we used nickel(II) acetate as the cyclization agent (Scheme 1). The reaction proceeded only with the nickel salt; attempts with other salts of copper(II), manganese(II), chromium(II), or cobalt(II) were unsuccessful. The ability of nickel(II) ion may arise from the tendency to form a square planar complex in the four-coordination state, while other ions are apt to form tetrahedral complexes.[9] The free two α-carbons at the terminals in precursor **4** could be set close to each other in a square-planar nickel(II) intermediate to accomplish cyclization.

Although nickel(II) ion was essential for ring closure, it brought forth a problem. The attempted demetalation and transmetalation of compound **5** totally failed. Overnight mixing of compound **5** with sulfuric acid at 50 °C caused no demetalation. Reductive demetalation with sulfuric acid and iron powder was also unsuccessful. Heating with sulfuric acid at 120 °C resulted in extensive decomposition. Boiling of **5** in dimethylformamide in the presence of excess zinc(II), cobalt(II), or copper(II) salts did not cause the transmetalation. It is well established that the stable

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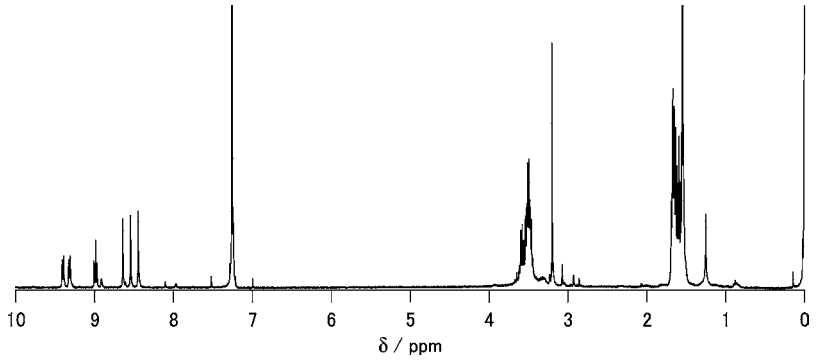

Figure 2. Proton NMR spectrum of compound **5** at 400 MHz in $CDCl_3$.

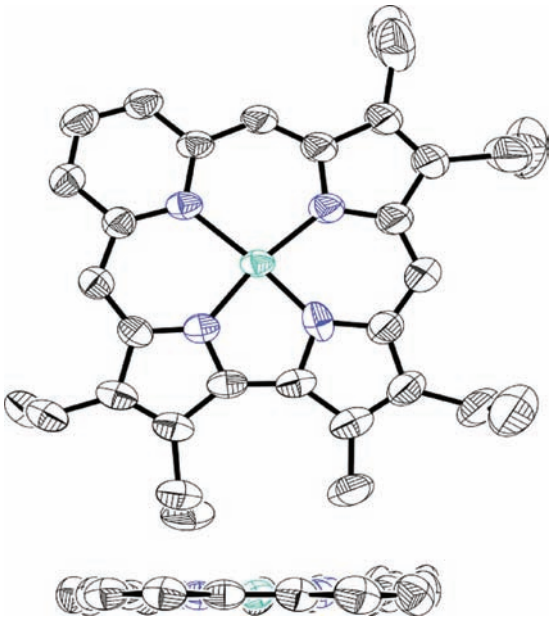

Figure 3. Crystal structure of compound **5** with 50% probability thermal ellipsoids. Upper, top view; lower, side view without the side chains. Hydrogen atoms are omitted for clarity.

nickel(II) ion in porphyrin is removed only with sulfuric acid after a prolonged treatment.[10] The resistance of **5** against demetalation may be explained in terms of the structure as well as the intrinsic stability of nickel(II) ion. X-ray analysis shows that the metal cavity is narrower and the Ni−N(pyrrole) bonds are shorter as compared with nickel(II) porphyrin (Figure 4). Thus, removal of the nickel(II) ion, firmly trapped in the pyricorrole cavity, was very difficult.

Rearrangement of the π-Conjugation Pathway. Although the free base pyricorrole is not available at present, nickel(II) pyricorrole **5** yet provides the opportunity to have insight into the aromaticity of porphyrinoid. Berlin and Breitmaier initially attempted pyridine incorporation into the porphyrin ring to perturb the π-electron conjugation system.[11] They oxidized a nonaromatic precursor dihydropyriporphyrin to prepare pyridine-containing porphyrin. However, unexpected products, dimeric porphyrin and pyriporphyrinone, were obtained. Successful pyriporphyrin synthesis was accomplished by Lash[12] and Latos-Grażyński.[13] Pyriporphyrin, however, was nonaromatic and unstable because insertion of an extra carbon into the porphyrin macrocycle broke the aromatic electron conjugation pathway. Pyriporphyrin was only stable provided that aryl groups were attached to the *meso*-bridges.[12,13] Lash and Chaney subsequently reported that pyriporphyrin without the *meso*-phenyl groups was stabilized when 3-hydroxypyridine, rather than pyridine, was present.[14] The keto−enol tautomerization in the 3-hydroxypyridine moiety allowed development of an 18π-electron circle. Contrary to pyriporphyrin and oxypyriporphyrin,[11−14] pyricorrole in the present report is stable enough, although it has an intact pyridine subunit. The stability of pyricorrole is primarily due to the same number of ring constituting $C_{20}N_4$ atoms as porphyrin. Under this circumstance, the 18π-electron circuit is readily developed in both porphyrin and pyricorrole. It is notable in the pyridine-involved π-conjugation pathway in Figure 4 that the pyridine has only 4π electrons. Loss of the local aromaticity in the pyridine moiety is likely to be compensated with the entire aromaticity by 18π electrons developed over the macrocycle.

Comparison with Porphyrin and Corrole. A notable feature of the pyricorrole core is the narrow coordination cavity after deletion of one *meso*-carbon (Figure 3). In this aspect, pyricorrole is closely related to corrole. However, pyricorrole exhibits similarity to porphyrin as well. As shown in Figure 4, pyricorrole is a divalent ligand like porphyrin and in contrast with trivalent corrole.[8] Another similarity of pyricorrole to porphyrin is available from NMR. It is important to note that the NMR spectrum of nickel complex **5** in Figure 2 exhibits sharp signals. The observation indicates that nickel(II) pyricorrole is diamagnetic, in agreement with nickel(II) porphyrin, while nickel(II) corrole is paramagnetic.[2,8]

Pyricorrole is structurally analogous to corrole where one *meso*-carbon is missing. However, the macrocycle still resembles porphyrin in that it is a divalent metal ligand and forms a diamagnetic nickel(II) complex. Pyricorrole accordingly looks like both porphyrin and corrole. The intermediary character of pyricorrole arises from the *meso*-carbon transfer into the pyrrole moiety, which is a milder structural rearrangement than the *meso*-carbon removal as found in corrole. The presence of many pyridine compounds reminds us of the derivatization of pyricorrole through the pyridine moiety. Preparation of the modified products is ongoing in our laboratory.

■ EXPERIMENTAL SECTION

Physical Measurements. *Spectroscopy.* Proton NMR spectra were recorded with a JEOL α400 (400 MHz) or ECA600 (600 MHz) instrument in the indicated solvent. The chemical shifts were referenced against internal tetramethylsilane. UV−vis spectra were obtained on a Shimadzu MPS-2000 spectrophotometer. Mass spectra were recorded on a JEOL Accu-TOF (time-of-flight) for compounds **1**−**4** using positive- and negative-mode ESI (electronspray ionization)-TOF

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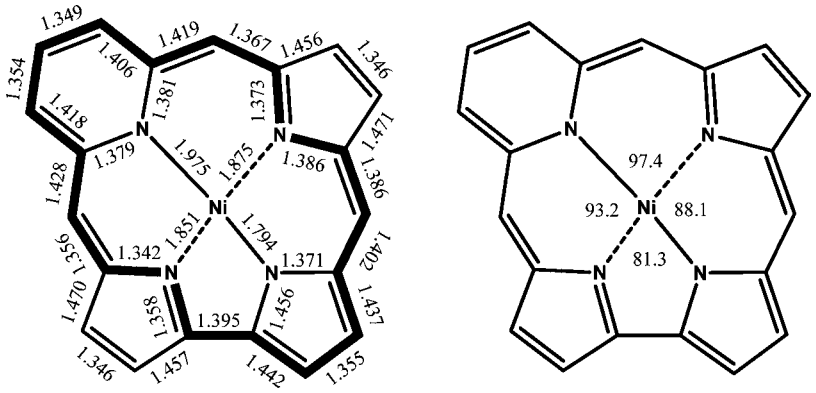

Figure 4. Molecular geometry of the core in compound **5**. Numerals are the bond lengths in Angstroms (left) and bond angles in degrees (right).

methods and Thermo Fischer Exactive for **5** using the positive-mode ESI-TOF method.

X-ray Analysis of Single Crystals. Data for single-crystal X-ray diffraction analyses were collected on a Bruker SMART APEXII CCD diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). Data collection and reduction were performed using *SMART* and *SAINT*, respectively. Structures for crystallography were solved by direct methods using *SHELXL97*[15] and refined using *SHELXL97* with the *Yadokari-XG* program.[16]

Sample Preparation. *Compound 1.* Pyridine-2,6-dicarbonyl dichloride (2.04 g, 10 mmol, Aldrich) was dissolved in 100 mL of dichloromethane, and aluminum chloride (3.18 g) was added. Methyl 3,4-diethylpyrrole-2-carboxylate (3.90 g, 20 mmol)[17] was combined to the solution before being refluxed overnight under vigorous stirring. The cooled mixture was diluted with chloroform (30 mL) and washed with aqueous sodium bicarbonate until neutral and then with water. The organic layer was evaporated to dryness, and the residue was dissolved in a minimum amount of hot chloroform. An equal volume of hot methanol was added, and the solution was placed on an ice bath. The crystalline product of **1** was collected after filtration and dried (3.36 g, 82%). Analytical sample was crystallized from chloroform/hexane. ESI-TOF MS (positive mode) (% intensity): $C_{27}H_{32}N_3O_6$ ($[M + H]^+$) calcd 494.22, found 494.25 (10%); $C_{27}H_{31}N_3NaO_6$ ($[M + Na]^+$) calcd 516.21, found, 516.23 (100%) (Figure S1, Supporting Information). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.19 (t, 6H, 2 $-CH_2CH_3$), 1.24 (t, 6H, 2 $-CH_2CH_3$), 2.82 (q, 4H, 2 $-CH_2CH_3$), 2.95 (q, 4H, 2 $-CH_2CH_3$), 3.52 (s, 6H, 2 -OCH_3), 8.21 (t, 1H, pyridine), 8.44 (d, 2H, pyridine), 11.25 (br s, 2H, NH) (Figure S2, Supporting Information).

Compound 2. A saturating amount of dry hydrogen chloride was bubbled into the methanol (70 mL) containing compound **1** (2.47 g, 5.00 mmol) and zinc powder (2.0 g, 30.6 mmol). The mixture was stirred overnight. The solution was diluted with chloroform (100 mL), and insoluble materials were filtered off. The organic layer was washed with aqueous sodium hydrogen carbonate until neutral and evaporated to dryness. The residue was dissolved in a minimum volume of hot chloroform and diluted with 2 vol of hot methanol. Water (10%, v/v) was added to the hot solution, and the mixture was placed on an ice bath. Solid compound **2** formed was collected by filtration and dried under vacuum (1.83 g, 74%). ESI-TOF MS (positive mode) (% intensity): $C_{27}H_{35}N_3NaO_4$ ($[M + Na]^+$) calcd 488.25, found 488.27 (100%) (Figure S3, Supporting Information). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.08 (t, 6H, 2 $-CH_2CH_3$), 1.16 (t, 6H, 2 $-CH_2CH_3$), 2.47 (q, 4H, 2 $-CH_2CH_3$), 2.74 (q, 4H, 2 $-CH_2CH_3$), 3.80 (s, 6H, 2 -OCH_3), 4.07 (s, 4H, *meso*-H), 6.96 (d, 2H, pyridine), 7.52 (t, 1H, pyridine), 9.38 (br s, 2H, NH) (Figure S4, Supporting Information).

Compound 3. Compound **2** (1.00 g, 2.15 mmol) was dissolved in a mixture of methanol (10 mL) and tetrahydrofuran (10 mL). Aqueous sodium hydroxide (0.64 g/10 mL) was added dropwise to the refluxing mixture over 30 min, and the solution was further refluxed overnight. The cooled solution was poured into cold water, and acetic acid was added to precipitate compound **3**. The diacid **3** was dried under vacuum (0.86 g, 92%). ESI-TOF MS (negative mode) (% intensity): $C_{23}H_{30}N_3$ ($[M - 2CO_2 - H]^-$) calcd 348.24, found 348.26 (25%); $C_{24}H_{30}N_3O_2$ ($[M - CO_2 - H]^-$) calcd 392.23, found 392.25 (100%); $C_{25}H_{30}N_3O_4$ ($[M - H]^-$) calcd 436.22, found 436.24 (20%) (Figure S5, Supporting Information). ^{1}H NMR (400 MHz, $CDCl_3$ + trace triethylamine, δ): 0.89 (t, 6H, 2 $-CH_2CH_3$), 1.03 (t, 6H, 2 $-CH_2CH_3$), 2.31 (q, 4H, 2 $-CH_2CH_3$), 2.63 (q, 4H, 2 $-CH_2CH_3$), 3.95 (s, 4H, *meso*-H), 6.96 (m, 2H, pyridine), 7.53 (t, 1H, pyridine), 10.73 (br s, 2H, NH) (Figure S6, Supporting Information).

Compound 4. Diacid **3** (200 mg, 0.457 mmol) was decarboxylated with trifluoroacetic acid (0.10 mL). After addition of *tert*-butyl 5-acetoxymethyl-3,4-diethylpyrrole-2-carboxylate[18] (129 mg, 0.459 mmol) in 2.0 mL of methanol (20 mL), the mixture was stirred overnight at room temperature. A small amount of aqueous sodium hydroxide was added to neutralize the solution cooled on an ice bath. The resultant off-white precipitates of compound **4** were collected by filtration and dried at room temperature (214 mg, 82%). ESI-TOF HRMS (positive mode) (% intensity): $C_{36}H_{51}N_4O_2$ ($[M + H]^+$) calcd 571.40, found 571.42 (100%) (Figure S7, Supporting Information). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 1.05 (m, 15H, 5 $-CH_2CH_3$), 1.54 (s, 9H, $-CO_2C(CH_3)_3$), 2.27 (s, 3H, ring $-CH_3$), 2.43 (m, 10H, 5 $-CH_2CH_3$), 3.82 (s, 2H, *meso*-H), 4.39 (s, 2H, *meso*-H), 4.48 (s, 2H, *meso*-H), 6.49 (s, 1H, pyrrole αH), 7.41 (d + d, 2H, pyridine), 8.08 (t, 1H, pyridine), 8.57 (br s, 1H, NH), 10.17 (br s, 1H, NH), 10.21(br s, 1H, NH) (Figure S8, Supporting Information).

Nickel(II) Pyricorrole 5. The terminal ester group of compound **4** (100 mg, 0.185 mmol) was deleted with trifluoroacetic acid (0.5 mL) at room temperature before neutralization with potassium bicarbonate (30 mg). The mixture was diluted with *N,N*-dimethylformamide (30 mL), and nickel(II) acetate tetrahydrate (700 mg, 2.81 mmol) was added. The solution was refluxed over 60 min to induce cyclization. The cooled solution was evaporated to dryness under reduced pressure, and the residue was purified with silica-gel column chromatography with chloroform. The fast-running green band was collected, dried, and recrystallized from hexane/chloroform to afford dark green microcrystals of **5** (5.3 mg, 6.0%). UV–vis ($CHCl_3$) λ (nm) (ε, mM^{-1} cm^{-1}); 267 (59.1), 325 (86.8), 399 (162), 85 (36.7), 667 (21.3), 727 (40.9). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.19 (t, 6H, 2 $-CH_2CH_3$), 1.24 (t, 6H, 2 $-CH_2CH_3$), 2.82 (q, 4H, 2 $-CH_2CH_3$), 2.95 (q, 4H, 2 $-CH_2CH_3$), 3.52 (s, 6H, 2 $-OCH_3$), 8.45, 8.54, 8.64 (s, each, 1H, *meso*-H), 8.99 (t, 1H, pyridine), 9.31, 9.45 (d, each 1H, pyridine). The UV–vis and proton NMR spectra are provided in Figures 1 and 2. ESI-TOF HRMS (positive mode) (% intensity): $C_{31}H_{35}N_4Ni$ ($[M + H]^+$) calcd 520.2131, found 520.2128 (100%) (Figure S9, Supporting Information). Crystal data: $C_{31}H_{34}N_4Ni$ = 521, monoclinic, space group C_2/c (No. 33), a = 26.683(2) Å, b = 14.4557(12) Å, c = 14.2249(10) Å, α = 90°, β = 108.0600(10)°, γ = 90°, V = 5108.2(7) Å^3, Z = 8, D_{calcd} = 1.356 g/cm^3, T = −100 °C, R_1 = 0.0739 ($I > 2\sigma(I)$), wR_2 = 0.2185 (all data), GOF = 1.077, CCDC-855249.

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■ ASSOCIATED CONTENT

Supporting Information

Proton NMR and mass spectra of compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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