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Synthesis of Free-Base 10-Azacorroles

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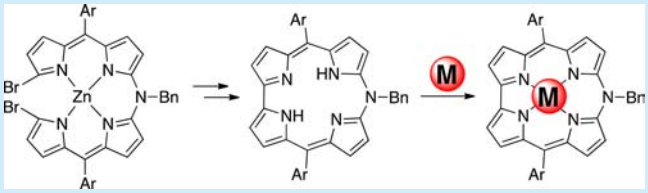
Supporting Information

ABSTRACT: A novel synthetic protocol has been developed for free-base 10-azacorroles. Ni(0)-mediated homocoupling of nitrogen-bridged bisdipyrrin Zn(II) complexes afforded a series of free-base 5,15-diaryl-10-azacorroles in good yields. Pd(II) and Cu(II) complexes have been prepared through metalation of free-base 10-azacorroles. Optical and electrochemical properties of 10-azacorrole metal complexes can be tuned by *meso*-aryl substituents and central metals. Cyclic voltammetry and theoretical calculations elucidated that the central metals of 10-azacorroles significantly affected their electronic properties.



Introduction of metals into the central cavity of porphyrins has been a useful method for fine-tuning of their optical and electrochemical properties. In addition, porphyrin metal complexes have been applied to a wide range of chemical research efforts in areas such as supramolecular chemistry, photosynthesis, catalysts, and so forth.[1,2] Such metal complexes have been usually prepared from their corresponding free-base porphyrins by treatment with various metal sources. Thus, the effective synthesis of free-base porphyrin derivatives is a key issue to expand their chemistry by metal coordination.

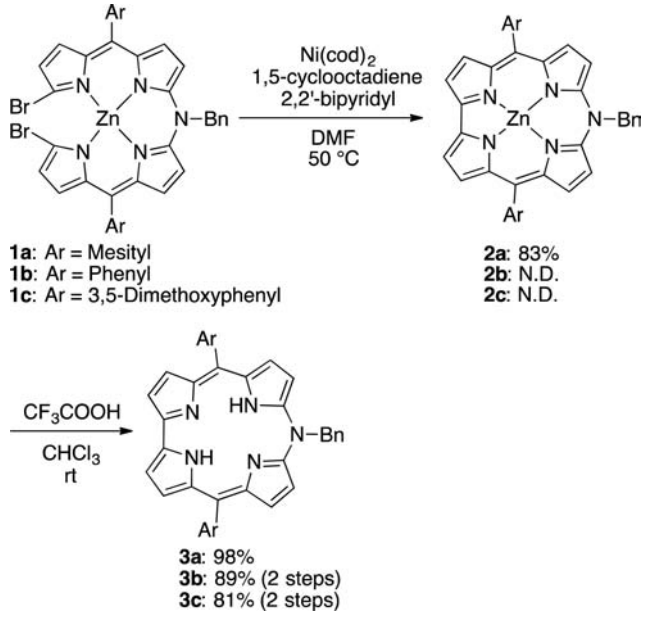
Corroles are a porphyrin analogue with one direct pyrrole–pyrrole linkage.[3,4] Recently, several research groups have developed the synthesis of heterocorroles, namely, corroles containing heteroatoms on their aromatic conjugation circuit.[5] In particular, installation of heteroatoms at the *meso*-positions dramatically changes its electronic structure. For example, Goldberg and co-workers have developed the chemistry of corrolazine, which has three nitrogen atoms at the *meso*-positions.[6,7] They accomplished the synthesis of free-base corrolazine through removal of phosphorus(V) from a corrolazine cavity under reductive conditions.[8] Corrolazine stabilizes high oxidation states of the central metals, enabling isolation of reactive intermediate in mimicking of biological oxidation system. Bröring and co-workers reported the synthesis of free-base *β*-alkyl-type 10-oxa-, 10-thia-, and 10-selenacorroles by reduction of their corresponding copper(II) complexes.[9,10]

Our group independently developed the synthetic protocols for *meso*-aryl-substituted 10-aza-, 10-oxa-, and 10-thiacorroles.[11] However, the central metals of these *meso*-aryl-10-heterocorroles have been limited to Ni(II) and Al(III) complexes, and preparation of free-base 10-heterocorroles has remained unsuccessful. Removal of Ni(II) and Al(III) proved to be difficult by known demetalation procedures such as treatment with H_2SO_4 or Grignard reagents.[12]

Here, we disclose a novel protocol to prepare free-base 10-azacorroles from nitrogen bridged bisdipyrrin Zn(II) complexes. This protocol efficiently provides a series of *meso*-aryl substituted 10-azacorroles. In addition, divalent metal complexes such as Zn(II), Cu(II), and Pd(II) have been successfully synthesized.

We prepared nitrogen-bridged bisdipyrrin Zn(II) complex **1a** according to the previous report. Cyclization of **1a** was accomplished under Yamamoto homocoupling conditions with $Ni(cod)_2$, 1,5-cyclooctadiene, and 2,2′-bipyridyl to produce Zn(II) 10-azacorrole **2a** in 83% yield (Scheme 1).[13]

Scheme 1. Preparation of Zn(II) 10-Azacorroles and Their Demetalation



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The formation of the 10-azacorrole skeleton was confirmed by the ^{1}H NMR spectrum of **2a**, which exhibited four doublet peaks of β-protons in the aromatic region. Finally, the structure of **2a** was unambiguously elucidated by X-ray diffraction analysis. Parts a and b of Figure 1 show the crystal structures of

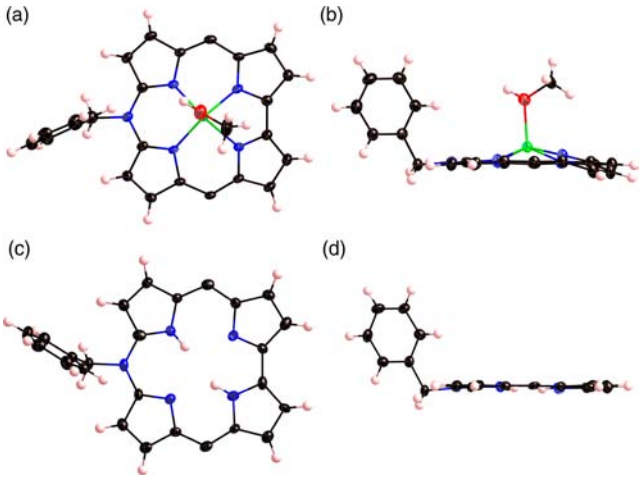


Figure 1. X-ray crystal structures of Zn(II)- and free-base 10-azacorroles. (a) Top view and (b) side view of **2a**. (c) Top view and (d) side view of **3a**. Mesityl substituents are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.

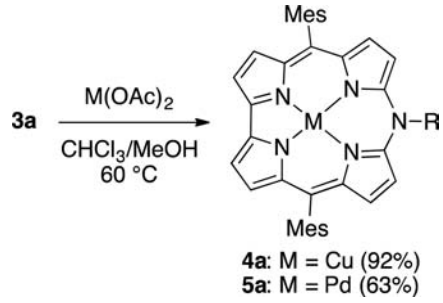
2a, in which one of pyrrole rings is tilted. In the crystal, the central Zn(II) metal was ligated by methanol, forming a pentacoordinate structure. The mean plane deviation was 0.088 Å, which is larger than the corresponding Ni(II) complex (0.020 Å). Such displacement is due to pentacoordinated conformation and the larger size of Zn(II) metal, which is located out of the mean plane.

Zn(II) metal in **2a** was easily removed by treatment with trifluoroacetic acid (TFA), producing the corresponding free-base 10-azacorrole **3a** in almost quantitative yield. The ^{1}H NMR spectrum of **3a** exhibited symmetric features, and inner NH protons of **3a** appeared at 5.23 ppm. The larger downfield shift of the NH proton as compared with free-base porphyrins would reflect the lower aromaticity of **3a**. This trend was also observed in other 10-heterocorroles.[10a] The highly planar structure of **3a** was revealed by X-ray diffraction analysis (Figure 1c,d). The position of inner NH protons could not be determined. However, the planar structure of **3a** indicates the existence of two NH protons in the central cavity because inner three NH protons should induce distortion as is observed in corroles. This was also supported by the ^{1}H NMR spectrum of **3a**, showing two integrated peak at 5.2 ppm, which could be assigned as inner NH protons.

On the basis of the present cyclization procedure, we prepared 10-azacorroles with various *meso*-aryl substituents. In the case of *meso*-phenyl and 3,5-dimethoxyphenyl groups, demetalation of Zn(II) metal complexes **2b** and **2c** proceeded during silica gel purification to furnish free-base azacorroles **3b** and **3c** directly in 89% and 81% yield, respectively.

With free-base **3a** in hand, we introduced various metals into its central cavity. Treatment of **3a** with $Cu(OAc)_2 \cdot H_2O$ gave Cu(II) complex **4a** in 92% yield. Pd(II) complex **5a** was obtained in 63% yield in the reaction with $Pd(OAc)_2$ (Scheme 2). The insertion of these metals was confirmed by high-resolution mass spectral analysis. The parent mass ion peaks of

Scheme 2. Metalation of Bisdipyrrins 2a and 2b with Cu(II) and Pd(II) ions



4a and **5a** were observed at m/z = 687.2403 (calcd for $(C_{43}H_{38}N_5Cu)^+$ = 687.2418) and m/z = 730.2160 (calcd for $(C_{43}H_{38}N_5Pd)^+$ = 730.2172). The structure of **5a** was elucidated by X-ray diffraction analysis (Figure 2), showing

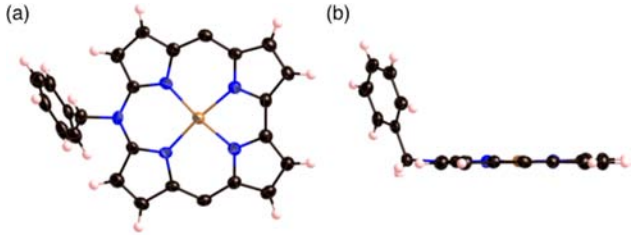


Figure 2. X-ray crystal structure of **5a**. (a) Top view and (b) side view. *meso*-Mesityl groups are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.

its highly planar conformation. The mean plane deviation of **5a** was 0.024 Å. The N–Pd bond lengths were 1.92 and 1.93 Å. These values are shorter than those of typical Pd(II) porphyrins (2.03 Å), reflecting smaller cavity of 10-azacorroles than those of porphyrins.[14]

Figure 3a shows UV/vis absorption and emission spectra of **3a**, **3b**, and **3c** in CH_2Cl_2. Compared with **3a**, **3b** and **3c** exhibited red-shifted Soret and Q bands, indicating the presence of electronic interaction between the azacorrole core and the *meso*-aryl group except in the case of **3a**. This is due to the more flexible conformation of other substituents than the mesityl group in **3a**. This tendency was also confirmed by electrochemical analysis. Cyclic voltammetry of **3a**, **3b**, and **3c** was performed in THF (Figure S21). The results are summarized in Table 1. Both the first oxidation potential and the first reduction potential of **3b** were decreased in comparison to **3a**, resulting in the small HOMO–LUMO gap. This result is in good agreement with the result of optical analysis. The fluorescent quantum yields of these azacorroles were almost identical (0.12 for **3a**, 0.088 for **3b**, and 0.10 for **3c**), indicating that the *meso*-aryl group does not significantly affect the excited-state dynamics.

Figure 3b illustrates UV/vis absorption and emission spectra of **2a**, **3a**, and **5a** in CH_2Cl_2. Zinc(II) complex **2a** exhibited a red-shifted but similar shaped spectrum as compared with **3a**. Zinc(II) complex **2a** and free-base **3a** showed red emission. The fluorescence quantum yields of **2a** and **3a** were 0.11 and 0.026, respectively. These features are similar to those of porphyrins. On the other hand, **5a** exhibited broad and split Soret-band as well as bathochromically shifted Q bands. Table 1 shows the result of electrochemical measurement of

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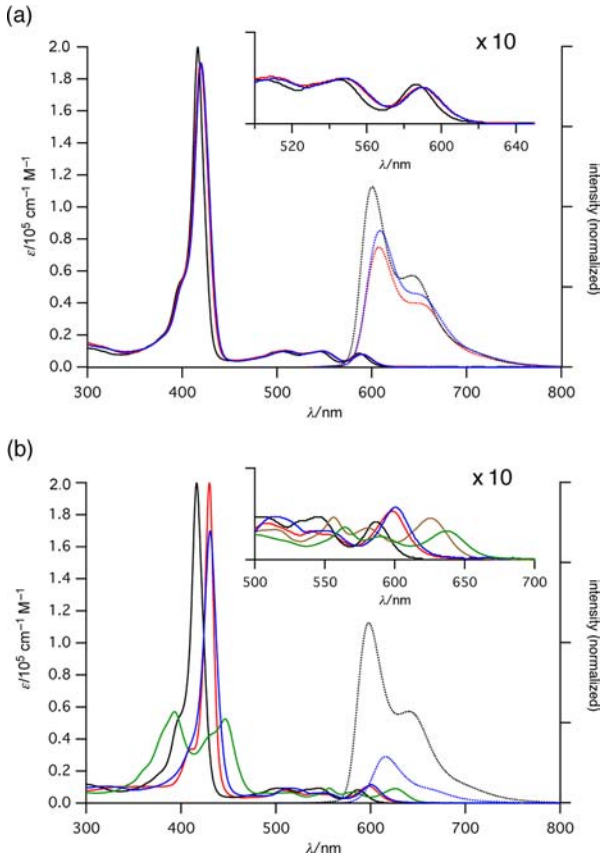

Figure 3. UV/vis absorption (solid line) and emission (dotted line) spectra of (a) **3a** (black), **3b** (red), and **3c** (blue) and (b) **2a** (blue), **3a** (black), **4a** (red), and **5a** (green) in CH_2Cl_2.

Table 1. Summary of Electrochemical Data[a,b]

compd	E_{red}^2 (V)	E_{red}^1 (V)	E_{ox}^1 (V)	E_{ox}^2 (V)	ΔE^c (V)
3a	−2.40	−2.01	0.357	0.697	2.37
3b		−1.87	0.327	0.689	2.20
3c	−2.23	−1.87	0.347	0.687	2.22
2a		−2.19	0.077	0.412	2.27
5a	−2.39	−1.94	0.360	0.716	2.30

[a]Potentials are shown versus ferrocene/ferrocenium couple. [b]Determined by differential pulse voltammetry. [c]$\Delta E = E_{ox}^1 - E_{red}^1$.

azacorroles **2a**, **3a**, and **5a** (Figure S22). As observed in the case of porphyrins, Zn(II) metalation lowered the first oxidation potential in comparison to the free base.

The different absorption features between **2a** and **5a** were further investigated by theoretical calculations. The absorption spectra of **2a** and **5a** were simulated by the time-dependent (TD) DFT method at the CAM-B3LYP/6-31G+LanL2DZ level (Figure S24). According to the calculations, two intense bands of **5a** at 393 and 447 nm could be assigned as transitions from HOMO−1 to LUMO and HOMO−3 to LUMO. On the other hand, the sharp Soret band of **2a** at 431 nm could be attributed to transitions from HOMO−1 to LUMO and from HOMO to LUMO+1. As reported previously, the low symmetry of 10-azacorroles resulted in the contribution of the HOMO−3 to LUMO transition into Soret and Q-bands. In fact, HOMO−3 of **5a** contains significant contribution of d orbitals on the central Pd metal to π-orbitals of azacorrole skeleton (Figure S23). Consequently, the transitions from these orbitals to LUMO become allowed to broaden the spectrum. This feature is not observed for normal porphyrins. Although the divalent nature and emission properties of 10-azacorroles are almost identical with those of porphyrin analogues, the different effects of central metals to the absorption properties highlight the specific feature of 10-azacorroles.

In summary, we have achieved an efficient synthesis of free-base 10-azacorroles with various *meso*-aryl substituents. This is the first synthesis of free-base *meso*-aryl-substituted 10-heterocorroles. Pd(II) and Cu(II) metal ions were inserted into the central cavity of 10-azacorroles. The structures of free-base, Zn(II), and Pd(II) 10-azacorroles were clearly elucidated by X-ray diffraction analysis. Cyclic voltammetry and theoretical calculations revealed the specific effect of central metals on optical properties of 10-azacorroles. These results expand the utility of 10-azacorroles in various applications. Further investigations on optical properties dependent on substituents are underway in our group.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, compound data, CIF files, and copies of NMR spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01323.

Experimental details, compound data, and copies of NMR spectra (PDF)
X-ray crystallographic data for **2a** (CIF)
X-ray crystallographic data for **3a** (CIF)
X-ray crystallographic data for **5a** (CIF)

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Notes

The authors declare no competing financial interest.

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