

10-Silacorroles Exhibiting NIR Absorption and Emission

Hiroto Omori, Satoru Hiroto,* and Hiroshi Shinokubo*^[a]

Abstract: 10-Silacorroles were obtained from the Pd-catalyzed silylative cyclization of a bis(α,α' -dibromodipyrryn) Ni^{II} precursor with dihydrosilanes. These 10-silacorroles show substantially red-shifted absorption bands relative to those of normal porphyrins and isocorroles. Notably, the corresponding free-base and Zn^{II} 10-silacorroles exhibit emissions in the NIR region. Theoretical calculations on these 10-silacorroles revealed the presence of $\sigma^*-\pi^*$ conjugation between the silyl group and the tetrapyrrole π -system, which significantly lowers their LUMO energy levels.

Silicon-containing π -conjugated molecules such as siloles, have attracted much attention as novel organic optoelectronic materials.^[1-3] The introduction of silicon into the π -conjugation system induces a substantial reduction of the HOMO–LUMO gap by lowering the LUMO energy level due to incorporation of the σ^* orbital of a Si–C bond to the π^* orbital ($\sigma^*-\pi^*$ conjugation). In addition, the rigid nature of the Si-bridged π -systems decelerates the non-radiative decay of the singlet-excited state, thus enhancing the emission properties.^[4]

Porphyrinoids are macrocyclic compounds with porphyrin-like oligopyrrole skeletons.^[5] The properties of porphyrinoids are affected substantially by the nature of their skeleton and other structural factors. In particular, the direct inclusion of heteroatoms into their π -conjugation circuit induces a dramatic change of their electronic structures.^[6] Recently, Bröring and co-workers, as well as our group, have independently explored the chemistry of 10-heterocorroles, which contain elements from groups 15 and 16, e.g. nitrogen, oxygen, sulfur, and selenium (Figure 1).^[7,8] However, the synthesis of 10-heterocorroles containing elements from group 14 has not yet been accomplished, except for isocorrole.^[9] Due to the aforementioned beneficial features of incorporating silicon in π -conjugated systems, 10-silacorroles should represent an attractive porphyrinoid target. Herein, we report the first synthesis of 10-silacorroles that exhibit absorption and emission in the near IR (NIR) region of the electronic spectrum. The present study also demonstrates that $\sigma^*-\pi^*$ conjugation is valid for large macrocyclic π -systems such as porphyrinoids. The biocompatibility of the porphyrin skeleton renders porphyrin-based NIR dyes promising materials for applications in bioimaging and photodynamic therapy.

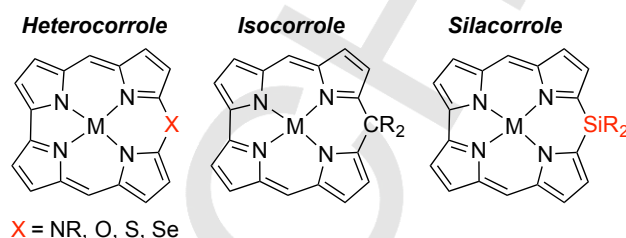


Figure 1. Chemical structures of heterocorroles, isocorrole, and silacorrole.

The synthesis of 10-silacorroles **2a** and **2b** was achieved in one step from bis(α,α' -dibromodipyrryn) Ni^{II} complex **1** via the Pd-catalyzed silylation reported by Yamanoi and Nishihara (Scheme 1).^[10] Treatment of **1** with diethylsilane in the presence of Pd(P(*t*-Bu)₃)₂ and 1,4-diazabicyclo[2.2.2]octane (DABCO) induced a twofold silylation under concomitant formation of a C–C bond, providing **2a** in 22% yield. The use of diphenylsilane afforded **2b** in 20% yield. The formation of **2a** was confirmed by ¹H NMR spectroscopy and mass spectrometry. The ¹H NMR spectrum of **2a** exhibited four doublet peaks at $\delta = 6.31, 6.25, 6.11,$ and 5.99 ppm for the β -pyrrolic protons, reflecting the non-aromatic nature of **2a**. Eventually, the structure of **2a** was unambiguously determined by single-crystal X-ray diffraction analysis (Figure 2a and 2b). In the crystal, **2a** adopts a highly planar conformation, in which the deviation from the mean plane consisted of 18 carbons and four nitrogen atoms on the macrocycle is 0.050 Å. The silicon atom is slightly displaced with respect to the mean plane (0.15 Å). The C(9)–Si bond length in **2a** [1.849(3) Å] is almost identical to that of siloles (1.86 Å),^[11] while the C(9)–Si–C(10) angle [107.63(14)°] is wider than that of hexaphenylsilole (93.2°). Similar features were observed in **2b** (Figure 2c and 2d), even though the displacement of the silicon atom from the macrocycle plane is slightly larger (0.41 Å) than that in **2a**.

We then examined the demetalation of **2a** and **2b**. Free-base 10-silacorroles **3a** and **3b** were obtained by the treatment of **2a** and **2b** with *p*-tolylmagnesium bromide in toluene, followed by the addition of aqueous HCl.^[12] In the ¹H NMR spectrum, the inner N-bound protons of **3a** appeared at $\delta = 15.1$ ppm, which is downfield-shifted compared to those of isocorrole ($\delta = 13.6$ ppm).^[9c] The structures of **3a** and **3b** were also determined by single-crystal X-ray diffraction analyses (Figure 2 and Figure S13).^[13] The free-base silacorroles **3a** and **3b** exhibited highly planar structures, and **3b** exhibited a wider C(9)–Si–C(10) angle [114.77(12)°] than Ni^{II} complex **2b** [107.92(16)°]. This result suggests that the macrocyclic framework in **2a** is contracted upon coordination to Ni^{II}. The distance between N(1) and N(2) in **3b** (2.66 Å) is indicative for the presence of hydrogen bonds within the cavity. This result is consistent with the downfield-shifted signals for the N-bound protons in **3b**.

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Scheme 1. Synthesis of free-base and metal-coordinated 10-silacorroles.

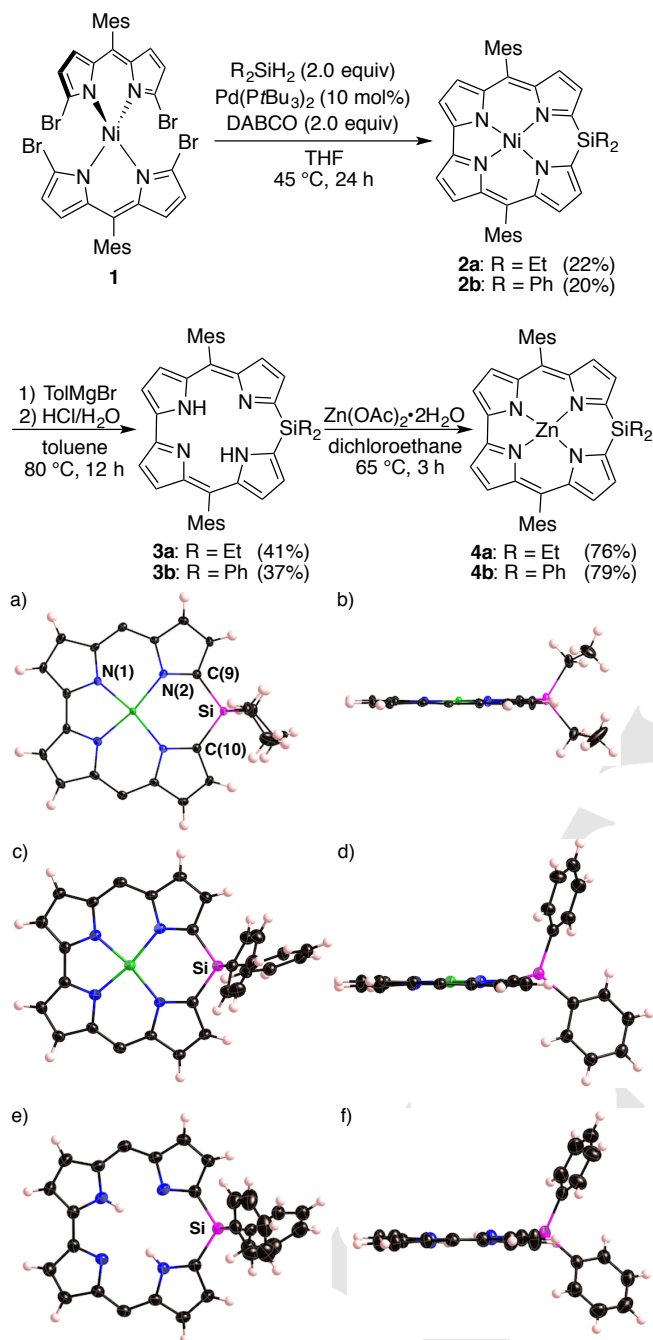


Figure 2. Molecular structures of **2a**, **2b**, and **3b**: a) top and b) side views of **2a**; c) top and d) side views of **2b**; e) top and f) side views of **3b** (atomic displacement parameters set at 50% probability; mesityl groups are omitted for clarity).

Treatment of **3a** and **3b** with zinc acetate in refluxing dichloroethane furnished the corresponding Zn^{II} complexes **4a** and **4b** in good yields (Scheme 1). Figure 3 displays the electronic absorption and emission spectra of **2a**, **3a**, and **4a** in CH₂Cl₂. All silacorroles exhibited Soret-like bands and Q-like

bands. The lowest-energy absorption band of silacorroles depends substantially on the metal ion incorporated. The bands are red-shifted in the order of **3a** < **4a** < **2a**. In particular, the band of **2a** reaches into the NIR region (918 nm). Moreover, the electronic structure of 10-silacorroles can be tuned by the substituents on silicon: phenyl derivatives **2b**, **3b**, and **4b** showed bathochromically shifted absorption bands relative to the corresponding ethyl derivatives (Figure S14).

Free-base and Zn^{II}-coordinated silacorroles in solution showed emissions in the NIR region (Figure 3). For free-base **3a** and Zn^{II}-complex **4a**, fluorescence quantum yields of 0.002 and 0.014 were measured, respectively. NIR emission is known for some expanded porphyrinoids, but the emission wavelengths of **3a** and **4a** are the most red-shifted among previously reported tetrapyrroles. The lower emission efficiency of **3a** compared to **4a** should be attributed to the structural flexibility. The Stokes shift of **4a** ($\Delta\nu = 321 \text{ cm}^{-1}$) is smaller than that of **3a** ($\Delta\nu = 1586 \text{ cm}^{-1}$). The emission lifetimes of **3a** and **4a** were 0.120 and 1.78 ns, respectively (Figure S15 and Table S3). These lifetimes and Stokes shifts clearly indicated that the emission was not phosphorescence but fluorescence.

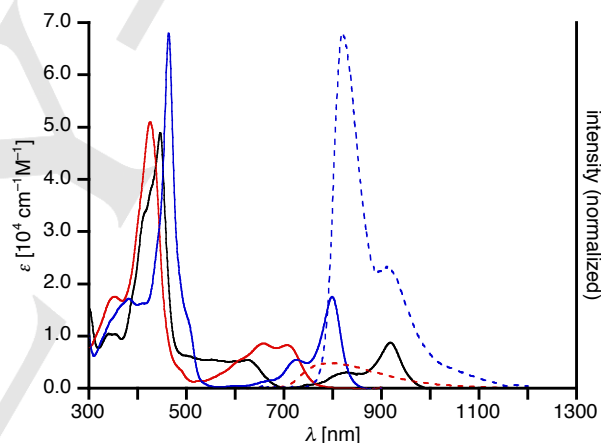


Figure 3. UV/vis/NIR absorption (solid lines) and emission spectra (dashed lines) of **2a** (black), **3a** (red), and **4a** (blue) in CH₂Cl₂.

To obtain insights into the electronic structure of 10-silacorroles, we performed electrochemical analysis by cyclic voltammetry. The oxidation and reduction potentials of **2a**, **3a**, **4a**, **2b**, **3b**, and **4b** were determined in CH₂Cl₂ (Table 1, Figure S16, and Table S4). For **2a**, **3a**, and **4a**, differences between the first oxidation potential and the first reduction potential ($\Delta E = E_{ox}^1 - E_{red}^1$) of 1.63, 1.93, and 1.64 V were observed, respectively. The decrease of ΔE according to **3a** > **4a** \approx **2a** is in good agreement with the results of the optical analyses. Compared to free-base **3a**, metal-coordinated complexes **2a** and **4a** showed a larger deviation regarding their E_{ox}^1 values than their E_{red}^1 values, indicating that the central metal affects the highest occupied molecular orbital (HOMO) more than the lowest unoccupied molecular orbital (LUMO). In comparison to diethyl derivative **2a**, diphenyl derivative **2b** exhibited higher E_{ox}^1 and E_{red}^1 values. The larger difference in E_{red}^1 than in E_{ox}^1 results in smaller ΔE values for the phenyl derivatives compared to the ethyl

derivative. This result is consistent with those obtained from the optical analyses.

Table 1. Oxidation and reduction potentials of **2a**, **3a**, **4a**, **2b**, **3b**, and **4b**.^a

Compound	E_{ox}^1	E_{red}^1	ΔE^b
2a	0.207	-1.42	1.63
3a	0.413	-1.52	1.93
4a	0.104	-1.54	1.64
2b	0.278	-1.33	1.57
3b	0.443	-1.44	1.85
4b	0.155	-1.45	1.61

^aAll potentials vs. the ferrocene/ferrocenium couple; ^b $\Delta E = E_{\text{ox}}^1 - E_{\text{red}}^1$

The analogy between 10-silacorroles and siloles implies that $\sigma^*-\pi^*$ conjugation between the silylene group and the π -system should also lower the LUMO level of 10-silacorroles, as in siloles. In order to determine the effect of the incorporation of silicon on the electronic structure of the 10-silacorrole, DFT calculations were carried out at the B3LYP/6-31G(d)+SDD level of theory, which showed that the LUMO of silacorrole is delocalized over the silicon atom and the adjacent carbon atoms as is the case for silole derivatives (Figure 4b).^[14] This result supports the notion of effective conjugation between the σ^* -orbital of the substituents on the silicon atom and the π^* -orbital of the tetrapyrrolic framework. A subsequent natural bond orbital (NBO) analysis disclosed a relatively large contribution of the σ^* -orbitals of the Si-C bonds to the LUMO (Table S6). In contrast, the LUMO of isocorrole exhibits no orbital overlap on the *meso*-carbon atom (Figure 4d). Moreover, the difference of LUMO levels between silacorroles and isocorroles are distinctly larger than those of HOMO levels (Figure S19). Consequently, the particularly low LUMO energy level observed for the 10-silacorroles should be due to the $\sigma^*-\pi^*$ conjugation. The LUMO of **3b** is partially located on the phenyl group (Figure S17),^[15] which suggests that the electronic structures of 10-silacorroles can be tuned via the substituents on silicon.

To determine the impact of the central metals on the absorption spectra, the metal effect was evaluated by DFT calculations (Figure S18). The relatively small MO coefficients on the metals suggest negligible $d-\pi$ interactions. Accordingly, the major factors contributing to the metal effect should be the inductive effect and the structural rigidification. In fact, the deviation of the C-C bond lengths around the *meso*-positions in the Ni^{II} complexes is smaller than that in the metal-free bases, supporting a more effective π -conjugation in the Ni^{II} complexes (Table S5).

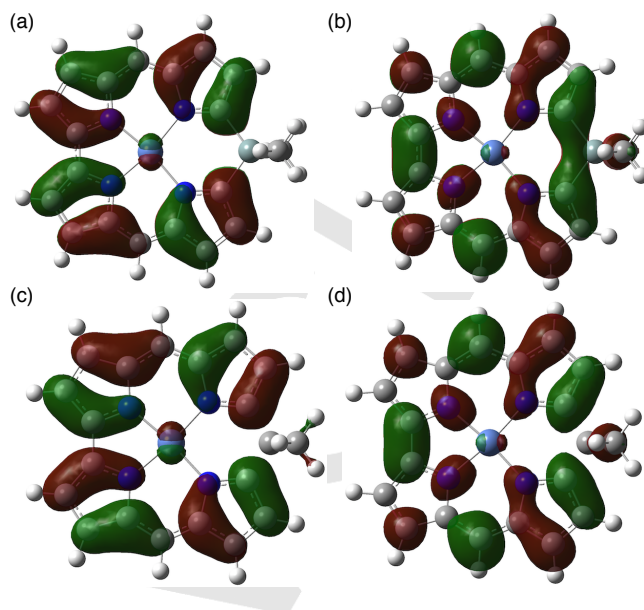


Figure 4. Schematic illustration of (a) HOMO and (b) LUMO of silacorrole Ni^{II} and (c) HOMO and (d) LUMO of isocorrole Ni^{II}. In (a) and (b), ethyl and mesityl groups in **2a** are replaced with methyl groups and hydrogens, respectively.

In conclusion, we have synthesized 10-silacorroles and their Ni^{II} and Zn^{II} complexes. The electrochemical and theoretical analysis revealed the presence of $\sigma^*-\pi^*$ conjugation between the silylene group and the tetrapyrrole system. These 10-silacorroles exhibit porphyrin-like absorption spectra that reach into the NIR region, owing to a significantly decreased LUMO level. The electronic structures of these 10-silacorroles can be tuned via the central metals and the substituents on silicon. The successful incorporation of silicon at the *meso*-position of porphyrin derivatives should thus substantially extend the chemistry of heteroporphyrinoids.

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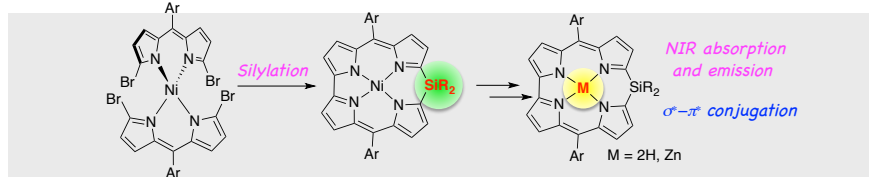
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Keywords: 10-heterocorroles • $\sigma^*-\pi^*$ conjugation • silicon • porphyrinoids • NIR emission

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A new family of heteroporphyrinoid, 10-silacorrole, has been prepared through Pd-catalyzed silylation of a dibromodipyrrole Ni^{II} precursor. 10-Silacorroles exhibited near IR absorption and emission. Theoretical analysis and electrochemical investigation revealed the presence of $\sigma-\pi^*$ conjugation between silicon atom and tetrapyrrolic macrocyclic skeleton.