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Peripherally Silylated Porphyrins

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Abstract: Silylation of peripherally lithiated porphyrins with silyl electrophiles has realized the first synthesis of a series of directly silyl-substituted porphyrins. The meso-silyl group underwent facile protodesilylation whereas the β-silyl group was entirely compatible with usual work-up and purification on silica gel. The meso-silyl group caused larger substituent effects to the porphyrin as compared with the β-silyl group. Silylation of β-lithiated porphyrins with 1,2-dichlorodisilane furnished β-to-β disilane-bridged porphyrin dimers. A doubly β-to-β disilane-bridged NiII-porphyrin dimer was also synthesized from a β/β-dilithiated NiII-porphyrin and characterized by X-ray crystallographic analysis to take a step-like oxidative dimerization of the Grignard species, because of the protonation instead occurred after hydrolysis, as well as quantum yields, thereby having been extensively investigated.[6,7] Despite their potential, there are no reports on porphyrinyl metal species with electrophilic reactions of these porphyrinyl metal species with electrophilic silylating reagents.

Porphyrrins are an important class of compounds playing a wide range of vital roles in living systems. Their attractive optical, electrochemical and biological properties have led to applications in various fields, such as materials science, biochemistry and catalysis.[1] Peripheral introductions of functional groups onto porphyrins can cause electronic perturbations of porphyrins and thus represent an effective means to modify the electronic properties and steric environments of porphyrins.[2] Silyl groups attached peripherally to a π-conjugated system have been demonstrated to interact with the π-system through π-π and σ*-π* conjugation.[3-5] Peripheral silylation of arenes generally gives rise to modifications of the optical and electronic properties of the parent arenes such as improved fluorescent quantum yields, thereby having been extensively investigated.[6,7] Despite their potential, there are no reports on peripherally silylated porphyrins,[8] because of the lack of suitable synthetic protocols to introduce a silyl group at porphyrin. We recently developed methods to generate highly reactive porphyrinyl Grignard[9] and lithium[10] reagents via halogen-metal exchange reactions. We disclose herein the first synthesis of peripherally silylated porphyrins through the reactions of these porphyrinyl metal species with electrophilic silylating reagents.

Our initial attempts to obtain Ni(II) meso-trimethylsilylporphyrin 2Ni by the reaction of meso-magnesiated porphyrin with trimethylsilyl cyanide[11] resulted in failure. Protonation instead occurred after hydrolysis, as well as oxidative dimerization of the Grignard species, because of the low nucleophilicity of the sterically demanding magnesium reagent.[9] We then turned our attention to more nucleophilic porphyrinyl lithium reagents.[10] Treatment of meso-iodoporphyrin with nBuLi at −98 °C followed by an addition of trimethylsilyl cyanide yielded desired 2Ni (Scheme 1, conditions a). Although the reaction was efficient (ca. 70% NMR yield), facile protodesilylation of 2Ni proceeded during purification on silica gel to isolate 2Ni in only 18% yield, along with the formation of the protonated product.[12,13] The instability of 2Ni may be ascribed to the electron-rich nature of the silylated meso-position.

In a similar fashion, we synthesized β-trimethylsilylporphyrin 3Ni via β-lithioporphyrin (conditions a). In contrast to 2Ni, 3Ni is stable under acidic conditions,[12] and is compatible with silica gel column chromatography to isolate 3Ni in 79% yield. It is worth noting that 3Ni was also accessible from the corresponding Grignard reagent in 67% yield (conditions b), reminding us of the smaller steric hindrance around the β-position.

These successes encouraged us to prepare β-to-β disilane-bridged porphyrin dimers with an expectation of interporphyrinic interaction through π(Si–Si)-π(porphyrin) conjugation.[2c,7] After more careful and precise preparation of β-

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Supporting information for this article is given via a link at the end of the document.

.Scheme 1. Synthesis and denickelation of silylated porphyrins. a) i) 1.5 equiv. nBuLi, THF, −98 °C, 30 min, ii) 2 equiv. TMSCN, THF, −98 °C to r.t., 2 h; b) i) 1.5 equiv. nBuLi, THF, −40 °C, 2 h, ii) 2 equiv. TMSCN, THF, −40 °C to r.t., 2 h; c) i) 1.00 equiv. nBuLi, THF, −98 °C, 30 min, ii) 0.45 equiv. Me2(CISiSiCiMe2), THF, −98 °C to r.t., 1 h; d) i) 2.00 equiv. nBuLi, THF, −98 °C, 30 min, ii) 0.47 equiv. Me2(CISiSiCiMe2), THF, −98 °C, 20 min; e) 0.47 equiv. Me2(CISiSiCiMe2), THF, −40 °C, 20 min; f) i) 10 equiv. 4-TolMgBr, toluene, r.t., 4 h, ii) 3 M HCl aq., CH2Cl2, r.t., 10 min; f) i) 40 equiv. 4-TolMgBr, 10 equiv. CH2CHSiPh, toluene, 50 °C, 4 h, ii) 3 M HCl aq., CH2Cl2, r.t., 10 min.
lithiated porphyrin with 1.00 equiv. of nBuLi, slow addition of 0.45 equivalents of 1,2-dichloro-1,2,2-tetramethylsilane provided singly β-to-β disilane-bridged porphyrin dimer 4Ni in 57% yield (conditions c).

Doubly β-to-β disilane-bridged porphyrin dimer 5Ni would be a fascinating target, which would take a more fixed conformation for more efficient interporphyrinic interaction, judging from Isobe's reports on disilane-bridged anthracene dimers.\[7\] To prepare 5Ni, β,β-dilithiated porphyrin\[14\] successfully generated from β,β-diiodoporphyrin under our conditions for iodine-lithium exchange\[10\] was utilized. Stepwise construction of two disilane-bridges was effective to suppress formation of unbridged and acyclic products, and double bridged dimer 5Ni was obtained in 4% yield by slowly adding the dichlorodisilane at –40 °C (conditions d).

In addition to NMR analysis (see Supporting Information (SI)), the structures of \(\text{meso}-silylporphyrin 2Ni\) and \(\beta\)-to-β disilane-bridged dimers 4Ni and 5Ni were unambiguously revealed by X-ray crystallographic analysis (Figure 1). \(\text{meso}-silylporphyrin 2Ni\) has a distorted porphyrin plane to avoid steric repulsion between the porphyrin plane and the trimethylsilyl group.\[15\] In the solid-state, singly bridged dimer 4Ni has a non-symmetric helical-step-like structure in which one \(\text{meso-aryl} \) group in one porphyrin is located just above the other porphyrin. In contrast, its \(^1\text{H}\) and \(^13\text{C}\) NMR spectra display a singlet peak for the methyl groups on the two silicon atoms, indicating free rotation of the disilane bridge in solution. Doubly bridged dimer 5Ni has a step-like structure with trans geometry, in which the four dihedral angles \(\phi_1\) and \(\phi_2\) between the Si–Si–Cβ planes and the Cβ–Cβ′–Cω–Si mean planes are ca. 75° (see SI). This conformation looks favorable for \(\sigma-\pi\) interaction between the two porphyrin units via the two Si–Si bonds.

The UV/vis absorption spectra of 2Ni–5Ni as well as the unsubstituted parent porphyrin 1Ni in CH\(_2\)Cl\(_2\) are shown in Figure 2. Each silylated porphyrin exhibits a typical absorption spectrum comprising a sharp Soret band in 400–450 nm and weak Q bands in 500–550 nm. \(\text{meso-Silylporphyrin 2Ni}\) shows the larger red-shift of the Soret and Q bands (\(\lambda_{\text{max}} = 421\) and 540 nm, respectively) than \(\beta\)-silylporphyrin 3Ni (\(\lambda_{\text{max}} = 414\) and 525 nm, respectively) due to the more efficient interaction at the meso position. Characteristically, dimers 4Ni and 5Ni show broadened Soret bands\[16\] as a consequence of small yet distinct exciton coupling between the two porphyrin units.

![Figure 1. X-Ray crystal structures. a) Top view and b) side view of 2Ni. c) Top view and d) side view of 4Ni. e) Top view and f) side view of 5Ni. The thermal ellipsoids are drawn at 30% probability. Solvent molecules, tert-butyl groups and aryl hydrogen atoms are omitted for clarity. Schematic representation of dihedral angle g) \(\phi_1\) and h) \(\phi_2\).](https://repository.kulib.kyoto-u.ac.jp)

![Figure 2. UV/vis absorption spectra of 1Ni–5Ni in CH2Cl2.](https://repository.kulib.kyoto-u.ac.jp)

To obtain further understanding of \(\sigma-\pi\) conjugation and interporphyrinic interaction in the dimers, DFT calculations were performed at the B3LYP/6-31G(d) (C,H,N,Si) + LANL2DZ (Ni) level using Gaussian09 package.\[17\] \(\text{meso-Silylporphyrin 2Ni}\) has a little narrower HOMO–LUMO gap (2.87 eV) than the parent porphyrin 1Ni (2.99 eV) while the frontier orbital energy gaps of \(\beta\)-silylporphyrins remain almost unchanged (see SI). Small yet obvious orbital densities are located at the Si–Me bonds in the HOMO and LUMO of \(\text{meso-silylporphyrin 2Ni}\) (Figure 3a and 3b) while such densities are negligible in those of \(\beta\)-silylporphyrins 3Ni, which is consistent with their UV/vis absorption spectra. The high HOMO density at the meso position as well as the strain around the \(\text{meso-trimethylsilyl group}\)\[19\] would explain the observed facile protodesilylation reaction. In dimers 4Ni and 5Ni, contributions of \(\sigma-\pi\) conjugations are mostly trivial in their frontier orbitals (see SI), reflecting the \(\beta\)-to-β connection. This is consistent with their absorption spectra that are not significantly perturbed. However, characteristically the HOMO of 5Ni has been calculated to exhibit small but distinct anti-bonding...
interaction between $\pi$-orbitals on the $\beta$-positions and $\sigma$-orbitals of the Si–Si bonds (Figure 3d).

Figure 3. Optimized structure and Kohn-Sham orbital representations obtained by DFT calculations at the B3LYP/6-31G(d) (C,H,N,Si) + LANL2DZ (Ni) level. a) HOMO, b) LUMO and c) Optimized structure of 2Ni. d) HOMO of 5Ni. tert-Butyl groups were replaced with hydrogen atoms to simplify the calculations.

Considering the instability of silylated porphyrins under typical denickelation conditions ($\text{H}_2\text{SO}_4$ in Inflourocacetic acid), denickelation of silylated porphyrins with a 4-tolylmagnesium bromide$^{[19]}$ was conducted to obtain freebase porphyrins for fluorescence study. While denickelation of 3Ni proceeded successfully (Scheme 1, conditions e), attempted denickelation of 4Ni resulted in failure probably due to the oxidative insertion of Ni(0), generated by the action of the Grignard reagent, into the Si–Si bond. To deactivate the Ni(0) species, we found that an addition of phenyl vinyl sulfide was effective to furnish denickelated product 4FB in 35% yield (conditions f).

Figure 4 represents the UV/vis absorption and fluorescence spectra of $\beta$-silylporphyrin 3FB, singly bridged dimer 4FB, and the parent porphyrin 1FB. $\beta$-Silylporphyrins 3FB and 4FB display spectra similar to that of 1FB with small red shifts. The Soret band of 4FB is broadened owing to exciton coupling.$^{[16]}$ The $\beta$-silyl groups on the periphery have limited effects on fluorescence quantum yields: 3FB ($\Phi_\text{F} = 0.037$), 4FB ($\Phi_\text{F} = 0.048$) and 1FB ($\Phi_\text{F} = 0.043$).

In summary, a series of peripherally silylated porphyrins were synthesized for the first time. meso-Silylporphyrin shows the larger red shift in the UV/vis absorption spectrum due to the more efficient $\sigma$-$\pi$ conjugation between the meso-silyl group and the porphyrin $\pi$ system, but is unstable under acidic conditions. In contrast, $\beta$-silylporphyrins are stable, and the electronic perturbation by the $\beta$-silyl group is small. $\beta$-to-$\beta$ Disilane-bridged porphyrin dimers were prepared and characterized to exhibit weak yet distinct interporphyrinic interaction. Further study is underway to explore the application of peripherally metalated porphyrins in our laboratory.

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Keywords: porphyrin • silylation • substituent effects • lithiation• porphyrin dimer


Screening of silylating reagents is given in Supporting Information (Table S1). For discussion about the favorable effect of cyanide in silylation of Grignard reagents, see: P. J. Lennon, D. P. Mack, Q. E. Thompson, Organometallics 1989, 8, 1121-1122.

Stirring meso-silylporphyrin \( 2\text{Ni} \) (3 \( \mu \)mol) in \( \text{CH}_2\text{Cl}_2 \) (5 mL) with 1 M HCl aq. (5 mL) for 30 min at r.t. quantitatively gave the protodesilylated product. In contrast, \( \eta^5\)-silylporphyrin \( 3\text{Ni} \) was compatible even with 3 M HCl aq.


Addition of D\(_2\)O to the dilithiated porphyrin prepared with 2.5 equiv. of \( \text{DBuLi} \) at \(-98^\circ\text{C}\) for 30 min gave Ni(II) \( 5.10,15\text{-tris}(\text{3,5-di-tert-butylphenyl})\)-2,18-dideuteroporphyrin (\( H/D = 5/95 \)) in 98% yield.

The mean plane deviation of \( 2\text{Ni} \) consisting of the porphyrinic 4 nitrogen atoms and 20 carbon atoms was calculated to be 0.326 Å (0.229 Å for the structure optimized by DFT calculations). This is larger than that of tetraphenylporphyrin nickel complex in a crystal. (0.292 Å): A. L. Maclean, G. J. Foran, B. J. Kennedy, P. Turner, T. W. Hambley, Aust. J. Chem. 1996, 49, 1273-1278.

The full widths at half maxima of Soret bands are \( 1\text{Ni} 1200 \text{ cm}^\text{-1} \), \( 2\text{Ni} 1200 \text{ cm}^\text{-1} \), \( 3\text{Ni} 1200 \text{ cm}^\text{-1} \), \( 4\text{Ni} 1900 \text{ cm}^\text{-1} \), \( 5\text{Ni} 1800 \text{ cm}^\text{-1} \), \( 1\text{FB} 600 \text{ cm}^\text{-1} \), \( 3\text{FB} 700 \text{ cm}^\text{-1} \) and \( 4\text{FB} 1700 \text{ cm}^\text{-1} \).

M. J. Frisch et al. Gaussian 09, revision C.02; Gaussian, Inc.; Wallingford, CT, 2009.

meso- and β-Silylated porphyrins and β-to-β disilane-bridged porphyrin dimers were synthesized for the first time via porphyrinyl-lithium reagents. A doubly β-to-β disilane-bridged NIII-porphyrin dimer has been also synthesized and characterized by single crystal X-ray crystallographic analysis to take a step-like structure, which is favorable for the electronic interactions between the two porphyrin units.