

Peripherally Silylated Porphyrins

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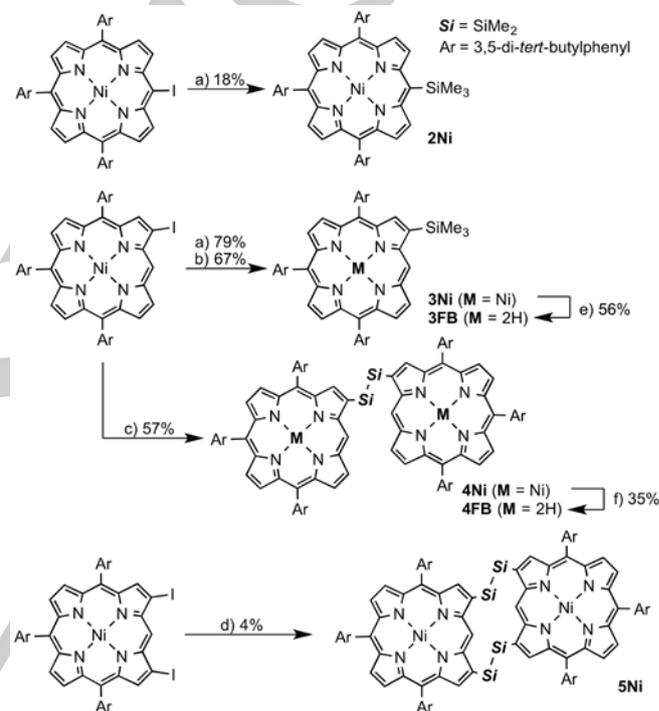
Abstract: Silylation of peripherally lithiated porphyrins with silyl electrophiles has realized the first synthesis of a series of directly silyl-substituted porphyrins. The *meso*-silyl group underwent facile protodesilylation whereas the β -silyl group was entirely compatible with usual work-up and 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 Ni^{II}-porphyrin dimer was also synthesized from a β,β -dilithiated Ni^{II}-porphyrin and characterized by X-ray crystallographic analysis to take a step-like structure favorable for interporphyrinic interaction. Denickelation of β -silylporphyrins was achieved upon treatment with a 4-tolylmagnesium bromide to yield the corresponding freebase porphyrins.

Porphyrins 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 on a π -conjugated system have been demonstrated to interact with the π -system through σ - 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 *n*BuLi 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.



Scheme 1. Synthesis and denickelation of silylated porphyrins. a) i) 1.5 equiv. *n*BuLi, THF, -98 °C, 30 min, ii) 2 equiv. TMSCN, THF, -98 °C to r.t., 2 h; b) i) 1.5 equiv. *i*PrMgCl·LiCl, THF, -40 °C, 2 h, ii) 2 equiv. TMSCN, THF, -40 °C to r.t., 2 h; c) i) 1.00 equiv. *n*BuLi, THF, -98 °C, 30 min, ii) 0.45 equiv. Me₂(Cl)SiSi(Cl)Me₂, THF, -98 °C to r.t., 1 h; d) i) 2.00 equiv. *n*BuLi, THF, -98 °C, 30 min, ii) 0.47 equiv. Me₂(Cl)SiSi(Cl)Me₂, THF, -98 °C, 20 min, iii) 0.47 equiv. Me₂(Cl)SiSi(Cl)Me₂, THF, -40 °C, 20 min; e) 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. CH₂CHSPH, toluene, 50 °C, 4 h, ii) 3 M HCl aq., CH₂Cl₂, r.t., 10 min.

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 σ (Si-Si)- π (porphyrin) conjugation.^[4c,7] After more careful and precise preparation of β -

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lithiated porphyrin with 1.00 equiv. of *n*BuLi, slow addition of 0.45 equivalents of 1,2-dichloro-1,1,2,2-tetramethyldisilane 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 doubly bridged dimer **5Ni** was obtained in 4% yield by slowly adding the dichlorodisilane at -98 °C and subsequently at -40 °C (conditions d).

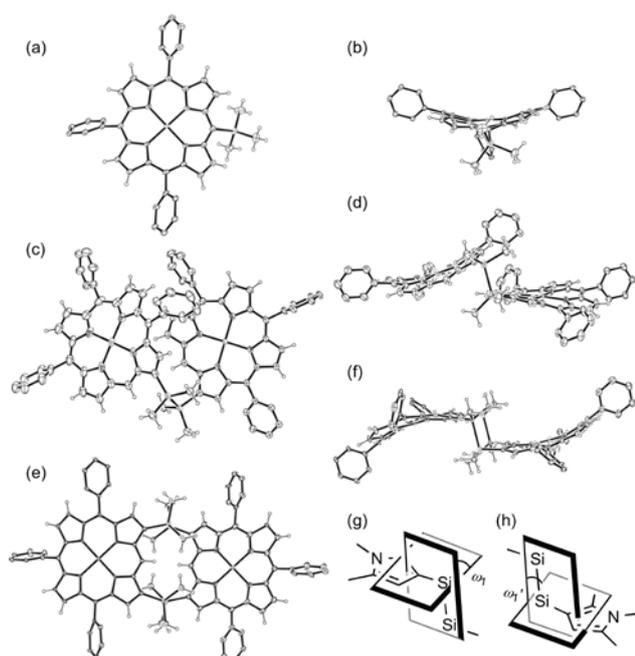


Figure 1. X-Ray crystal structures. a) Top view and b) side view of **2Ni**. c) Top view and d) side view of **4Ni**. e) Top view and f) side view of **5Ni**. The thermal ellipsoids are drawn at 30% probability. Solvent molecules, *tert*-butyl groups and aryl hydrogen atoms are omitted for clarity. Schematic representation of dihedral angle g) ω_1 and h) ω_1' .

In addition to NMR analysis (see Supporting Information (SI)), the structures of *meso*-silylporphyrin **2Ni** and β -to- β disilane-bridged dimers **4Ni** and **5Ni** were unambiguously revealed by X-ray crystallographic analysis (Figure 1). *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 *meso*-aryl group in one porphyrin is located just above the other porphyrin. In contrast, its ^1H and ^{13}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 ω_1 and ω_1' between the Si-Si-C β planes and the C β -C β' -C α -Si mean planes are *ca.* 75° (see SI). This conformation looks favorable for σ - π 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_2Cl_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. *meso*-Silylporphyrin **2Ni** shows the larger red-shift of the Soret and Q bands ($\lambda_{\text{max}} = 421$ and 540 nm, respectively) than β -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.

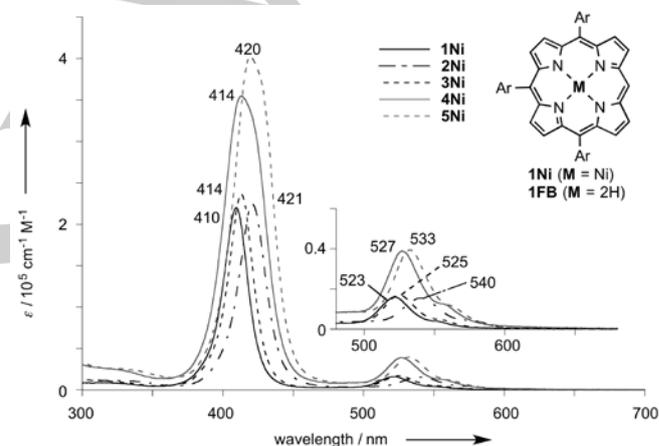


Figure 2. UV/vis absorption spectra of **1Ni**–**5Ni** in CH_2Cl_2 .

To obtain further understanding of σ - π 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] *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 β -silylporphyrins remain almost unchanged (see SI). Small yet obvious orbital densities are located at the Si–Me bonds in the HOMO and LUMO of *meso*-silylporphyrin **2Ni** (Figure 3a and 3b) while such densities are negligible in those of β -silylporphyrin **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 *meso*-trimethylsilyl group^[15] would explain the observed facile protodesilylation reaction. In dimers **4Ni** and **5Ni**, contributions of σ - π conjugations are mostly trivial in their frontier orbitals (see SI), reflecting the β -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 p-orbitals on the β -positions and σ -orbitals of the Si–Si bonds (Figure 3d).

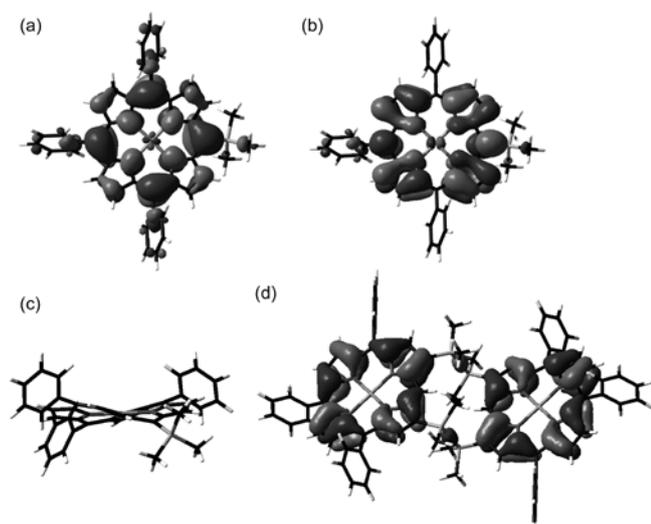


Figure 3. Optimized structure and Kohn-Sham orbital representations obtained by DFT calculations at the B3LYP/6-31G(d) (C,H,N,Si) + LANL2DZ (Ni) level. a) HOMO, b) LUMO and c) Optimized structure of **2Ni**. d) HOMO of **5Ni**. *tert*-Butyl groups were replaced with hydrogen atoms to simplify the calculations.

Considering the instability of silylated porphyrins under typical denickelation conditions (H_2SO_4 in trifluoroacetic acid), denickelation of silylated porphyrins with a 4-tolylmagnesium bromide^[18] 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).

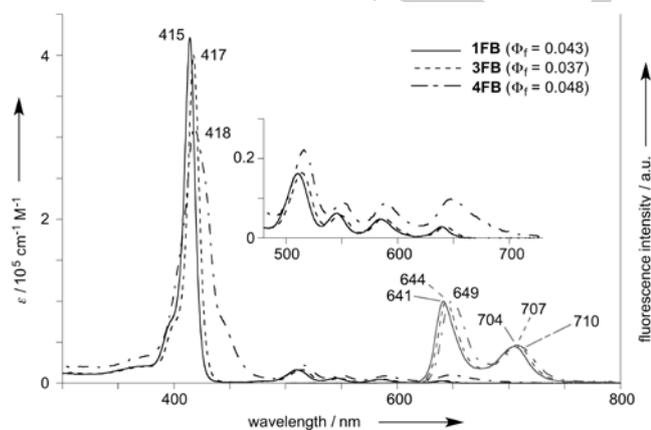


Figure 4. UV/vis absorption (solid lines) and fluorescence (dashed lines) spectra of **1FB**, **3FB** and **4FB** in CH_2Cl_2 .

Figure 4 represents the UV/vis absorption and fluorescence spectra of β -silylporphyrin **3FB**, singly bridged dimer **4FB**, and the parent porphyrin **1FB**. β -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 β -silyl groups on the periphery have limited effects on fluorescence quantum yields: **3FB** ($\Phi_f = 0.037$), **4FB** ($\Phi_f = 0.048$) and **1FB** ($\Phi_f = 0.043$).

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 σ - π conjugation between the *meso*-silyl group and the porphyrin π system, but is unstable under acidic conditions. In contrast, β -silylporphyrins are stable, and the electronic perturbation by the β -silyl group is small. β -to- β 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.

Acknowledgements

This work was supported by Grants-in-Aid from MEXT (Nos.: 25107002 “Science of Atomic Layers”) and from JSPS (Nos.: 25220802 (Scientific Research (S)), 24685007 (Young Scientists (A)), 26620081 (Exploratory Research)). H.Y. thanks Kansai Research Foundation for Technology Promotion and The Asahi Glass Foundation for financial support. K.F. acknowledges a JSPS Fellowship for Young Scientists.

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

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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 Ni^{II}-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.