

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-disilane-bridged Ni²⁺-porphyrin dimer was also synthesized from a β,β-dilithiated Ni²⁺-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-tolymagnesium 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 π-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 porphyrinylolithium reagents.[10] Treatment of meso-lithoporphyrin 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,[13] 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.[14-17] After more careful and precise preparation of β-

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**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. iPrMgClLiCl, 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(CISi)(SiCl)(CH₂)Me₂, THF, –98 °C to r.t., 1 h; d) i) 2.00 equiv. nBuLi, THF, –98 °C, 30 min, ii) 0.47 equiv. Me₂(CISi)(SiCl)(CH₂)Me₂, THF, –98 °C, 30 min, iii) 0.35 equiv. iPrMgClLiCl, THF, –40 °C, 2 h, e) 2.00 equiv. 4-TolMgBr, toluene, r.t., 4 h, ii) 3 M HCl aq., CH₂Cl₂, r.t., 10 min; f) i) 4.0 equiv. 4-TolMgBr, 10 equiv. CH₃CH₂SPh, toluene, 50 °C, 4 h, ii) 3 M HCl aq., CH₂Cl₂, r.t., 10 min.

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![Diagram of porphyrin structures](image-url)
lithiated porphyrin with 1.00 equiv. of nBuLi, slow addition of 0.45 equivalents of 1,2-dichloro-1,2,2,2-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-diodoporphyrin 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 four dihedral angles g) ω and h) α'.
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 (H2SO4 in Influoacetic acid), denickelation of silylated porphyrins with a 4-tolylmagnesium bromide 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 1FB, 3FB, singly bridged dimer 4FB, and the parent porphyrin 1FB. β-Silylporphyrin 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. The β-silyl groups on the periphery have limited effects on fluorescence quantum yields: 3FB (Φf = 0.037), 4FB (Φf = 0.048) and 1FB (Φf = 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.: 25220602 (Scientific Research (S)), 24685007 (Young Scientists (A)), 26620081 (Exploratory Research)). H.Y. thanks Kansai Glass Foundation for financial support. K.F. acknowledges a JSPS Fellowship for Young Scientists.

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

Figure 4. UV/vis absorption (solid lines) and fluorescence (dashed lines) spectra of 1FB, 3FB and 4FB in CH2Cl2.

Stirring meso-silylporphyrin 2Ni (3 µmol) in CH2Cl2 (5 mL) with 1 M HCl aq. (5 mL) for 30 min at r.t. quantitatively gave the protodesilylated product. In contrast, μ-silylporphyrin 3Ni was compatible even with 3 M HCl aq.


Addition of D2O to the dilithiated porphyrin prepared with 2.5 equiv. of BuLi at –98 °C for 30 min gave Ni(II) 5, 10,15-tris(3,5-di-tert-butylphenyl)-2,18-dideuterioporphyrin (4H+/D+ = 5/95) in 98% yield.

The mean plane deviation of 2Ni consisting of the porphyric 4 nitrogen atoms and 20 carbon atoms was calculated to be 0.326 Å (0.292 Å for the structure optimized by DFT calculations). This is larger than that of tetraphenylporphyrin nickel complex in a crystal. (0.223 Å): A. L. Maclean, G. J. Foran, B. J. Kennedy, P. Turner, T. W. Hambly, Aust. J. Chem. 1996, 49, 1273-1278.

The full widths at half maxima of Soret bands are 1Ni 1200 cm−1, 2Ni 1200 cm−1, 3Ni 1200 cm−1, 4Ni 1900 cm−1, 5Ni 1800 cm−1, 1FB 600 cm−1, 3FB 700 cm−1 and 4FB 1700 cm−1.

meso- and β-Silylated porphyrins and β-to-β disilane-bridged porphyrin dimers were synthesized for the first time via porphyrinylithium 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.