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Porphyrinoids

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Near-IR Absorbing Nickel(II) Porphyrinoids Prepared by Regioselective Insertion of Silylenes into Antiaromatic Nickel(II) Norcorrole**

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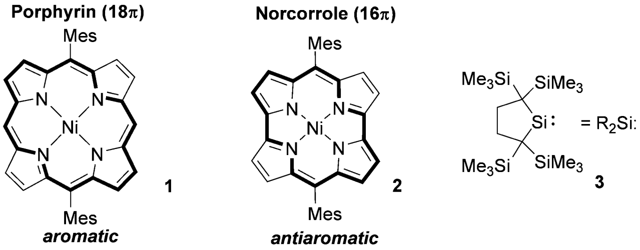
Abstract: *The treatment of an antiaromatic norcorrole Ni^{II} complex with a kinetically stabilized silylene provided ring-expansion products in excellent yields through the highly regio- and stereoselective insertion into the β-β pyrrolic C–C bonds. The resultant Ni^{II} porphyrinoid monoinsertion product exhibited relatively strong near-IR absorption bands due to the small HOMO–LUMO gap in spite of the disrupted cyclic π-conjugation by the silicon atom.*

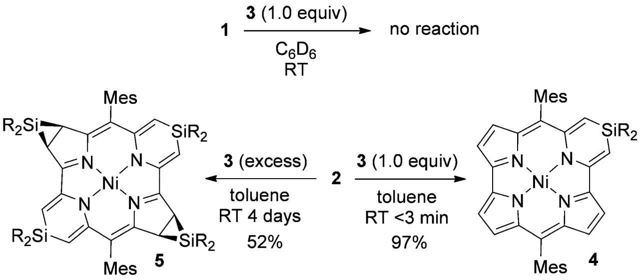
The introduction of main-group elements such as silicon into π-conjugated systems has been quite successful for the creation of novel functional materials that exhibit intriguing optoelectronic properties.[1] To rapidly access silicon-containing π-conjugated systems, the insertion of silylenes into π systems is particularly effective. Silylenes, which are divalent silicon compounds, are highly reactive intermediates that often undergo addition to unsaturated compounds to provide three-membered rings or insertion products.[2] For example, the reaction of silylenes with benzene affords silacycloheptatrienes in good yields through addition/ring opening under thermal or photo-irradiated conditions.[3] However, large π-conjugated systems such as porphyrins have not been investigated as reaction partners in the silicon-insertion reaction with silylenes.

Norcorrole is a ring-contracted porphyrinoid that lacks two of the *meso*-carbon atoms found in regular porphyrins (Scheme 1).[4] We recently isolated the norcorrole Ni^{II} complex **2** as an air-stable material. It exhibits a distinct antiaromatic nature because of its highly planar structure and the presence of 16 π electrons along the conjugation circuit.[5] In addition, upon treatment with *meta*-chloroperoxybenzoic acid (*m*CPBA), oxygen insertion into the carbon–carbon bond between the two pyrrole units of **2** affords the aromatic 18 π electron oxacorrole Ni^{II} complex. This type of atom insertion enables the rapid construction of novel π-conjugated systems. Although several antiaromatic porphyrinoids have been isolated, such reactions of antiaromatic porphyrins have not been examined. Herein, we report a silicon-insertion reaction of silylene **3**[6] into **2** to afford ring-expansion products in excellent yields. Furthermore, we analyze the antiaromaticity of silicon-containing porphyrinoid **4** by spectroscopy and theoretical analysis.[7]



Scheme 1. Structures of Ni^{II} porphyrin **1**, Ni^{II} norcorrole **2**, and kinetically stabilized silylene **3**. The bold lines indicate the conjugation circuits. Mes = 2,4,6-trimethylphenyl.

To evaluate the propensity for silicon insertion, stabilized silylene **3** was reacted with porphyrin **1** and norcorrole **2** (Scheme 2). Whereas no reaction was observed upon treatment of 5,15-dimesitylporphyrin Ni^{II} complex **1** with **3**, Ni^{II} norcorrole **2** instantly reacted with **3** in three minutes at room temperature to provide **4** as a single product in 97 % yield. The structure of **4** was unambiguously elucidated by X-ray diffraction analysis and found to be silicon-containing porphyrinoid **4**, which is formed by the insertion of **3** into the β-β pyrrole carbon–carbon linkage (Figure 1 a,b). No other regioisomers were detected in the reaction mixture.



Scheme 2. Reactions of Ni^{II} porphyrin **1** and Ni^{II} norcorrole **2** with stable silylene **3**.

Treatment of **2** with an excess of **3** (8.0 equiv) provided, judging from its high-resolution mass spectrum, four-fold addition product **5** as the major product in 52 % yield. The structure of **5** was also determined by X-ray diffraction analysis (Figure 1 c,d). Interestingly, this adduct has two silacyclopropanes fused to the pyrrole units in a *cis* fashion. The presence of the silacyclopropane moiety suggests that the azasilacyclohexadiene rings in **4** and **5** likely result from the ring opening of an initial silacyclopropane adduct, as has been reported for the formation of silacycloheptatriene from benzene.[3]

Kinetically stabilized silylene **3** exclusively reacted with **2** at the β-β pyrrolic bond. To determine whether the present

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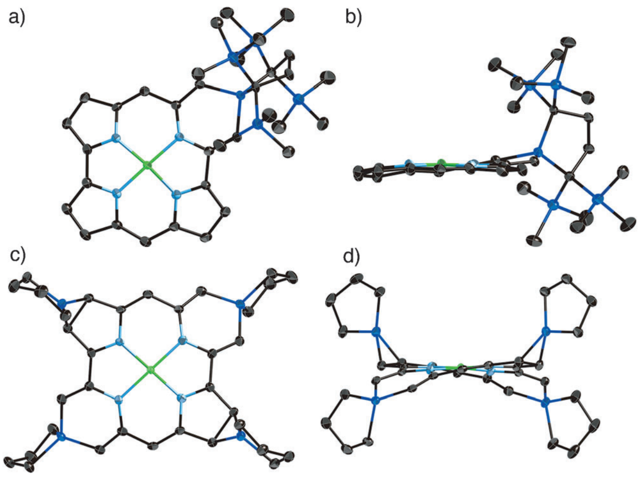
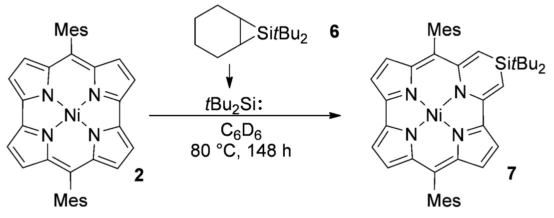


Figure 1. X-ray crystal structures of **4** and **5**. a) Top view and b) side view of **4**, and c) top view and d) side view of **5**. Thermal ellipsoids are scaled at the 50% probability level. The hydrogen atoms, mesityl groups, and trimethylsilyl groups in (c) and (d) are omitted for clarity.

selectivity is specific to **3**, we investigated the reaction of **2** with di(*tert*-butyl)silylene generated in situ from silacyclopropane precursor **6** (Scheme 3).[8] The reaction was sluggish; however, some insertion product **7** was obtained in 72% conversion. In the ^{1}H NMR spectrum of **7**, the chemical shifts of pyrrole protons were nearly the same as those of the pyrrole protons in **4**.[9] On the basis of this result, it was concluded that di(*tert*-butyl)silylene undergoes insertion with the same regioselectivity.



Scheme 3. Silylene transfer from silacyclopropane **6** to norcorrole **2**.

Because of the presence of the sp^3 silicon atom, the cyclic π-conjugation is disrupted in **4**. Surprisingly, however, the UV/Vis/NIR absorption spectrum of **4** exhibited broad and strong absorption bands in the low-energy region compared to those observed for typical porphyrinoids containing four nitrogens (Figure 2a). The absorption edge of **4** extended to 1300 nm, suggesting a small HOMO–LUMO gap. Thus, the electrochemical properties of **4** were investigated by cyclic voltammetry. Porphyrinoid **4** exhibited two reversible reduction waves at −1.12 and −1.81 V and one reversible oxidation wave at 0.30 V (Supporting Information, Figure S7). The narrow gap between the first oxidation and reduction potentials (1.42 V) is consistent with the optical analysis. Results of DFT calculations also indicated a small HOMO–LUMO gap (1.82 eV) of **4** (Figure S8).

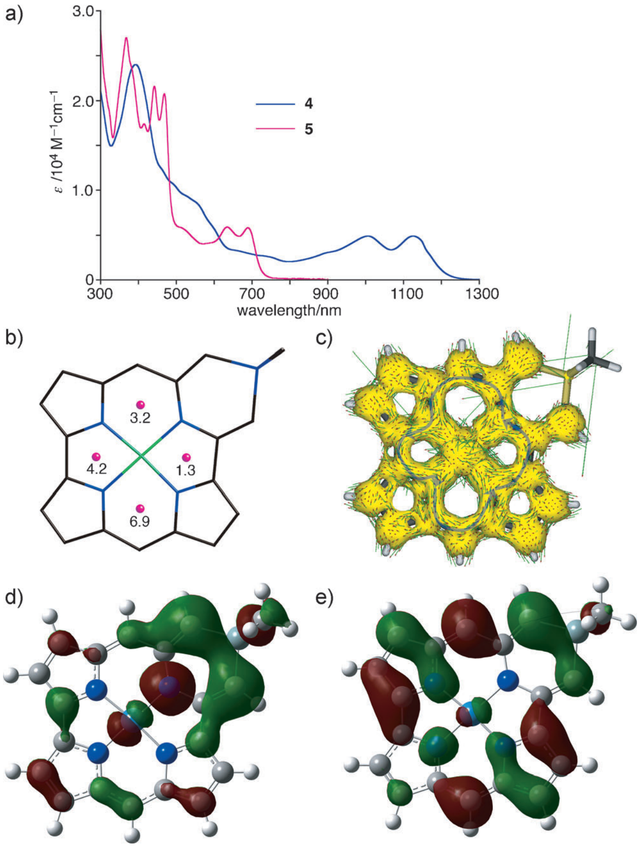
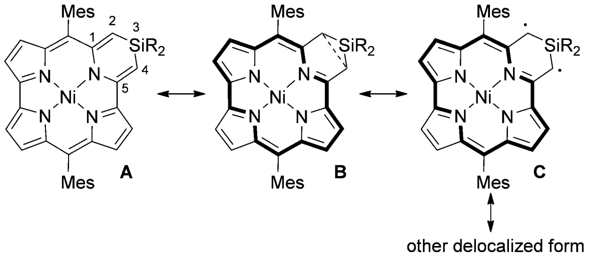


Figure 2. a) UV/Vis/NIR absorption spectra of **4** and **5** in CH_2Cl_2. b) NICS values of **4** calculated at the B3LYP/631SDD level. c) AICD plot of **4** at an isosurface value of 0.05. d) HOMO and e) LUMO of **4**.

In the ^{1}H NMR spectra of nonaromatic acyclic dipyrrins, the pyrrole proton peaks typically appeared in the 6.0–7.0 ppm range. The pyrrole proton signals of **4**, on the other hand, were shifted upfield in the 5.2–6.1 ppm region.[10] In addition, the calculated nucleus-independent chemical shift (NICS) values were small but positive, which suggests a weak antiaromatic nature for **4** (Figure 2b).[11] Furthermore, the anisotropy of the induced current density (AICD) exhibited counterclockwise current density, which also indicates the antiaromaticity of **4** (Figure 2c).[12,13]

The small HOMO–LUMO gap and weak antiaromaticity of **4** cannot be explained by the normal resonance structure **A**, which should have no cyclic π conjugation (Scheme 4). One can, however, consider another resonance structure, **B**, with cyclic 16 π electron conjugation and partial π-bonding character between the two carbon atoms (C2 and C4)



Scheme 4. Resonance structures of silicon-containing porphyrinoid **4**.

adjacent to the silicon.[14] The C2–C4 distance is 2.776 Å in the X-ray structure. The natural bond orbital analysis suggests a non-negligible Wiberg bond index between the C2 and C4 atoms (0.11), as well as decreased double bond characters for the C1–C2 (1.64) and C4–C5 (1.77) bonds. The calculated HOMO also indicated significant orbital overlap between the two carbon atoms, supporting a bonding interaction between C2 and C4 (Figure 2d). In addition, the CASSCF(2,2) calculation suggested approximately an 8% contribution of the biradical resonance structure **C**. In fact, a toluene solution of **4** showed a weak ESR signal, the intensity of which was clearly dependent on temperature (Figure S9). Such behavior is typical of delocalized singlet biradicals.[15] It was thus concluded that the narrow HOMO–LUMO gap and antiaromaticity of **4** can be explained by contributions from the resonance structures **B** and **C**.

In conclusion, highly regioselective insertion of silylenes into norcorrole Ni^{II} complex **2** provided silicon-containing porphyrinoids in excellent yields. In spite of the disrupted cyclic π conjugation by the silicon atom, the resultant porphyrinoid **4** exhibited relatively strong NIR absorption bands due to the small HOMO–LUMO gap. The weak antiaromatic character of **4** was elucidated on the basis of spectroscopic and theoretical analyses. The present study demonstrates that atom-insertion reactions into reactive antiaromatic π systems enable the efficient construction of novel π-conjugated systems with fascinating properties. Further studies on the reactivity of antiaromatic norcorroles are currently underway in our group.

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Keywords: antiaromaticity · insertion · NIR absorption · porphyrinoids · silylenes

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[1] a) S. Ponomarenko, S. Kirchmeyer in *Silicon Polymers*, *Vol. 235* (Ed.: A. M. Muzafarov), Springer, Berlin, **2011**, pp. 33; b) S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa, K. Tamao, *Chem. Eur. J.* **2000**, *6*, 1683; c) S. Yamaguchi, K. Tamao, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327; d) A. Fukazawa, S. Yamaguchi, *Chem. Asian J.* **2009**, *4*, 1386; e) S. Yamaguchi, K. Tamao, *Chem. Lett.* **2005**, *34*, 2; f) S. Yamaguchi, C. Xu, *J. Synth. Org. Chem. Jpn.* **2005**, *63*, 1115; g) M. Hissler, P. W. Dyer, R. Réau, *Coord. Chem. Rev.* **2003**, *244*, 1; h) J. Liu, J. Y. Lam, B. Tang, *J. Inorg. Organomet. Polym.* **2009**, *19*, 249.

[2] a) Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479; b) P. P. Gaspar, R. West in *The Chemistry of Organic Silicon Compounds*, *Vol. 2*, *Part 3* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, chap. 43, p. 2463; c) N. J. Hill, R. West, *J. Organomet. Chem.* **2004**, *689*, 4165.

[3] a) H. Suzuki, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.* **1994**, *116*, 11572; b) H. Suzuki, N. Tokitoh, R. Okazaki, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2471; c) M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **2002**, *124*, 3830; d) M. Kira, S. Ishida, T. Iwamoto, A. de Meijere, M. Fujitsuka, O. Ito, *Angew. Chem.* **2004**, *116*, 4610; *Angew. Chem. Int. Ed.* **2004**, *43*, 4510.

[4] a) M. Bröring, S. Köhler, C. Kleeberg, *Angew. Chem.* **2008**, *120*, 5740; *Angew. Chem. Int. Ed.* **2008**, *47*, 5658; b) A. Ghosh, I. H. Wasbotten, W. Davis, J. C. Swarts, *Eur. J. Inorg. Chem.* **2005**, 4479.

[5] T. Ito, Y. Hayashi, S. Shimizu, J.-Y. Shin, N. Kobayashi, H. Shinokubo, *Angew. Chem.* **2012**, *124*, 8670; *Angew. Chem. Int. Ed.* **2012**, *51*, 8542.

[6] a) M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **1999**, *121*, 9722; b) M. Kira, T. Iwamoto, S. Ishida, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 258; c) M. Kira, *Chem. Commun.* **2010**, *46*, 2893.

[7] For core-modified porphyrinoids by silicon, see: a) J. Skonieczny, L. Latos-Grażyński, L. Szterenberg, *Chem. Eur. J.* **2008**, *14*, 4861; b) J. Skonieczny, L. Latos-Grazynski, L. Szterenberg, *Org. Biomol. Chem.* **2012**, *10*, 3463.

[8] Unfortunately, porphyrinoid **7** could not be isolated by silica-gel column chromatography.

[9] For a review on silylene transfer with silacyclopropanes, see: A. K. Franz, K. A. Woerpel, *Acc. Chem. Res.* **2000**, *33*, 813.

[10] The ^{29}Si NMR spectrum of **4** showed a signal for the spiro silicon atom at $\delta = -7.7$ ppm, which is upfield-shifted as compared to those in silacycloheptatrienes.[3c] This also implies the presence of the paratropic ring current effect in porphyrinoid **4**.

[11] The NICS value has been successfully used as a measure of aromaticity; see: a) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842; b) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. J. Jiao, N. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.

[12] AICD represents the 3D image of delocalized electron densities with a scalar field and illustrates the paramagnetic term of the induced current density; see: a) D. Geuenich, K. Hess, F. Köhler, R. Herges, *Chem. Rev.* **2005**, *105*, 3758; b) R. Herges, D. Geuenich, *J. Phys. Chem. A* **2001**, *105*, 3214.

[13] AICD plots have been successfully used in analyses of various porphyrinoids; see: a) M.-C. Yoon, J.-Y. Shin, J. M. Lim, S. Saito, T. Yoneda, A. Osuka, D. Kim, *Chem. Eur. J.* **2011**, *17*, 6707; b) T. Higashino, J. M. Lim, T. Miura, S. Saito, J.-Y. Shin, D. Kim, A. Osuka, *Angew. Chem.* **2010**, *122*, 5070; *Angew. Chem. Int. Ed.* **2010**, *49*, 4950; c) J. S. Lee, J. M. Lim, M. Toganoh, H. Furuta, D. Kim, *Chem. Commun.* **2010**, *46*, 285.

[14] For partial π bonding between two parallel p orbitals on two carbon atoms bridging a silicon atom, see: a) J. Ma, Y. Ding, K. Hattori, S. Inagaki, *J. Org. Chem.* **2004**, *69*, 4245; b) M. Abe, C. Ishihara, A. Tagegami, *J. Org. Chem.* **2004**, *69*, 7250.

[15] For leading references on biradicals, see: a) M. Abe, *Chem. Rev.* **2013**, *113*, 7011; b) M. Abe, J. Ye, M. Mishima, *Chem. Soc. Rev.* **2012**, *41*, 3808; c) Z. Sun, Z. Zeng, J. Wu, *Chem. Asian J.* **2013**, *8*, 2894; d) C. Lambert, *Angew. Chem.* **2011**, *123*, 1794; *Angew. Chem. Int. Ed.* **2011**, *50*, 1756; e) Z. Sun, Q. Ye, C. Chi, J. Wu, *Chem. Soc. Rev.* **2012**, *41*, 7857.