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# Structural Interconversion and Regulation of Optical Properties of Stable Hypercoordinate Dipyrrin−Silicon Complexes

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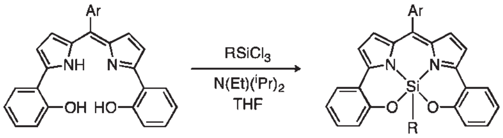
*Supporting Information*

**ABSTRACT:** Novel pentacoordinate dipyrrin−silicon complexes showed efficient red or near-IR fluorescence, and the structural interconversion between silanol and siloxane derivatives resulted in significant changes in the optical properties.

Dipyrrins are widely used as monoanionic bidentate ligands, and their complexes show unique optical properties.[1] In particular, dipyrrin−boron complexes (BODIPYs) have attracted much attention because of their strong and tunable fluorescence properties.[2] Dipyrrin complexes with other elements such as Zn,[3] Cu,[4] In,[5] Ga,[5] and Sn[6] are also intriguing because different coordination geometries and/or complexation stoichiometries lead to versatile properties and applications. Although many kinds of dipyrrin complexes have been synthesized, dipyrrin−silicon complexes have not been reported to date.

Silicon atoms often exert a considerable influence on the optical properties of fluorophores.[7] In addition, hypercoordinate silicon compounds such as pentacoordinate and hexacoordinate silicon complexes generally exhibit completely different or reverse reactivity (e.g., more facile bond cleavage) than the usual tetracoordinate silicon compounds.[8] For example, pentacoordinate siloxane derivatives, which have Si−O−Si units, easily undergo hydrolysis to give the corresponding silanol (Si−OH) derivatives, whereas tetracoordinate siloxanes are much more stable than the corresponding silanols.[9] Reversible bond formation and dissociation between the hypercoordinate and the usual tetracoordinate silicon compounds are responsible for switching of the fluorescence properties.[10]

Scheme 1. Synthesis of Silicon Complexes 3-R and 4-R



**1**: (Ar = mesityl)
**2**: (Ar= Ph)

**3-Me** (Ar = mesityl, R = Me)
**3-Ph** (Ar = mesityl, R = Ph)
**4-Me** (Ar= Ph, R = Me)
**4-Ph** (Ar= Ph, R = Ph)

The $N_2O_2$-type dipyrrins, which contain 2-hydroxyphenyl groups at the pyrrole α-positions, adopt six-membered-ring coordination and provide trianionic tetradentate chelation sites to B and Al, affording red-fluorescent B and Al complexes in high yield.[11] We are convinced that the $N_2O_2$-type dipyrrins are strong candidates for functional modulation of hypercoordinate silicon compounds on the basis of the pentacoordinate silanol−siloxane structural interconversion because the pentacoordinate structure of silicon compounds is favored by five- or six-membered-ring chelation. We also expect $N_2O_2$-type dipyrrin−Si complexes to show near-IR (NIR) fluorescence because of the expected planar structure of the fluorophores. Recent interest in NIR emission has grown because of its potential application to biosensors and solar batteries. The combination of dipyrrin and silicon would enable the switching of red or NIR fluorescence properties of the dipyrrin complexes by using the peculiar reactivity and properties of hypercoordinate silicon compounds.

Herein we describe the first synthesis and characterization of hypercoordinate silicon complexes with $N_2O_2$-type dipyrrins, which are interconvertible between the pentacoordinate silanol and siloxane. These dipyrrin silicon complexes exhibit different fluorescence properties in the red and NIR regions. Consequently, the unusual dynamic interconversion between the hypercoordinate silicon compounds by reversible hydrolysis/dehydration results in significant changes in the optical properties.

Ligands **1** and **2** were synthesized according to a reported procedure.[11b] The silicon complexes **3-R** and **4-R** (R = Me, Ph), in which the silicon atom bears a methyl or phenyl group, were obtained in moderate yields by the reactions with $MeSiCl_3$ or $PhSiCl_3$, respectively, in the presence of NEt(*i*Pr)$_2$ (Scheme 1). In the case of the $N_2$-type 3,5,8-triphenyldipyrrin, however, the starting material was recovered in the reactions with $Me_3SiCl$, $Me_2SiCl_2$, $MeSiCl_3$, and $SiCl_4$ under similar conditions.

Silicon complexes **3-R** and **4-R** were stable under aerobic conditions and readily purified by column chromatography on silica gel. The obtained complexes were soluble in chloroform and characterized by spectroscopic measurements ($^1$H, $^{13}$C, and $^{29}$Si NMR; ESI-MS) and elemental analysis. The $^1$H NMR spectra in $CDCl_3$ showed a $C_s$-symmetric spectral pattern. **3-R** exhibited a single set of proton resonances for the two hydroxyphenylpyrrole moieties, while the two *o*-methyl groups of the mesityl ring appeared as two singlets. The proton resonances of the methyl groups on the silicon atoms appeared at 0.09 and 0.04 ppm for **3-Me** and **4-Me**, respectively. In addition, the $^{29}$Si NMR spectra showed singlet signals at −117.4, −116.6, −130.5, and −129.8 ppm for **3-Me**, **4-Me**, **3-Ph**, and **4-Ph**, respectively. These shifts are characteristic of pentacoordinate silicon atoms.

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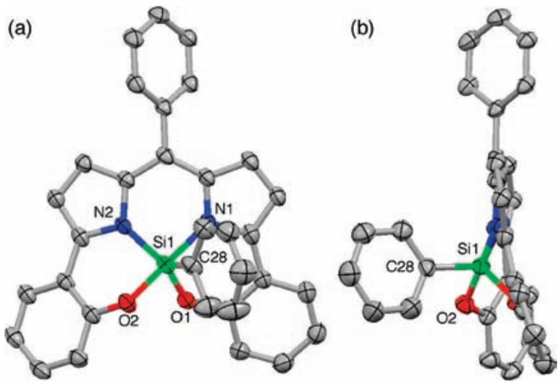
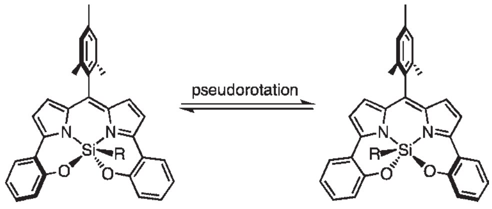


**Figure 1.** Crystal structure of one enantiomer of **4-Ph** in the solid state: (a) top view; (b) side view. Thermal ellipsoids are displayed at the 50% level. Colors: C, gray; N, blue; O, red; Si, green. Hydrogen atoms have been omitted for clarity.

### Scheme 2. Pseudorotation between Two Structures of 3-R



X-ray structural analysis of single crystals of **4-Ph** showed that the silicon atom is in a distorted trigonal-bipyramidal (TBP) coordination environment (Figure 1).[12,13] The atoms N1 and O2 form the axis of the bipyramid, with an O2−Si1−N1 angle of 177.80(9)°. The atoms N2, O1, and C28 are in the equatorial plane of the bipyramid, and the angles N2−Si1−C28, O1−Si1−N2, and C28−Si1−O1 are ~120° each.[14] **4-Ph** has a chiral structure and exists as a racemate in the crystals. Although the $C_1$-symmetric pentacoordinate structure was observed in the crystal structure, the $^1$H NMR spectrum suggested a $C_s$-symmetric spectral pattern as seen for **3-R**. Since pentacoordinate silicon compounds are known to undergo intramolecular isomerization according to the widely accepted Berry pseudorotation mechanism,[15] the observed $C_s$-symmetric $^1$H NMR spectral pattern was attributed to fast interconversion between the two structures on the NMR time scale (Scheme 2).

The obtained silicon complexes showed intense fluorescence in the NIR region (Table 1). **3-Me** and **3-Ph** showed higher fluorescence quantum yields than **4-Me** and **4-Ph**. This is most likely due to the restricted rotation of the mesityl group.[3] The substituents on the silicon atom also affected the optical properties. **3-Ph** and **4-Ph** showed absorption and fluorescence peaks at wavelengths longer than those of **3-Me** and **4-Me**.

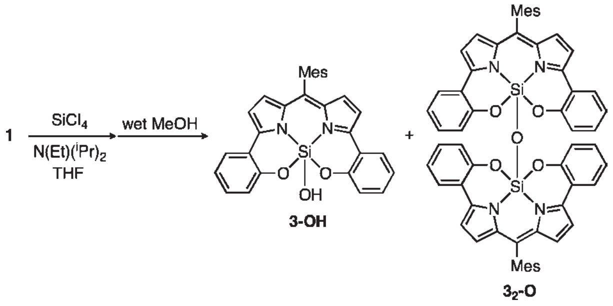
We then examined the reactions of ligand **1** with $SiCl_4$ to make a pentacoordinate silicon complex with a chlorine atom, which could then be replaced by another substituent. Indeed, the monodipyrrin complex **3-OH** and disiloxane derivative **$3_2$-O** were obtained after quenching the reaction with wet MeOH (Scheme 3). The silanol **3-OH** (41%) was almost exclusively isolated, and the yield of **$3_2$-O** was extremely low (<1%). This unusual formation of the silanol is ascribed to the intrinsic properties of the hypercoordinate silicon compounds.

### Table 1. Optical Properties of the Dipyrrin−Silicon Complexes in $CHCl_3$

| | $\lambda_{abs}$/nm | $\lambda_{fluor}$/nm | $\Phi_F$ |
|---|---|---|---|
| **3-Me** | 606 | 649 | 0.76 |
| **4-Me** | 606 | 648 | 0.012 |
| **3-Ph** | 612 | 662 | 0.72 |
| **4-Ph** | 613 | 660 | 0.03 |
| **3-OH** | 605 | 626 | 0.81 |
| **$3_2$-O** | 573, 601 | 664,[a] 671[b] | 0.44,[a] 0.37[b] |

[a] After excitation at 601 nm. [b] After excitation at 573 nm.

### Scheme 3. Synthesis of Silicon Complexes 3-OH and $3_2$-O



The $^1$H NMR spectra of **3-OH** and **$3_2$-O** indicated $C_s$-symmetric dipyrrin moieties. The $^{29}$Si NMR spectra showed singlets at −141.2 and −148.6 ppm for **3-OH** and **$3_2$-O**, respectively. These spectra also suggested the formation of pentacoordinate silicon complexes. The IR spectrum of **3-OH** showed the O−H stretching vibration peak at 3440 cm$^{-1}$ and no asymmetric Si−O−Si stretching vibration band at 1112 cm$^{-1}$, which was observed in **$3_2$-O**. The electrospray ionization (ESI) mass spectrum of **$3_2$-O** showed a peak at $m/z$ 959.3, consistent with a disiloxane structure. The diffusion constants obtained using diffusion-ordered NMR spectroscopy (DOSY) are $6.0 \times 10^{-10}$ and $7.3 \times 10^{-10}$ m$^2$/s for **$3_2$-O** and **3-OH**, respectively. These results are consistent with **3-OH** being the monomeric product, as the diffusion constant of **3-Me** is $7.7 \times 10^{-10}$ m$^2$/s. Finally, X-ray structural analysis revealed that the two silicon dipyrrin moieties of **$3_2$-O** were connected by a $\mu$-oxo oxygen (O3) located at the inversion center, indicating a linear Si−O−Si arrangement (Figure 2).[13,16,17]

Although the usual tetracoordinate siloxanes are resistant toward hydrolysis, disiloxane **$3_2$-O** was hydrolyzed to **3-OH** by refluxing in wet MeOH. The $^1$H NMR spectrum in $CDCl_3$ showed the formation of **3-OH** and **$3_2$-O** in a ratio of 95:5. Very interestingly, this hydrolysis−dehydration process was reversible. The dehydration of **3-OH** by refluxing in hexane gave **$3_2$-O** with high efficiency (**$3_2$-O**:**3-OH** = 90: 10).

Disiloxane **$3_2$-O** showed two absorption bands at 573 and 601 nm (Table 1). This spectral pattern may suggest an interaction between the two silicon−dipyrrin moieties. **$3_2$-O** showed two different fluorescence peaks at 671 and 664 nm upon excitation at 573 and 601 nm, respectively.[18] In contrast, **3-OH** showed much sharper absorption and fluorescence spectral bands than **$3_2$-O** (Figure 3). **3-OH** had twice the fluorescence quantum yield (0.81) as **$3_2$-O** (~0.4). Thus, the definitely different optical properties can be well-controlled in an off/on switching fashion by the facile dehydration/hydration process on

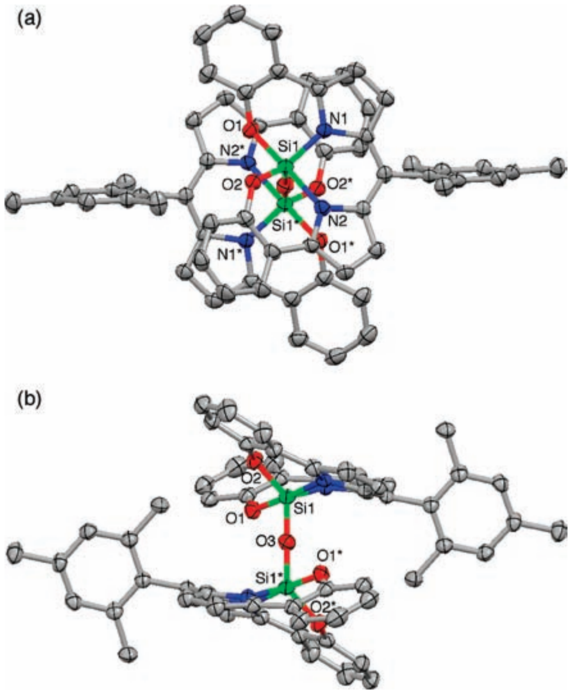


**Figure 2.** Crystal structure of **3$_2$-O**: (a) top view; (b) side view. Thermal ellipsoids are displayed at the 50% level. Colors: C, gray; N, blue; O, red; Si, green. Hydrogen atoms have been omitted for clarity.

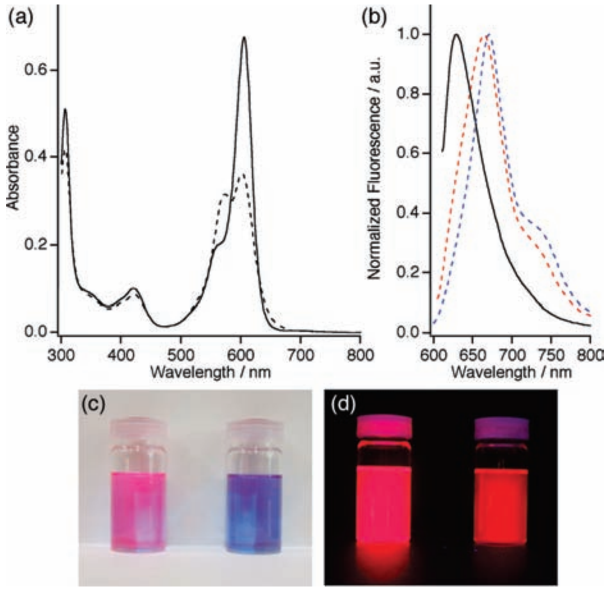


**Figure 3.** (a) Absorption and (b) fluorescence spectra of **3-OH** (solid line) and **3$_2$-O** (dashed line) in CHCl$_3$. The samples were excited at 605 nm (**3-OH**), 573 nm (**3$_2$-O**, blue line), and 601 nm (**3$_2$-O**, red line). (c, d) Photographs of **3-OH** (left) and **3$_2$-O** (right) were taken under (c) ambient light and (d) UV light (365 nm).

the basis of the unique reactivities of the hypercoordinate dipyrrin−silicon complexes.

In conclusion, the first synthesis of hypercoordinate silicon complexes with N$_2$O$_2$-type dipyrrins, red/NIR-fluorescent silicon analogues of BODIPY, has been accomplished. Structural interconversion between the pentacoordinate silanol and siloxane by utilizing their peculiar reactivities provided unprecedented regulation of the optical properties. The results obtained here promise versatile applications using this off/on switching ability by interconversion between the hypercoordinate silicon compounds.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Crystallographic data (CIF), synthetic procedures, and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal data for **4-Ph**: C$_{33}$H$_{22}$N$_2$O$_2$Si, $M$ = 506.62; triclinic; $a$ = 10.0066(5) Å, $b$ = 11.3661(6) Å, $c$ = 12.8556(9) Å, $\alpha$ = 62.181(2)°, $\beta$ = 77.287(2)°, $\gamma$ = 70.1211(14)°; $U$ = 1212.79(12) Å$^3$; $T$ = 120(2) K; space group $P\bar{1}$ (No. 2); $Z$ = 2; 12001 reflns measured, 5484 unique ($R_{\mathrm{int}}$ = 0.0395); $R_1$ = 0.0627 [$I > 2\sigma(I)$], $wR_2$ = 0.1564 (all data), GOF($F^2$) = 1.101.

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(14) The pentacoordination characters %TBP$_a$ and %TBP$_e$ were determined as 95.3 and 99.7%, respectively, indicating a nearly ideal TBP structure for **4-Ph**. See: Tamao, K.; Hayashi, T.; Ito, Y. *Organometallics* **1992**, *11*, 2099.

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(16) Crystal data for **3$_2$-O**: C$_{60}$H$_{46}$N$_4$O$_5$Si$_2$, $M$ = 959.20; triclinic; $a$ = 10.6926(12) Å, $b$ = 10.9105(9) Å, $c$ = 11.2603(12) Å, $\alpha$ = 65.661(2)°, $\beta$ = 76.871(3)°, $\gamma$ = 87.781(3)°; $U$ = 1161.2(2) Å$^3$; $T$ = 120(2) K; space group $P\bar{1}$ (No. 2); $Z$ = 1,; 11621 reflns measured, 5296 unique

($R_{\mathrm{int}}$ = 0.0621); $R_1$ = 0.0562 [$I > 2\sigma(I)$], $wR_2$ = 0.1617 (all data), GOF($F^2$) = 1.095.

(17) %$\mathrm{TBP_a}$ and %$\mathrm{TBP_e}$ were determined as 95.5 and 99.8%, respectively, for **$3_2$-O**.

(18) This probably resulted from interconversion of the two isomers by pseudorotation and/or two different transitions of **$3_2$-O**.