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Synthesis of Dibenzo[*b,f*]silepins with a Benzoquinolyl Ligand

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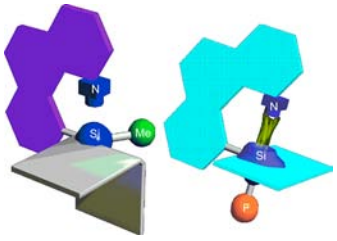
ABSTRACT



A benzo[*h*]quinolyl ligand provided pentacoordinate character for silicon in dibenzo[*b,f*]silepins. Substituents on the silicon center determined both conformations of the dibenzosilepin and luminescence properties in relation to charge transfer.

Silicon in organic molecules has shown various coordination and oxidation numbers and is a key unit to provide attractive structures and unique properties. Tetracoordinate silicon compounds with C−Si single bonds are so stable under air that many π-conjugated organosilicons have been already applied to organic electronics devices.[1,2] In recent years, stabilizing strategies for low valent silicon species have been radically developed. Kinetically stabilized disilenes[3] and silabenzenes[4] exhibited a bathochromic shift in UV−vis absorption spectra as compared with the corresponding hydrocarbons.

Synthesis of hypervalent silicon compounds was also achieved mainly by two methods.[5] One includes the addition of anions with high affinity to the silicon center, such as fluoride or alkoxide.[6] The other involves intra- or intermolecular donation from the neutral donor unit. The neutral silicon complexes usually require electron-withdrawing substituents on the silicon center[7] or rigid polydentate ligands[8] to exist stably. The pentacoordinate center obtained by these methods shows a trigonal-bipyramidal geometry giving two inequivalent sites of substitution, apical and equatorial. The apical positions are generally occupied by dative moieties or electronegative substituents.[9] In the case of π-conjugated organosilicon compounds, it was found the coordination number influenced optical properties.[10] Switching between the tetra- and pentacoordinate state of the silicon compounds induces changes not only in the structure but also in the

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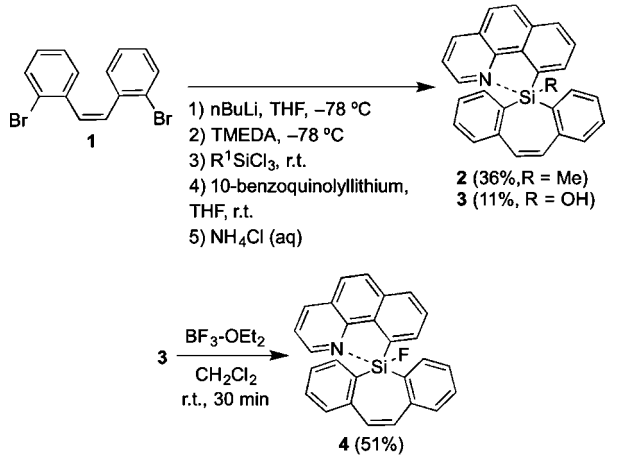
electronic states, resulting in intriguing optical characteristics such as stimuli-responsive changes.[11]

Recently, we demonstrated that a simple bidentate ligand, 10-benzo[*h*]quinoline, can stabilize pentacoordinate structures with N−Si dative bonds in trimethylsilyl, trifluorosilyl, and diethynyl(methyl)silyl derivatives.[12] Pentacoordination of the silicon center induced a bathochromic shift and fluorescence from the benzo[*h*]quinolyl ligand. The characteristic optical property was related to the orbitals localized on the benzoquinolyl ligand, only depending on the degree of the fixation of the ligand.

To construct a cooperative system between substituents on the pentacoordinate silicon center, we herein report the synthesis and properties of benzo[*h*]quinolyldibenzo[*b*,*f*]-silepins with a bending structure by the benzylidene group. The apical and equatorial positions of silicon produce two distinct patterns for placement of the 1,2-diarylethene moiety. Tuning of the conformation was achieved by the substituent on the silicon center (Me or F). Moreover, we observed the conformation and substituent influenced charge transfer efficiencies between the dibenzosilepin moiety and the benzoquinolyl ligand by photoirradiation.

Scheme 1. Synthesis of Benzo[*h*]quinolyldibenzo[*b*,*f*]silepins[a]



[a] TMEDA: *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine. R^1: Me for **2**, $O(CH_2)_2O(CH_2)_2OEt$ for **3**.

Entry to the desired dibenzo[*b*,*f*]silepins begins with a dibrominated 1,2-diphenylethene **1** and its dilithiation (Scheme 1).[13] The dilithiated species reacted with trichloro(methyl)silane followed by addition of 10-benzo[*h*]quinolyllithium to give the methylated benzo[*h*]quinolyldibenzo[*b*,*f*]silepin **2**. To prepare the fluorinated dibenzo[*b*,*f*]silepin, synthesis of an alkoxylated dibenzo[*b*,*f*]silepin was executed using the same procedure for **2** utilizing an alkoxytrichlorosilane. After column chromatography and recrystallization, the products were separated. Although the structures were not definitively determined by the ^{1}H NMR spectra because of the diverse peaks, elemental analysis and mass spectra supported that the product was hydrolyzed during purification, resulting in hydroxylated dibenzo[*h*]quinolyldibenzo[*b*,*f*]silepin **3**. Boron trifluoride diethyl etherate successfully exchanged the hydroxy group of **3** for fluoride to give compound **4**.

The solid-state structures of the obtained dibenzosilepins were determined by X-ray diffraction analysis (Figure 1). In compound **2**, the methyl group, which is electron donating, occupied the equatorial position. Therefore, the diphenylethene moiety was arranged in the apical-equatorial manner. The structure of **3** also looked like an apical-equatorial conformation (Supporting Information, Figure S9). The benzoquinoline's nitrogen, however, pointed to the hydroxy group. This means that the structure of **3** was governed not only by pentacoordination of the silicon center but also by a H-bond. In compound **4**, fluoride occupied the apical position and directed the diphenylethene moiety to an equatorial-equatorial conformation. As the N−Si distance shortens in the order **3** (2.818 Å) > **2** (2.761 Å) > **4** (2.341 Å), the sum of the three angles formed by the equatorial atoms increases in the order **3** (341.55°) < **2** (343.84°) < **4** (353.26°). The order suggests that the H-bond disturbed the pentacoordination of the silicon center and that fluoride enhanced the pentacoordinate character. The angle N1−Si1−F1 (174.54(10)°) in **4** was closer to 180° than that of N1−Si1−C28 (169.6°) in **2**, indicating that the silicon center strongly interacted with the electron pair from the N-atom. The pentacoordinate characters, $\%TBP_a$ and $\%TBP_e$,[14] were determined as 25% and 42% for **3**, 30% and 49% for **2**, and 55% and 79% for **4**, respectively. From these values, the configurations around the silicon center are intermediate structures between tetrahedron and trigonal-bipyramid. The dihedral angles between phenyl and vinylene moieties of **2** and **4** were 46° and 29° (averaged four dihedral angles, and neglecting front or back side of

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the surface), respectively. The conformation of the diphenylethene moiety, apical-equatorial and equatorial-equatorial, plays a crucial role in the silepin structure.

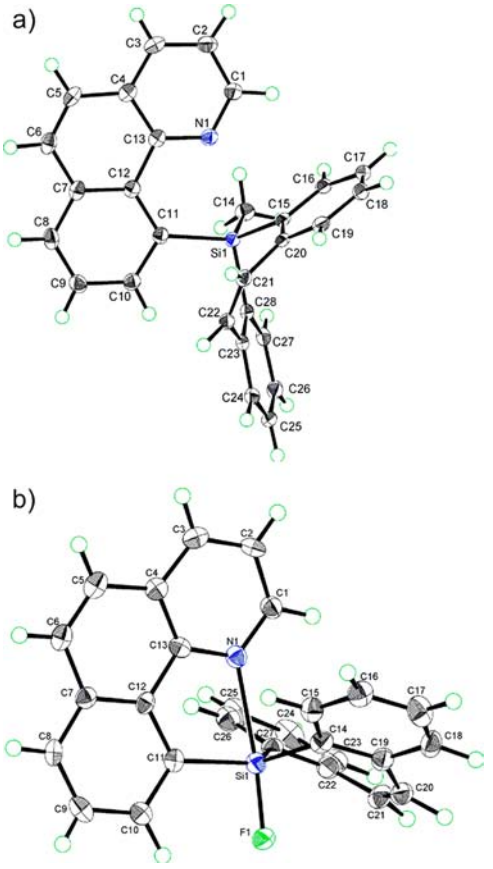

Figure 1. X-ray crystal structures of (a) **2** and (b) **4** with thermal ellipsoids drawn to the 50% probability level. Selected bond lengths [Å] and angles [deg]: **2**: Si1−N1 = 2.761, Si1−C15 = 1.8782(19), Si−C28 = 1.897(2), C28−Si1−C11 = 104.47(8), C14−Si1−C28 = 107.73(9), C15−Si1−C28 = 99.00(8), C14−Si1−C15 = 113.09(9), N1−Si1−C28 = 169.6, C19−C20−C21−C22 = 134.4(2), C21−C22−C23−C24 = 134.8(2); **4**: Si1−N1 = 2.341(2), F1−Si1−C11 = 97.04(12), F1−Si1−C27 = 99.34(11), F1−Si1−C14 = 99.78(12), C27−Si1−C11 = 120.34(15), C14−Si1−C11 = 119.98(15), C27−Si1−C14 = 112.94(15), N1−Si1−F1 = 174.54(10), C18−C19−C20−C21 = 149.7(4), C18−C19−C20−C21 = 153.4(4).

The structures of **2** and **4** in the solution state were investigated by NMR spectroscopy at rt. The ^{29}Si NMR signal of **4** (δ = −40.3 ppm) appeared in the upper field compared to that of **2** (δ = −20.2 ppm), representing a strong N−Si interaction in **4**. Although the extent of the pentacoordination character was different, both of them showed an upfield shift by the nitrogen's electron pair as compared with tetracoordinate analogues ($\delta \approx -10$ ppm).[2] In the ^{1}H NMR spectra of **2**, no separation of the peak derived from the apical-equatorial conformation was observed, implying rotation of the diarylethene moiety in the solution state. While there was only one ^{1}H NMR signal (2 protons) of **2** between 6.0 and 7.0 ppm assignable to the vinylene group, two signals (2 and 4 protons) appeared in ^{1}H NMR spectra of **4**. One is assignable to the vinylene group, and the other is assignable to the 3,4,6,7-protons of dibenzo[*b,f*]silepin shielded by the benzoquinolyl ring. This shielding indicates that the equatorial-equatorial conformation of the diphenylethene moiety remained in the solution state due to the strong electron-withdrawing character of fluoride.

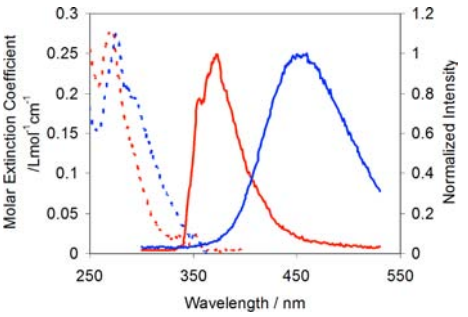

Figure 2. UV−vis (left, dotted line) and normalized photoluminescence spectra (right, solid line, excited at absorption maxima) of **2** (red) and **4** (blue) in CH_2Cl_2 (1.0×10^{-5} M).

Figure 2 displays the UV−vis absorption and photoluminescence spectra of **2** and **4** excited at the absorption maxima in dichloromethane ($c = 1.0 \times 10^{-5}$ M). The absorption peak of **4** with a shoulder around 300 nm slightly shifted to a longer wavelength region as compared with that of **2**. Moreover, compounds **2** and **4** showed absorption bands around 350 nm assignable to the transition between frontier orbitals of benzo[*h*]quinoline.[15] In photoluminescence spectra, compound **4** showed a larger Stokes shift than compound **2**, and those peak shapes were different. The photoluminescence spectrometry in other solvents (cyclohexane, tetrahydrofuran, and *N,N*-dimethylformamide) revealed that the peak position of **2** also remained (Table 1 and Figure S10). The peak of **4** shifted to a longer wavelength region as the solvent polarity increased. It can be deduced that fluorescence was derived from the local excited state of the benzoquinolyl ligand in compound **2** and from the charge transfer state from the dibenzosilepin moiety to the benzoquinolyl ligand in compound **4**.

Table 1. Optical Properties of the Pentacoordinate Silicon Complexes

compd	$\lambda_{abs,\ max}$ [nm][a]	$\lambda_{em,cy}$ [nm][b]	$\lambda_{em,\ DCM}$ [nm][c]	$\lambda_{em,\ DMF}$ [nm][d]	Φ_F[e]
2	270	352	373	372	<0.01
4	276	415	464	472	<0.01

[a] Absorption maxima: Dichloromethane (1.0×10^{-5} M). [b] Fluorescence maxima: Cyclohexane (1.0×10^{-5} M). [c] Fluorescence maxima: Dichloromethane (1.0×10^{-5} M). [d] Fluorescence maxima: *N,N*-Dimethylformamide (1.0×10^{-5} M). [e] Absolute fluorescence quantum yield: Dichloromethane (1.0×10^{-5} M).

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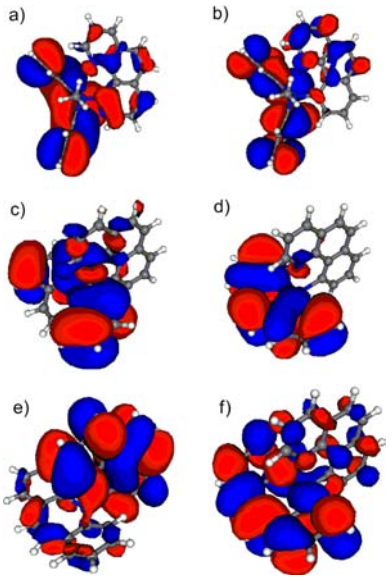

Figure 3. Kohn–Sham orbital diagrams: (a) HOMO of **2**, (b) LUMO+2 of **2**, (c) HOMO−3 of **4**, (d) HOMO of **4**, (e) LUMO of **4**, and (f) LUMO+2 of **4**.

To obtain a better understanding of the structures and properties of the obtained benzoquinolyldibenzosilepins, density functional theory (DFT) calculations of **2** and **4** were performed.[16] The structures were optimized by RI-TPSS-D3(BJ)/def2-SVP, and the N–Si distances (2.738 Å for **2** and 2.410 Å for **4**) were almost identical to those of the crystal structures.[17] The optimization was applied to the opposite conformers, equatorial-equatorial for **2** and apical-equatorial for **4**. Single-point calculation of them (RIJCOSX-PW6B95-D3(BJ)/def2-TZVP)[18] revealed that the apical-equatorial conformation of **2** was more stable by +0.69 kcal/mol at 298 K than the equatorial-equatorial conformation. This small stabilization was inefficient in maintaing the conformation. In **4**, the equatorial-equatorial conformation was more stable by +3.10 kcal/mol at 298 K than the apical-equatorial conformation. This value supports the fixed structure in the solution state. Corresponding with the absorption data, it was found that the HOMO–LUMO band gap of **4** (2.37 eV) is smaller than that of **2** (2.77 eV). Figure 3 displayed the frontier orbitals of **2** and **4** which are responsible for the transition. The conformation hardly changed the distribution of the orbital lobes. Time-dependent DFT calculation (RIJCOSX-PBE0/def2-TZVPP)[19] with Tamm–Dancoff approximation (TDDFT/TDA)[20] suggests that excitation between the orbitals mainly localized on the dibenzosilepin moiety (HOMO → LUMO+2) was likely to occur for **2** (λ = 286 nm, f = 0.1962) and **4** (λ = 310 nm, f = 0.2854). In the **4**, an additional transition was permitted from the orbital localized on the dibenzosilepin moiety to that on the benzoquinolyl ligand (HOMO−3 → LUMO, λ = 299 nm, f = 0.2709). The large oscillation strength of this transition can be explained in terms of the symmetric structures of the complexes. The equatorial-equatorial conformation is categorized to possessing C_s symmetry. In this symmetry, the transition from the orbital with the phase reversal at the symmetric plane to the orbital without phase inversion is accepted. Thus, the oscillation strength can be enlarged. The results from TDDFT/TDA calculation mean that the fixed equatorial-equatorial conformation and fluoride could be responsible for the electronic interaction, inducing charge transfer from the dibenzosilepin moiety to the benzoquinolyl ligand.

In conclusion, benzo[*h*]quinolyldibenzo[*b*,*f*]silepins were synthesized successfully, and their pentacoordination of the silicon center was confirmed by X-ray diffraction analysis, NMR spectroscopy, and DFT calculation. It was found that the methyl and fluoride derivatives favored the apical-equatorial and equatorial-equatorial conformation, respectively. The fixed equatorial-equatorial conformation and the electron-withdrawing substituent on the silicon center provided a large Stokes shift in absorption and luminescence spectra. Modification and functionalization of the new π-conjugated organosilicon molecules are currently underway.

Supporting Information Available. Synthetic procedures, NMR spectra, and the X-ray crystal structure of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

(16) ORCA (version 2.9): F. Neese et al.; see Supporting Information.

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