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COMMUNICATION

Tetracoordinate silicon complexes of 1,2-bis(indol-2-yl)benzene as blue-emitting dyes in the solid state

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Cite this: DOI: 10.1039/x0xx00000x

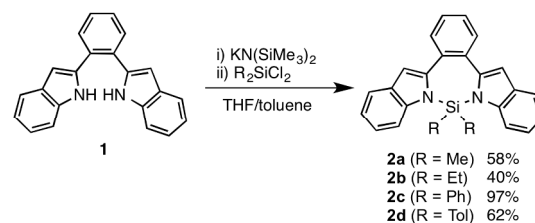
Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

1,2-Bis(indol-2-yl)benzene was prepared and found to serve as an effective bidentate ligand to form stable silicon complexes bearing two N—Si bonds. These complexes take boat-shaped 2,6-diaza-1-silepin structures, which undergo a butterfly-like conformational motion whose activation barriers were determined by shape analysis of variable-temperature ^1H NMR spectra. These silicon complexes exhibit blue emissions in solution and in the solid-state both with high efficiency.

Organosilicon compounds have been known to have potentials as electroluminescent molecules, electron transporting materials and blue-emitting dyes.¹ A variety of molecular designs have thus been invented to lead to the exploration of versatile organosilicon compounds. In most cases, the carbon–silicon bond formation is a key step to synthesise organosilicon compounds such as arylsilanes, siloles and silepins.^{1–3} On the other hand, organosilicon compounds bearing nitrogen–silicon bonds have been still rare, probably due to the intrinsic lability of nitrogen–silicon bonds.⁴ As a rare example, Nabeshima *et al.* reported $\text{N}_2\text{O}_2\text{C}$ -type pentacoordinate silicon complexes of dipyrromethenes bearing two 2-hydroxyphenyl groups that showed strong fluorescence in near infrared (NIR) region.⁵ Recently, Wagler *et al.* have developed tetracoordinate silicon complexes of 1,1-bis(pyrrol-2-yl)ethene whose emission properties are dependent upon the substituents at the silicon and silicon complexes bearing $\text{N}_2\text{O}_2\text{X}_2$ -type hexa-coordinations.⁶ Silicon complexes of porphyrinoids and phthalocyanines are also known as representative complexes bearing nitrogen–silicon bonds, and most of them are fluorescent.⁷ Here we report on 1,2-bis(indol-2-yl)benzene that can serve as a new bidentate ligand to form tetracoordinate silicon complex bearing two N—Si bonds. This report offers a new insight for stabilities of organosilicon complexes bearing N—Si bonds as well as for creation of new fluorophores in the solid-state.



Scheme 1 Synthesis of 2a-d.

We chose 1,2-bis(indol-2-yl)benzene (**1**) as a novel bidentate ligand because of its flexibility to form structurally less constrained silicon complexes and conjugative character of a 1,2-phenylene bridge. In addition, **1** was easily prepared by a coupling reaction of 2-borylindole with 1,2-diiodobenzene in 70% yield (See ESI†). Silicon incorporation has been achieved by deprotonation of the two indolic NH protons with potassium bis(trimethylsilyl)amide followed by addition of dialkyl- or diaryldichlorosilane. After the mixtures were stirred for 12 h, these reactions gave silicon complexes **2a-d** in moderate to good yields (Scheme 1). Complexes **2a-d** were fairly stable during aqueous work up and purification by column chromatography on silica. While complex **2a** undergoes *ca.* 10% decomplexation after storing for 3 months under aerobic conditions, complexes **2b-d** are more stable, being intact after storing even for several months. These stabilities probably stem from a chelate effect associated with the bidentate ligand as well as kinetic stabilisation by the ethyl or aryl substituents at the silicon atom.

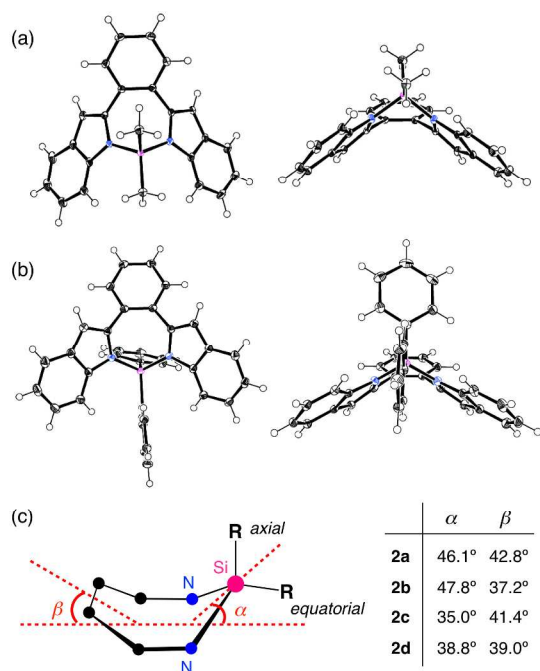


Fig. 1 X-Ray crystal structures of (a) **2a** and (b) **2c**. The thermal ellipsoids were scaled to 50% probability. Solvent molecules were omitted for clarity. (c) A schematic representation of the boat-shape, and a summary of bent-angles.

The solid-state structures of **2a-d** have been revealed by single-crystal X-ray diffraction analysis (Fig. 1 and Fig. S11-12, ESI†). The 1,2-bis(indol-2-yl)benzene ligand takes a V-shaped conformation by coordinating to the silicon atom with N—Si bond lengths of 1.772(1) and 1.765(1) Å for **2a**, 1.763(2) and 1.761(2) Å for **2b**, 1.761(1) and 1.761(1) Å for **2c** and 1.767(1) and 1.761(1) Å for **2d**, respectively. The central 2,6-diaza-1-silepin moiety takes a boat-shaped conformation as is the case in pristine silepins reported by Komatsu and coworkers.³ As shown in Figure 1c, the bent angles α of dialkyl-substituted analogs (46.1° in **2a** and 47.8° in **2b**) are larger than those of diaryl-substituted ones (35.0° in **2c** and 38.8° in **2d**), in line with DFT optimised structures (Fig. S13, ESI†). On the other hand, the bent angles β looks independent of the substituents on the silicon atom. Because of this boat-shaped conformation, the two substituents on the silicon atom are not equivalent, being located at an equatorial and an axial position. Indeed, the ¹H NMR spectrum of **2b** exhibits two sets of ethyl signals at −60 °C, which coalesce into a single broad set at −20 °C and finally become a single set of sharp signals at 60 °C (Fig. S5, ESI†). These temperature-dependent ¹H NMR spectra suggest a conformational inversion of the boat-shaped 2,6-diaza-1-silepin ring as shown in Figure 2a. We then conducted line-shape analyses of variable-temperature ¹H NMR spectra of **2a** and **2d** in order to determine inversion rates (*k*), whereby the singlet signals of the methyl and tolyl groups were used as probes.⁸ The ¹H NMR spectra of **2d** measured in toluene-*d*₈ at various temperatures are shown in Figure 2b. The activation parameters of this conformational dynamics have been determined: $E_a = 13.26$ kcal/mol, $\Delta H^\ddagger = 12.80$ kcal/mol, $\Delta S^\ddagger = 9.30$ cal/mol·K and $\Delta G_{298}^\ddagger = 10.03$ kcal/mol.⁹ In a similar manner, the activation parameters of **2a** have been determined as follows: $E_a = 17.94$ kcal/mol, $\Delta H^\ddagger = 17.40$ kcal/mol, $\Delta S^\ddagger = 20.30$ cal/mol·K and $\Delta G_{298}^\ddagger = 11.35$ kcal/mol (Fig. S4, ESI†). The activation energy and the thermal enthalpy of **2a** are larger than

those of **2d** probably due to the larger α angle as indicated above, that also explain the large positive entropy. The ²⁹Si{¹H} NMR spectra were measured in toluene-*d*₈ at −80 °C, which exhibit signals at 1.51 ppm for **2a**, 3.03 ppm for **2b**, −22.09 ppm for **2c** and −22.21 ppm for **2d**.

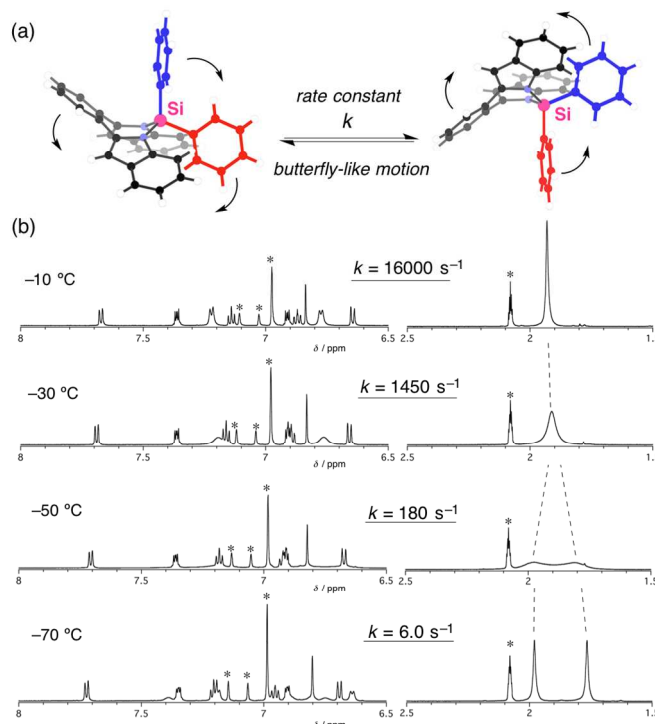


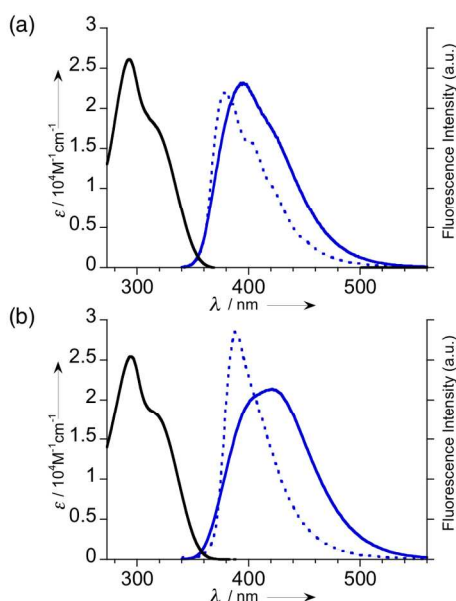
Fig. 2 (a) Representation of butterfly-like motion. (b) VT-¹H NMR spectra of **2d** in toluene-*d*₈. * indicates solvent peaks.

These silicon complexes exhibit absorption bands around 300 nm with a shoulder peak around 320 nm and blue emissions in the range of 350–550 nm as shown in Figure 3 and Table 1. The fluorescence quantum yields of **2a** and **2b** in CH₂Cl₂ are both 0.58, being identical to that of the ligand itself, while the quantum yields of **2c** and **2d** are enhanced to 0.65 and 0.62.^{9,10} In addition, the solid-state emissions are clearly observable for these silicon complexes. Interestingly, the quantum yields of **2a-d** in the solid state are comparable to those in CH₂Cl₂, whereas the ligand **1** only exhibited a weak emission in the solid state. The blue-shifted emission in the solid state should be attributed to the fixed conformations since the emission peak of **2c** observed in 133 K in methylcyclohexane is similarly blue-shifted (Fig. S24, ESI†). The efficient solid-state emission may be accounted for by the suppression of excited energy deactivation process related to the boat-shape conformational change. In addition, the substituents at the silicon atoms may prevent the whole molecule from intermolecular stacking that is in principle crucial for solid-state emission.¹¹

Table 1. Optical properties of **1** and **2a-d**.

compd.	λ_{abs} [nm]	λ_{em} [nm]	$\Phi_{\text{F,DCM}}$	λ_{powder} [nm]	$\Phi_{\text{F,powder}}$
1	293	422	0.58 ^[b]	440	0.09 ^[a]
2a	293	395	0.58 ^[a]	379	0.55 ^[a]
2b	294	394	0.58 ^[a]	390	0.49 ^[a]
2c	294	421	0.65 ^[c]	388	0.54 ^[a]
2d	295	419	0.62 ^[b]	386	0.71 ^[a]

[a] excited at 330 nm. [b] excited at 340 nm. [c] excited at 350 nm

**Fig. 3** UV/Vis absorption (black) and emission (blue) spectra of (a) **2a** and (b) **2c** in CH_2Cl_2 (solid lines) and in the solid state (dashed lines).

In summary, 1,2-bis(indol-2-yl)benzene was newly prepared and found to serve as an effective bidentate ligand to form stable silicon complexes bearing two N—Si bonds. The activation energies of “butterfly-like motion” have been determined by line-shape analysis of temperature variable ^1H NMR spectra. These silicon complexes exhibit blue emissions in solution and in the solid-state both with high efficiency. Further explorations of novel fluorescent silicon complexes are underway in our laboratory.

This work was supported by Grant-in-Aid from JSPS (No. 25220802 (Scientific Research (S)) and No. 26810021 (Young Scientist (B))).

Notes and references

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†Crystallographic data for **2a**: $\text{C}_{24}\text{H}_{20}\text{N}_2\text{Si}_1 \cdot (\text{CHCl}_3)$. $M_w = 483.88$, monoclinic $P2_1/c$ (No. 14), $a = 10.6810(19)$, $b = 19.442(4)$, $c = 11.152(2)$ Å, $\beta = 101.368(4)^\circ$, $V = 2270.4(7)$ Å³, $Z = 4$, $D_c = 1.416$ g/cm³, $R_1 = 0.0277$ ($I > 2.0\sigma(I)$), $wR_2 = 0.0758$ (all data), $S = 1.039$, CCDC 1050753. **2c**: $(\text{C}_{34}\text{H}_{24}\text{N}_2\text{Si}_1)_2 \cdot (\text{C}_4\text{H}_8\text{O})$. $M_w = 1049.39$, monoclinic $C2/c$ (No. 15), $a = 21.767(4)$, $b = 12.983(2)$, $c = 19.854(4)$ Å, $\beta = 108.480(4)^\circ$, $V = 1996.68(6)$ Å³, $Z = 4$, $D_c = 1.306$ g/cm³, $R_1 = 0.0461$ ($I > 2.0\sigma(I)$), $wR_2 = 0.1126$ (all data), $S = 1.073$, CCDC 1050755.

†Electronic Supplementary Information (ESI) available: Experimental procedures, spectral data for all new compounds, photophysical data and crystallographic data of **2b** (CCDC 1050754) and **2d** (CCDC 1050756). For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c000000x/

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