COMMUNICATION

Synthesis, Structures and Photophysical Properties of Hexacoordinated Organosilicon Compounds with 2-(2-Pyridyl)phenyl Groups

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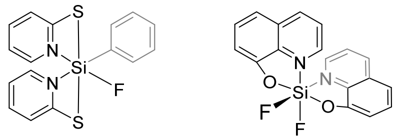
We synthesised novel hexacoordinated organosilicon compounds with two 2-(2-pyridyl)phenyl groups. Single-crystal X-ray structure analyses indicated that Lewis acid-base interactions exist between the silicon atom and two nitrogen atoms of the pyridine rings, and that hexacoordinated organosilicon compounds have slightly distorted octahedral structures in the solid state. The hexacoordinated organosilicon compounds are stable in air, water, heat, acids, and bases. Fluorescent quantum yield increased dramatically and a significant red-shift of the maximum fluorescence wavelength was observed with the introduction of amino groups on the 2-(2-pyridyl)phenyl aromatic rings. The fluorescent colours of a hexacoordinated organosilicon compound with two amino groups can be switched by protonation and deprotonation (neutralisation) of the amino groups.

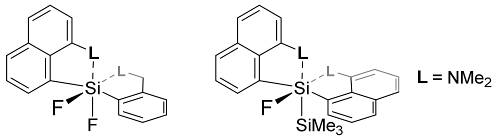
Hypervalent organosilicon compounds, such as pentacoordinated and hexacoordinated organosilicons, are important intermediates in synthetic organic reactions[1] and organic functional materials.[2] Thus, it is of interest to synthesise hypervalent organosilicon compounds and investigate their properties. There have been many reports on the synthesis of pentacoordinated organosilicon compounds,[1b] such as organosilicates[3] and π-conjugated molecules with intramolecular Lewis acid-base interactions between the silicon and nitrogen/oxygen atoms.[4,5] We recently reported the synthesis and photophysical properties of pentacoordinated organosilicon compounds with a 2-(2-pyridyl)phenyl group, which can be regarded as silafluorene equivalents.[6,7]

Additional hexacoordinated organosilicon compounds, such as hexacoordinated silicates[1b,8] and hexacoordinated organosilicon compounds with Lewis acid-base interactions (Fig. 1a) have been reported.[4a,b,9,10] However, the synthesis of neutral hexacoordinated organosilicon compounds with C,N-bidentate ligands are less developed (Fig. 1b).[10a,c,d,g] Our previous reports on the synthesis of pentacoordinated organosilicon compounds with a 2-(2-pyridyl)phenyl group[6,7] inspired us to design and synthesize hexacoordinated organosilicon compounds which contain two C,N-bidentate ligands and form two silafluorene equivalent moieties (Fig. 1c).

(a) Hexacoordinated organosilicon compounds containing pyridine ligands[9b,c]



(b) C,N-bidentate hexacoordinated organosilicon compounds[10a,d]



(c) **This work:** Hexacoordinated organosilicon compounds with 2-(2-pyridyl)phenyl groups

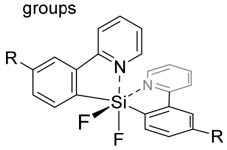


Fig. 1. Examples of hexacoordinated organosilicon compounds.

Hexacoordinated silicon compound **2a** was synthesised by lithiation of 2-(2-bromophenyl)pyridine (**1a**), followed by treatment of the formed 2-(2-lithiophenyl)pyridine with tetrachlorosilane and replacement of the chlorine atoms of the formed diaryldichlorosilane intermediate with silver fluoride (Scheme 1).[11] In this synthesis, **2a** was obtained in 65% yield as a white solid.[12] Interestingly, organosilicon compound **2a** was stable in air, water, heat, acids, and bases.

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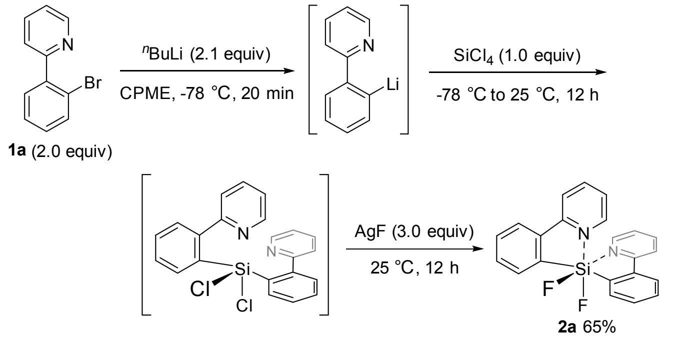
† Electronic Supplementary Information (ESI) available: General experimental procedure and characterization data for hexacoordinated organosilicon compounds **2a**-**2c**. See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis of hexacoordinated silicon compound **2a**

The structure of compound **2a** in the solid state was determined by single-crystal X-ray structure analysis (Fig. 2).[13] Analysis reveals that **2a** comprises a hexacoordinated silicon (with N atoms *trans* to F atoms) in the solid state and has a slightly distorted octahedral structure; Lewis acid-base interactions exist between the silicon centre and the two nitrogen atoms of the pyridine moieties (Si–N bond lengths = 2.09 and 2.12 Å). In addition, the two 2-pyridylphenyl moieties are almost perpendicular to each other.

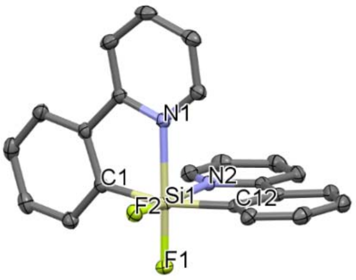


Fig. 2. Single crystal X-ray structure of hexacoordinated silicon compound **2a**. The ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected distances [Å]: Si1–N1 2.0949(11), Si1–N2 2.1172(11), Si1–F1 1.6610(8), Si1–F2 1.6586(8), Si1–C1 1.9064(13), Si1–C12 1.9111(13). Selected angles [°]: N1–Si1–N2 85.74(4), N1–Si1–C12 88.89(5), N1–Si1–F1 173.53(5), N1–Si1–F2 88.94(4), N1–Si1–C1 80.83(5), N2–Si1–C12 80.25(5), N2–Si1–F1 89.43(4), N2–Si1–F2 173.17(4), N2–Si1–C1 88.03(5), C12–Si1–F1 94.53(5), C12–Si1–F2 95.38(5), C12–Si1–C1 164.98(6), F1–Si1–F2 96.19(4), F1–Si1–C1 94.73(5), F2–Si1–C1 95.35(5).

Next, we synthesized hexacoordinated silicon compounds **2b** and **2c** with amino and trifluoromethyl groups on the aromatic rings (Fig. 3), respectively. Single-crystal X-ray structure analysis of **2b** indicates that the silicon atom in **2b** also is hexacoordinated via intramolecular Lewis acid-base interactions in the solid state.[13]

Although compounds **2a**–**c** exist as hexacoordinated structures in the solid state, some small signals are observed at around 9.25 ppm in the ^1H NMR spectrum (in $CDCl_3$ solution) of **2a** (Fig. S5); several weak signals are also detected in the ^{19}F NMR spectrum (Fig. S7). Two triplets are observed at -129.5 ppm (major) and -153.3 ppm (minor) in the ^{29}Si NMR spectrum (Fig. S8). These results suggest that hexacoordinated compound **2a** exists as a mixture of hexacoordinated isomers or species with different coordination numbers in solution. ^1H and ^{19}F NMR spectra of **2c** in $CDCl_3$ solution are similar to those of **2a** (Figs. S14–S16). In contrast, the hexacoordinated silicon compound **2b** is observed as a single component in ^1H and ^{13}C NMR spectra (Figs. S10 and S11).[14] In addition, a triplet at -125.1 ppm is observed in the ^{29}Si NMR spectrum in $CDCl_3$ solution (Fig. S13). Although a ligand exchange reaction of **2b** and DMAP (2 equiv) was investigated, coordination of DMAP to complex **2b** was not observed in ^1H NMR spectrum at 25 °C (Fig. S17).

The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of **2a**–**2c**, and their energy levels, were calculated by DFT calculations at the B3LYP/6-31G(d) level of theory (Fig. 4). The HOMO–LUMO energy gap of **2b** (3.76 eV) is smaller than that of **2a** (4.66 eV) and **2c** (4.75 eV) because the HOMO energy level of **2b** significantly increases by the amino groups which are strong electron-donating groups. Unlike **2a** and **2c**, the HOMO and HOMO-1 of **2b** are delocalized on the dimethylaniline moieties, whereas the LUMO and LUMO+1 are distributed on the pyridine moieties (Fig. S3).

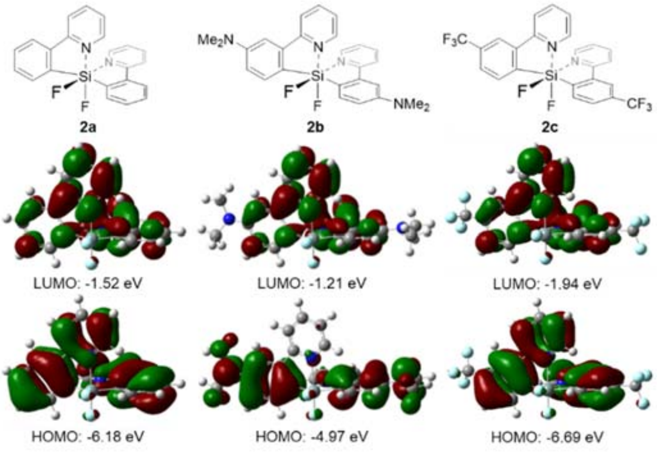


Fig. 4. HOMO and LUMO distributions and energy levels of hexacoordinated organosilicon compounds **2a**–**2c**.

The optical properties of compounds **2a** and **2b** in CH_2Cl_2 solution were examined by UV/Vis absorption and photoluminescence spectroscopy (Fig. 5). Compared to **2a**, the absorption of **2b** is observed at a longer wavelength (368 nm). Considering that **2b** exists as a single structure in solution, it is reasonable to suggest that the longer wavelength absorption is derived from the hexacoordinated structure of **2b**. TD-DFT calculations for hexacoordinated compound **2b** at the B3LYP/6-31G(d) level of theory indicate that the broad absorption around 368 nm comprises four peaks derived from HOMO→LUMO (λ_{cal} = 390 nm), HOMO-1→LOMO (λ_{cal} = 387 nm), HOMO→LUMO+1 (λ_{cal} = 381 nm), and HOMO-1→LUMO+1 (λ_{cal} = 380 nm) transitions (Table S20 and Fig. S4). The results suggest that the longest wavelength absorption (λ = 368 nm) has intramolecular charge-transfer (ICT) character, which is also supported by the red-shift in absorption observed with increasing solvent polarity (Fig. S1).

Compounds **2a**–**c** fluoresces in CH_2Cl_2 solution (Fig. 5a). Compounds **2a** and **2c** showed similar optical properties. On the other hand, introducing two amino groups on the aromatic rings results in a longer maximum fluorescent wavelength for **2b** in CH_2Cl_2 solution; fluorescent quantum yield also increased dramatically (λ_{em} = 528 nm, Φ_F = 0.12, Fig. 5b). Red-shift in florescence was observed with increasing solvent polarity (Fig. S1), which suggested that **2b** has ICT character in emission. The maximum fluorescence wavelength (λ_{em} = 529 nm) in a powder solid of **2b** is almost the same as that in CH_2Cl_2 solution (Fig. S2).

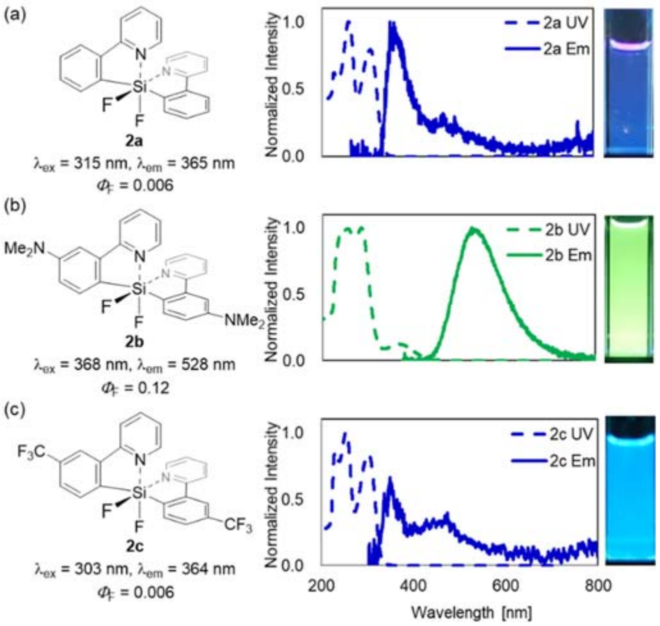


Fig. 5. Optical properties of compounds **2a**–**2c**.

The silicon compound with two amino groups, **2b,** changes fluorescence colour via protonation and deprotonation of the amino groups (Fig. 6). The colour switches from green to yellow after the addition of trifluoroacetic acid (TFA). This colour change is reversible with the addition of trimethylamine (TEA).

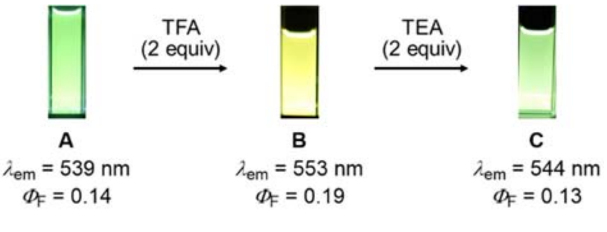


Fig. 6. Switching of fluorescent colours of organosilicon compound **2b**.

Conclusions

In summary, we synthesised novel hexacoordinated silicon compounds by lithiation of 2-(2-bromophenyl)pyridine derivatives, followed by treatment of the formed lithiated 2-phenylpyridines with tetrachlorosilane, then replacement of the chlorine atoms of the formed diaryldichlorosilane intermediates with silver fluoride. The structures of the hexacoordinated silicon compounds were determined by single-crystal X-ray structure analysis. Lewis acid-base interactions exist between the silicon atom and two pyridine nitrogen atoms, and the hexacoordinated organosilicon compounds have slightly distorted octahedral structures. The hexacoordinated organosilicon compounds are stable in air, water, heat, acids, and bases. The hypervalent silicon compounds exhibited fluorescent properties. Longer maximum fluorescent wavelengths and dramatically increased fluorescent quantum yields resulted when two amino groups were introduced on the aromatic rings. The fluorescent colours of a hexacoordinated organosilicon compound containing two amino groups can be switched by protonation and neutralization. We propose that these hexacoordinated organosilicon compounds offer new insights into organosilicon chemistry and contribute to the field of organic functional materials.

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Conflicts of interest

There are no conflicts to declare.

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12 Please see the Supplemental Information for the optimization of reaction conditions (Table S1).

13 Please see the Supplemental Information for the detail. CCDC 1987499 (**2a**), 1987501 (**2b**), and 1987500 (**2c**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

14 In ^{19}F NMR, the other kind of peak was slightly detected. Please see the Supplemental Information for the detail.