J. Am. Chem. Soc. **2000,** *122,* 6793−6794

Photophysical Properties Changes Caused by Hypercoordination of Organosilicon Compounds: From Trianthrylfluorosilane to Trianthryldifluorosilicate

Shigehiro Yamaguchi,* Seiji Akiyama, and Kohei Tamao*

Institute for Chemical Research, Kyoto University
Uji, Kyoto 611-0011, Japan

Received March 24, 2000

Modification of π-electron systems by the main group elements represents a new direction toward the construction of organic materials with unusual electronic structures and with unique functions such as sensory materials. One promising way is the use of specific orbital interactions between carbon π-conjugated systems and the main-group element moieties.[1] Another potential way may be to take advantage of the hypercoordination abilities of the main-group elements. The latter involves the electronic and structural perturbations induced by hypercoordination. For example, in the case of the group 14 compounds having extended π-electron systems as substituents, the structural change from tetrahedral to trigonal bipyramidal by pentacoordination would cause a change in the interligand through-space interaction, as visualized in Figure 1. This perturbation by the structural change in addition to the intrinsic electronic perturbation by the hypercoordination would substantially change the properties of the π-systems. However, little attention has been paid to this possibility so far,[2] despite extensive studies on the hypercoordinate main-group element compounds from the viewpoints of their syntheses, structures and reactivities.[3] In this contribution, we present the first example of controlling the photophysical properties derived from the hypercoordination of group 14 elements.

As a group 14 compound having extended π-conjugated substituents, tri(9-anthryl)fluorosilane **1**[4] was used in this study. In comparison with anthracene itself ($\lambda_{\mathrm{abs},0-0}$ 376 nm, $\lambda_{\mathrm{em},0-0}$ 381 nm, Φ_f 0.31 in THF), compound **1** has red-shifted absorption and emission maxima and a significantly lower quantum yield ($\lambda_{\mathrm{abs},0-0}$ 401 nm, $\lambda_{\mathrm{em},0-0}$ 416 nm, Φ_f 0.033 in THF).[4] These unique photophysical properties, due to the through-space interaction between the anthryl groups, render it a suitable material for the present study.

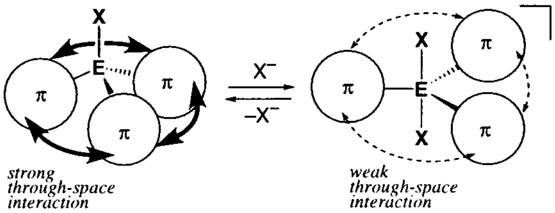


Figure 1. Schematic representation of the change in the through-space interaction between π-ligands by hypercoordination of the central group 14 element.

The addition of fluoride ion to the fluorosilane **1** afforded trianthryldifluorosilicate **2**: The use of KF/[2.2.2]cryptand as a fluoride source[5] made it possible to isolate the silicate $\mathbf{2}\cdot\mathrm{K}^+$/cryptand in 74% yield as air-stable, pale yellow crystals, as shown in Scheme 1.[6]

A comparison of the crystal structure of the silicate $\mathbf{2}\cdot\mathrm{K}^+$/cryptand with that of **1** reveals the structural changes by hypercoordination.[7] One of two crystallographically independent structures of **2** is shown in Figure 2. The structure of **1** has already been reported in our previous report.[4] While the silane **1** has a tetrahedral structure with a rather flat geometry around the central silicon atom ($\sum\angle\mathrm{C}_{ipso}-\mathrm{Si}-\mathrm{C}_{ipso} = 345.7°$), the silicate **2** has a nearly ideal trigonal bipyramidal structure ($\angle\mathrm{F}-\mathrm{Si}-\mathrm{F}$, av 176.6°, $\sum\angle\mathrm{C}_{ipso}-\mathrm{Si}-\mathrm{C}_{ipso} = 360°$). In both compounds, the three anthryl groups are arranged in a propeller-like fashion: The C−C−Si−F dihedral angles are in the range of 37.1−44.1° for **1** and 41.5−53.1° for **2**. The change from **1** to **2** causes a slight elongation of the Si−F and $\mathrm{Si}-\mathrm{C}_{ipso}$ bond lengths by ~0.09 and 0.07 Å, respectively. As a result of the expansion of the $\mathrm{C}_{ipso}-\mathrm{Si}-\mathrm{C}_{ipso}$ angles and the elongation of the $\mathrm{Si}-\mathrm{C}_{ipso}$ bond lengths, the $\mathrm{C}_{ipso}\text{- - -}\mathrm{C}_{ipso}$ nonbonded distances between the anthryl groups are 0.1−0.3 Å elongated from **1** (3.18−3.19 Å) to **2** (3.28−3.45 Å). These structural changes due to the pentacoordination crucially affect the photophysical properties as described below.

The changes in the UV−visible absorption and fluorescence spectra have been investigated by the addition of $n\text{-Bu}_4\mathrm{NF}$ (TBAF) as a fluoride source into a THF solution of trianthrylfluorosilane **1**, as shown in Figure 3. In the UV−visible absorption spectra, as the amount of TBAF increases, new bands of the silicate $\mathbf{2}\cdot\mathrm{NBu}_4^+$ appear at about 10 nm shorter wavelengths relative to **1**, along with the disappearance of the absorption bands of **1**. In the fluorescence spectra, a more dramatic change has been observed. Thus, upon the formation of the silicate $\mathbf{2}\cdot\mathrm{NBu}_4^+$, the intensity of the emission significantly increases with about 20 nm hypsochromic shifts of the emission maxima. The quantum yield determined with anthracene as a standard increases more than 20 times from **1** (Φ_f 0.033) to **2** (Φ_f 0.64).[8] This notable change is visualized in Figure 4. It is thus demonstrated that the "off-on" behavior of the anthryl fluorophore can be controlled on the basis of the coordination number of the silicon atom.

---

(1) For examples: (a) Salzner, U.; Lagowski, J. B.; Pickup, P. G.; Poirier, R. A. *Synth. Met.* **1998**, *96*, 177. (b) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379. (c) Yuan, Z.; Taylor, N. J.; Ramachandran, R.; Marder, T. B. *Appl. Organomet. Chem.* **1996**, *10*, 305. (d) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112. (e) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10776. (f) Noda, T.; Shirota, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9714. (g) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.*, **1998**, 3693. (h) Yamaguchi, S.; Itamai, Y.; Tamao, K. *Organometallics* **1998**, *17*, 4910. (i) Deschamps, E.; Ricard, L.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1158. (j) Hay, C.; Vilain, D. L.; Deborde, V.; Toupet, L.; Réau, T. *Chem. Commun.* **1999**, 345. (k) Mao, S. S.; Tilley, T. D. *Macromolecules* **1997**, *30*, 5566. (l) Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Antolini, L.; Pudova, O.; Bongini, A. *J. Org. Chem.* **1998**, *63*, 5497. (m) Jiang, B.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9744.

(2) Corriu and co-workers reported the effect of hypercoordination toward the oxidation potentials in a series of ferrocenylsilicates: Cerveau, G.; Chuit, C.; Colomer, E.; Corriu, R. J. P.; Reyé, C. *Organometallics* **1990**, *9*, 2415.

(3) Hypercoordinate silicon compounds, reviews: (a) Tandura, S. N.; Alekseev, N. V.; Voronkov, M. G. *Top. Curr. Chem.* **1986**, *131*, 99. (b) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; p 1241. (c) Chuit, C.; Corriu, R. J. P.; Reyé, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (d) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z.; Apeloig, Y., Eds.; John Wiley: Chichester, 1998; Vol. 2, Part 2, p 1339.

(4) Yamaguchi, S.; Akiyama, S.; Tamao, K. *Organometallics* **1998**, *17*, 4347.

(5) Yamaguchi, S.; Akiyama, S.; Tamao, K. *Organometallics* **1999**, *18*, 2851.

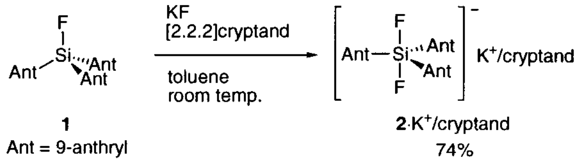
(6) **(6)**$\mathbf{2}\cdot\mathrm{K}^+$/[2.2.2]cryptand: mp 167 °C dec. ^{1}H NMR (acetone-d_6) δ 2.55 (t, J = 4.6 Hz, 12H), 3.55 (t, J = 4.6 Hz, 12H), 3.58 (s, 12H), 6.41−6.47 (m, 6H), 7.01−7.06 (m, 6H), 7.82 (d, J = 8.1 Hz, 6H), 8.33 (s, 3H), 8.76 (d, J = 9.2 Hz, 6H). ^{13}C NMR (THF-d_8) δ 54.43, 68.17, 71.00, 122.15, 124.00, 126.97, 128.23, 132.83, 135.76, 137.64, 154.00 (t, $^2J_{\mathrm{CF}}$ = 39.0 Hz). ^{19}F NMR (acetone-d_6) δ −49.71. ^{29}Si NMR (THF-d_8) δ −93.70 (t, $^1J_{\mathrm{SiF}}$ = 272.2 Hz). UV−vis (THF) $\lambda_{\max}$ nm (log ϵ) 392 (4.53), 372 (4.46), 353 (4.18). Anal. Calcd for $\mathrm{C_{60}H_{63}F_2KN_2O_6Si}$: C, 71.12; H, 6.27; N, 2.76. Found: C, 71.41; H, 6.14; N, 2.93.

(7) Crystal data of $\mathbf{2}\cdot\mathrm{K}^+$/[2.2.2]cryptand·1,2-dimethoxyethane (instrument; Rigaku RAXIS-IV): $\mathrm{C_{64}H_{73}F_2N_2O_8KSi}$, FW = 1103.47, crystal size 0.50 × 0.50 × 0.20 mm, orthorhombic, $Pca2_1$ (No. 29), a = 26.6314(3) Å, b = 24.9190(4) Å, c = 17.2996(2) Å, V = 11480.5(4) Å^3, Z = 8, D_c = 1.277 g cm^{-3}, μ (Mo Kα) = 1.77 cm^{-1}, number of unique reflections = 12949, temperature −100 °C, R = 0.035, R_w = 0.053, and GOF = 1.18.

(8) Enhancement of the fluorescence of anthracene by silyl groups: Kyushin, S.; Ikarugi, M.; Goto, M.; Hiratsuka, H.; Matsumoto, H. *Organometallics* **1996**, *15*, 1067.

10.1021/ja001042q CCC: $19.00

Scheme 1



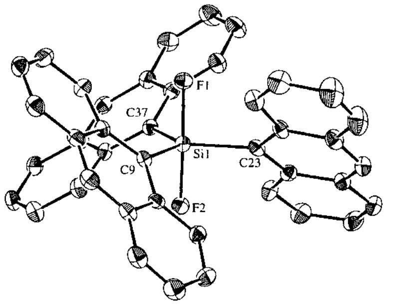


Figure 2. ORTEP drawing of **2**·K$^+$/[2.2.2]cryptand (50% probability for thermal ellipsoids). One of two crystallographically independent molecules is shown here and K$^+$/[2.2.2]cryptand is omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Si1−F1 1.716(2), Si1−F2 1.710(2), Si1−C9 1.955(3), F1−Si1−F2 176.59(9), C9−Si1−C23 114.1(1), C9−Si1−C37 122.7(1), C23−Si1−C37 123.2(1), F1−Si1−C9 91.48(10).

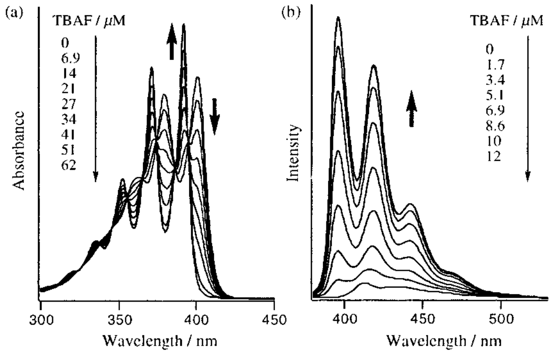


Figure 3. Spectral changes upon the addition of TBAF to **1** in THF: (a) UV−vis absorption spectra: **1**, 40 μM; (b) fluorescence spectra: **1**, 0.2 μM.

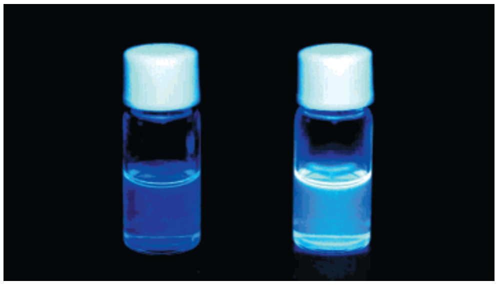


Figure 4. A picture of THF solutions of **1** (left) and **1** + TBAF (right) under irradiation of light at 365 nm.

Table 1. Photophysical Properties Changes from Triarylfluorosilanes to the Corresponding Difluorosilicates[a]

		UV−vis		FL	
compound[b]		$\lambda_{abs,0-0}$/nm	log ϵ	$\lambda_{em,0-0}$/nm[c]	Φ_f[d]
Ant_3SiF	(**1**)	401	4.48	416	0.033
$[Ant_3SiF_2]^-$	(**2**)[e]	392	4.61	396	0.64
Ant_2PhSiF	(**3**)	397	4.26	409	0.17
$[Ant_2PhSiF_2]^-$	(**4**)[e]	391	4.33	395	0.46
$AntPh_2SiF$	(**5**)	393	3.91	405	0.86
$[AntPh_2SiF_2]^-$	(**6**)[e]	391	3.87	399	0.76
$NpPh_2SiF$	(**7**)	286	3.94	332[f]	0.14[f]
$[NpPh_2SiF_2]^-$	(**8**)[e]	286	3.84	338[f]	0.061[f]
$PhenPh_2SiF$	(**9**)	302	4.11	353[f]	0.11[f]
$[PhenPh_2SiF_2]^-$	(**10**)[e]	303	4.12	359[f]	0.19[f]

[a] The experiments were carried out by the addition of stock THF solution of *n*-Bu_4NF to THF solution of silanes. The data for silicates are those at the saturated points of the spectral changes. [b] Ant = 9-anthryl, Np = 1-naphthyl, and Phen = 9-phenanthryl. [c] Excited at 366 nm. [d] Determined with reference to anthracene, unless otherwise stated. [e] Countercation: *n*-Bu_4N^+. [f] Excited at 254 nm and the quantum yields determined with reference to naphthalene.

To clarify the general trends of the changes from the silanes to silicates, photophysical properties of a series of similar triarylfluorosilanes, Ant_2PhSiF (**3**), $AntPh_2SiF$ (**5**), $NpPh_2SiF$ (**7**), and $PhenPh_2SiF$ (**9**), and the corresponding silicates, **4**, **6**, **8**, and **10**, respectively, have been investigated.[9,10] The data are summarized in Table 1, together with those of **1** and **2**. There are two notable trends as follows. (1) The hypercoordination causes no significant shifts in the absorption and emission maxima, except for the cases of the dianthryl-silane **3** and -silicate **4**, but their shifts are still smaller relative to those of the trianthryl pair **1** and **2**.[11] (2) No striking changes in the quantum yields of the fluorescence are also observed from the silanes to the silicates. On the basis of these results, the changes observed from **1** to **2** are found to be significant and should be mainly ascribed not to the intrinsic electronic perturbation by the hypercoordination but to the decrease in the degree of the through-space interaction between the anthryl groups by the structural change from tetrahedral **1** to trigonal bipyramidal **2**, as observed in the crystal structures.

The large spectral change from **1** to **2** in the fluorescence spectra enabled us to estimate the binding constant of **1** toward fluoride to be 2.8 (± 0.2) × 10^4 M^{-1} at 20 °C in THF.[12,13] When other anionic species such as Cl^-, Br^-, I^-, ClO_4^-, and BF_4^- as their *n*-Bu_4N^+ salts were added to the silane **1** in place of TBAF, no changes were observed both in the UV−visible absorption and fluorescence spectra. This apparently relies on the specific affinity of the silicon atom with the fluorine atom. It should also be noted that the produced fluorosilicate **2** can be reversed to the silane **1** by washing with excess water without any decomposition. These features suggest the present trianthrylsilane works as a new type of chemoselective fluorescent sensor of the fluoride ion.[14]

Acknowledgment. The authors gratefully thank Professor O. Kajimoto (Kyoto University) for helpful discussions. This work was partly supported by a Grant-in-Aid (No. 11740349) from the Ministry of Education, Science, Sports and Culture of Japan.

Supporting Information Available: Experimental procedures and data for all new compounds and crystal structural data for **2**·K$^+$/cryptand (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA001042Q

---

(9) The silicates **4**, **6**, **8**, and **10** have been isolated and fully characterized as the salts of K$^+$/[2.2.2]cryptand: See the Supporting Information.

(10) Tamao, K.; Yoshida, J.-i.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics* **1982**, *1*, 355.

(11) The blue shifts of the $\lambda_{abs,\,0-0}$ and $\lambda_{em,\,0-0}$ from **3** to **4** should be ascribed to the change in the degree of the through-space interaction between the two anthryl groups.

(12) The molar ratio analysis actually showed a 1:1 stoichiometry of the complexation of **1** with fluoride. The binding constant was determined from the Benesi−Hildebrand plot. As a reference, the binding constant of dianthrylsilane **3** toward fluoride ion was determined to be 2.9 (± 0.1) × 10^4 M^{-1} at 20 °C in THF, although in the cases of other silanes the changes were too small to determine the binding constants.

(13) Tamao, K.; Hayashi, T.; Ito, Y. *J. Organomet. Chem.* **1996**, *506*, 85.

(14) (a) Dusemund, C.; Sandanayake, K. R. A. S.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1995**, 333. (b) Yamamoto, H.; Ori, A.; Ueda, K.; Dusemund, C.; Shinkai, S. *Chem. Commun.* **1996**, 407. (c) Cooper, C. R.; Spencer, N.; James, T. D. *Chem. Commun.* **1998**, 1365. (d) Nicolas, M.; Fabre, B.; Simonet, J. *Chem. Commun.* **1999**, 1881. (e) Black, C. B.; Andrioletti, B.; Try, A. C.; Ruiperez, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10438.