Organometallics **1998,** *17,* 4347−4352

Articles

Synthesis, Structures, Photophysical Properties, and Dynamic Stereochemistry of Tri-9-anthrylsilane Derivatives

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Received June 9, 1998

A series of tri-9-anthrylsilanes having various substituents, such as −F, −H, −OH, −OMe, vinyl, and ethynyl, have been prepared, and their UV−vis absorption and fluorescence spectra have been determined. Chiral propeller-like arrangements of three anthryl groups have been confirmed by X-ray structural analysis of the fluoro and vinyl derivatives. In solution, however, all the trianthrylsilanes prepared herein undergo enantiomerization at room temperature. The free energies of enantiomerization are about 8−10 kcal mol^{-1}, determined by variable-temperature ^{1}H NMR. The propeller-like structure significantly reduces the quantum yield of fluorescence of the anthracene chromophore.

Introduction

Anthracene-bound organosilicon compounds are of interest from the viewpoint of the structural and electronic modification of the peculiar anthracene π-electron systems by silicon substituents. Extensive studies have been conducted to date not only on their fundamental photophysical properties[1−6] and chemical reactivities[7−14] but also on their application as new precursors for sol−gel materials[15] and as new materials for organic electroluminescent (EL) devices.[16,17] However, most of the studies reported so far have been concerned with silicon compounds containing only one 9-anthryl group on silicon. Only a few reports have dealt with the di-9-anthrylsilanes,[3,4] in which their photochemical intramolecular dimerization of the two anthryl groups has been investigated. As to organosilanes having three anthryl groups, i.e., trianthrylsilanes, there have been no published reports.

Considering the bulky and flat geometry of the anthryl group, trianthrylsilanes would have C_3 symmetry propeller-like chiral structures, as shown in Scheme 1. Stereoisomerization of propeller-like molecules is an old but still attractive subject to design new chiral molecules.[18,19] Mislow and co-workers have studied in detail the dynamic stereochemistry of trimesitylsilane, tri-*o*-xylylsilane, and related compounds, which also have propeller-like structures.[18] For instance, a free energy ($\Delta G^{\ddagger}$) of enantiomerization for trimesitylsilane, $(Mes)_3SiH$, is 10.9 kcal mol^{-1} as determined by variable-temperature (VT) ^{1}H NMR, and its enantiomerization occurs at room temperature.[18a] In

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S0276-7333(98)00477-4 CCC: $15.00

Scheme 1

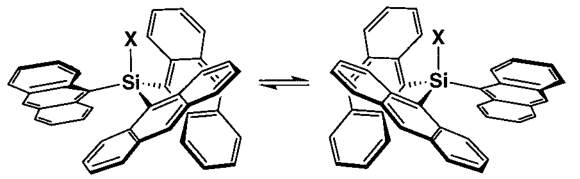
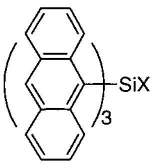
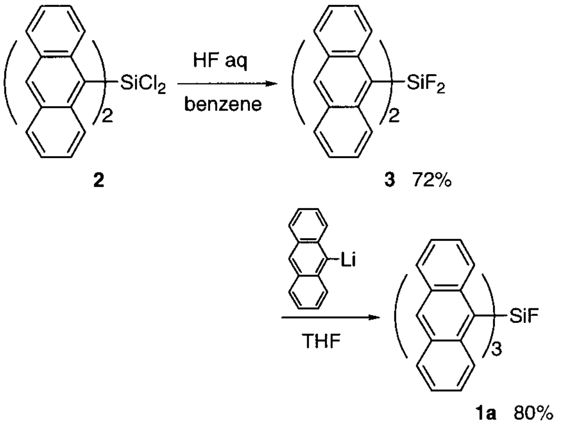


Chart 1



1a (X = F)
1b (X = H)
1c (X = OH)
1d (X = OMe)
1e (X = $CH=CH_2$)
1f (X = $C\equiv CSiMe_3$)

Scheme 2

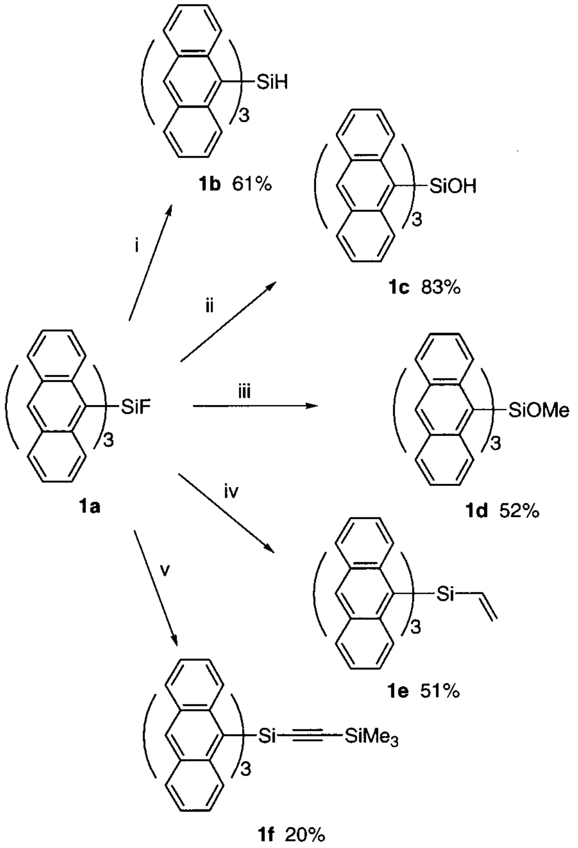


this context, we were interested in the case of trianthrylsilanes, because of their potential as a new kind of optically active chromophore. We now report the synthesis, crystal structures, and UV−vis and fluorescence spectra of a series of trianthrylsilane derivatives **1** having various axis substituents (Chart 1). Their VT ^1H NMR spectra have also been measured to evaluate the free energies of their enantiomerization.

Results and Discussion

Synthesis of Trianthrylsilane Derivatives. Trianthrylhalosilanes have been prepared as key precursors for various trianthrylsilane derivatives. Thus, dichlorosilane **2** was prepared by the reaction of silicon tetrachloride with 2 molar amount of 9-anthryllithium in 80% yield. Although an attempt to prepare trianthrylchlorosilane by the reaction of **2** with 9-anthryllithium failed, the coupling reaction of dianthryldifluorosilane **3**, prepared in 72% yield by the fluorination of dichlorosilane **2** with aqueous HF, with 9-anthryllithium successfully gave a trianthrylfluorosilane **1a** in 80% yield, as shown in Scheme 2.

Scheme 3



Reagents and conditions: i) $LiAlH_4$ (1 mol. amount), THF, 0 °C. ii) NaOH (2.6 mol. amount), THF/H_2O, rt. iii) NaOMe (2 mol. amount), MeOH, rt. iv) (CH_2=CH)MgBr (2.5 mol. amount), reflux. v) $Me_3SiC\equiv CLi$ (1.5 mol. amount), reflux.

A series of trianthrylsilane derivatives **1b**−**1f** having various axis substituents were obtained from the fluorosilane **1a**, as shown in Scheme 3. Thus, the reduction of **1a** with $LiAlH_4$ in THF afforded the hydrosilane **1b** in 61% yield. The hydrolysis of **1a** under alkaline conditions gave the corresponding silanol **1c** in 83% yield. Nucleophilic substitution reactions on the silicon center of **1a** successfully proceeded with NaOMe, (vinyl)MgBr, and $Me_3SiC\equiv CLi$ to yield **1d**−**1f**, respectively, in moderate yields. However, when slightly more bulky nucleophiles such as MeMgBr, PhLi, and allyllithium were employed, the reaction did not take place even in the presence of CuCN[20] and under heating, probably due to the steric hindrance of the bulky anthryl groups. All the trianthrylsilanes **1** are air stable yellow compounds.

Crystal Structures of Trianthrylsilanes. An X-ray crystal structure analysis has been carried out for fluorosilane **1a** and vinylsilane **1e**. Their crystal data and their selected bond distances, bond angles, and torsion angles are summarized in Tables 1and 2. The structures are shown in Figures 1and 2, together with atom-labeling systems. Both trianthrylsilanes **1a** and **1e** have propeller-like arrangements of three anthryl groups, but not being exactly in C_3 symmetry. The torsion angles between the axis Si−X bonds (X = F(1) for **1a** and C(43) for **1e**) and the anthracene planes vary in the range 33−60°. In both cases, the crystals are racemic mixtures. It should be noted here that trianthrylsilanes have rather flat geometries around the central silicon atoms. The sum of the three C_{ipso}−Si(1)−C_{ipso} angles is 345.7° and 340.0° for **1a** and **1e**, respectively, which are about halfway from an ideal sp^3 silicon atom (328.5°) to an imaginary "sp^2 silicon atom" (360°). The average C_{ipso}−Si(1)−X angles are 102.8° and 105.6° for **1a** and **1e**, respectively. These values are

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[20] Lennon, P. J.; Mack, D. P.; Thompson, Q. E. *Organometallics* **1989**, *8*, 1121.

Table 1. Crystal and Intensity Collection Data for Trianthrylsilanes

	1a	**1e**
formula	$C_{42}H_{27}SiF$	$C_{44}H_{30}Si$
mol wt	578.76	586.81
cryst dimens, mm	0.70 × 0.10 × 0.10	0.30 × 0.20 × 0.20
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
cell consts		
a, Å	19.4849(7)	19.3630(8)
b, Å	12.7621(8)	13.1047(6)
c, Å	12.6063(6)	13.1373(3)
β, deg	108.348(2)	109.466(2)
V, Å^3	2975.4(2)	3143.0(2)
Z	4	4
D_{calcd}, g cm^{-3}	1.292	1.240
temp, °C	−100	−100
radiation	Mo Kα (λ = 0.710 70 Å)	
μ(Mo Kα), cm^{-1}	1.16	1.06
$2\theta_{\max}$, deg	55.2	55.2
no. of collected rflns	5657	6353
no. of unique rflns	3753 ($I > 3\sigma(I)$)	4949 ($I > 3\sigma(I)$)
rfln/parameter ratio	9.43	12.16
R^a	0.040	0.038
$R_w{}^b$	0.053	0.057
goodness of fit	1.18	1.29

[a] $R = \sum||F_o| - |F_c||/|\sum|F_o|$. [b] $R_w = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega F_o{}^2]^{1/2}$.

Table 2. Selected Bond Distances and Angles for Trianthrylsilanes

	1a	**1e**
Bond Distances (Å)		
Si(1)−C(9)	1.883(2)	1.914(2)
Si(1)−C(23)	1.894(2)	1.906(2)
Si(1)−C(37)	1.883(2)	1.912(2)
Si(1)-X^a	1.615(1)	1.885(2)
Bond Angles (deg)		
C(9)−Si(1)−C(23)	115.48(9)	112.69(6)
C(9)−Si(1)−C(37)	115.24(10)	107.78(6)
C(23)−Si(1)−C(37)	114.94(9)	118.69(7)
C(9)−Si(1)−X^a	102.62(9)	105.95(7)
C(23)−Si(1)−X^a	102.05(9)	105.62(7)
C(37)−Si(1)−X^a	103.79(9)	105.10(7)
Torsion Angles (deg)		
X−Si(1)−C(9)−C(11)^a	−37.1(2)	−43.8(1)
X−Si(1)−C(23)−C(25)^a	−44.1(2)	−59.8(1)
X−Si(1)−C(37)−C(39)^a	−39.1(2)	−33.1(1)

[a] X = F(1) and C(43) for **1a** and **1e**, respectively.

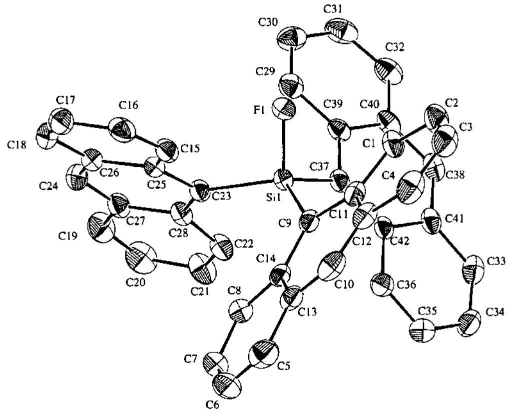

Figure 1. ORTEP drawing of **1a** (50% probability for thermal ellipsoids).

similar to those of a crystal structure of trimesitylsilyl azide Mes_3SiN_3 ($\sum C_{ipso}-Si-C_{ipso} = 342.1°$ and average $C_{ipso}-Si-N = 104.4°$),[21] suggesting comparable steric crowding around the central silicon atoms for the trianthrylsilanes and trimesitylsilanes.

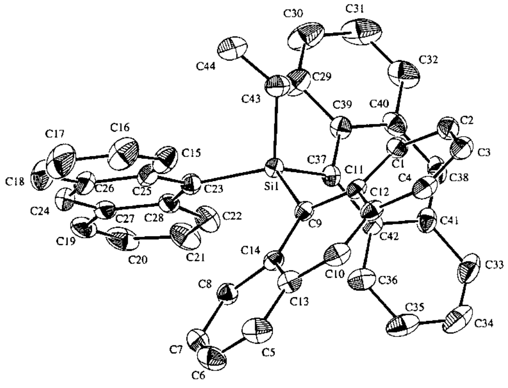

Figure 2. ORTEP drawing of **1e** (50% probability for thermal ellipsoids).

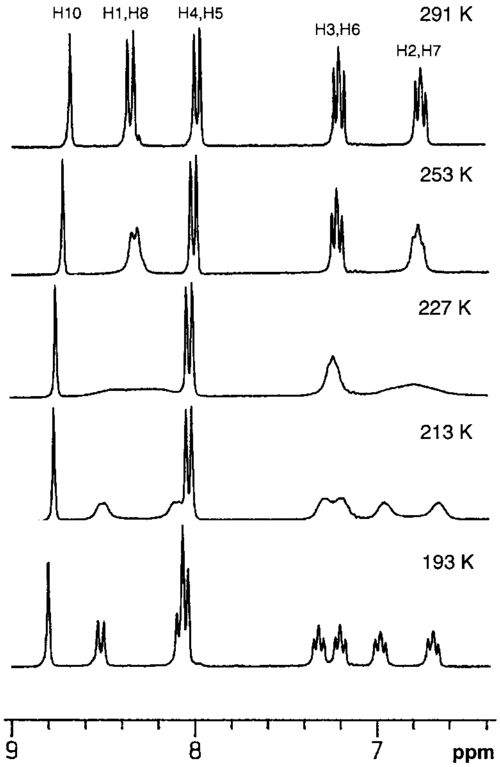

Figure 3. Stacked plot for the variable-temperature ^1H NMR spectra of **1f**.

Dynamic Stereochemistry of Trianthrylsilanes in Solution. In the ^1H NMR spectra at room temperature, all the trianthrylsilanes **1** showed one singlet (H10), only two doublets [(H1, H8) and (H4, H5)], and two quasi triplets [(H2, H7) and (H3, H6)] for the anthracene protons, indicating that their rapid enantiomerization occurs at this temperature. To evaluate the free energy ($\Delta G^{\ddagger}$) of their enantiomerization, we carried out VT ^1H NMR measurements. As a representative result, the ^1H NMR spectra of the tri(anthryl)(ethynyl)silane **1f** at low temperatures are shown in Figure 3. At decreasing temperatures, one doublet at 8.34 ppm (assigned to H1 and H8) and two quasi triplet at 6.76 ppm (H2 and H7) and at 7.21 ppm (H3 and H6) broadened, coalesced, and finally resulted in two doublets and four quasi triplets. Based on the coalescence temperatures of the peaks for H1 and H8, the free

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[21] Zigler, S. S.; Haller, K. J.; West, R.; Gordon, M. S. *Organometallics* **1989**, *8*, 1656.

Table 3. Free Energies of the Enantiomerization of Trianthrylsilanes

compound	X	$\Delta G^{\ddagger}_T$ (T, K)[a] (kcal mol^{-1})	$\Delta\nu$[b] (Hz)
1a	F	9.7 (213)	201.1
1b	H	9.3 (203)	171.8
1c	OH	7.9 (173)	162.1
1d	OMe	*c*	*c*
1e	CH=CH$_2$	9.0 (203)	360.4
1f	C≡CSiMe$_3$	10.6 (227)	116.4

[a] Coalescence temperature of the signals of H1 and H8. [b] Separation of the signals of H1 and H8. [c] Not coalesed above 173 K.

Table 4. Photophysical Properties of Trianthrylsilanes

compound	UV−vis[a] λ_{max}/nm (log ϵ)	FL[a] λ_{em}/nm[b] (Φ_f)[c]
1a (X = F)	363 (4.19), 380 (4.41), 402 (4.45)	434 (3.6 × 10^{-2})
1b (X = H)	360 (4.21), 379 (4.46), 401 (4.51)	432 (2.8 × 10^{-2})
1c (X = OH)	362 (4.19), 380 (4.40), 402 (4.43)	434 (1.5 × 10^{-2})
1d (X = OMe)	361 (4.20), 379 (4.39), 401 (4.40)	439 (5.6 × 10^{-3})
1e (X = CH=CH$_2$)	365 (4.19), 382 (4.40), 404 (4.43)	437 (1.7 × 10^{-2})
1f (X = C≡CSiMe$_3$)	364 (4.19), 382 (4.42), 404 (4.45)	438 (4.0 × 10^{-2})
(9-anthryl)SiPh$_2$F (**4**)	356 (3.77), 374 (3.92), 394 (3.85)	426 (5.2 × 10^{-1})

[a] In chloroform. [b] Maximum wavelength in emission spectra. The excitation wavelength is 366 nm. [c] Based on anthracene (Φ = 0.29, in hexane) as a standard.

energy was estimated by using the Eyring equation to be 10.5 kcal mol^{-1}. The coalescence temperature and the estimated $\Delta G^{\ddagger}$ values for **1** are summarized in Table 3. Trianthrylsilanes have about 8−10 kcal mol^{-1} of free energy, which is slightly less than those of the trimesitylsilane and tri-*o*-xylylsilane derivatives (10−12 kcal mol^{-1}).[18a] Among a series of trianthrylsilanes, we could not find a general relationship between the $\Delta G^{\ddagger}$ and the nature of the axis substituents, while oxygen functionalities seem to facilitate the isomerization, the reason still unknown at this time.

UV−Visible and Fluorescence Spectra of Trianthrylsilanes. The UV−vis absorption and fluorescence spectral data for the trianthrylsilanes are summarized in Table 4, which also contains the 9-anthryldiphenylfluorosilane (**4**) data for comparison. Trianthrylsilanes **1** have their absorption bands with fine structures in the region of 300−430 nm. A comparison of the absorption maxima between **1a** and **4** shows that the absorption maxima of the trianthryl silicon compounds are about 10 nm longer than the monoanthryl derivative. In the fluorescence spectra, trianthrylsilanes show broad emission bands around 430 nm, here again being nearly 10 nm longer than that of the monoanthryl derivative, according to a comparison between **1a** and **4**. The low quantum yields and lack of fine structures of the emission bands (Figure 4) are noted as features of the trianthrylsilanes, which are probably due to the congested spatial arrangements of the three anthracene chromophores in the molecule. Among a series of trianthrylsilanes, the axis substituents faintly affect both the absorption maxima and emission wavelengths, while the quantum yields vary.

Conclusion

For the design of C_3 symmetry chiral molecules with functions such as fluorescence, we have noted here the trianthrylsilane skeleton. A series of trianthrylsilanes have been prepared for the first time, and their structure, photophysical properties, and dynamic stereochemistry have been investigated. The trianthrylsilanes indeed have a propeller-like arrangement for the three flat anthryl groups. The degree of crowding around the silicon center is comparable to that in trimesitylsilane derivatives. Despite the steric congestion, however, all the trianthrylsilanes prepared herein undergo enantiomerization at room temperature in solution, the free energy ($\Delta G^{\ddagger}$) being about 8−10 kcal mol^{-1}. It has also been found that the propeller-like structure significantly reduces the quantum yield of fluorescence of the anthracene chromophore. These fundamental data will be helpful for the further design of chiral chromophores as well as chiral silanes with C_3 symmetry.

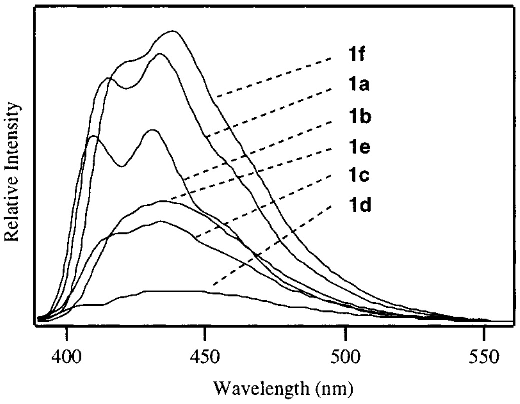

Figure 4. Fluorescence spectra of trianthrylsilanes **1**. The excitation wavelength is 366 nm.

Experimental Section

General Procedures. Melting point (mp) determinations were performed by using a Seiko DSC6200 and a Yanaco MP-S3 instrument. ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were measured using a JEOL EX-270 (270 MHz for ^{1}H, 67.8 MHz for ^{13}C, 254 MHz for ^{19}F, and 53.5 MHz for ^{29}Si) spectrometer in appropriate solvents. Chemical shifts are reported in δ ppm with reference relative to the residual protio-solvent peak for ^{1}H and ^{13}C, to CFCl$_3$ for ^{19}F, and to TMS for ^{29}Si, respectively. UV−visible absorption spectra were measured with a Shimadzu UV-3100PC spectrometer in spectral grade chloroform. Fluorescence spectra were measured with a Perkin-Elmer LS50B spectrometer in degassed spectral grade chloroform. Thin-layer chromatography (TLC) was performed on plates coated with a 0.25 mm thickness of silica gel 60F-254 (Merck). Column chromatography was performed by using Kieselgel 60 (70−230 mesh; Merck). Diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone before use. Other all solvents were dried over appropriate desiccants and distilled under nitrogen. All reactions were carried out under a nitrogen atmosphere unless otherwise stated.

Di-9-anthryldichlorosilane (2). To an ether (25 mL) solution of 9-bromoanthracene (2.57 g, 10 mmol) was added a hexane solution of *n*-BuLi (1.57 M, 7.0 mL, 11 mmol) at −78 °C. The mixture was allowed to warm to 0 °C and stirred for 30 min. The mixture was added dropwise to an ether (10 mL) solution of silicon tetrachloride (0.58 mL, 5 mmol) at 0 °C and stirred for 2 h to form yellow precipitates, which were collected by filtration. Toluene (200 mL) was added to the precipitates, and the resulting suspension was stirred and filtered to remove the insoluble salt. The filtrate was concentrated to give pure **2** (1.81 mg, 3.99 mmol) in 80% yield as moisture-sensitive yellow crystals: mp 128 °C (dec). ^{1}H NMR (C$_6$D$_6$): δ 6.92−6.98 (m, 4H), 7.04−7.09 (m, 4H), 7.70 (d, J = 8.6 Hz, 4H), 8.25

(s, 2H), 9.03 (d, J = 8.9 Hz, 4H). ^{13}C NMR (C_6D_6): δ 74.23, 75.69, 77.11, 78.17, 78.73, 80.76, 83.04, 85.48. ^{29}Si NMR (C_6D_6): δ 3.50. MS (EI) *m*/*e* (relative intensity) 454 (93), 452 (M^+, 100). Anal. Calcd for $C_{28}H_{18}C_{l2}Si$: C, 74.17; H, 4.00. Found: C, 74.38; H, 4.05.

Di-9-anthryldifluorosilane (3). A toluene (250 mL) solution of **2** (8.80 g, 19.4 mmol) was added slowly to a 47% hydrofluoric acid (200 mL, ca. 4.7 mol) solution in an open flask at room temperature, and the mixture was stirred for 45 min. After separating from the aqueous layer, the organic layer was washed with H_2O (50 mL × 2) quickly, followed by drying over Na_2SO_4 and filtration. The filtrate was condensed under reduced pressure to afford pure **3** (6.03 mg, 14.3 mmol) in 74% yield as yellow crystals: mp 197 °C. ^{1}H NMR (C_6D_6): δ 7.02−7.15 (m, 8H), 7.72 (d, J = 8.1 Hz, 4H), 8.25 (s, 2H), 8.95 (d, J = 8.6 Hz, 4H). ^{13}C NMR (acetone-d_6): δ 125.96, 126.07 (t, $^2J_{C-F}$ = 17.1 Hz), 127.69 (t, $^3J_{C-F}$ = 3.7 Hz), 128.19, 130.62, 132.25, 134.46, 138.22. ^{29}Si NMR (acetone-d_6): δ −20.51 (t, $^1J_{Si-F}$ = 296.34 Hz). ^{19}F NMR (acetone-d_6): δ −116.97. MS (EI) *m*/*e* (relative intensity) 420 (M^+, 100). Anal. Calcd for $C_{28}H_{18}F_2Si$: C, 79.97; H, 4.31. Found: C, 79.86; H, 4.15.

Tri-9-anthrylfluorosilane (1a). An ether (20 mL) solution of 9-anthryllithium, prepared from 9-bromoanthracene (3.15 g, 12.3 mmol) and *n*-BuLi (7.5 mL, 12.3 mmol), was added dropwise to a THF (15 mL) solution of **3** (4.68 g, 11.1 mmol) at −78 °C over 30 min. The mixture was warmed to room temperature over 20 min and stirred for an additional 2 h to form yellow precipitates, which were collected by filtration. Toluene (50 mL) was added to the precipitates, and the resulting suspension was stirred and then filtered to remove insoluble salts. The filtrate was concentrated under reduced pressure to afford pure **1a** (5.13 g, 8.8 mmol) in 80% yield as yellow crystals: mp 316 °C. ^{1}H NMR (C_4D_8O): δ 6.81−6.87 (m, 6H), 7.21−7.26 (m, 6H), 8.01 (d, J = 8.1 Hz, 6H), 8.25 (dd, J = 9.4 and 2.4 Hz, 4H), 8.72 (s, 3H). ^{13}C NMR (C_4D_8O): δ 125.60, 126.75, 128.92 (d, $^3J_{C-F}$ = 3.7 Hz), 130.24, 132.54, 133.33, 133.51 (d, $^2J_{C-F}$ = 14.6 Hz), 137.81. ^{29}Si NMR (C_4D_8O): δ −2.86 (d, $^1J_{Si-F}$ = 278.94). ^{19}F NMR (C_4D_8O): δ −136.7. MS (EI) *m*/*e* (relative intensity) 578 (M^+, 100). UV−vis ($CHCl_3$) λ_{max} nm (log ϵ): 402 (4.45), 380 (4.41), 363 (4.19). Anal. Calcd for $C_{42}H_{27}FSi$: C, 87.16; H, 4.70. Found: C, 87.17; H, 4.70.

Tri-9-anthrylhydrosilane (1b). To a THF (2.0 mL) solution of **1a** (267 mg, 0.46 mmol) was added $LiAlH_4$ (18 mg, 0.46 mmol) at 0 °C. The mixture was stirred for 30 min at the same temperature, followed by slow addition of ethyl acetate (1.0 mL) to quench the excess $LiAlH_4$. After filtration of the salts, the filtrate was concentrated under reduced pressure. The residue was recrystallized from toluene to afford **1b** (158 mg, 0.28 mmol) in 61% yield as yellow crystals: mp 300 °C (dec). ^{1}H NMR (C_4D_8O): δ 6.86−6.92 (m, 6H), 7.21−7.27 (m, 6H), 7.48 (s, 1H), 8.00 (d, J = 8.6 Hz, 6H), 8.28 (d, J = 9.5 Hz, 6H), 8.66 (s, 3H). ^{13}C NMR (C_4D_8O): δ 125.55, 236.79, 238.82, 130.35, 132.40, 132.56, 132.43, 138.22. ^{29}Si NMR (C_4D_8O): δ −41.38. MS (EI) *m*/*e* (relative intensity) 560 (M^+, 20), 382 (60), 214 (100). UV−vis ($CHCl_3$) λ_{max} nm (log ϵ): 401 (4.51), 379 (4.46), 360 (4.21). Anal. Calcd for $C_{42}H_{28}Si$: C, 89.96; H, 5.03. Found: C, 90.13; H, 5.27.

Tri-9-anthrylhydroxysilane (1c). To a THF (4 mL) solution of **1a** (289 mg, 0.5 mmol) was added an aqueous solution (2 mL) of NaOH (53 mg, 1.3 mmol) at room temperature in the air, and the mixture was stirred for 4 h. The mixture was extracted with toluene. The organic layer was washed with water and dried over K_2CO_3. After filtration, the filtrate was concentrated to afford pure **1c** (238 mg, 0.42 mmol) in 83% yield as yellow crystals: mp 256 °C (dec). ^{1}H NMR (C_4D_8O): δ 6.45 (s, 1H), 6.69−6.75 (m, 6H), 7.14−7.19 (m, 6H), 7.95 (d, J = 8.6 Hz, 6H), 8.41 (d, J = 8.6 Hz, 6H), 8.60 (s, 3H). ^{13}C NMR (C_4D_8O): δ 125.23, 125.59, 129.02, 129.84, 130.22, 131.89, 132.63, 137.73, 138.25. ^{29}Si NMR (C_4D_8O): δ −17.41. MS (EI) *m*/*e* (relative intensity) 576 (M^+, 30), 178 (100). UV−vis ($CHCl_3$) λ_{max} nm (log ϵ): 402 (4.43), 380 (4.40), 362 (4.19). Anal. Calcd for $C_{42}H_{28}OSi$: C, 87.46; H, 4.92. Found: C, 87.69; H, 4.96.

Tri-9-anthrylmethoxysilane (1d). To a THF (8 mL) solution of **1a** (579 mg, 1.0 mmol) was added a MeOH (3 mL) solution of MeONa (108 mg, 2.0 mmol) at room temperature. After stirring for 1 h, the reaction mixture was evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel (hexane/benzene = 2/1, R_f = 0.68) to afford pure **1a** (306 mg, 0.52 mmol) in 52% yield as yellow crystals: mp 259 °C. ^{1}H NMR (C_4D_8O): δ 3.33 (s, 3H), 6.74−6.79 (m, 6H), 7.15−7.20 (m, 6H), 7.95 (d, J = 8.4 Hz, 6H), 8.35 (d, J = 8.9 Hz, 6H), 8.62 (s, 3H). ^{13}C NMR (C_4D_8O): δ 54.48, 125.35, 125.93, 129.88, 129.99, 132.34, 132.59, 136.35, 137.86. ^{29}Si NMR (C_4D_8O): δ −14.38. MS (EI) *m*/*e* (relative intensity) 590 (M^+, 40), 178 (100). UV−vis ($CHCl_3$) λ_{max} nm (log ϵ): 401 (4.40), 379 (4.39), 361 (4.20). Anal. Calcd for $C_{43}H_{30}OSi$: C, 87.42; H, 5.12. Found: C, 87.67; H, 5.15.

Tri-9-anthrylvinylsilane (1e). To a THF (16 mL) solution of **1a** (1.16 g, 2 mmol) was added a THF solution of vinylmagnesium bromide (2.0 M, 2.5 mL, 5.0 mmol) at room temperature. The reaction mixture was refluxed with stirring for 1 h. After filtration of the salt, the filtrate was concentrated by rotary evaporation. The residue was subjected to column chromatography on silica gel (hexane/benzene = 2/1, R_f = 0.30) to give **1e** (600 mg, 1.0 mmol) in 51% yield as yellow crystals: mp 300 °C. ^{1}H NMR (C_4D_8O): δ 5.14 (dd, J = 3.0 and 19.7 Hz, 1H), 5.69 (dd, J = 3.0 and 14.4 Hz, 1H), 6.65−6.71 (m, 6H), 6.80 (dd, J = 19.7 and 14.4 Hz, 1H), 7.14−7.20 (m, 6H), 7.97 (d, J = 8.6 Hz, 6H), 8.18 (d, J = 8.9 Hz, 6H), 8.64 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 124.55, 124.58, 128.99, 129.88, 131.34, 131.54, 133.80, 135.69, 137.05, 139.34. ^{29}Si NMR (C_4D_8O): δ −26.48. MS (EI) *m*/*e* (relative intensity) 586 (M^+, 40). UV−vis ($CHCl_3$) λ_{max} nm (log ϵ): 404 (4.43), 382 (4.40), 365 (4.19). Anal. Calcd for $C_{44}H_{30}Si$: C, 90.06; H, 5.15. Found: C, 90.15; H, 5.21.

Tri-9-anthryl((trimethylsilyl)ethynyl)silane (1f). To a THF (2 mL) solution of trimethylsilylacetylene (0.22 mL, 1.5 mmol) was added a hexane solution of *n*-BuLi (1.59 M, 0.94 mL, 1.5 mmol) at 0 °C. The mixture was stirred for 1 h. The resulting solution was added to a THF (6 mL) solution of **1a** (579 mg, 1.0 mmol), followed by reflux with stirring for 30 min. After concentration by rotary evaporation, water was added and the mixture was extracted with EtOAc. The organic layer was washed with water (4 mL × 3), dried over Na_2SO_4 and filtered. After concentration of the filtrate, the resulting mixture was recrystallized from benzene to give pure **1f** (198 mg, 0.3 mmol) in 20% yield as yellow crystals: mp 317 °C (dec). ^{1}H NMR (C_4D_8O): δ −0.26 (s, 9H), 6.72−6.78 (m, 6H), 7.17−7.22 (m, 6H), 7.28 (s, 1H), 7.98 (d, J = 8.6 Hz, 6H), 8.35 (d, J = 8.9 Hz, 6H), 8.67 (s, 3H). ^{13}C NMR (C_4D_8O): δ −0.72, 116.96, 119.35, 125.47, 125.64, 129.92, 130.31, 132.67, 132.74, 132.90, 137.89. ^{29}Si NMR (C_4D_8O): δ −44.48, −18.91. MS (EI) *m*/*e* (relative intensity) 656 (M^+, 100). UV−vis ($CHCl_3$) λ_{max} nm (log ϵ): 404 (4.45), 382 (4.42), 364 (4.19). Anal. Calcd for $C_{47}H_{36}Si$: C, 85.93; H, 5.52. Found: C, 86.37; H, 5.31.

9-Anthryldiphenylfluorosilane (4). To an ether (10 mL) solution of 9-anthryl bromide was added a hexane solution of *n*-BuLi (1.6 M, 2.8 mL, 4.5 mmol) at −78 °C. The mixture was gradually warmed to 0 °C over 40 min. Diphenyldifluorosilane (0.88 g, 4 mmol) was added to the mixture at 0 °C and stirred at room temperature for 3 h. After removal of the salt by filtration, the filtrate was concentrated by rotary evaporation. The residue was subjected to column chromatography on silica gel (hexane/benzene = 12/1, R_f = 0.24) to give **4** (577 mg, 1.53 mmol) in 38% yield as white crystals: mp 116−118 °C. ^{1}H NMR (C_4D_8O): δ 7.28−7.46 (m, 10H), 7.65 (d, J = 6.5 Hz, 4H), 8.05 (d, J = 8.4 Hz, 2H), 8.38 (d, J = 8.1 Hz, 2H), 8.70 (s, 1H). ^{13}C NMR (acetone-d_6): δ 126.38, 126.96 (d, $^2J_{C-F}$ = 12.2 Hz), 127.42, 129.45 (d, $^3J_{C-F}$ = 7.3 Hz), 129.76, 130.91, 132.37,132.74, 133.82, 135.73 (d, $^2J_{C-F}$ = 17.1 Hz), 136.10, 139.28. ^{29}Si NMR (C_6D_6): δ 1.68 (d, $^1J_{Si-F} = 284.3$ Hz). ^{19}F NMR (acetone-d_6): δ -148.64. MS (FAB) *m*/*e* (relative intensity) 378 (M^+, 50). UV−vis ($CHCl_3$) λ_{max} nm (log ϵ): 394 (3.85), 374 (3.92), 356 (3.77). Anal. Calcd for $C_{26}H_{19}FSi$: C, 82.50; H, 5.06. Found: C, 82.40; H, 4.91.

X-ray Crystal Structure Determination of 1a and 1e. Single crystals of **1a** and **1e** suitable for X-ray crystal analysis were obtained by recrystallization from benzene and toluene/ether mixed solvent, respectively. The intensity data were collected at 173 K on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo Kα radiation from a rotating-anode generator operating at 50 kV and 100 mA to a maximum 2θ value of 55°. A total of 17 oscillation images (4.00°), each being exposed for 60 min, and a total of 24 oscillation images (3.00°), each being exposed for 60 min, were collected for **1a** and **1e**, respectively. The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structures were solved by direct methods in SIR92,[22] and full-matrix least-squares refinement was carried out for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions but not refined. All the calculations were performed using the teXsan crystallographic package of Molecular Structure Corp. The crystal data and analytical conditions are listed in Table 1. Further details are given in the Supporting Information.

Acknowledgment. This work was partly supported by a Grant-in-Aid (No. 09239103) from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: Tables of complete crystal data and intensity collection data, atomic coordinates, anisotropic displacement parameters, and bond distances and angles for **1a** and **1e** (12 pages). Ordering information is given on any current masthead page.

OM9804778

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