First C_2 Symmetrical Siloles: Synthetic, Structural, and Photophysical Studies of 7-Sila-7*H*-dibenzo[*c,g*]fluorenes

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The syntheses of 7-sila-7*H*-dibenzo[*c,g*]fluorenes **1** were effected via dilithiation of 2,2′-dibromo-1,1′-binaphthyl (**2**) followed by cyclization of the resulting dianion with dihalosilanes: Me_2SiCl_2, Ph_2SiCl_2, and Ph_2SiF_2. The X-ray structural analysis of 7-sila-7,7-diphenyl-7*H*-dibenzo[*c,g*]fluorene (**1b**) provided the first geometrical parameters of the 7-sila-7*H*-dibenzo[*c,g*]fluorene derivative in which the silole skeleton was found to be twisted in the C_2 symmetrical conformation due to the significant steric repulsion of the binaphthyl group fixed within the van der Waals radii. The photophysical study and semiempirical PM3 calculation suggested the presence of significant $\sigma^*-\pi^*$ conjugation in the LUMO of the 7-sila-7*H*-dibenzo[*c,g*]fluorene **1** like a silole.

Introduction

Siloles (silacyclopentadienes) have attracted much attention as a quite unique π-electron system due to the unusually low-lying LUMO arising from the $\sigma^*-\pi^*$ conjugation.[1] Especially, since Tamao demonstrated the novel synthetic methodology and many potential applications, there has been explosively growing interest in siloles and silole-containing polymers.[2,3] However, neither chiral nor C_2 symmetrical silole has been reported. Because siloles have characteristic photophysical properties in the UV−visible region, chiral silole derivatives would provide access to a new class of compounds in the material sciences.

We anticipated that the silole skeleton of the 7-sila-7*H*-dibenzo[*c,g*]fluorene **1** would be C_2 symmetrical due to the steric repulsion of the binaphthyl group. Thus, the 7-sila-7*H*-dibenzo[*c,g*]fluorene **1** should be the prospective chiral silole derivative. 7-Sila-7,7-dimethyl-7*H*-dibenzo[*c,g*]fluorene (**1a**) was recently isolated by Lucchi and Fabris as the first 7-sila-7*H*-dibenzo[*c,g*]fluorene derivative.[4] They reported that 3,5-disila-3,3,5,5-tetramethyl-3,5-dihydro-dinaphtho[2,1-*c*:1′,2′-*e*]azepine subjected to flash chromatography was transferred to **1a**. Quite recently, we reported that **1a** was produced from dilithiation of 2,2′-dibromo-1,1′-binaphthyl (**2**) followed by cyclization of the resulting dianion with $XMe_2SiSiPh_2X$ (X = F, Cl).[5] However, neither the synthetic study nor the characteristic details of the 7-sila-7*H*-dibenzo[*c,g*]fluorene **1** have ever been investigated. With the aim of developing a route to the chiral silole derivative, we herein report the first synthetic, structural, and photophysical studies of the 7-sila-7*H*-dibenzo[*c,g*]fluorene **1**.

Results and Discussion

The most straightforward route to the 7-sila-7*H*-dibenzo[*c,g*]fluorene **1** would be the cyclization of **2** with corresponding dihalosilanes. Thus, at the beginning, we investigated the preparation of the known 7-sila-7,7-dimethyl-7*H*-dibenzo[*c,g*]fluorene (**1a**) using Me_2SiCl_2 (eq 1). To the intermediate 2,2′-dilithio-1,1′-binaphthyl prepared from **2** using *n*-BuLi (2.5 equiv) in THF at −70 °C was added slowly a solution of Me_2SiCl_2 (1.6 equiv) in THF, and the reaction mixture was then stirred for 2 h at −70 °C to give **1a** in 38% yield as a white powder. The identity of **1a** was confirmed by its ^1H NMR spectrum, which was consistent with the data reported in the literature.[4,5] Because **1a** was in hand, we also investigated the synthesis of the novel 7-sila-7,7-diphen-

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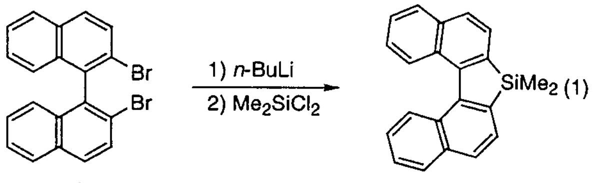
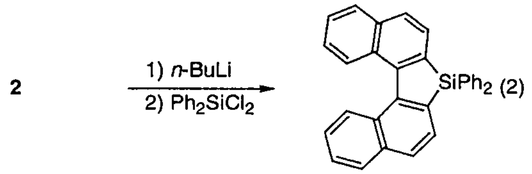
yl-7*H*-dibenzo[*c*,*g*]fluorene (**1b**) by a similar procedure in order to prepare single crystals suitable for an X-ray diffraction study. As expected, **1b** was obtained as colorless crystals. However, the yield (8.7%) was much lower than that of the less sterically hindered **1a** (eq 2). More reactive Ph_2SiF_2 also gave the slightly improved results (eq 3). The yields susceptible to the steric factors of the complementary dihalosilanes suggest that the 7-sila-7*H*-dibenzo[*c*,*g*]fluorene **1** possessed significant strain resistant to the cyclization reaction.



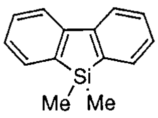
2 **1a** (38%)



2 **1b** (8.7%)

$$\mathbf{2} \xrightarrow[2)\ Ph_2SiF_2]{1)\ n\text{-BuLi}} \mathbf{1b}\ (9.6\%) \qquad (3)$$

Two alternative views of the molecular structure of 7-sila-7,7-diphenyl-7*H*-dibenzo[*c*,*g*]fluorene (**1b**) are shown in parts a and b of Figure 1. The cell constants and data collection parameters are summarized in Table 1. The important geometrical parameters are shown in Table 2. In contrast with the completely planar biaryl analogues such as 1,1-dimethyldibenzosilole (**3**) and 4,4-diphenyldithienosilole (**4**),[6,7] the silole unit of **1b** is significantly twisted in the slightly deformed C_2 symmetrical conformation with a C2−C1−C11−C12 torsion angle of 22.5(2)°. On the other hand, the bond lengths and bond angles of the silole skeleton are within the range of a typical silole. As predicted in the synthetic study, **1b** was found to be highly strained due to the steric repulsion of the binaphthyl group fixed within the van der Waals radii (H(C8)−H(C18) = 2.32 Å). In fact, the torsion angle of the acyclic C9−C1−C11−C19 moiety (34.9(3)°) is expanded outward by 12.4° more than that of the silylene-bridged C2−C1−C11−C12 moiety (22.5(2)°). Four trivalent carbons in the silole unit are also deformed from the idealized trigonal shape. In particular, the C2 and C12 carbons directly bridged by the silylene group are distorted by 9.1° in Si1−C2/C1−C2−C3 and by 13.0° in Si2−C12/C11−C12−C13, respectively.



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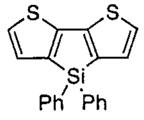

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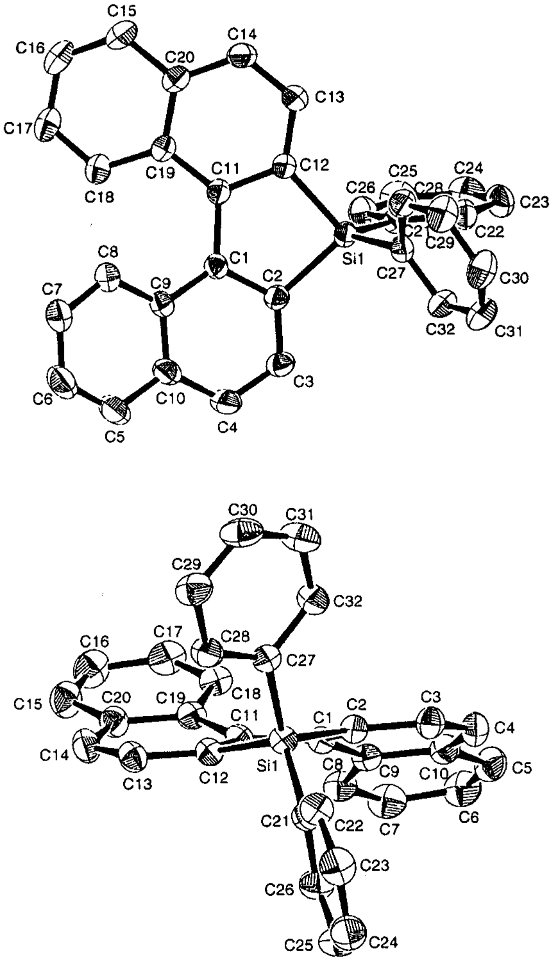

Figure 1. (a, top) Molecular structure of **1b** with thermal ellipsoids at the 30% probability level. (b, bottom) Alternative view of **1b** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Summary of Crystal Data and Intensity Collection Parameters for 1b

empirical formula	$Si_1C_{32}H_{22}$
fw	434.61
cryst syst	monoclinic
space group	$P2_1/c$ (#14)
a, Å	14.876(1)
b, Å	11.552(1)
c, Å	15.507(1)
β, deg	116.509(5)
V, Å^3	2384.8(3)
Z	4
D_{calcd}, g/cm^3	1.210
μ(Cu Kα), mm^{-1}	0.983
$2\theta_{max}$, deg	154.3
no. of unique reflns	4921
no. of used reflns ($I > 3.00\sigma(I)$)	4060
R	0.047
R_w	0.071

The 7-sila-7*H*-dibenzo[*c*,*g*]fluorene **1** showed interesting photophysical properties distinct from the corresponding acyclic analogues, 2,2′-bissilyl-substituted 1,1′-binaphthy **5** and $(2\text{-Np})_2SiR_2$ **6**, which are the silyl-substituted binaphthyls missing the silole skeleton. Their UV−visible absorption and fluorescence data are summarized in Table 3. As shown in the structural analysis, the two naphthyl groups of 7-sila-7*H*-dibenzo-

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(6) The optimized geometry of **3** was determined at the B3LYP/6-31G(d) level of theory using the Gaussian 98 programs.

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Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) of 1b

Bond Lengths			
Si1−C2	1.855(2)	Si1−C12	1.864(2)
C1−C2	1.393(2)	C1−C11	1.502(2)
C11−C12	1.398(2)	H(C8)−H(C18)	2.32
Bond Angles			
C2−Si1−C12	91.80(7)	Si1−C2−C1	109.0(1)
C2−C1−C11	113.4(1)	C1−C11−C12	114.0(1)
Si1−C12−C11	108.0(1)		
Torsion Angles			
Si1−C2−C1−C11	15.1(2)	Si1−C12−C11−C1	17.6(2)
C2−C1−C11−C12	22.5(2)	C9−C1−C11−C19	34.9(3)

Table 3. UV−Visible Absorption and Fluorescence Data for 1, 5, and 6

	UV absorption[a]		fluorescence[a]
compd	λ_{max}/nm	ϵ	λ_{max}/nm[b]
1a	360	9530	422
1b	367	7750	430
5a	289	12 600	344
5b	290	12 500	347
6a	271	12 100	339
6b	271	7750	341

[a] In C_6H_{12}. [b] Excited at the absorption maximum wavelength.

[*c*,*g*]fluorene **1** are fixed in a narrow torsion angle. Thus, their π-orbitals should significantly overlap through the binaphthyl juncture. In fact, the absorption and fluorescence spectra of 7-sila-7,7-dimethyl-7*H*-dibenzo[*c*,*g*]-fluorene (**1a**) remarkably red-shifted more than those of 2,2′-bis(trimethylsilyl)-1,1′-binaphthyl (**5a**) and (2-Np)$_2$SiMe$_2$ (**6a**), in which the π-conjugation between two naphthyl groups is completely broken by their geometrical or structural restrictions.[8] 7-Sila-7,7-diphenyl-7*H*-dibenzo[*c*,*g*]fluorene (**1b**) also showed the similar red-shifted spectra in comparison with 2,2′-bis(dimethylphenylsilyl)-1,1′-binaphthyl (**5b**) and (2-Np)$_2$SiPh$_2$ (**6b**). It is noteworthy that the absorption and emission maximum wavelengths of the diphenylsilylene-bridged **1b** red-shifted by 7 and 8 nm further than those of the dimethylsilylene-bridged **1a**, respectively. In contrast, neither **5** nor **6** missing the silole skeleton showed such a silicon effect in the absorption and fluorescence spectra. There is no doubt that the silole unit plays an important role in the remarkable silicon effect in the photophysical properties of the 7-sila-7*H*-dibenzo[*c*,*g*]-fluorene **1** that arises from the significant mixture of a σ^*-orbital of the exocyclic σ-bonds on silicon with a π^*-orbital of the binaphthyl moiety, that is, the $\sigma^*-\pi^*$ conjugation, like a silole. In fact, Tamao recently reported that the more electronegative 1,1-substituents of siloles tend to give longer absorption maximum wavelengths.[9] The semiempirical PM3 calculation also shows the presence of significant $\sigma^*-\pi^*$ conjugation in the LUMO of **1a**. In contrast, in the case of the carbon analogue, 7,7-dimethyl-7*H*-dibenzo[*c*,*g*]fluorene (**7**), the $\sigma^*-\pi^*$ conjugation in the LUMO is almost negligible. The shapes of the LUMO of **1a** and **7** are visualized in Figure 2.

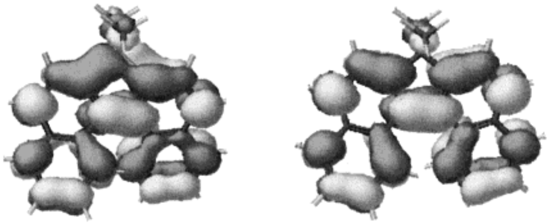
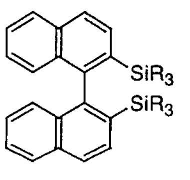
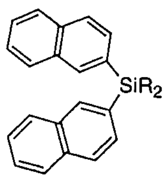


Figure 2. (a, left) PM3-calculated LUMO of **1a**. (b, right) PM3-calculated LUMO of **7**. The threshold level is 0.025.

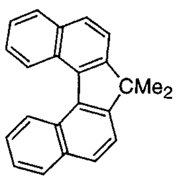
In conclusion, in the course of our research on the chiral silole chemistry, the first general method for the synthesis of the 7-sila-7*H*-dibenzo[*c*,*g*]fluorene **1** has been developed based on dilithiation of 2,2′-dibromo-1,1′-binaphthyl (**2**) followed by cyclization of the resulting dianion with dihalosilanes. The X-ray structural analysis, photophysical study, and semiempirical PM3 calculation revealed that 7-sila-7*H*-dibenzo[*c*,*g*]fluorene **1** is a promising candidate as a C_2 symmetrical chiral silole derivative. Asymmetric synthesis of the 7-sila-7*H*-dibenzo[*c*,*g*]fluorene **1** as well as its application to the material sciences is now under investigation in our laboratory.



5a: SiR$_3$ = SiMe$_3$
5b: SiR$_3$ = SiMe$_2$Ph



6a: SiR$_2$ = SiMe$_2$
6b: SiR$_2$ = SiPh$_2$



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Experimental Section

General Comments. ^{1}H (499.9 MHz) and ^{13}C (125.7 MHz) NMR spectra were measured on a Varian Unity 500 plus NMR spectrometer. ^{13}C NMR (75.47 MHz) and ^{29}Si (59.6 MHz) NMR spectra were measured on a Bruker AVANCE 300 NMR spectrometer. ^{1}H (200 MHz) NMR spectra were measured on a Varian Gemini 200H NMR spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to internal CDCl$_3$ (^{1}H δ 7.24 ppm; ^{13}C δ 77.0 ppm) relative to Me$_4$Si at δ 0.00 ppm. ^{29}Si chemical shifts were referred to Me$_4$Si (^{29}Si δ 0.00 ppm) as an external standard. UV absorption spectra were recorded on a Jasco V-550 UV/vis spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4010 fluorescence spectrophotometer. Low- and high-resolution mass spectra were obtained on a JEOL GCmate mass spectrometer. Melting points are uncorrected and were measured on a Yanaco MP-500D melting point apparatus. Density functional theory (B3LYP/6-31G(d)) calculation was performed on a Silicon Graphics Indigo2000 workstation.[10] Semiempirical calculations were performed using the PM3 method in the MOPAC installed on a Macintosh PowerBook G3.[11] Medium-pressure liquid chromatography (MPLC) was done on a Jasco PRC-50 using a silica gel packed

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column. Tetrahydrofuran (THF) was dried over and distilled from sodium benzophenone ketyl prior to use. 2,2′-Dibromo-1,1′-binaphthyl (**2**) was prepared according to published procedures.[9a] All reactions were carried out under nitrogen.

Preparation of 7-Sila-7,7-dimethyl-7*H*-dibenzo[*c,g*]-fluorene (1a) via the Cyclization of 2 with Me_2SiCl_2. To a solution of **2** (250 mg, 0.607 mmol) in THF (5 mL) was added a hexane solution of *n*-BuLi (1.0 mL, 1.50 M, 1.50 mmol) at −70 °C, and the reaction mixture was stirred for 30 min. After the reaction mixture was cooled to −90 °C, a solution of Me_2SiCl_2 (126 mg, 0.977 mmol) in THF (5 mL) was added slowly. After the addition was complete, the reaction mixture was warmed to −70 °C and stirred for an additional 2 h until the dark red dilithio dianion completely faded. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with hexane. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel with hexane. The crude product was subjected to MPLC (hexane) to afford **1a** (70.7 mg, 0.228 mmol) in 38% yield as a white powder: mp 36−38 °C (lit.[4] a colorless oil); ^{1}H NMR ($CDCl_3$, 499.9 MHz) δ 0.46 (s, 6H), 7.34−7.38 (m, 2H), 7.47−7.51 (m, 2H), 7.80 (d, J = 7.5 Hz, 2H), 7.88 (d, J = 7.5 Hz, 2H), 7.92 (d, J = 8.3 Hz, 2H), 7.98 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ −3.33, 124.26, 125.74, 127.82, 127.90, 128.26, 128.48, 129.72, 135.73, 139.87, 147.12; ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ 3.02; MS, *m/z* (%) 310 (M^+, 100), 295 (40); HRMS found, 310.1175; calcd for $C_{22}H_{18}Si$, 310.1178.

Preparation of 7-Sila-7,7-diphenyl-7*H*-dibenzo[*c,g*]-fluorene (1b) via the Cyclization of 2 with Ph_2SiCl_2. To a solution of **2** (311 mg, 0.755 mmol) in THF (5 mL) was added a hexane solution of *n*-BuLi (1.3 mL, 1.50 M, 1.95 mmol) at −70 °C, and the reaction mixture was stirred for 30 min. After the reaction mixture was cooled to −90 °C, a solution of Ph_2SiCl_2 (343 mg, 1.36 mmol) in THF (5 mL) was added slowly. After the addition was complete, the reaction mixture was warmed to −70 °C and stirred for an additional 4 h until the dark red dilithio dianion completely faded. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with hexane. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel with hexane. The crude product was subjected to MPLC (cyclohexane) to give the pure **1b** (28.6 mg, 0.228 mmol) in 8.7% yield as a white powder, which was recrystallized from a solution of the compound in diethyl ether at room temperature to give colorless crystals: mp 194−196 °C (dec); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.28−7.42 (m, 8H), 7.51 (ddd, J = 8.1, 6.8, 1.2 Hz, 2H), 7.62−7.70 (m, 4H), 7.83−8.05 (m, 8H); ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ 12.36; MS, *m/z* (%) 434 (M^+, 97), 356 (100), 355 (93), 278 (31); HRMS found, 434.1487; calcd for $C_{32}H_{22}Si$, 434.1491. Anal. Calcd for $C_{32}H_{22}Si$: C, 88.44; H, 5.10. Found: C, 88.27; H, 5.06.

Preparation of 7-Sila-7,7-diphenyl-7*H*-dibenzo[*c,g*]-fluorene (1b) via the Cyclization of 2 with Ph_2SiF_2. To a solution of **2** (200 mg, 0.485 mmol) in THF (5 mL) was added a hexane solution of *n*-BuLi (1.1 mL, 1.50 M, 1.65 mmol) at −70 °C, and the reaction mixture was stirred for 30 min. After the reaction mixture was cooled to −90 °C, a solution of Ph_2SiF_2 (187 mg, 0.85 mmol) in THF (5 mL) was added slowly. After the addition was complete, the reaction mixture was warmed to −70 °C and stirred for an additional 4 h until the dark red dilithio dianion completely faded. Further workup as in the reaction with Ph_2SiCl_2 give the pure **1b** (20.3 mg, 0.468 mmol) in 9.6% yield as a white powder.

Preparation of $(2\text{-Np})_2SiMe_2$ (6a). A solution of Me_2SiCl_2 (323 mg, 2.50 mmol), 2-bromonaphthalene (1.01 g, 4.88 mmol), and magnesium (169 mg, 6.95 mmol) in THF (7 mL) was stirred for 20 min at room temperature, then heated to reflux for an additional 30 min. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with Et_2O. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was subjected to flash chromatography (silica gel, hexane) to give the almost pure product, which was further purified by the bulb-to-bulb distillation to give the pure **6a** (472 mg, 1.51 mmol) in 62% yield as a colorless oil: bp 160−180 °C/0.5 mmHg; ^{1}H NMR ($CDCl_3$, 499.9 MHz) δ 0.69 (s, 6H), 7.43−7.49 (m, 4H), 7.59 (dd, J = 8.0 Hz, J = 1.0 Hz, 2H), 7.79−7.82 (m, 6H), 8.04 (s, 2H); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ −2.3, 125.9, 126.4, 127.1, 127.7, 128.1, 130.4, 132.9, 133.8, 135.0, 135.6; ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ −7.21; MS, *m/z* (%) 312 (M^+, 30), 297 (100); HRMS found, 312.1326; calcd for $C_{22}H_{20}Si$, 312.1334. Anal. Calcd for $C_{22}H_{20}Si$: C, 84.56; H, 6.45. Found: C, 84.80; H, 6.60.

Preparation of $(2\text{-Np})_2SiPh_2$ (6b). To a solution of 2-bromonaphthalene (200 mg, 4.52 mmol) in THF (10 mL) was added a hexane solution of *n*-BuLi (3.8 mL, 1.50 M, 5.7 mmol) at −70 °C, and the reaction mixture was stirred for 30 min. After the reaction mixture was cooled to −90 °C, a solution of Ph_2SiF_2 (621 mg, 2.82 mmol) in THF (5 mL) was added slowly. After the addition was complete, the reaction mixture was warmed to −70 °C and stirred for an additional 2 h until the dark red dilithio dianion completely faded. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with hexane. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was subjected to flash chromatography (silica gel, hexane) to give the almost pure product, which was further purified by the bulb-to-bulb distillation to give the pure **6b** (702 mg, 1.61 mmol) in 36% yield as white powder. The essentially pure **6b** for the measurement of UV absorption and the fluorescence spectra was obtained by recrystallizations from hexane; mp 154−157 °C; ^{1}H NMR ($CDCl_3$, 499.9 MHz) δ 7.34−7.54 (m, 10H), 7.62−7.68 (m, 6H), 7.75 (d, J = 7.5 Hz, 2H), 7.84 (d, J = 8.5 Hz, 4H), 8.07 (s, 2H); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 126.0, 126.8, 127.1, 128.0, 128.4, 129.7, 131.7, 132.1, 132.1, 132.9, 134.0, 134.1, 136.5, 137.8; ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ −13.66; MS, *m/z* (%) 436 (M^+, 91), 359 (80), 232 (100); HRMS found, 436.1655; calcd for $C_{32}H_{24}Si$, 436.1647. Anal. Calcd for $C_{32}H_{24}Si$: C, 88.03; H, 5.54. Found: C, 87.83; H, 5.77.

X-ray Crystallography. Single crystals of **1b** suitable for the X-ray diffraction study were obtained from a solution of the compound in diethyl ether at room temperature. Diffraction data were collected on a Rigaku Denki AFC7S diffractometer with a rotation anode (50 kV, 30 mA) using graphite-monochromated Cu Kα (λ = 1.54178 Å). The data were collected at a temperature of 23 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 154.3°. The structures were solved by direct methods[12] and expanded using Fourier techniques.[13] The cell constants and data collection parameters are summarized in Table 1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4060 observed reflections ($I > 3.00\sigma(I)$) and 298 variable parameters and converged (least parameter shift was 0.77 times its esd) with unweighted and weighted agreement factors: $R = 0.047$, $R_w = 0.071$, and R1 = 0.047 for $I > 3.00\sigma(I)$ data. Neutral atom scattering were taken from Cromer and Waber.[14] Anomalous dispersion effects were included in F_{calc},[15] and the values for Df' and Df'' were those of Creagh and McAuley.[16] The values for the mass attenuation coefficients

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are those of Creagh and Hubbell.[17] All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[18]

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Supporting Information Available: Spectroscopic data for **1**, **5**, and **6** and X-ray diffraction data for **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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