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Synthesis and Photophysical Properties of Asymmetric Substituted Silafluorenes

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Supporting Information

ABSTRACT: Several 1,3-diphenyl-substituted silafluorene compounds were synthesized and characterized as potential fluorescent materials for OLED fabrication and bioimaging. Introducing phenyl groups into the silafluorene ring at the 1- and 3-positions led to a red shift in the emission, resulting in blue light emitting compounds (λ_{max} 368–375 nm in solution; λ_{max} 362–371 and 482 nm in the solid state), and improved the quantum yield efficiency both in solution and as solids. Aggregation enhanced emission of the silafluorenes (AEE) was also investigated. Theoretical MO calculations were carried out



to aid in understanding the optical properties of these molecules. Since these compounds might be useful in bioimaging, their toxicity was also investigated in skin fibroblast cells. All compounds were found to be nontoxic to the investigated cell cultures.

INTRODUCTION

Dibenzoannulated analogues of silacyclopentadienes, or silafluorenes, have high electron affinities^{1–3} and are promising potential materials as electron transporters and emitters for fabrication of organic light emitting diodes (OLEDs)⁴ and photovoltaic cells.^{5–9} Silafluorene conjugates are also anticipated to be useful alternatives for expanding the repertoire of traditional fluorescent dyes in many biological assays and fluorescent imaging techniques.¹⁰ Important features of useful fluorophores for such applications include high absorption, high quantum yield, high stability with respect to photobleaching, and compatibility with biological systems.

Silafluorenes having 2-fold symmetric structures can be prepared by coupling of o,o'-dilithiobiphenyl with chlorosilanes¹¹ and by thermolysis of phenylchlorosilanes.¹² Substituted silafluorenes have been synthesized by [2 + 2 + 2]cycloaddition of Si-bridged 1,6-diynes with alkynes in the presence of an Ir(I)—phosphine catalyst,¹³ by intramolecular sila-Friedel—Crafts cyclization,¹⁴ by addition of a silyl group to an alkyne,¹⁵ and by the cross-coupling reaction of siliconbridged biaryls.¹⁶ Asymmetric silafluorenes are of interest, as asymmetrically aryl-substituted 9,9-spiro-9-silabifluorene (SSF) derivatives prepared through the cyclization of the corresponding 2,2-dilithiobiphenyls with silicon tetrachloride have demonstrated remarkably high absolute photoluminescence quantum yields (1/4PL): 30-55%.¹⁷ We were interested in synthesizing new blue light emitting silafluorenes. With molecular modification, the electronic and optical properties of π -conjugated compounds can be tuned;² thus, attaching conjugating substituents to the symmetric silafluorene ring can lead to red shifting, driving the emission maximum from the UV into the blue region.³ Attaching different groups to the silicon atom in the silafluorene ring also influences the fluorescence quantum yield efficiency.¹⁸

In this paper we provide a new route for synthesizing 1,3diphenyl-9-silafluorene derivatives. We report X-ray structural analysis and photophysical properties, including AEE characteristics and solid-state fluorescence, for both previously synthesized and novel silafluorene derivatives. Also included are the cell toxicity studies of compounds 3, 4, 6, and 6'.

RESULTS AND DISCUSSION

2,2'-Dilithio-3,5-diphenylbiphenyl (1) was synthesized by the reaction of 1-bromo-2,4,6-triphenylbenzene with *n*-butyllithium in diethyl ether.^{19,20} This reaction gave the desired product in over 90% yield in diethyl ether, but in THF or in hexane only 1-lithio-2,4,6-triphenylbenzene was obtained. Thus, it appears that the Li-coordinating diethyl ether molecules²¹ are crucial for

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the second lithiation step to occur on a neighboring phenyl ring at the *ortho* position.

9,9-Dichloro-1,3-diphenyl-9-silafluorene (2) and 1,1',3,3'-tetraphenyl-9-silaspirofluorene (3) were synthesized by the reaction of 1 with silicon tetrachloride, similarly to the procedure for their unsubstituted analogues²² (Scheme 1).

Scheme 1. Synthesis of Silafluorene 2



When 1 was treated with an 8-fold excess of SiCl₄ at -95 °C, the yield of 2 was almost 90%. However, the yield substantially decreased when a 2–4-fold excess of SiCl₄ was used, and spirosilafluorene 3 was formed in 50% yield. When 1 molar equiv of silicon tetrachloride was used, the yield of 3 reached 90%. In the reaction of 1 with dichlorodiphenylsilane the diphenylsilafluorene 4 was obtained in high yield (Scheme 2).

Scheme 2. Synthesis of Diphenylsilafluorene 4



Metalation of Dichlorosilafluorene 2. Reaction of dichlorosilafluorene **2** with excess metallic Li in THF at room temperature gives the 9,9-dilithiosilafluorene $5^{.22,23}$ The formation of dianion **5** was confirmed by the treatment of the mixture with Me₃SiCl, upon which 9,9-bis(trimethylsilyl)-1,3-diphenyl-9-silafluorene (**6**) was formed (Scheme 3).

Scheme 3. Metalation of Silafluorene 2



Silafluorene **6** was obtained previously by a radical intramolecular ring closure reaction.²⁴ 9,9-Bis(phenyldimethylsilyl)-1,3-diphenyl-9-silafluorene (**6**') was synthesized similarly in the reaction of 5 and phenyl(dimethyl)chlorosilane.

The structures of **2**, **3**, **4**, **6**, and **6**' were confirmed by ¹H, ¹³C, and ²⁹Si NMR and X-ray structure analysis, as presented in the Supporting Information.

Photophysical Properties. The photophysical properties of silafluorenes **3**, **4**, **6**, and **6**' are shown in Table 1.

The photophysical properties of 9,9-spirosilafluorene (7) and 9,9-diphenylsilafluorene (8) (Figure 1) were compared with those of 3, 4, 6, and 6' in order to investigate the effect of introducing phenyl substituents at positions 2 and 4 on the silafluorene moiety. 7 and 8 were synthesized by following known procedures.²²

Phenyl substituents can affect the optical properties of silafluorenes in several ways. They can enhance the free mobility of π electrons and the charge transportation in excited states, increasing the quantum yield efficiency. However, phenyl substituents can also provide nonradiative extinction pathways and thereby reduce quantum yield efficiency in solution. Finally, in the solid state angular phenyl rings may prevent aggregation, increasing the photoefficiency.

All investigated silafluorenes give blue emission. In solution the emission ranges lie between 340 and 450 nm (Figures 2–4), while in the solid state the emission ranges are broader, and for 6 and 6' additional peaks appear, resulting a broad emission from 320 to 500–550 nm (see the Supporting Information).

The highest molar extinction was observed for the new asymmetric spirosilafluorene 3, while the highest quantum yield efficiency in organic solvent as well as in the solid state was measured for compound 4. The solid-state quantum yield efficiency of 4 (0.42) approaches that of the more complex silafluorenes of Lee et al.¹⁷ (0.31–0.54), obtained via a much longer synthesis.

On comparison of the UV spectrum of 3 to that of 7 and the spectrum of 4 to that of 8, the absorption below 300 nm is more intense for 3 and 4 due to the additional phenyl groups. The broad absorption bands at 300-340 nm are also more intense in the case of 3 and 4, as these bands belong to the silafluorene ring, and the absorption can be enhanced by the conjugating phenyl substituents (see Theoretical Calculations).

The fluorescence emission maxima for silafluorenes 3, 4, 6, and 6' were red-shifted by about 20 nm in comparison to the maxima of unsubstituted silafluorenes 7 and 8. Fluorescence spectra recorded in dichloromethane show that the intensity of emission of the new phenyl-substituted silafluorenes is greater than that of the unsubstituted analogues.

Different substituents on the silicon atom of the silafluorene ring do not influence significantly the energy of the emission but do affect the intensity. As shown in Table 1, electrondonating substituents on the silicon atom enhance the fluorescence quantum yield efficiency, while electron-withdrawing groups decrease it. Furthermore, 3, 4, 7, and 8 have more extended conjugated systems than 6 and 6', which also influences the intensity.

Although some symmetric silafluorenes were already prepared in the 1950s, aggregation induced emission (AIE) or aggregation enhanced emission (AEE) of the reported silafluorenes was usually not investigated,^{25,26} and AEE was observed only for some ring-fused dibenzosiloles.²⁷ Compounds showing AEE characteristics are beneficial for sensitive sensing processes (with detection limits down to 0.1 ppm) and selectivity, enabling the development of biological probes to detect proteins, DNA, and RNA.²⁸

Aggregation enhanced emission (AEE) for our compounds was examined in THF-water solutions (see the Supporting Information). Compounds 4 and 7 show no significant increase in fluorescence intensity when aggregated, but they do not undergo quenching either. Compounds 6, 6', and 8 show typical AEE characteristics. Their fluorescence intensity

Table 1. Photophysical Properties of Silafluorenes 3, 4, 6, 6', 7, and 8^a

	UV-vis			fluorescence in CH_2Cl_2		solid state fluorescence		
silafluorene	$\lambda_{ m max}$, nm	λ_{ex} nm	$\log \epsilon \text{ (at } \lambda_{\text{ex}})$	λ_{\max} nm	$\Phi_{ m fl}$	λ_{ex} nm	λ_{\max} nm	$\Phi_{ m fl}$
3	265	330	3.49	375	0.13	325	371	0.15
4	265	330	3.03	368	0.17	325	361	0.42
6	260	330	3.16	368	0.09	325	365; 482	0.12
6'	260	330	3.34	368	0.07	325	362; 482	0.13
7	280	320	3.23	358	0.10	325	368	0.21
8^b	281	310	2.97	348	0.10	325	340; 355	0.16

^{*a*}Definitions: λ_{max} absorption or fluorescence maximum; λ_{ex} excitation wavelength; ε , molar absorption coefficient; Φ_{fl} , fluorescence quantum yield efficiency, estimated for CH₂Cl₂ solutions relative to 2-aminopyridine standard in 0.1 M H₂SO₄ aqueous solution. ^{*b*}Also reported by Yabusaki et al. (with excitation wavelength 250 nm.¹⁸



Figure 1. Structures of compounds 7 and 8.



Figure 2. UV absorption and fluorescence emission of compounds 3 and 4 in CH_2Cl_2 .



Figure 3. UV absorption and fluorescence emission of compounds 6 and 6' in CH_2Cl_2 .

increases rapidly with aggregation. Compound 3 has a peculiar maximum in fluorescence intensity when the water content of its THF solution is increased (Figure 5).

This phenomenon suggests that for **3** there is a structural change in the aggregates as the water/THF ratio changes. Crystallization enhanced emission (CEE) may be occurring,



Figure 4. UV absorption and fluorescence emission of compounds 7 and 8 in CH_2Cl_2 .



Figure 5. AEE characteristics of 3 in a THF-water mixture.

and the solid -state emission verifies this presumption. Accordingly, near the maximum the nanoaggregated particles probably exhibit a crystalline structure, and then with increasing water content, and presumably with increasing aggregate size, amorphous particles are formed.²⁹

In compounds **3**, **4**, **6**, **6**', and **8** there are two or four phenyl groups that provide a nonradiative extinction pathway by their free rotation. In the case of usual organic fluorescent molecules $\pi - \pi$ stacking can occur in nanoaggregates, resulting in quenching upon aggregation.³⁰ In the nanoaggregates of the investigated silafluorenes the $\pi - \pi$ stacking is partially hindered by the asymmetric substitution or by the nonplanar structure of the silafluorene frame. Restriction of intramolecular rotation (RIR) of the phenyl groups probably plays an important role in AEE as well, since the quantum yield efficiency increases with the hindrance of nonradiative extinction pathways. RIR was

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investigated in ethylene glycol; details are described in the Supporting Information.

In the solid state, on comparison of 7 to 3, the difference in the emission maximum decreases as well as the quantum yield efficiency. In contrast, on comparison of 4 to 8, phenyl substitution causes a red shift in the emission maximum and an increase in the quantum yield efficiency, prominently in the solid state. Compounds 6 and 6' exhibit behavior different from that of the other compounds. Si–Si bonds have a strong effect on the optical properties. This is especially true for 6', but both compounds show intense aggregation enhanced emission and their quantum yield efficiency is also increased in the solid state. 6 and 6' have a second emission peak around 482 nm in the solid state. These emission bands can be assigned to the conjugation of the Si–Si bond and the silafluorene (and phenyl) ring.³¹

When the solid compounds are observed visually, the brightest compounds are 6 and 6' (Figure 6). The reason for



Figure 6. Fluorescence of crystals under UV lamp (from left: 3, 4, 6, 6', 7, and 8, respectively).

this might be that only 6 and 6' have their major emission in the region of blue and cyan (or sky blue) colors, while all the other compounds emit mostly violet light.

Finally, light-emitting devices with the structure ITO/m-MTDATA (40 nm)/NPB (20 nm)/4 (20 nm)/TPBi (40 nm)/ LiF (1 nm)/Al (100 nm) and ITO/m-MTDATA (40 nm)/ NPB (20 nm)/6 (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm) were fabricated. At 15 V this device emitted blue light at 448 nm with a maximum luminance of 2890 cd/m². Its onset voltage was 4.4 V, the peak external quantum efficiency 1.7%, and the current efficiency 2.11 cd/A at 5.36 mA/cm² current density. The second device containing compound **6** also emitted blue light at 464 nm with a maximum luminance of 962 cd/m² at 20 V. Its onset voltage was 8.6 V, the peak external quantum efficiency 0.7%, and the current efficiency 1.08 cd/A at 27.6 mA/cm² current density. (For further details see the Supporting Information.) The results above suggest that compound 4 is the most promising candidate for the manufacture of electroluminescence devices.

Theoretical Calculations. Molecular orbital calculations were performed with the TD-DFT method at the B3LYP/6-31G* level using the Gaussian 09 package. The calculated energies from HOMO-3 to LUMO+3 are shown in Figure 7. The new phenyl-substituted silafluorene compounds were compared to their unsubstituted versions and to their carbon analogues.

On comparison of the silafluorenes with their carbon analogues, all energy levels show a decrease, but this is greater for the LUMO levels than the HOMO levels; thus, the HOMO-LUMO gap is decreased. Compound 7 shows the greatest decline of 0.23 eV. On comparison of the phenylsubstituted silafluorenes with their unsubstituted analogues (3 and 4 with 7 and 8), the HOMO levels are raised slightly and the LUMO levels are lowered, narrowing the HOMO-LUMO gap by 0.22 and 0.19 eV, respectively. This is in good agreement with the UV spectra, where 7 and 8 have absorption at around 280 nm while the silafluorene ring of 3 and 4 absorbs at 298 nm, which shows up as a shoulder because of the very intense peak of the substituent phenyl groups.

Due to the decrease of the HOMO–LUMO gap in the phenyl-substituted silafluorenes, significant changes were expected in the emission spectra as well. The measured results show that the originally UV-emitting compounds can be tuned with phenyl substitution and with significant red shift turned into blue-emitting compounds.

Molecular orbital calculations were carried out also for electronically advantageous conformations, where the phenyl groups are in the same plane with the silafluorene ring and the aromatic rings can conjugate. These conformations are at the rotation barrier maxima; thus, the probability of these conformations is low, but according to the calculated excited states they are responsible for the broad absorption bands in the UV spectra at around 330 nm (see the Supporting Information). The conjugating phenyl groups do not cause a large change in the HOMO levels but lower the LUMO levels and decrease the HOMO–LUMO gap by 0.23–0.35 eV (Figure 8).



Figure 7. Calculated molecular orbital levels at optimized geometries in the energy minimum.

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Figure 8. Calculated molecular orbital levels for phenyl-substituted silafluorenes and their carbon analogues at rotational maxima of the phenyl groups.

Toxicity Assays. The silafluorenes in this study emit blue light, which is not ideal for in vivo imaging but is suitable for biological research. As an initial exploration of their potential utility, a selection of the compounds reported in Table 1 was assayed for cytotoxicity in Normal Adult Human Primacy Dermal Fibroblasts cell line (NHDF from ATCC cat. #PCS-201-012). Cells were treated for 72 h with each test compound, and then the amount of live cells was quantified using an ATP determining assay reagent, Cell Titer Glo (Promega, cat. #G7572). ATP measurement is becoming more widely accepted as an indicator of the number of viable cells present. When cell viability is lost and membrane integrity is compromised, there is a rapid drop in the level of ATP present, resulting from the combination of a loss of the cell's ability to synthesize more ATP and the removal of any remaining ATP by the action of ATPases.

The IC50 values were determined using curve-fitting software (xlfit 5.0 (IDBS)) to find the concentration at which point 50% cytotoxicity is observable. Cell viability and proliferation remained intact for **3**, **4**, **6**, and **6'** in normal fibroblast cells below concentrations of 100 μ M, and the IC50 values appear to be above 100 μ M for each of the studied compounds. The lack of cytotoxicity of these molecules presents them as suitable agents for bioimaging purposes.

CONCLUSIONS

9,9-Dichloro-1,3-diphenylsilafluorene and its four derivatives were synthesized in only three- or five-step reactions. All compounds were found to be stable, crystalline, blue-emitting compounds. The optical properties were investigated in dichloromethane solution, in aggregate form, and in the solid state as well. Furthermore, compounds **4** and **6** were tested in electroluminescence devices (see the Supporting Information).

Theoretical calculations showed that phenyl substitution on the silafluorene ring leads to a decrease in the HOMO–LUMO gap. In good agreement with this result, the new asymmetric phenyl-substituted compounds show significant red shifts in the UV and emission spectra in comparison to their unsubstituted analogues. Due to the fact that these additional phenyl groups can conjugate with the silafluorene ring, they also increase the fluorescence emission intensity. The observed intensity increase in solution was less than that expected, probably because the rotating phenyl groups also provide a nonradiative extinction pathway. As this rotation was hindered in aggregates and in the solid state, enhanced emission was observed. All compounds showed increased quantum yield efficiency in the solid state: up to 42% for compound **4**.

The effect of different substituents on the silicon atom was also studied. Substitution on the silicon atom did not significantly influence the emission maxima or range in solution. Phenyl groups were found to be the most beneficial, as they increased the fluorescence emission intensity, while organosilyl groups caused decreased the fluorescence emission intensity and thus decreased the fluorescence quantum yield efficiency.

Si-Si bond containing compounds **6** and **6'** exhibit characteristics different from those of the other silafluorenes. They showed the most intense AEE characteristics, and both compounds have a second emission maximum at 482 nm in the solid state.

All compounds were found to be potential blue light emitting OLED materials; from the electroluminescence results compound **4** is an especially promising candidate. According to toxicity assays on human skin fibroblast cells, all compounds are potential candidates also in bioimaging.

EXPERIMENTAL SECTION

General Synthetic Procedure, Reagents, and Solvents. Triphenylbenzene, bromine, *n*-BuLi (1.6 M solution in hexane), silicon tetrachloride, and carbon disulfide were purchased from Aldrich and used without further purification. All solvents were distilled from sodium benzophenone ketyl in standard stills. Procedures involving air- and moisture-sensitive materials were carried out using standard a Schlenk line under a nitrogen atmosphere.

FT-IR spectra were obtained on a Mattson Polaris FT-IR spectrometer (ATR). ¹H, ¹³C, and ²⁹Si NMR spectra were recorded in CDCl₃. ²⁹Si NMR was recorded on a Varian INOVA-500 spectrometer at 500 MHz for ¹H (99.38 MHz for ²⁹Si). ¹H NMR and ¹³C NMR spectra were recorded on a Varian MercuryPlus 300 spectrometer at $\bar{3}00$ MHz for 1H and 75.40 MHz for ^{13}C nuclei. The crystal structure evaluations for 2, 3, 4, 6, and 6' data collections were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K α (λ = 0.71073 Å) radiation or on a Bruker SMART APEXII diffractometer with Cu K α (λ = 1.54178 Å) radiation, depending on the parameters of the single crystal. Mass spectra were recorded with a Bruker REFLEX II spectrometer using the MALDI technique and anthracene matrix. UV and fluorescence spectra were recorded on a HP 8452 UV-visible spectrophotometer and F-4500 fluorescence spectrophotometer. Solid-state fluorescence measurements were carried out according to the method described by de Mello et al.,³² using 325 nm CW light from a He-Cd laser for excitation and an Ocean Optics USB2000 miniature fiber optics spectrometer.

Fluorescence quantum yield efficiency was estimated relative to a 2-aminopyridine standard in 0.1 M $\rm H_2SO_4$ aqueous solution using the equation

$$(\Phi_{\rm fl})_{\rm x} = (\Phi_{\rm fl})_{\rm st} (Grad_{\rm x}/Grad_{\rm st}) (\eta_{\rm x}^2/\eta_{\rm st}^2)$$

where $(\Phi_{\rm fl})_x$ is the quantum efficiency of an unknown compound, $(\Phi_{\rm fl})_{\rm st}$ is the quantum efficiency of the standard, *Grad* is the slope of the plot of integrated fluorescence intensity vs absorbance, and η is the refractive index of the solvent (x and st refer to the unknown compound and the standard, respectively).³³

Bromotriphenylbenzene was obtained as described by Kohler and Blanchard³⁴ in the reaction of triphenylbenzene with bromine in carbon disulfide. 1-Bromo-2,4,6-triphenylbenzene can be obtained after recrystallization from ethanol with minimum 90% yield in high purity. (The purity was verified by ¹H and ¹³C NMR³⁵)

2,2'-Dilithio-3,5-diphenylbiphenyl (1). This compound was synthesized in the reaction of bromotriphenylbenzene with 2 equiv of n-BuLi in a hexane-diethyl ether mixture. A 5.0 g (13 mmol) portion of bromotriphenylbenzene was dissolved in 40 mL of diethyl ether and

10 mL of hexane and cooled to -78 °C, and 17 mL (27 mmol) of *n*butyllithium in 1.6 M solution in hexane was added dropwise to the suspension within 1 h. The solution was stirred for a further 3 h at low temperature and then 4 h at room temperature. After the reaction was completed, the volatile compounds were evaporated from the solvents under reduced pressure.

9,9-Dichloro-1,3-diphenyl-9-silafluorene (2). A solution of 1 (13 mmol in 50 mL of Et₂O) was added dropwise to a solution of SiCl₄ (33 mL, 129 mmol) in Et₂O (160 mL) at -95 °C. The reaction mixture was stirred at -95 °C and then warmed to room temperature by spontaneous evaporation of the cooling bath overnight. A yellow solution and a white precipitate were obtained. The white precipitate, mostly LiCl, was removed by filtration, and excess SiCl₄ and solvents were removed under vacuum. The residue was dissolved in Et₂O. After crystallization at -20 °C from Et₂O, 4.66 g (89%) of 2 was obtained. Selected data for 2 are as follows. ¹H NMR (300.133 MHz, CDCl₂): δ 7.3–8.1 (aromatic). ¹³C NMR (75.403 MHz, C_6D_6): δ 149.7 (C_9), 147.3 (C_q), 146.8 (C_q), 145.1 (C_q), 142.0 (C_q), 140.6 (C_q), 133.2 (CH), 132.6 (CH), 132.1 (C_q), 130.2 (CH), 129.4 (CH), 129.2 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 127.6 (CH), 121.5 (CH), 119.0 (CH), 0.2 (SiCH₃). ²⁹Si NMR (99.314 MHz, C_6D_6): δ +5.8 ppm.

1,1',3,3'-Tetraphenyl-9-silaspirofluorene (3). To 13 mmol of 1 in 75 mL of a hexane/Et₂O solution was added 6.5 mmol (1 equiv) of SiCl₄ at -78 °C. The temperature was raised to room temperature, and the reaction mixture was stirred overnight. After the reaction was complete, the solvents and excess SiCl₄ were removed by pumping and Et₂O was added to dissolve the solid residue. After crystallization at -20 °C from Et_2O, 3.93 g (91%) of 3 was isolated: mp 255 °C. $^1\mathrm{H}$ NMR (300.133 MHz, CDCl₃): δ 6.763-7.895 (aromatic) and 6.496-7.688 ppm. ¹³C NMR (75.403 MHz, CDCl₃): δ 150.9 (C_a), 149.6 (C_q) , 149.3 (C_q) , 144.4 (C_q) , 142.6 (C_q) , 141.5 (C_q) , 135.5 (C_q) , 133.8 (CH), 131.1 (C_q), 131.0 (CH), 129.0 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 126.8 (CH), 126.6 (CH), 121.3 (CH), 118.7 (CH).²⁹Si NMR (99.314 MHz, CDCl₃): δ -6.8 ppm. IR: 628.34, 694.51, 733.33, 753.63, 837.22, 881.05, 1026.99, 1068.40, 1129.87, 1255.32, 1389.83, 1442.45, 1492.46, 1545.74, 1591.50, 3027.69, 3049.51 cm⁻¹. MS (MALDI) m/z (%): 635.3 (25), 636.2 (40), 637.2 (26), 638.2 (8), 639.2 (2).

1,3,9,9-Tetraphenyl-9-silafluorene (4). To 13 mmol of 1 in 75 mL of a hexane/Et₂O solution was added 13.0 mmol (3.3 g) of Ph₂SiCl₂ in 20 mL of hexane at -78 °C. The temperature was raised to room temperature, and the reaction mixture was stirred overnight. After the reaction was complete, the solvents were removed by pumping and Et₂O was added to dissolve the solid residue. Following crystallization at -20 °C from diethyl ether 5.6 g (90%) of 4 was obtained: mp 185 °C. ¹H NMR (300.133 MHz, CDCl₃): δ 7.113-8.094 ppm (aromatics). ¹³C NMR (75.403 MHz, CDCl₃): δ 148.5 (C_{a}) , 144.4 (C_{a}) , 144.2 (C_{a}) , 142.5 (C_{a}) , 141.3 (C_{a}) , 142.2 (C_{a}) , 137.4 (C_q), 135.9 (CH), 134.2 (CH), 133.2 (C_q), 130.8 (CH), 130.0 (CH), 129.3 (CH), 129.0 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.5 (CH), 125.3 (CH), 121.4 (CH), 119.0 (CH). ²⁹Si NMR (99.314 MHz, CDCl₃): δ –10.3 ppm. IR: 652.47, 695.32, 758.03, 880.16, 1026.95, 1114.90, 1387.66, 1429.90, 1494.83, 1589.17, 3025.82, 3056.90 cm⁻¹. MS (MALDI) m/z (%): 485.1 (5), 486.1 (53), 487.1 (28), 488.1 (9), 489.1 (5).

9,9-Dilithio-1,3-diphenyl-9-silafluorene (5). A solution of 9,9dichloro-1-silafluorene **2** (5.0 g, 13 mmol) in THF (180 mL) was stirred with lithium metal (1.0 g, 130 mmol) at 0 °C for 2 h. After stirring for 10 min the reaction mixture turned red. The color of the solution then changed to a deep purple. (Unfortunately, we were not able to record ²⁹Si NMR signal of the dianion because of the presence of a paramagnetic species formed as a result of over-reduction of the dilithio-dianion, as has been described previously.²²) The reaction mixture was treated with excess Me₃SiCl at 0 °C to give 9,9bis(trimethylsilyl)-1,3-diphenyl-9-silafluorene (6). The volatiles were removed under reduced pressure, and the residue was extracted with hexane (250 mL). The hexane solution was washed with distilled water, dried over MgSO₄, and filtered. Upon crystallization from the residue at room temperature, 3.84 g (98.6%) of white crystals of bis(trimethylsilyl) derivative **6** was obtained: mp 143 °C. ¹H, ¹³C, and ²⁹Si NMR of **6** were similar to that of prepared in ref 14. ¹H NMR (300.133 MHz, CDCl₃): δ -0.03 (CH₃Si), 7.3–7.8 (aromatic). ¹³C NMR (75.403 MHz, CDCl₃): δ 150.4 (C_q), 148.7 (C_q), 148.3 (C_q), 145.7 (C_q), 142.1 (C_q), 141.5 (C_q), 141.2 (C_q), 137.8 (C_q), 134.0 (CH), 129.0 (CH), 128.9 (CH), 128.5 (CH), 128.4 (CH), 127.7 (CH), 127.6 (CH), 127.4 (CH),126.7 (CH), 126.4 (CH), 121.5 (CH), 119.0 (CH), -0.5 (SiCH₃). ²⁹Si NMR (99.314 MHz, CDCl₃): δ -13.6 (SiCH₃), -40.3(Si-SiCH₃). IR: 625.46, 693.83, 758.45, 829.97, 1028.95, 1242.82, 1493.06, 1590.58, 2891.10, 2945.37, 3039.92, 3059.24 cm⁻¹. MS (MALDI) *m*/*z* (%): 480.7 (62), 481.7 (23), 482.7 (15).

9,9-Bis(phenyldimethylsilyl)-1,3-diphenyl-9-silafluorene (6'). This compound was prepared very similarly to **6**, but **5** was treated with phenyl(dimethyl)chlorosilane: mp 129 °C. ¹H NMR (300.133 MHz, CDCl₃): δ 0.11 (CH₃Si) 7.1–8.1 (aromatic). ¹³C NMR (75.403 MHz, CDCl₃): δ 150.4 (C_q), 148.6 (C_q), 148.3 (C_q), 145.4 (C_q), 142.2 (C_q), 141.4 (C_q), 140.1 (C_q), 138.5 (C_q), 137.2 (C_q), 134.7 (CH), 134.2 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.6 (CH), 128.4 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 126.6 (CH), 126.5 (CH), 121.3 (CH), 119.0 (CH), -2.6 (SiCH₃). ²⁹Si NMR (99.314 MHz, CDCl₃): δ –16.5 (SiCH₃), -41.6 (Si-SiCH₃). IR: 645.61, 693.73, 730.52, 758.61, 801.75, 832.42, 877.53, 1106.78, 1249.12, 1425.81, 1500.43, 1592.29, 2955.58, 3051.63 cm⁻¹. MS (MALDI) *m*/*z* (%): 605.0 (58), 606.0 (28), 606.9 (14).

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving NMR, IR, UV, and fluorescence spectra, crystallographic data, and detailed results of the toxicity assays for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org. The crystal structures are also available free of charge from the Cambridge Crystallographic Data Center; the CCDC codes are 890700, 890701, 890702, 890703, 890704, 890705, and 890706 for compounds 7, 3, 8, 4, 6, 2, and 6', respectively.

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Notes

The authors declare no competing financial interest.

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