Synthesis and Characterization of Luminescent 2,7-Disubstituted Silafluorenes

Douglas W. Hammerstroem, Janet Braddock-Wilking*, and Nigam P. Rath

Department of Chemistry and Biochemistry and Center for Nanoscience, University of Missouri St Louis, St. Louis, Missouri 63121, United States.

ABSTRACT: The synthesis and characterization of a series of six new highly fluorescent 2,7-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafluorenes was investigated utilizing a modified multi-step synthetic pathway in which the final step utilizes palladium-catalyzed cross-coupling conditions to incorporate a variety of conjugated – alkynyl(aryl) groups at the 2,7-positions. These new compounds were characterized utilizing X-ray crystallography as well as multinuclear NMR, EA, TGA, DSC, UV-Vis, and fluorescence spectroscopic techniques. The new silafluorene compounds show a strong absorption band in the visible region with a maximum in the region of 374-388 nm and an emission maximum in the range of 403-420 nm. The solution-state quantum efficiencies for the luminescence are high and range from 0.80-0.89. All of the compounds show high thermal stability as determined by DSC and TGA analysis.

INTRODUCTION

Conjugated π -electron systems containing silicon have received substantial attention for their use as components for a wide variety of optical and electronic applications such as organic light emitting diodes (OLEDs), photovoltaic devices, field-effect transistors (FETs), and as chemical and biological sensors.¹⁻¹⁸ The unique optoelectronic properties found in these silicon systems arises from the $\sigma^*-\pi^*$ conjugation between the σ^* orbital of the two exocyclic groups at the silicon center and π^* orbital of the butadiene unit of the ring resulting in a low energy LUMO level.^{16,17} Incorporation of conjugated organic moieties on the ring allows for further electronic tuning.¹⁻²² Silafluorenes represent a relatively new class of photoluminescent molecules which demonstrate smaller band gaps, deep blue emission, high electron affinity, improved thermal stability, and greater quantum yields than that of their fluorene and carbazole analogs.^{15,23-30} Silafluorenes are analogs of 9,9-dialkylfluorenes, which have been of interest due to their deep blue emission and their ability to be incorporated into polysilafluorenes.^{11,24,26,27,30-37} Commercially available blue emitting polyfluorenes generally have a much shorter lifetime compared to that of red and green emitters. As a result, there has been increased interest in strong blue emitters with high quantum efficiency, lifetime, and color purity. Unfortunately, some polyfluorenes can undergo a decrease in emission and spectral broadening resulting in a low-energy green band over time.³⁸⁻⁴⁰

The synthesis of silafluorenes has traditionally been through the reaction of an *o,o*-dilithiobiphenyl with an appropriate dichlorosilane.^{7,8} Silafluorenes containing substituents at the 2,7- or 3,6-positions have been prepared by a similar reaction starting from a tetrahalobiphenyl precursor followed by the subsequent incorporation of a variety of organic substituents through a cross-coupling reaction.^{7,8,30,32,36,41} More recently, a number of transition metal-mediated syntheses of silafluorenes have been developed.⁸ 2,7- and 3,6-Dihalogenated silafluorenes have also been widely used for the preparation of new silafluorene-based polymers.⁸ Recently, a relatively simple, inexpensive, and high-yielding route to a tetra-halogenated biphenyl system has been developed by Huang et. al.,⁴² and recently improved by Ozin et. al.⁴³ In this method, commercially available *o*-dianisidine can be brominated to form 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (**1**), which by utilizing the *para*-directing methoxy substituents, can undergo iodination to form 2,2'-diiodo-4,4'-dibromodiphenyl (**2**). 2,7-Dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene (**3**) can then be synthesized through a lithium-halogen exchange with (**2**) which preferentially exchanges with the iodo substituents to form the 2,2'-dilithio-4,4'-dibromodiphenyl intermediate.^{42,43} However, in our experience, this reaction was low yielding for the preparation of (**3**). Using a modified method we were able to substantially reduce the experimental time and increase the yield of (**3**). With this improved route, the final step involving the synthesis of new 2,7- disubstituted silafluorenes (**4a-f**), was achieved by a standard palladium-catalyzed Sonagashira cross-coupling of (**3**) with the desired -alkynyl(aryl) linkages containing different terminal aryl groups. The synthesis and characterization of the new silafluorenes are described in the following sections.

RESULTS AND DISCUSSION

Synthesis and Characterization. The substituted biphenyl compounds **1** and **2** were prepared using a previously published procedure (Scheme 1).⁴³ Preparation of 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (**1**), proceeds via a Sandmeyer reaction in which the commercially available *o*-dianisidine amino groups are exchanged for bromides.⁴³ While glass tubing can be used to extend the stem of the dropping funnel below the surface of the solution to prevent side reaction with atmospheric O₂,⁴³ the reaction vessel can alternatively be purged with an inert atmosphere in order to achieve the same effect.

Preparation of 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (**2**), was directed by the 5,5'-methoxy groups in order to undergo the 2,2'-iodination reaction. Compound (**3**), 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafuorene, was obtained by a newly modified method developed from previously published methods.⁴²⁻⁴⁴ High yields of (**3**) were obtained by scrupulous control of all experimental parameters (see the Experimental Section) aided by utilizing an appropriately sized reaction vessel capable of accommodating a magnetic stirrer large enough to stir the reaction mixture as rapidly as practically possible such that a vortex formed. It was also imperative the level of the reaction mixture within the vessel was maintained beneath that of the bath, such that any added liquid N₂ did not result in localized freezing within the reaction mixture, especially during the period in which the mixture formed a slurry. Silafluorenes (**4a-f**) were prepared from the reaction of (**3**) with an appropriate -alkynynyl(aryl) precursor using palladium-catalyzed Sonagashira cross-coupling conditions^{42,44} as outlined Scheme 1. While compound (**3**) was not visibly fluorescent, silafluorenes (**4a-f**) exhibited mild fluorescence in solution after stirring for 30 min at 80 °C during their synthetic preparation. The silafluorenes were isolated as yellow crystalline powders in moderate to good yields (54-79%, based on the starting silafluorene **3**), and faintly shimmered blue in ambient lighting conditions, even at low (1x10⁻⁷ M) concentrations. These new compounds were characterized using X-ray crystallography, thermal analysis (DSC/TGA), elemental analysis, as well as multinuclear NMR, IR, UV-Vis, and fluorescence spectroscopic techniques and the results are discussed herein. The known compounds (**1-3**) were characterized by ¹H and ¹³C{¹H} NMR spectroscopy and the spectra showed good agreement with the literature values.^{42,43} Silafluorenes (**4a-f**) exhibited several characteristic proton and carbon NMR shifts.

For example, the ^1H NMR spectral data showed the diagnostic resonances as singlets at ca. δ 7.85 and 4.10, which were associated with the isolated proton between the methoxy substituent and the five-membered ring, and the $-\text{OCH}_3$ protons, respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR data revealed alkynyl carbon resonances in the range of δ 85-87 and 93-95, and the carbon bearing the methoxy substituents as well as the β -carbon of the central 5-membered ring of the heterocycle exhibited resonances at ca. δ 162 and 150-151, respectively. These chemical shifts were also similar to the previously reported values for related 2,7-disubstituted-3,6-dimethoxy-9,9-diphenylsilafluorenes.^{44,45} The silafluorenes (**4a-f**) all exhibited a $^{29}\text{Si}\{^1\text{H}\}$ NMR resonance at -17.6 ppm.

X-ray Crystal Structures. Crystals of sufficient quality for silafluorenes **4a-f** were grown by slow evaporation from CHCl_3 (or CDCl_3) solutions as thin yellow needles. Compound **4a** refined with one molecule of chloroform per two molecules of **4a**. The structures were solved and refined to reasonable geometries and residual electron densities and are summarized in Table 1 (see Experimental Section). The molecular structures of **4a-f** are shown in Figures 1-6, respectively with selected bond distances and angles. The bond distances found in **4a-f** are within the expected range and are similar to related silafluorene structures.³⁸ The exocyclic Si-C bonds in **4a-f** ranged from ca. 1.79-1.86 Å, whereas the endocyclic Si-C bonds ranged from ca. 1.85-1.95 Å. The C-Si-C exocyclic bond angles were significantly larger, ca. 108-115°, compared to the C-Si-C endocyclic angles, ca. 85-92°, as expected due to the constraints of the ring system. All of the compounds exhibit similar structural parameters within the silafluorene core to that of previously published 2,7-disubstituted-3,6-dimethoxy-9-silafluorene analogs.⁴³⁻⁴⁵ For compounds **4a-4f** varying amounts of twisting of the terminal aryl groups with respect to the silafluorene core were observed (see Figures 1-6). The related compound, 2,7-(ethynylphenyl)-3,6-dimethoxy-9,9-diphenylsilafluorene exhibited a molecular structure whereby one of the terminal phenyl groups is essentially coplanar with the silafluorene core (torsion angle 7.39°) whereas the other terminal phenyl group is almost perpendicular (torsion angle 89.24°).³⁸ Compounds **4a-f** all crystallized in essentially a parallel arrangement, but are offset partially due to the phenyl rings on the silylene moiety, which sterically block the majority of intermolecular overlap. Compound **4e** crystallized with the longest intermolecular distances of 7.025 Å, eliminating any possibility of π - π stacking interactions. Compounds **4a-d** and **4f** all possess intermolecular distances of 4.080-4.184 Å, but are offset such that there is minimal intermolecular orbital overlap between conjugated systems (see Supporting Information).

Figure 1. Molecular structure of **4a**. Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability

Figure 4. Molecular structure of **4d**. Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability

level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for **4a**: Si1-C1 = 1.865(2), Si1-C12 = 1.862(3), Si1-C37 = 1.861(3), Si1-C31 = 1.869(3), C1-C6 = 1.407(4), C6-C7 = 1.489(3), C7-C12 = 1.411(3), C13-C14 = 1.195(4), C21-C22 = 1.197(4), C37-Si1-C31 = 111.56(12), C6-C1-Si1 = 109.70(17), C1-C6-C7 = 114.9(2), C12-C7-C6 = 114.3(2), C7-C12-Si1 = 109.95(18), C12-Si1-C1 = 91.16(11), C2-C3-C15-C16 = 2.19, C11-C10-C23-C28 = 49.54.

Figure 2. Molecular structure of **4b**. Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for **4b**: Si1-C1 = 1.867(3), Si1-C12 = 1.869(3), Si1-C37 = 1.867(3), Si1-C31 = 1.867(3), C6-C7 = 1.477(4), C1-C6 = 1.416(4), C7-C12 = 1.413(4), C13-C14 = 1.193(4), C22-C23 = 1.200(4), C37-Si1-C31 = 108.97(13), C6-C1-Si1 = 109.1(2), C1-C6-C7 = 114.9(3), C12-C7-C6 = 115.5(3), C7-C12-Si1 = 108.7(2), C1-Si1-C12 = 91.70(13), C2-C3-C15-C16 = 178.12, C11-C10-C24-C29 = 152.81.

Figure 3. Molecular structure of **4c**. Hydrogen atoms and solvent molecules have been removed for clarity.

level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for **4d**: Si1-C1 = 1.854(3), Si1-C12 = 1.860(3), Si1-C49 = 1.861(3), Si1-C43 = 1.863(3), C6-C7 = 1.493(4), C1-C6 = 1.405(4), C7-C12 = 1.413(4), C13-C14 = 1.194(4), C27-C28 = 1.198(4), C49-Si1-C43 = 108.78(15), C6-C1-Si1 = 108.9(2), C1-C6-C7 = 115.3(3), C12-C7-C6 = 114.3(3), C7-C12-Si1 = 108.9(2), C1-Si1-C12 = 92.13(15), C2-C3-C15-C16 = 1.31, C11-C10-C29-C34 = 11.3.

Figure 5. Molecular structure of **4e**. Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for **4e**: Si1-C1 = 1.8667(17), Si1-C12 = 1.8700(17), Si1-C47 = 1.8631(18), Si1-C41 = 1.8660(18), C6-C7 = 1.494(2), C1-C6 = 1.407(2), C7-C12 = 1.414(2), C13-C14 = 1.191(2), C27-C28 = 1.195(2), C47-Si1-C41 = 110.12(8), C6-C1-Si1 = 109.48(12), C1-C6-C7 = 114.97(15), C12-C7-C6 = 114.58(14), C7-C12-Si1 = 109.31(12), C1-Si1-C12 = 91.48(7), C2-C3-C15-C16 = 32.68, C17-C18-C21-C22 = 37.13, C11-C10-C29-C34 = 168.89, C33-C32-C35-40 = 33.34.

Figure 6. Molecular structure of **4f**. Hydrogen atoms and solvent molecules have been removed for clarity.

<p>Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for 4c: Si1-C1= 1.916(7), Si1-C12 = 1.955(8), Si1-C37 = 1.791(8), Si1-C43 = 1.802(9), C1-C2 = 1.406(8), C2-C3 = 1.420(9), C3-C4 = 1.392(9), C4-C5 = 1.388(9), C5-C6 = 1.375(9), C6-C7 = 1.472(9), C1-C6 = 1.414(9), C7-C12 = 1.408(9), C13-C14 = 1.201(7), C25-C26 = 1.211(8), C37-Si1-C43= 115.3(5), C6-C1-Si1= 114.3(5), C1-C6-C7= 113.0(7), C12-C7-C6= 115.1(7), C7-C12-Si1= 112.1(5), C1-Si1-C12= 85.4(3), C2-C3-C15-C16 = 83.63, C11-C10-C27-C32= 134.61.</p>	<p>Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for 4f: Si1-C1 = 1.8551(10), Si1-C12 = 1.8638(9), Si1-C47 = 1.8594(10), Si1-C41 = 1.8682(10), C6-C7 = 1.4848(12), C1-C6 = 1.4086(12), C7-C12 = 1.4151(13), C13-C14 = 1.2046(13), C26-C27 = 1.2063(13), C47-Si1-C41 = 108.82(4), C6-C1-Si1 = 110.45(6), C1-C6-C7 = 114.02(8), C12-C7-C6 = 114.94(8), C7-C12-Si1 = 109.43(6), C1-Si1-C12 = 91.10(4), C2-C3-C15-C16 = 113.79, C11-C10-C28-C37 = 4.99.</p>
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Electronic Transitions. Recently, Cai and West and coworkers reported two tetraphenylsilole-containing cyclosiloxanes that show essentially 100% solid-state fluorescence quantum yields and strong AEE behavior.⁴⁶ Cai and West et al. also reported the synthesis and characterization of three related cyclotetrasiloxanes that contain silafluorene and/or silole-based ring systems that also exhibit high solid-state quantum yields ($\Phi_f = 0.65$ -0.78).⁴⁷ Previously, they reported a series of four ring-shaped siloxane derivatives containing silafluorene units that showed high quantum efficiency in the solid state ($\Phi_f = 0.35$ -0.54).⁴⁸ Pusztai and coworkers synthesized two highly fluorescent blue-emitting bis(diquinaldinatoalumino)-9-silafluorenes that exhibited high quantum efficiency in solution and in the solid-state.⁴⁹

All of the new silafluorenes were observed to have strong blue emission both in solution and the solid state, whose physical properties vary upon the alkynyl(aryl) linkages employed. All compounds exhibit similar absorption and emission spectra. The normalized UV-vis absorption and emission spectra of **4a-f** are shown in Figure 7, and are labeled in the order of their absorptive and emissive energies (**4a** > **4b** > **4c** > **4d** > **4e** > **4f**). Details of their photophysical properties are summarized in Table 2. The absorption spectra are dominated by an intense absorption band appearing between 373 – 388 nm. For silafluorenes **4a-4f** these bands arise from π - π^* transitions where the electron transitions are from the initial and excited states, which are HOMO/HOMO₋₁ and LUMO/LUMO₊₁, respectively, and are significantly delocalized over the entire bridged silafluorene network.^{20,29} The median absorption of 376 nm for **4a-4f** is in agreement with the theoretical absorption maxima around 371 nm for 2,7-(silafluorenyl)silafluorene while the absorption at ca. 288 nm is due to the silafluorene core.²⁰ The emission spectra for **4a-4f** (Figure 7b) show two major bands with the highest energy band being the most intense and appearing in the range of 403-420 nm. The related previously synthesized silafluorene analogs exhibit similar experimental absorption and emission values as those found for **4a-4f**, except for the terminal triphenylamine derivative

which showed red-shifted absorption and emission properties.^{44,45} In general, strong π -donor and π -acceptor substituents can exhibit considerably red-shifted absorption and emission maxima with respect to groups which are primarily inductive, while extending conjugation also results in red-shifted spectra.^{41,50} Compounds **4a-4f** follow this general trend. The new compounds, **4a-4c** incorporate inductive substituents to their -alkynyl(aryl) substituents, while **4d-4f** incorporate π -accepting substituents which also extend the conjugation. The absorption and emission maxima are nearly identical for **4a-4c**, but within the subset, **4a** incorporates an inductively electron-withdrawing substituent and possesses the highest energy absorptions and emissions with respect to **4b** and **4c**, which possess progressively more inductively donating substituents. These inductive effects are in agreement with previously predicted and observed trends.^{41,44,45,49-52} For **4d-f**, the trend in increasing red-shifted maxima follows that of effective extended conjugation. The phenoxy substituted alkynyl(aryl) compound (**4d**) exhibits very similar emission maxima but has a slightly lower quantum efficiency ($\lambda_{em} = 410, 434 \text{ nm}$, $\Phi_f = 0.87$) to that of the previously published 4-methoxyphenyl substituted-alkynyl(aryl) ($\lambda_{em} = 410, 435 \text{ nm}$, $\Phi_f = 0.94$).⁴⁵ Compound **4e** is red-shifted with respect to **4d**, likely due to its increased conjugation through absence of the oxygen atom. Li and Xu reported the preparation of two difurobenzosilole derivatives from an electrophilic double cyclization reaction starting from the corresponding 2,7-disubstituted alkynyl(4-methoxyphenyl) derivative. The resulting difurobenzosilole derivatives exhibited very high quantum efficiency in in solution ($\Phi_f = 0.93-0.99$).⁴⁵

The compound with the most red-shifted maxima of all previously discussed is **4f**, which is red-shifted with respect to **4e** likely due to the increased conjugation through a fused-ring system rather than the freely rotating rings in **4e**. Compounds **4a-4f** all exhibit very high quantum yields ($\Phi_f = 0.80-0.89$) in the order of **4b** > **4d** > **4c** > **4f** > **4e** > **4a**.

Figure 7. (a) Normalized UV/Vis and (b) fluorescence spectra of **4a-f** in CH₂Cl₂.

Table 2. UV–Visible and Fluorescence Spectral Data for silafluorenes **4a-f**.

Compound	λ_{max}^a absorbance (nm)	$\log \epsilon$	λ_{max}^b fluorescence (nm)	Φ_f^c	T_m^d/T_d^e (°C)
4a	285, 336, 373	4.80	403, 426	0.80	245/350
4b	287, 340, 374	4.93	405, 426	0.89	251/363
4c	288, 340, 375	4.90	405, 429	0.85	301/403
4d	288, 340, 377	4.90	410, 434	0.87	226/362
4e	292, 340, 384	4.82	417, 440	0.82	290/450
4f	280, 340, 388	4.95	420, 445	0.84	280/448

All measurements performed in CH₂Cl₂. ^a1x10⁻⁵ M. ^b1x10⁻⁶ M. ^cExcitation at 350 nm with anthracene as the standard. ^dMelting points measured by DSC. ^eDecomposition temperatures (5% weight loss) measured by TGA. The Φ_F is the average value of repeated measurements within $\pm 5\%$ error.

The thermal properties for **4a-f** were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the results are listed in Table 2. DSC analyses of **4a-f** showed relatively high melting points, while no glass transition temperatures were observed. The TGA results indicate all of the new compounds have good thermal stability. The decomposition temperatures (T_d) corresponding to 5% weight loss were measured as 345, 395, 401, 370, 401, 445 °C for **4a-f**, respectively. The order of stability in terms of thermal decomposition is **4e** > **4f** > **4c** > **4b** > **4d** > **4a**, which are much higher compared to a related carbon-based fluorene analog.⁵³ Previous studies have shown that thermal stability may be increased through the incorporation of a heteroatom (i.e. silicon) in place of a carbon center in some spiro-silabifluorene systems or by increasing the molecular volume.²²⁴

While **4a** exhibits the highest energy absorption and emission maxima, it also has the lowest quantum yield. Compound **4b** provides the greatest quantum yield while having nearly identical maxima to that of **4a**, with the added benefit of marginally greater thermal stability. The most thermally stable compound, **4e**, is substantially red-shifted compared to that of **4a** but with a similar quantum yield.

In conclusion, a series of 2,7-disubstituted-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafluorenes with different -alkynyl(aryl) substituents were synthesized and characterized in good yields ranging from 54-79%. All of the new silafluorenes described herein exhibit a high energy emission maxima between 403-420 nm and high fluorescence quantum yields in the range of 0.80-0.89 with fluorescence in both the solution and solid states. Further studies of this class of molecules with different -alkynyl(aryl) and aryl substituents are currently underway.

EXPERIMENTAL SECTION

General Procedures. Reactions were carried out under an argon atmosphere using standard Schlenk techniques with solvents dried and purified by standard methods, unless otherwise noted. Tetrahydrofuran was distilled from sodium and 9-fluorenone. Chloroform, dichloromethane, acetonitrile, methanol, pentane, and hexane were used as received. *O*-dianisidine was purchased from Alfa Aesar. The compounds, 1-ethynyl-3-fluorobenzene, 1-ethynyl-4-phenoxybenzene, 2-ethynyl-6-methoxynaphthalene, 4-ethynylbiphenyl, 4-ethynyltoluene, 4-*tert*-butylphenylacetylene, and *n*-butyllithium in hexanes (1.6 M) were all purchased from Sigma Aldrich and used without further purification. Dichlorodiphenylsilane was purchased from Sigma Aldrich and distilled from potassium carbonate under argon prior to use. Both 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (**1**) and 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (**2**) were synthesized according to a literature procedure.³⁷ All NMR spectra were collected on an Agilent 600 MHz (¹H recorded at 600 MHz, ¹³C at 126 MHz, and ²⁹Si at 99.38 MHz) or

on a Bruker Avance-300 MHz (^1H recorded at 300 MHz, ^{13}C at 75 MHz, and ^{19}F at 282 MHz) at ambient temperature unless otherwise noted). Chloroform- d_1 was purchased from Cambridge Isotopes, Inc. Elemental analyses were performed by Robertson Microlit Labs, Inc., Ledgewood, NJ. A JEOL M Station-JMS 700 mass spectrometer was used to obtain high resolution mass spectra by fast atom bombardment (FAB) or (EI) conditions, using 3-nitrobenzyl alcohol (NBA) as a matrix and dichloromethane as a solvent. X-ray intensity data were measured using a Bruker Apex II diffractometer equipped with a CCD area detector. Melting point determinations were obtained on a Mel-Temp melting point apparatus and are uncorrected. UV-vis and fluorescence spectra were measured at room temperature on a Cary 50 Bio UV-visible and Cary Eclipse Fluorescence spectrophotometer, respectively. The relative fluorescence quantum yield in solution was determined for compounds **4a-4f** using anthracene (1×10^{-6} M) in CH_2Cl_2 as the reference standard. Emission spectra were measured using the λ_{max} value for each compound as determined by the absorption spectra. The differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) data were recorded on a TA Instruments Q2000 and Q500 instrument, respectively under nitrogen atmosphere. The thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 under nitrog

Preparation of 2,7-Dibromo-3,6-dimethoxy-9,9-diphenyl-silafluorene (3) To flame-dried four-necked flask equipped with an addition funnel, thermometer, and magnetic stirrer under argon, 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (5 g, 8.01 mmol) was dissolved in THF (160 mL). The solution was chilled to $-95\text{ }^\circ\text{C}$ in a methanol/ N_2 bath. At $95\text{ }^\circ\text{C}$, there is risk of the methanol bath freezing and fracturing the four-necked flask. Addition of water ($\text{H}_2\text{O}:\text{MeOH}$, 1:4) mitigates this possibility, resulting in a slush. 10.27 mL *n*-BuLi (1.6 M in hexanes) was then added dropwise over 2.5 min to the rapidly stirring solution, while not allowing the reaction mixture temperature to exceed $-90\text{ }^\circ\text{C}$ in order to ensure selectivity for a lithium-iodine exchange. The clear solution immediately turned yellow after the first drop of *n*-BuLi was added, and developed into a bright yellow slurry as half of the total volume of *n*-BuLi is added before redissolving as *n*-BuLi addition is completed. Immediately after addition of *n*-BuLi was complete, dichlorodiphenylsilane (3.37 mL, 16.03 mmol) was injected by syringe in one portion. The pale yellow reaction mixture was immediately removed from the bath and allowed to stir at room temperature overnight. The reaction mixture was then quenched with saturated ammonium chloride solution and extracted with chloroform. The organic layer was then washed with brine, dried with magnesium sulfate, and filtered. The solvent was then removed by rotoevaporation. The product was then purified by chromatography (silica gel, dichloromethane/hexane 1/1) and recrystallized in dichloromethane:ethanol. The resulting white crystalline powder (3.36 g, 76%) was then collected by filtration and confirmed by comparison to literature values.^{37,65}

General procedure for preparation of 2,7-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafluorenes.

To a flame-dried 15 mL three-necked flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene (0.250 g, 0.453 mmol), Pd(PPh₃)₄ (0.052 g, 0.045 mmol), and CuI (0.018 g, 0.092 mmol) were added, followed by piperidine (5.2 mL, 52.5 mmol) and -alkynyl(aryl) (1.34 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation.

Preparation of 2,7-(1-ethynyl-3-fluorobenzene)-3,6-dimethoxy-9,9-diphenylsilafluorene (4a). The compound was prepared following the general procedure, using 1-ethynyl-3-fluorobenzene as the -alkynyl(aryl). The product was received as a bright yellow powder (0.190 g, 67% yield). Mp: 251-252 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. ¹H NMR (600 MHz, CDCl₃): δ 7.88 (s, 2H), 7.65 (d, ³J_{HF} = 7 Hz, 4H), 7.49 – 7.41 (m, 2H), 7.41 – 7.28 (m, 10H), 7.27 – 7.23 (m, 2H), 7.05 – 7.00 (m, 2H), 4.09 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 162.8, 162.5 (d, ¹J_{C-F} = 246 Hz), 150.3, 139.0, 135.6, 132.2, 130.4, 129.9 (d, J_{C-F} = 9 Hz), 128.5, 128.3, 127.6 (d, J_{C-F} = 3 Hz), 125.5 (d, J_{C-F} = 9 Hz), 118.4 (d, J_{C-F} = 15 Hz), 115.6 (d, ²J_{C-F} = 21 Hz), 112.5, 104.0, 93.5 (d, ⁴J_{C-F} = 3 Hz), 87.2, 56.1. ²⁹Si{¹H} NMR (119 MHz, CDCl₃): δ -17.6. ¹⁹F NMR (564 MHz, CDCl₃): δ -113.1 (m). Anal. Calcd for C₄₂H₂₈F₂O₂Si: C, 79.98; H, 4.47. Found: C, 80.01; H, 4.22. HRMS (EI): calcd. for C₄₂H₂₈F₂O₂Si: 631.19049; found 630.18268.

Preparation of 2,7-(4-ethynyltoluene)-3,6-dimethoxy-9,9-diphenylsilafluorene (4b). The compound was prepared following the general procedure, using 4-ethynyltoluene as the -alkynyl(aryl). The product was received as a bright yellow powder (0.178 g, 63% yield). Mp: 246-247 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. ¹H NMR (600 MHz, CDCl₃): δ 7.88 (s, 2H), 7.67 – 7.64 (m, 4H), 7.48 – 7.40 (m, 6H), 7.39 – 7.34 (m, 6H), 7.17 – 7.12 (m, 4H), 4.08 (s, 6H), 2.36 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 162.5, 150.0, 138.9, 138.4, 135.6, 132.5, 131.6, 130.3, 129.1, 128.39, 128.31, 120.5, 113.0, 104.0, 95.0, 85.6, 56.1, 21.6. ²⁹Si{¹H} NMR (119 MHz, CDCl₃): δ -17.64. Anal. Calcd for C₄₄H₃₄O₂Si: C, 84.85; H, 5.50. Found: C, 84.60; H, 5.54. HRMS (EI): calcd. for C₄₄H₃₄O₂Si: 622.23279; found 622.234.

Preparation of 2,7-(4-tert-butylphenylacetylene)-3,6-dimethoxy-9,9-diphenylsilafluorene (4c). The compound was prepared following the general procedure, using 4-tert-butylphenylacetylene as the -alkynyl(aryl). The product was received as a bright yellow powder (0.253 g, 79% yield). Mp: 341-342 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. ¹H NMR (600 MHz, CDCl₃): δ 7.88 – 7.86 (m, 2H), 7.67 – 7.64 (m, 4H), 7.50 – 7.47 (m, 4H), 7.45 – 7.40 (m, 2H), 7.39 – 7.34 (m, 10H), 4.07 (s, 6H), 1.32 – 1.30 (m, 18H). ¹³C{¹H} NMR

(151 MHz, CDCl₃): δ 162.6, 151.5, 150.0, 138.9, 135.6, 132.5, 131.4, 130.3, 128.4, 128.3, 125.4, 120.6, 113.2, 104.1, 94.9, 85.6, 56.2, 34.9, 31.3. ²⁹Si{¹H} NMR (119 MHz, CDCl₃): δ -17.6. Anal. Calcd for C₅₀H₄₆O₂Si: C, 84.94; H, 6.56. Found: C, 84.69; H, 6.45. HRMS (EI): calcd. for C₅₀H₄₆O₂Si: 706.985; found 706.32666.

Preparation of 2,7-(1-ethynyl-4-phenoxybenzene)-3,6-dimethoxy-9,9-diphenylsilafluorene (4d).

The compound was prepared following the general procedure, using 1-ethynyl-4-phenoxybenzene as the -alkynyl(aryl). The product was received as bright yellow needle-like crystals (0.240 g, 68% yield). Mp: 227-229 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. ¹H NMR (600 MHz, CDCl₃): δ 7.87 (s, 2H), 7.66 – 7.65 (m, 4H), 7.52 – 7.51 (m, 4H), 7.45 – 7.41 (m, 2H), 7.39 – 7.34 (m, 10H), 7.14 (t, *J* = 12 Hz, 2H), 7.04 (d, *J* = 12 Hz, 4H), 6.96 (d, *J* = 6 Hz, 4H), 4.08 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 162.6, 157.6, 156.6, 150.0, 138.8, 135.6, 133.3, 132.4, 130.3, 130.0, 128.4, 128.3, 123.9, 119.5, 118.4, 118.2, 113.0, 104.0, 94.3, 85.6, 56.1. ²⁹Si{¹H} NMR (119 MHz, CDCl₃): δ -17.6. Anal. Calcd for C₅₄H₃₈O₄Si: C, 83.26; H, 4.92. Found: C, 82.97; H, 4.83. HRMS (EI): calcd. for C₅₄H₃₈O₄Si: 778.25397; found 778.252.

Preparation of 2,7-(4-ethynylbiphenyl)-3,6-dimethoxy-9,9-diphenylsilafluorene (4e).

The compound was prepared following the general procedure, using 4-ethynylbiphenyl as the -alkynyl(aryl). The product was received as a bright yellow powder (0.183 g, 54% yield). Mp: 326-328 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. ¹H NMR (600 MHz, CDCl₃): δ 7.91 (s, 2H), 7.69 – 7.66 (m, 4H), 7.64 – 7.57 (m, 12 H), 7.47 – 7.42 (m, 6H), 7.40 – 7.34 (m, 8H), 4.11 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 162.6, 150.1, 140.9, 140.5, 138.9, 135.6, 132.4, 132.1, 130.4, 128.9, 128.4, 128.3, 127.7, 127.1, 127.0, 122.5, 112.9, 104.0, 94.7, 87.0, 56.2. ²⁹Si{¹H} NMR (119 MHz, CDCl₃): δ -17.6. Anal. Calcd for C₅₄H₃₈O₂Si: C, 86.83; H, 5.13. Found: C, 86.73; H, 4.96.

Preparation of 2,7-(2-ethynyl-6-methoxynaphthalene)-3,6-dimethoxy-9,9-diphenylsilafluorene (4f).

The compound was prepared following the general procedure, using 2-ethynyl-6-methoxynaphthalene as the -alkynyl(aryl). The product was received as a bright yellow powder (0.185 g, 54% yield). Mp: 294-295 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. ¹H NMR (600 MHz, CDCl₃): δ 8.01 (s, 2H), 7.93 (s, 2H), 7.73– 7.67 (m, 8H), 7.60 – 7.57 (m 2H), 7.46 – 7.42 (m, 2H), 7.40 – 7.37 (m, 6H), 7.19 – 7.14 (m, 2H), 7.12 – 7.11 (m, 2H), 4.12 (s, 6H), 3.93 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 162.6, 158.4, 150.0, 138.9, 135.6, 134.2, 132.5, 131.4, 130.3, 129.5, 129.2, 128.6, 128.4, 128.3, 126.8, 119.4, 118.5, 113.1, 105.9, 104.0, 95.4, 86.0, 56.2, 55.5. ²⁹Si{¹H} NMR (119 MHz, CDCl₃): δ -17.6. Anal. Calcd for C₅₂H₃₈O₄Si: C, 82.73; H, 5.074.92. Found: C, 82.45; H, 4.97. HRMS (EI): calcd. for C₅₂H₃₈O₄Si: 754.25397; found 752.252.

X-ray Structure Determination of 4a-f. Crystals of X-ray diffraction quality were grown by slow evaporation of chloroform or dichloromethane solutions of **4a-f**. Crystals of appropriate dimensions were mounted on MiTeGen cryoloops in random orientations. Preliminary examination and data collection were performed using a Bruker X8 Kappa Apex II Charge Coupled Device (CCD) Detector system single crystal X-Ray diffractometer equipped with an Oxford Cryostream LT device. All data were collected using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a fine focus sealed tube X-Ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consist of combinations of ω and ϕ scan frames with typical scan width of 0.5° and counting time of 15 seconds/frame at a crystal to detector distance of 4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages⁵⁵ were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of reflections harvested from the complete data set. Collected data were corrected for systematic errors using SADABS⁵⁵ based on the Laue symmetry using equivalent reflections. A summary of crystal structure parameters are listed in Table 1. Complete crystal data and intensity data collection parameters are listed in supporting information. Structure solution and refinement were carried out using the SHELXTL- PLUS software package⁵⁶. The structures **4a**, **4c**, **4e** and **4f** were in triclinic space group P-1 whereas structures **4b** and **4d** were solved and refined in monoclinic space group P2₁/c. All structures were solved by direct methods and refined successfully in the listed space groups. Full matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. All hydrogen atoms were treated using appropriate riding model (AFIX m3). The final residual values and structure refinement parameters are listed in Table 1. A half (0.5) molecule of CHCl₃ was found in the **4a** lattice. One of the C₆H₅F motifs was disordered and was refined over 2 orientations of 50% occupancies. Disorder model was refined with geometry and displacement parameter restraints. The molecule, **4c** is disordered over two sites with Si as the anchor atom. The 2 orientations were refined with partial occupancy of 52:48%. The refinement was carried with SAME restraint for the two orientations. In case of the molecule **4f**, overlapping partial occupancy CH₂Cl₂ solvents were located in the lattice which could not be modeled. Therefore Palton/Squeeze⁵⁷ was used to remove the solvent contributions. The naphthalene ring disorder was resolved with 2 orientations (93:7%). Complete listings of positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms are listed in supplementary material. A table of calculated and observed structure factors is available in electronic format.

Table 1. Crystallographic and Data Collection Parameters for 4a-f^a

	4a	4b	4c	4d	4e	4f
Formula	C ₈₅ H ₅₇ Cl ₃ F ₄ O ₄ Si ₂	C ₄₄ H ₃₄ O ₂ Si	C ₅₀ H ₄₆ O ₂ Si	C ₅₄ H ₃₈ O ₄ Si	C ₅₄ H ₃₈ O ₂ Si	C ₅₂ H ₃₈ O ₄ Si
fw	1380.83	622.80	706.96	778.93	746.93	754.91
cryst syst	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
space group	P $\bar{1}$	P2 ₁ /c	P $\bar{1}$	P2 ₁ /c	P $\bar{1}$	P $\bar{1}$
<i>a</i> , Å	10.8704(9)	12.7069(6)	8.6693(4)	15.6365(9)	12.3161(3)	9.3163(7)
<i>b</i> , Å	11.9328(10)	11.9563(5)	12.6841(6)	15.7339(9)	13.1757(3)	12.8339(10)
<i>c</i> , Å	15.0473(13)	23.0436(11)	18.8639(8)	17.2706(10)	13.7692(4)	19.0752(14)
α , deg	83.471(5)	90	82.507(2)	90	114.7461(10)	80.503(4)
β , deg	71.515(5)	102.887(3)	83.597(2)	109.642(3)	103.0238(15)	84.054(4)
γ , deg	68.378(5)	90	78.312(2)	90	90.6655(12)	70.047(4)
<i>V</i> , Å ³	1720.9(3)	3412.8(3)	2006.21(16)	4001.7(4)	1962.77(9)	2111.7(3)
<i>Z</i>	1	4	2	4	2	2
<i>d</i> _{calc} , g/cm ³	1.332	1.212	1.170	1.293	1.264	1.187
μ , mm ⁻¹	0.233	0.106	0.098	0.108	0.104	0.101
R1, ^b wR2 ^c	0.0818, 0.1720	0.1299, 0.1538	0.0863, 0.1584	0.1376, 0.1259	0.0736, 0.1139	0.0718, 0.1541
goodness-of-fit on <i>F</i> ²	1.033	1.009	1.015	0.995	1.019	1.048

^a λ = 0.71073 Å (Mo), *T* = -100(2) K. ^b R1 = $(\sum ||F_o| - |F_c||) / \sum |F_o|$. ^c wR2 = $[(\sum w(F_o^2 - F_c^2)^2) / \sum w(F_c^2)^2]^{1/2}$. All crystals were yellow needles.

ASSOCIATED CONTENT

Supporting Information

¹H, ¹³C{¹H}, and ¹⁹F (for **4a**) NMR spectra, DSC and TGA data, and crystallographic data for silafluorenes **4a-f**. The Supporting Information is available free of charge via the internet at <http://pubs.acs.org>. The crystal structures are available free of charge from the Cambridge Crystallographic Data Center; The CCDC codes are: CCDC-1411567 (**4a**), CCDC-1411568 (**4b**), CCDC-1411569 (**4c**), CCDC-1411570 (**4d**), CCDC-1411571 (**4e**), and CCDC-1411572 (**4f**).

AUTHOR INFORMATION

Corresponding Author

*E-mail (J. Wilking), wilkingj@umsl.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We acknowledge funding from the National Science Foundation (CHE-1362431) for support of this work, and for funding for the Agilent DD2 600 MHz NMR spectrometer (MRI-0959360) and Apex-II diffractometer (MRI, CHE-0420497).

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