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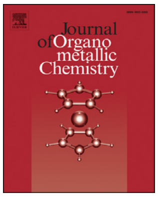

Synthesis and characterization of luminescent 2,7-disubstituted silafluorenes

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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 to 0.89. All of the compounds show high thermal stability as determined by DSC and TGA analysis.

1. 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 σ*–π* 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

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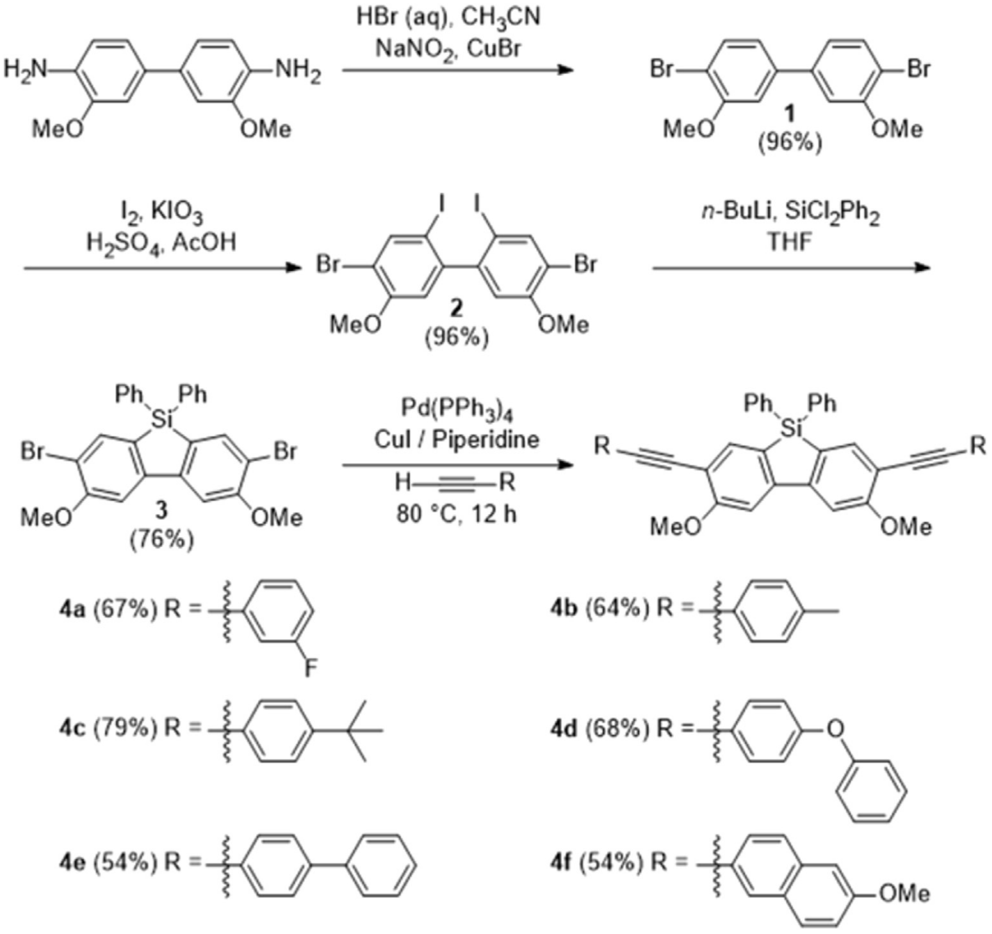
this improved route, the final step involving the synthesis of new 2,7- disubstituted silafluorenes (**4a-f**), was achieved by a standard palladium-catalyzed Sonagashira cross-coupling of (**3**) with the desired -alkynyl(aryl) linkages containing different terminal aryl groups. The synthesis and characterization of the new silafluorenes are described in the following sections.

2. Results and discussion

2.1. 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 O_2 [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-diphenylsilafluorene, 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 N_2 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 (1×10^{-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 ^{1}H and ^{13}C{^{1}H} 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 ^{1}H 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 $-OCH_3$ protons, respectively. The ^{13}C{^{1}H} NMR data revealed alkynyl carbon



Scheme 1. Synthesis of silafluorenes **4a**–**4f**.