

Synthesis and Photoluminescence of Silole Derivatives

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Abstract

The syntheses of 9,9'-spiro-9-silabifluorene as well as 1,1-dichloro-1-silafluorene and 1,1-dimethyl-1-silafluorene through the formation of 2,2'-dibromobiphenyl have been emphasized with good yields. Their fluorescence spectra are obtained using photoluminescence spectrometer and assumed to be the precursors of the development of polymers.

Key words: Silicon, Fluorescence, Silafluorene

1. Introduction

Silicon-containing π -conjugated compounds, especially siloles, have emerged as a new class of electrolyte materials with good electron transport properties in OLEDs^[1-12]. The reason grounds that siloles have a relatively lowest unoccupied molecular orbital (LUMO) level due to the σ^* - π^* conjugation between the σ^* orbitals of silicon and the π^* orbital of the butadiene fragment, resulting in a high electron affinity.

Spirosilafluorene derivatives may be useful in light emitting diodes for display devices. The spiro-silafluorene unit is well known and has been synthesized with silicon atom at the site of the fusion. The synthesized compound contains two biphenyl moieties, resulting in a strained structure. In another attempt, silafluorenes (dibenzosiloles) i.e. 1,1-dichloro-1-silafluorene and 1,1-dimethyl-1-silafluorene have been produced. The starting material for all the silafluorenes and spiro-silafluorene is regarded the same. The spiro-linked molecules compared to the corresponding non-spiro linked parent compounds exhibit greater morphological stability and more fluorescence.

The π -conjugated organic materials with electronically rigid backbones have attracted considerable interest in both academic research and industrial applications due to increasing potential as active components for a wide range of electronic and photoelectronic devices.

Polysilafluorene derivatives have emerged as a promising class of blue light-emitting conjugated polymers for use in polymer-based emissive displays, because of photoluminescent yields^[1].

Silafluorenes (dibenzosiloles) have unusual electronic and optical properties. These compounds are strongly fluorescent and electroluminescent organic light-emitting diodes. We anticipate the discovery of more novel compounds. These ring compounds have novel electronic properties. The reason behind this is that the lowest unfilled molecular orbital of silafluorene lies at very low energy level, making these compounds highly electroactive and strongly fluorescent. Light emitting conjugated polymers are of interest both for their broad technological applications because they are model systems to gain fundamental understanding of the properties of soft organic and biological matter^[2].

Polysilafluorenes and their derivatives have received a great deal of attention and are evolving as a major class of materials for light emitting diodes (LEDs).

2. Experimental Section

2.1. Measurements

All manipulations involving air sensitive reagents were carried out under an atmosphere of dry argon gas using standard Schlenk and Vacuum techniques. ¹H NMR spectra were recorded on a Bruker 300 MHz spectrometer. CDCl₃ was used as NMR solvent. Tetramethylsilane (TMS) was used as internal reference. Fluorescence spectra were recorded with a Perkin Elmer LS55 Luminescence Spectrometer. Melting point

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measurements were carried out with conventional methods.

2.2. Materials

All commercially available chemicals, reagents and solvents were used as received without further purification, unless otherwise stated. Solvents like tetrahydrofuran (THF) and diethyl ether were purchased from Aldrich Chemical Co. Inc. and were distilled with sodium and benzophenone under argon before use.

2.3. Synthesis

2.3.1. Synthesis of 2,2'-dibromobiphenyl

To a stirred solution of 1,2-dibromobenzene (11.8 g, 0.05 mol) in anhydrous tetrahydrofuran (100 mL) for 30 min was added n-butyllithium (10 mL, 0.025 mol, 2.5 M in n-hexane). The mixture solution was cooled to the minimum temperature of dry ice/acetone mixture (-78°C). The rate of addition of n-butyllithium should be dropwise over a period of 30 minutes under the mentioned temperature. The reaction mixture was allowed to warm up to room temperature with stirring and then was hydrolyzed with approximately 1.2 mL of 5% hydrochloric acid. Then the volatile liquids were removed under reduced pressure. To this residue was added anhydrous diethyl ether (100 mL) and stirred for a while. An original organic layer and a white precipitate were obtained. The white precipitate, mostly lithium chloride, was removed by filtration under argon and removable liquids (filtrate) were evaporated under reduced pressure. The residue was kept under sublimation to give 5.9 g (75.64% yield) of white-needle like crystals of 2,2'-dibromobiphenyl. The melting point was to be 80°C. ¹H-NMR (300 MHz, CDCl₃): δ=(TMS, ppm) 7.59(d, 2H), 7.31(t, 2H), 7.21(d, 2H), 7.16(t, 2H).

2.3.2. Synthesis of 9,9'-spiro-9-silabifluorene

To a stirred solution of 2,2'-dibromobiphenyl (3.12 g, 10 mmol) in anhydrous diethyl ether (50 mL) for 30 min was added n-butyllithium (8 mL, 20 mmol, 2.5 M in n-hexane). This reaction mixture was cooled to the temperature of dry ice/acetone mixture (-78°C). The rate of addition of n-butyllithium should be dropwise over a period of 10 minutes under the mentioned temperature. The solution mixture (initially turned to slurry for a while) was allowed to warm up to room temperature

with stirring for 6 hours. Silicon tetrachloride (0.85 g, 5 mmol) was added dropwise to the mixture and stirred for 12 hours at room temperature. The contents were evaporated under reduced pressure. To this residue was added anhydrous diethyl ether (100 mL) and stirred for a while. A yellow solution and a white precipitate were obtained. The white precipitate was removed by filtration under argon atmosphere. The reaction mixture was concentrated under reduced pressure and crystallized to give 0.83 g (50% yield) of spiro-silabifluorene as white crystals. ¹H-NMR (300 MHz, CDCl₃): δ=(TMS, ppm) 7.92(d, 4H), 7.50(t, 4H), 7.40(d, 4H), 7.21(t, 4H).

2.3.3. Synthesis of 1,1-dichloro-1-silafluorene

To a stirred solution of 2,2'-dibromobiphenyl (3.12 g, 10 mmol) in anhydrous diethyl ether (50 mL) for 30 min was added n-butyllithium (8 mL, 20 mmol, 2.5 M in n-hexane). This mixture solution was cooled to the minimum temperature of dry ice/acetone mixture (-78°C) during which the rate of addition of n-butyllithium should be dropwise over a period of 10 minutes. The mixture solution (initially turned to slurry for a while) was allowed to warm up to room temperature with stirring for 6 hours. Silicon tetrachloride (43 mmol in excess, 5 mL) was added dropwise to the mixture at liquid nitrogen freezing temperature (-196°C) and allowed to warm up and stirred for 12 hours at room temperature. The contents were evaporated under reduced pressure. To this residue was added anhydrous diethyl ether (100 mL) and stirred for a while. A yellow solution and a white precipitate were obtained. The white precipitate, mostly LiCl, was removed by filtration under argon atmosphere. The reaction mixture was concentrated under reduced pressure and was kept under sublimation to give the white product 1.6 g (65% yield). ¹H-NMR (300 MHz, CDCl₃): δ=(TMS, ppm) 7.91 (d, 2H), 7.50 (t, 2H), 7.39 (d, 2H), 7.20 (t, 2H).

2.3.4. Synthesis of 1,1-dimethyl-1-silafluorene

This dibenzosilole was synthesized using the same procedure described for the previous silafluorene except that in this case dimethyldichlorosilane is used in place of silicon tetrachloride as was used. Colourless solid was obtained as a product in 55% yield. ¹H-NMR (300 MHz, CDCl₃): δ=(TMS, ppm) 7.83 (d, 2H), 7.64 (d, 2H), 7.45(t, 2H), 7.27 (t,2H), 0.43 (s, 6H).

3. Results and Discussion

3.1. Synthesis and Characterization

Here we have reported high yield synthesis of spiro-silabifluorene. The spiro-silabifluorene was synthesized from 1,2-dibromobenzene (1) as follows. This follow-up specifies that one equivalent of *n*-butyllithium reacts with two equivalents of 1,2-dibromobenzene (i.e. *o*-dibromobenzene), dissolved in tetrahydrofuran, to give 2,2'-dibromobiphenyl in yields more than 75% (Fig. 1.) as the starting material for spiro-silabifluorene. This reaction finds extensive use for the preparation of 2,2'-dibromobiphenyl which is an important intermediate in the preparation of some cyclic organo-silicon compounds^[5].

Unlikely using diethyl ether as a dissolving solvent, two equivalents of 2,2'-dibromobiphenyl reacting with four equivalents of *n*-butyllithium and further with one equivalent of silicon tetrachloride gives 9,9'-spiro-9-silabifluorene with 70% yield. An argument is in hand that the solvent plays a crucial role in the reaction of *n*-butyllithium with the *o*-dibromobenzene. Because when 1,2-dibromobenzene interacts with *n*-butyllithium using the solvent diethyl ether in place of tetrahydrofuran under identical conditions and amounts, 2,2'-dibromobiphenyl could not be separated out.

It is assumed that with the process of a halogen-metal interconversion, the reaction between *o*-dibromobenzene and *n*-butyllithium formed *o*-bromophenyllithium (2) as an intermediate leading to couple with further with *o*-dibromobenzene gives the 2,2'-dibromobiphenyl (3). In the same way the reaction employed at temperatures, using liquid nitrogen and dry ice/acetone mixture separately gives the almost same quantity of 2,2'-dibromobiphenyl. This preparation can be taken as a key

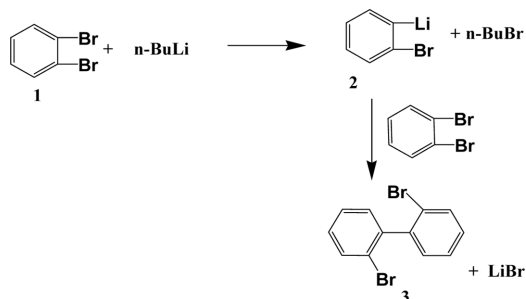


Fig. 1. Synthesis of 2,2'-dibromobiphenyl.

mediator for the synthesis of several organo-silicon compounds.

The lithiation of 2,2'-dibromobiphenyl at dry ice/acetone temperature giving 2,2'-dilithiobiphenyl (4) and then treatment with silicon tetrachloride at room temperature gives mostly 9,9'-spiro-9-silabifluorene (5) (Fig. 2). But latter step at very cooled condition (i.e. liquid nitrogen freezing temperature at -196°C) gives 1,1-dichloro-1-silabifluorene. However when the reaction has been carried out under reflux condition, better yields would have been obtained. A care should be taken while running the reaction to maintain the temperature.

Similarly one equivalent of 2,2'-dibromobiphenyl reacting with two equivalents of *n*-butyllithium further on one hand with one equivalent of silicon tetrachloride gives to 1,1-dichloro-1-silabifluorene^[4,5] (Fig. 3) with 70% yield and on the other hand with one equivalent of

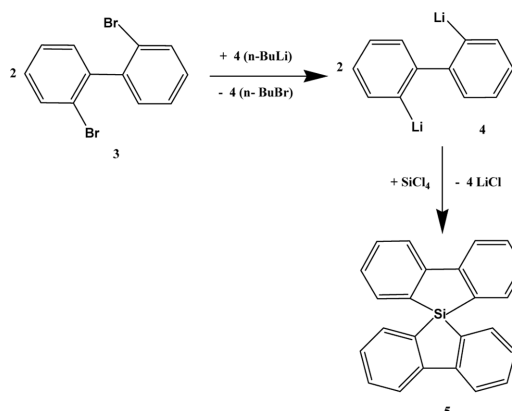


Fig. 2. Synthesis of 9,9'-spiro-9-silabifluorene.

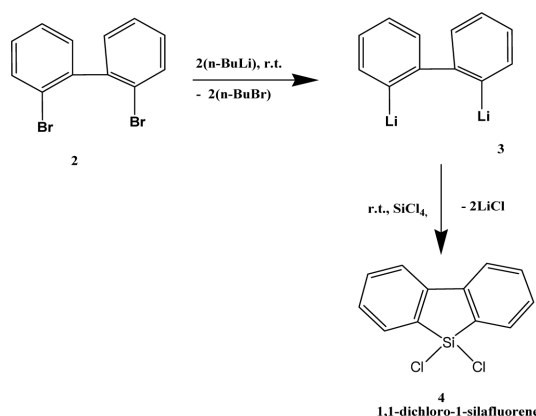


Fig. 3. Synthesis of 1,1-dichloro-1-silabifluorene.

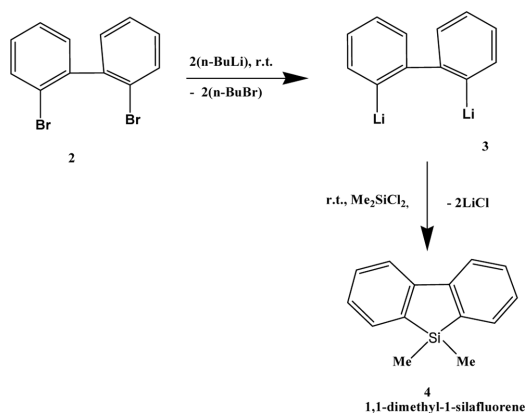


Fig. 4. Synthesis of 1,1-dimethyl-1-silafluorene.

dichloro dimethyl silane gives to 1,1-dimethyl-1-silafluorene (Fig. 4).

The most direct route to the corresponding silafluorenes (dibenzosiloles) would be the selective trans-lithiation of the 2,2'-dibromo substituents and subsequent cyclization with a tetrahalo- or dialkyldihalosilane. The silafluorenes have aromatic benzene rings fused to both cyclopentadiene double bonds. In preparing cyclic organosilicon compounds via a cyclization reaction, the yield of cyclic product increased as the number of chlorine atoms attached to silicon was increased. Apparently the higher polarity of a silicon-chlorine bond renders the silicon atom more susceptible to attack by nucleophilic reagents^[6].

3.2. Optical Properties

The photoluminescence of symmetric spiro-silabifluorene i.e. 9,9'-spiro-9-silabifluorene was measured in tetrahydrofuran at a concentration of 1×10^{-6} M at room temperature as shown in Fig. 5. Upon excitation of 315 nm, symmetric spiro-silabifluorene however shows

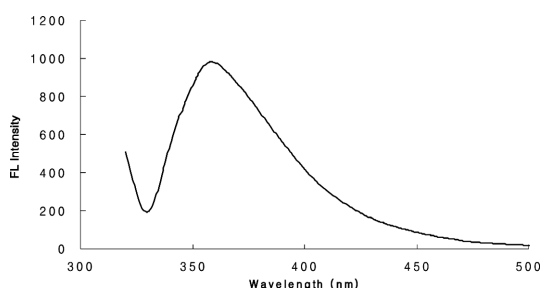


Fig. 5. Photoluminescence of 9,9'-spiro-9-silabifluorene.

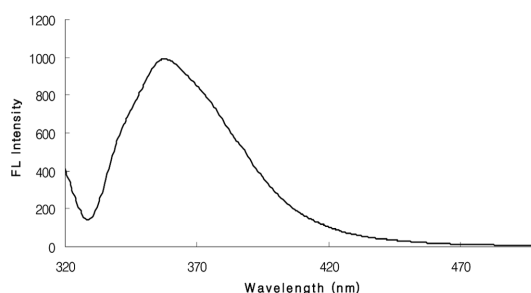


Fig. 6. Photoluminescence of 1,1-dichloro-1-silafluorene.

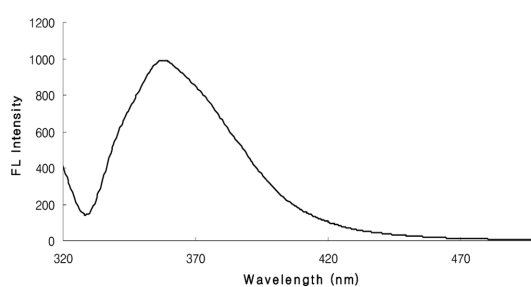


Fig. 7. Photoluminescence of 1,1-dimethyl-1-silafluorene.

the fluorescence emission centered at 365 nm. The photoluminescence of 1,1-dichloro-1-silafluorene was measured in tetrahydrofuran at a concentration of 1×10^{-6} M at room temperature as shown in Fig. 6. Upon excitation at 310 nm, this silafluorene shows emission centered at 360 nm. Similarly 1,1-dimethyl-1-silafluorene reveals emission centered at 351 nm upon excitation as shown in Fig. 7.

4. Conclusion

The syntheses of 9,9'-spiro-9-silabifluorene as well as 1,1-dichloro-1-silafluorene and 1,1-dimethyl-1-silafluorene through the formation of 2,2'-dibromobiphenyl have been emphasized with good yields. They are assumed to be the precursors of the development of polymers.

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