Investigation of Photoluminescence Properties for Dibenzosiloles and Tetrabenzospirosilole

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Abstract

Silicon-containing π-conjugated compounds, especially silacyclopentadienes (siloles), have emerged as a new class of electroactive materials with good electron transport properties in OLEDs. 9,9'-spiro-9-silabifluorene compound as well as its starting material 2,2'-dibromobiphenyl have been synthesized with higher yields. Spirosilabifluorene is expected to be an efficient host material for the blue-light emitting diodes. 9,9'-spiro-9-silabifluorene, 1,1-dichloro-1-silafluorene, and 1,1-dimethyl-1-silafluorene were characterized by ^{1}H-NMR, UV/Vis and photoluminescence spectroscopy.

Key words : Symmetric, Spirosilafluorene, Photoluminescence, Optical property

1. Introduction

Silicon-containing π-conjugated compounds, especially siloles, have emerged as a new class of electrolyte materials with good electron transport properties in O-LEDs.[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.[13]

Spirosilafluorene derivatives may be useful in light emitting diodes for display devices. The spirosilaflu-orene 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 spirosilaflu-orene 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 inter-est 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 promis-ing 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-emit-ting diodes. We anticipate the discovery of more novel compounds. These ring compounds have novel elec-tronic properties. The reason behind this is that the low-est unfilled molecular obital of silafluorene lies at very low energy level, making these compounds highly elec-troactive and strongly fluorescent. Light emitting con-jugated polymers are of interest both for their broad technological applications because they are model sys-tems to gain fundamental understanding of the properties of soft organic and biological matter.[2] Polysilafluorenes and their derivatives have received a great deal of atten-tion and are evolving as a major class of materials for light emitting diodes (LEDs).

2. Experiment

2.1. Materials and Measurements

All commercially available chemicals, reagents and solvents were used as received without further purifi-cation, unless otherwise stated. Solvents like tetrahydro-

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furan(THF) and diethyl ether were purchased from Aldrich Chemical Co. Inc. and were refluxed with sodium and benzophenone under Argon before use. All manipulations involving air-sensitive reagents were carried out under an atmosphere of dry Argon using standard Schlenk and Vacuum techniques. ^{1}H-spectra was recorded on a Bruker 300 MHz spectrometer. Tetramethylsilane (TMS) was used as internal reference (δ=0.00 ppm). Fluorescence spectra were recorded with a Perkin Elmer LS55 Luminescence spectrometer. Melting point measurements were carried out with conventional methods.

2.2. Syntheses
2.2.1. Synthesis of 2,2'-Dibromobiphenyl

To a stirred solution of 1.2-dibromobenzene (11.8 g, 0.05 mol) in anhydrous tetrahydrofuran (100.0 mL) for 30 min was added n-butyllithium (10.0 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 (100.0 mL) and stirred for a while. An original organic layer and a white precipitate were obtained. The white precipitate, mostly lithium chloride (LiCl), was removed by filtration under argon and removable liquids 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 80°C.

2.2.2. Synthesis of 9,9'-Spiro-9-silabifluorene

To a stirred solution of 2,2'-dibromobiphenyl (3.12 g, 10.0 mmol) in anhydrous diethyl ether (50.0 mL) for 30 min was added n-butyllithium (8.0 mL, 20.0 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 awhile) was allowed to warm up to room tem-

perature with stirring for 6 hours. Silicon tetrachloride (0.85 g, 5.0 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 (100.0 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 spirosilabifluorene as white crystals. CDCl3 was used as NMR solvent. Tetramethylsilane(TMS) was used as internal reference(δ=0.00 ppm)

^{1}H-NMR (300 MHz, CDCl3) : δ (TMS, ppm) = 7.92 (d, 4H), 7.50 (t, 4H), 7.40 (d, 4H), 7.21 (t, 4H).

2.2.3. 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).

^{1}H-NMR (300 MHz, CDCl3): δ (TMS, ppm) = 7.91 (d, 2H), 7.50 (t, 2H), 7.39 (d, 2H), 7.20 (t, 2H).

2.2.4. 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

Here we have reported high yield synthesis of spirosilabifluorene. The spirosilabifluorene 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% (scheme 1) as the starting material for spirosilabifluorene. 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]
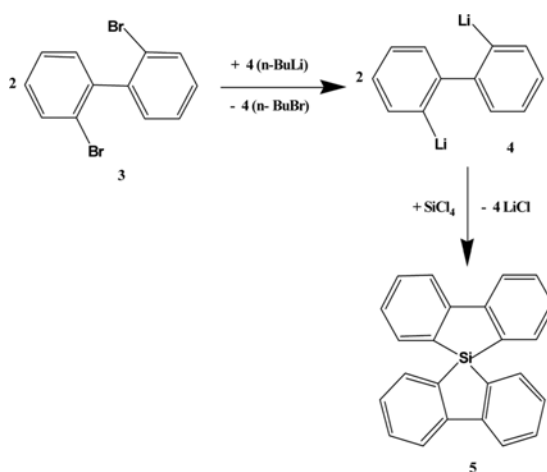
Unlikely using diethyl ether as a dissolving solvent, two equivalents of 2,2'-dibromobiphenyl reacting with four equivalents of n-butyllithium and further with one equivalent of silicon tetrachloride gives 9,9'-spiro-9-silabifluorene with 70% yield. An argument is in hand that the solvent plays a crucial 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 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) (scheme 2). But latter step at very cooled condition (i.e. liquid nitrogen freezing temperature at -196°C) gives 1,1-dichloro-1-silafluorene. Howeve when the reaction
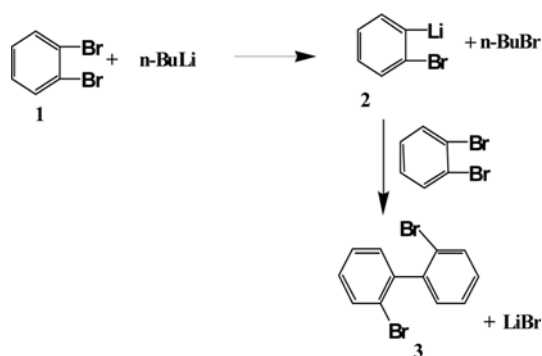

Scheme 1. Synthesis of 2,2'-dibromobiphenyl.

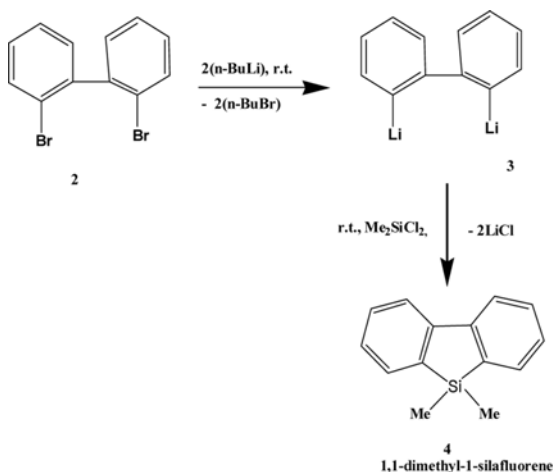Scheme 2. Synthesis of 9,9'-spiro-9-silabiluorene.

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-silafluorene[4,5] (scheme 3) with 70% yield and on the other hand with one equvalent of dichloro dimethyl silane gives to 1,1-dimethyl-1-silafluorene (scheme 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 chlo-
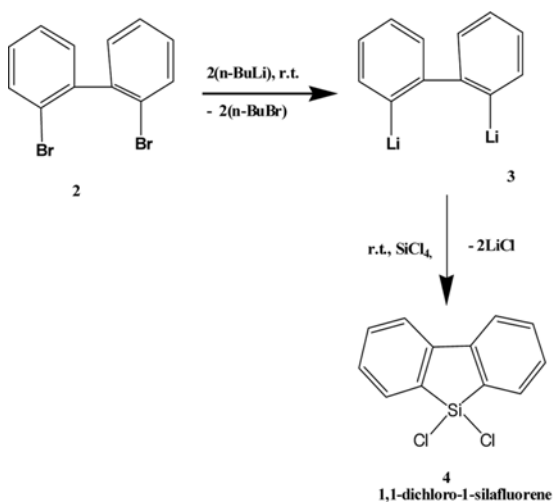
Scheme 3. Synthesis of 1,1-dichloro-1-silafluorene.

Fig. 1. Photoluminescence of 9,9'-spiro-9-silabifluorene.

Fig. 2. Photoluminescence of 1,1-dichloro-1-silafluorene.
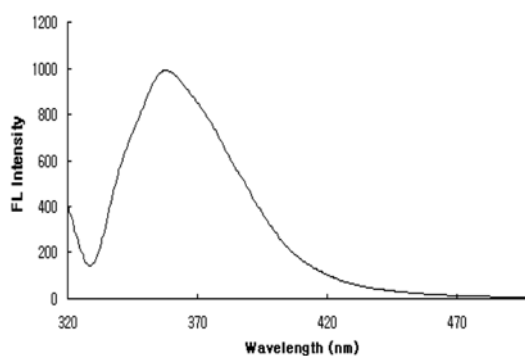
Scheme 4. Synthesis of 1,1-dimethyl-1-silafluorene.

Fig. 3. Photoluminescence of 1,1-dimethyl-1-silafluorene.

rine 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]

The photoluminescence of symmetric spirosilabiflu-orene 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 Figure 1. Upon excitation of 315 nm, symmetric spirosilabifluorene however shows the fluorescence emission centered at 365 nm. The pho-toluminescence of 1,1-dichloro-1-silafluorene was meas-ured in tetrahydrofuran at a concentration of 1×10^{-6} M at room temperature as shown in Figure 2. Upon exci-tation at 310 nm, this silafluorene shows emission cen-
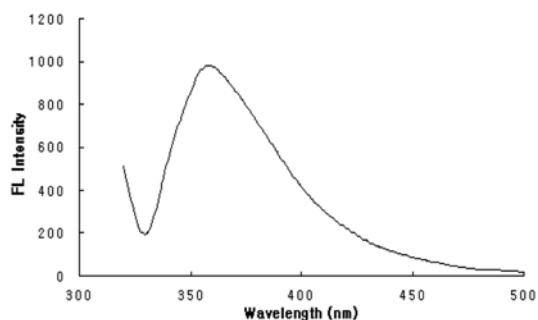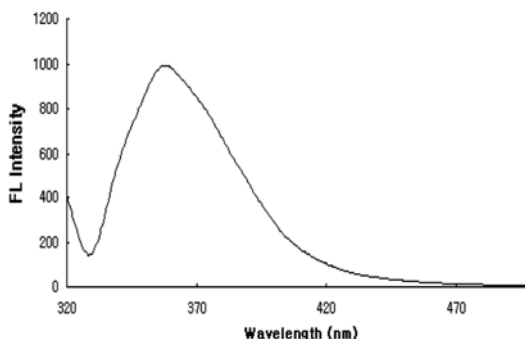
tered at 360 nm. Similarly 1,1-dimethyl-1-silafluorene reveals emission centered at 351 nm upon excitation as shown in Figure 3.

4. Conclusions

The syntheses of 9,9'-spiro-9-silabifluorene as well as 1,1-dichloro-1-silafluorene and 1,1-dimethyl-1-silaflu-orene 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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