



A thesis submitted for Doctor of Philosophy

Synthesis and Optical Characterization of Silole Derivatives and Silicon Nanoparticles

By

Arun Kumar Sharma

A thesis submitted to Department of Chemistry under Graduate School of Chosun University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

Supervisor: Prof. Honglae Sohn, Ph.D.

Department of Chemistry

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This is to certify that Doctor's thesis of

Arun Kumar Sharma

has fulfilled the requirements for Graduate School of Chosun University.

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ABSTRACT

Synthesis and Optical Characterization of Silole Derivatives and Silicon Nanoparticles

Arun Kumar Sharma Supervisor: Prof. Honglae Sohn, Ph. D. Co- Advisor: Prof. Sungdong Cho, Ph. D. Department of Chemistry Graduate School of Chosun University

Part 1

Nanocrystalline porous silicon surfaces have been used to detect nitroaromatic compounds in vapor phase. The mode of photoluminescence is emphasized as a sensing attitude or detection technique. Quenching of photoluminescence from nanocrystalline porous surfaces as a transduction mode is measured upon the exposure of nitroaromatic compounds. Reversible detection mode for nitroaromatics is, too, observed. To verify the detection afore-mentioned, photoluminescent freshly prepared porous silicons are functionalized with different groups. The mechanism of quenching of photoluminescence is attributed to the electron transfer behaviors of quantum-sized nano-crystallites in the porous silicon matrix to the analytes (nitroaromatics). An attempt has been done to prove that the surfacederivatized photoluminescent porous silicon surfaces can act as versatile substrates for sensing behaviors due to having a large surface area and highly sensitive transduction mode.

Part 2

We describe the synthesis and characterization of silicon nanoparticles prepared by the soluton reduction of SiCl₄. These reactions produce Si nanoparticles with surfaces that are covalently terminated. The resultant organic derivatized Si nanoparticles as well as a probable distribution of Water-soluble Si nanoparticles are observed and characterized by photoluminescence(PL) spectroscopy. This work focuses originally on the organic- and water-soluble silicon nanoparticles in terms of the photoluminescence. Further this work displays probably the first layout of hydrogen terminated Si nanoparticles synthesized in solution at room temperature.

Part 3

The silole derivatives (dibenzosiloles or the silafluorenes) i.e. 1,1-dichloro-1-silafluorene and 1,1-dimethyl-1-silafluorene as well as 9,9'-spiro-9silabifluorene compounds were synthesized from 1,2-dibromobenzene, nbutyllithium and silicon tetrachloride in higher yields characterized by NMR spectroscopy. The dibenzosiloles are expected to be efficient host materials for the blue-light emitting diodes.

Part 1

Synthesis of Functionalized Porous Silicon Surfaces and Quenching of Their Photoluminescence by Nitroaromatics

1.1. Introduction

Nitroaromatics are the compounds composed of aromatic compounds with mono- or poly-nitrate groups. Nitroaromatics are carcinogenic and mutagenic substances that are typical contaminants of military sites. Nitroaromatics are frequently used as solvents and as precursors to other high value organic compounds, such as pharmaceuticals. In addition, some nitroaromatics are either themselves explosive or are precursors to other explosive materials. An explosive is defined as a material that can be initiated to undergo very rapid, self-propagating decomposition that results in the formation of more stable material, the liberation of heat, or the development of a sudden pressure effect through the action of heat on produced or adjacent gases. All of these outcomes produce energy that a weapon's effectiveness is measured by the quantity of energy or damage potential delivered to the target. Chemical explosive is a compound or a mixture of compounds which, when subjected to heat, impact, friction, or shock, undergoes very rapid, self-propagating, heat- producing decomposition.

Many species containing nitro group detonate by way of heat or shock and are useful as explosives, as is the case with several commonly known nitroaromatics. Their analysis is necessary for process, research and development, explosive, forensic, environmental, and other reasons. Only few aromatic compounds, bearing one nitro group as a substituent of the aromatic ring, are produced as secondary metabolites by microorganisms. The majority of nitroaromatic compounds in the biosphere are industrial chemicals such as explosives, dyes,

polyurethane foams, herbicides, insecticides and solvents. Detection of unrecovered land mines[1] is a growing international problem. Unrecoverd land mines are a legacy that continues to harm people long after the hostilities cease. The most widely used tool for land mine detection today is the hand-held metal detector. Metal detectors widely used as portable instrumentation for field explosive detection, can not locate the plastic casing of modern land mines. Trained dogs are expensive and difficult to maintain and are easily fatigued[2]. Due to growing environmental concerns, nitroaromatic compounds have been targeted for monitoring because of their inherent biological toxicity. There is a significant motivation for the development of rapid, stable, inexpensive and robust sample analysis protocols for this class of analytes in both the military and civilian sectors[3]. Other applications include forensic investigations, such as post-blast residue determinations[4,5].

The identification and quantification of traces of nitroaromatic explosives have attracted a great attention during the last few years due to their extensive security and pollution problems for humans and ecosystems[6]. Consequently a great number of analytical methods have been developed for monitoring these compounds, for example, mass spectrometry[7], ion mobility spectrometry[8], electrochemical methods[9], fluorescence[10], chemiluminescence[11], surface enhanced Raman spectroscopy[12], nuclear quadrupole resonance[13], energydispersive X-ray diffraction[14], neutron activation analysis, electron capture detection[5-11] and cyclic voltammetry[15]. These techniques are highly selective,

but some are expensive and others are not easily fielded in a small, low-power package. Most detection methods for explosives are only applicable to vapor sample because of interference problems encountered in aquous media. Compared to other analytical techniques, fluorescence is more attractive because of its high sensitivity, high selectivity and multiple choices in signals and parameters like emission intensity, maximum wavelength etc.[16].

Chemical sensors for nitroaromatics[17,18] which offer new approaches to the rapid detection of ultra-trace analytes from explosives, have attracted attention because explosives are very important chemical species to be detected[19,20]. Detection of nitroaromatics is desirable since there are millions of unexploded land mines scattered worldwide[1]. Detection of nitroaromatics based upon adsorption into polymers has been reported. Chemo-selective polymers on surface acoustic wave (SAW) device provide a detection limit of 235 ppt for dinitrotoluene (DNT)[21]. Cyclic voltammetry using gold microelectrode covered with nonvolatile electrolyte shows a detection limit of 7 ppb for the trinitrotoluene (TNT)saturated air[22]. Organic polymers have been used to detect DNT and TNT under static conditions with a detection limit of several ppb[23]. Finally silicon polymers exhibit a detection limit of 4 ppb for the TNT-saturated air[24].

Here we report that very sensitive detection of TNT, DNT, nitrobenzene (NB), and picric acid (PA) has been achieved with different modifications of porous silicon (PSi) surfaces via: 1) as-prepared fresh PSi, 2) oxidized PSi, 3) hydrosilylated PSi with 1-dodecene, 4) hydrosilylated PSi with phenylacetylene, and 5) hydrosilylated PSi with 2,3,4,5-tetraphenyl-1-methyl-1-vinylsilacyclopenta-2,4-diene (methylvinyl silole) using photoluminescence quenching of the silicon crystallites as a transduction mode. Porous silicon films are electrochemically etched from crystalline silicon wafers in an aquous solution of [25]. Chemical modification of the porous silicon films stabilizes them from oxidation and provides the selectivity of analyte adsorption in the pores[26,27,28]. Transduction modes based on photoluminescence quenching have been developed for the potential to constitute sensitive, reusable sensors[29,30,31]. Condensation of analytes in the pores can lead to photoluminescence quenching via energy or electon transfer process[32,33].

1.2. Background of Study

Porous silicon is a high surface area network (morphology) of hydride terminated silicon whose efficient room temperature luminescence has attracted much interest for a wide range of applications. Initial excitement in the early 1990s focused upon the potential to use light-emitting silicon in optoelectronic devices that could be easily integrated with existing silicon-based technology. Till date, it is assumed that light emission most likely results from quantum confinement effects within silicon nanocrystallites and nanowires imbedded within the porous matrix. Since the discovery of light emission, porous silicon has been shown to serve as the platform for a broad range of applications, such as sensing and bioanalysis, utilizing a number of transduction schemes. For instance, Sailor and Harper demonstrated the sensitivity of the photoluminescence with respect to NO concentration in Ar, rendering porous silicon an useful chemo-sensor for this compound and other gases.

Hydosilylation of alkyne and alkenes on non-oxidized hydride terminated porous silicon derivatizes the surface with alkenyl and alkyl functionalities respectively. A very broad range of chemical groups may be incorporated. The reactions are assumed to protect and stabilize porous silicon surfaces from atmosphere or direct attack without compromising its material properties such as visible room-temperature photoluminescence. Material hydrosilylation of unsaturated hydrocarbons and siloles shows a slower surface oxidation observed by FTIR analysis. The influence of modified surfaces of the porous silicon on photoluminescence was investigated and was illustrated to depend upon organic moities. We have found that hydrosilylation of unsaturated carbon-carbon bonds on the native hydride-terminated porous silicon can be induced at room temperature, depending upon organic fragments. Insertion of alkene or alkyne into surface Si-H groups yields alkyl or alkenyl termination respectively. The hydrophobic surfaces capped with a monolayer of alkyl chains were reported to be stabilized under chemically demanding, basic conditions as compared to unfunctionalized porous silicon. However, the oxidation of freshly prepared hydride terminated porous silicon surface has been shown as a ground label to compare the other hydrosilylated products in terms of surface modifications.

Although the modifications have been carried out to be emphasized on

hydride terminated porous silicon surfaces, this very part focuses on, 'sensitive detection' of certain nitroaromatic compounds such as TNT, DNT, NB, and PA. Detection was observed in vapor phase with porous silicon surfaces using photoluminescence quenching of the silicon crystallites as a transduction mode. Porous silicon surfaces are electrochemically etched from crystalline silicon wafers in an aquous solution of hydrofluoric acid. The most exciting feature of this part is that the mechanism of PL quenching refers to the electron transfer process of quantum sized nanocrystallites in the porous silicon matrix to the analytes.

1.3. Experimentals and Instrumentation

1.3.1. Materials and Methods

Silicon wafer (silicon sense, n-type, <100> orientation, P-doped, 1-10 ohm) were purchased from Siltron Inc. Aquous HF (49%) and absolute ethanol (95%) were brought from Scientific Fisher. The alkene and alkyne i.e. 1-dodecene and phenyl acetylene were ordered from Aldrich, sparged with dry argon and used. Out of the nitroaromatics here used for sensing, DNT (97%), PA (98%), and NB (99%) are purchased from Aldrich. TNT was synthesized in the laboratory. Methylvinyl silole was synthesized in the laboratory using general procedures. The required materials lithium, diphenylacetylene, and methylvinyl silane were purchased from Aldrich.

Toluene was distilled from sodium and benzophenone. Air-sensitive procedures were carried out with standard Schlenk techniques (ChemGlass dual

manifold vacuum/argon lines). Thermal hydrosilylation was carried out by reflux and photochemical hydrosilylations were carried out under white bulb light and UV-light.

1.3.2. Etching Set-up for Porous Silicon Surface

The electrochemical etching was performed on silicon wafers to create porous surfaces which possess a network of pores to give rise to luminescence. The etching set-up was maintained in a laboratory hood where a suitable management is made for upwards flow of gas created during etching. Princeton 363 galvonostat/potentiostat was used for passage of required current density. 30 mW/cm² white light illumination was derived from a 300 W tungsten filament bulb. A 1.1 cm² exposed area of a polished crystalline n-type silicon wafer was kept for etching in a Teflon cell. Prior to this, the procedure involves the use of an aluminium foil as a cathode underneath the silicon chip. Viton O-ring seal was fixed over the chip and covered with an electrolyte/etchant in the form of a mixture of aquous HF (49%) and absolute ethanol (95%) in required proportion (1:1) as an anode.



Figure 1.1. Experimental setup for the formation of porous silicon surface.

1.3.3. Photoluminescence (Fluorescence) Measurement

For the measurement of photoluminescence exhibited by various groups functionalized porous silicon surface, the Ocean Optics 2000 spectrometer is used[29,30,32, 34,35,36,37,38,39]. Two excitation sources blue-LED with λ_{max} 460 nm and UV-LED with 380 nm are used. The pointers for detection and light source are adjusted at an average angle of 45° to each other.



Figure 1.2. Photograph of the optical bench setup.

1.3.4. FT-IR Spectroscopy

The modes of all the functionalized porous silicon surfaces can be verified by using Fourier-transform infra-red spectra. The spectra are taken by Nicolet 5700 FTIR spectrometer with the adjustment of transmission mode, spectral resolution at 4 cm⁻¹ as well as with the expression of wavelength range between 500-4000 cm^{-1.}

1.4. Formation of Porous Silicon Surface

Photoluminescent silicon samples were prepared under ambient air through a galvonostatic etch[8]. The mentioned-above silicon wafers were cleaned before use by soaking and rinsing with ethanol for a while to make smooth for pore formation. Galvonostatic etching was carried out using 1: 1 ratio of HF (49%) and absolute ethanol (95%) solutions as the electrolyte/ethant. 1.1 cm² exposed area of a polished crystalline n-type silicon wafer was etched for 5 min in a Teflon cell at 300 mA/cm² under white light illumination. After etching, the porous silicon samples were rinsed copiously with ethanol and dried under a gentle nitrogen flow. After drying the porous silicon surface, chips were kept in Schlenk flask under vacuum for 5 min.

$$2 \operatorname{Si} + 6 \operatorname{H} \operatorname{F} + 2 \operatorname{h}^{+} \longrightarrow \operatorname{Si} + \operatorname{H}_{2} \operatorname{Si}_{6} + 2\operatorname{H}^{+} + \frac{1}{2} \operatorname{H}_{2}$$
Porous Si Surface

Scheme 1.1. Chemical equation for the formation of porous silicon surface.



Figure 1.3. FESEM image of fresh porous silicon surface.

1.5. Availability of Nitroaromatic Compounds

Nitroaromatic (NACs) are the compounds composed of aromatic compounds with mono- or poly-nitro groups. However all the nitroaromatics (displayed in blue color) except TNT are used as received without purification.



Scheme 1.2. Chemical structures of some nitroaromatics.

1.5.1. Synthesis of TNT

TNT is synthesized from DNT as shown in scheme 2. About 5 g of DNT is administered in the Schlenk flask under argon. Then sulphuric acid and nitric acid

are added one by another. The whole reaction contents were run with stirring at 90°C for 3 hrs. When the reaction is over, it is evaporated to dryness under reduced pressure. It is dissolved in toluene and filtered and recrystallized to give light yellow colored product for detection point of view.



2,4-dinitritoluene

2,4,6-trinitrotoluene

Scheme 1.3. Chemical equation for the synthesis of TNT.

1.6. Illustration of the Vapor Sensing (detection of nitroaromatics)

As DNT, TNT, or PA are very sensitive to explosive characteristics, they or other NACs are used in very minimum amount. A fixed amount of analytes are generally and gently kept in U-tube for detection. Saturated air is flown to the Utube from its one arm to create saturated vapor which is then passed out from the other arm to the sensing agent. A portion of glass wool (as shown in figure) is introduced in the U-tube before adding the compound. This glass wool functions to prevent direct contact (flow of tiny particles) of the compound with the sensing agent (surface-derivatized porous silicon surface). Prior to detection, saturated air is blown to the compound in the U-tube to create saturated vapor of the compound. If there is not saturated vapor formed perfectly, lapses of quenching of photoluminescence intensity from porous silicon would appear.



Figure 1.4. Experimental setup for analyte-vapor sensing.

1.7. Synthesis of 1-Methyl-1-vinyl 2,3,4,5-tetraphenyl Silole

There are two steps for the synthesis of methylvinyl silole. Diphenyl acetylene (18 g, 100 mmol) and lithium (2.76 g, 400 mmol) are kept in a 250 mL schlenk flask under argon followed by 120 mL distilled ether and stirred for more than 1 hour. Then the solution in the flask is kept under liquid nitrogen bath until the solution changes to solid portion.



Scheme 1.4. Chemical equation for the synthesis of 1- methyl-1-vinyl silole.

Then dichloromethylvinyl silane (200 mmol) was added to the mixture for about half an hour followed by ether and stirred for overnight. The solution is allowed to settle until two layers appear. The upper layer is cannulated in another evacuated flask under argon and placed in -20 °C for recrystallization to give the required product. The remaining solution in the original flask is added with further ether and stirred for 30 min and allowed to settle for repeating the process. The product is characterized by ¹H and ¹³C NMR spectra, UV-vis absorption spectra and photoluminescence measurement.

1.8. Surface-derivatization of Porous Silicon

1.8.1. Thermal Oxidation

For appropriate luminescence, the fresh PSi is oxidized by keeping it in hot oven at 300 $^{\circ}$ C for 2 minutes. Exceeding this temperature, the luminescence may be lost or reduced. Fresh PSi is oxidized, when it is exposed to an open atmosphere for a long period. The oxidation occurs as follows.



Scheme 1.5. Oxidation of fresh PSi.

1.8.2. Hydrosilylation

We have found that both unsaturated carbon-carbon and silicon-carbon bonds

can be linked to the native hydride-terminated porous silicon with the help of different hydrophobic groups by the mechanism of hydrosilylation. For present study, the hydrosilylations were carried out as follows. If there is oxygen atom in the surface of fresh PSi, the hydrosilylation may be reduced or blocked.

(i) Thermal : The substrate along with PSi chip is refluxed either in appropriate solvent or in neat condition

(ii) Photochemical:

- (a) By keeping in UV-box at 306 nm
- (b) By keeping under white light of 300 W

Hydrosilylation has been carried out here for three compounds with probable reaction given below.

i) **1- dodecene**



Scheme 1.6. Hydrosilylation of PSi with 1-dodecene.

Fresh PSi is introduced in a schlenk flask and added 5 mL of 1-dodecene under argon and reflux is maintained for overnight. Similarly fresh PSi is covered with the solvent in UV-tube and kept in the UV-box for 24 hrs with the porous surface front inclined towards UV-light. Likewise fresh PSi is covered with the solvent in the Teflon cell as in the etching and kept under white-light at a distance of around 30 cm for 12 hrs

ii). Methylvinyl silole



Scheme 1.7. Hydrosilylation of PSi with methyl vinyl silole.

iii) Phenyl acetylene



Scheme 1.8. Hydrosilylation of PSi with phenylacetylene.

Fresh PSi is introduced in a schlenk flask and added 0.2 g of methylvinyl silole followed by 25 mL of tolune under argon and reflux is maintained for 24 and 48 hrs. Similarly fresh PSi is covered with the solvent in UV-tube and kept in the UV-Box for 14 and 24 hrs with the porous surface front inclined towards UV-light. Likewise fresh PSi is covered with the solvent in the Teflon cell as in the etching and kept under white-light at a distance of around 30 cm for 8, 14 and 24 hrs.

Fresh PSi is introduced in a shlenk flask and added 5 mL of phenylacetylene under argon and reflux is maintained for 4 hrs. Similarly fresh PSi is covered with the solvent in UV-tube and kept in the UV-box for 20 hrs with the porous surface front inclined towards UV-light. Likewise fresh PSi is covered with the solvent in the Teflon cell as in the etching procedure and kept under white light with 300 W at a distance of around 20 cm for 12 hrs

1.9. Results and Discussion

1.9.1. Effects of etching parameters on emission characteristics of PSi

The most common fabrication technique of PSi is electrochemical etching of a crystalline silicon wafer in HF etchant solution. The electrochemical process allows for precise control of the properties of PS such as thickness of the porous layer, porosity, and average pore diameter. The control of these properties of PSi was shown to depend on variables such as (i) HF concentration in the used electrolyte, (ii) applied current density, (iii) time period for etching, and (iv) the thickness of PSi etc. Depending on the etching parameters, for example current density, HF concentration, or substrate doping type and level, the physical properties of PSi can be varied [8]. When the feature size of the pores of PSi is less than a few nanometers, various quantum-size effects occur, which make PSi even more fascinating. The well-studied PSi morphology can range from spongy-like microporous (pore size < 10 nm) and branchy mesoporous silicon (pore size 10–50 nm) to the classical macroporous silicon (pore size 50 nm–20 μ m).

1.9.2. Surface-derivatization (Functionalization)

Widespread application of porous silicon is contingent, however, upon the stabilization of the material which deteriorates in ambient conditions due to oxidation and adsorption of impurities from air[40]. Corrosion of porous silicon occurs gradually or rapidly and thus a general method to stabilize the surface is crucial[41]. Ideally, the methodology should not only render the surface robust but should also allow for incorporation of a broad range of chemical functionalities upon demand to tailor the surface for specific applications.

The ability to controllably and permanently attach organic molecules to nanocrystalline silicon surfaces is also interesting within the burgeoning field of nanotechnology and for creation of molecular-scale architectures on semiconductor substrates. As monolayers on single-crystal non-oxidized silicon surfaces bound through silicon-carbon bonds have been to result in extremely stable flat surfaces [42,43,44], a similar approach has been pursued on porous silicon[45]. The nanoscale architecture of porous silicon is inherently fragile, and thus rapid and efficient syntheses under room-temperature conditions are preferable. The influence of silicon surface states has been implicated in photoluminescence (PL) mechanisms, leading to great interest in techniques which can change the chemical makeup of the surface residues [28]. The silicon hydride $(Si-H_x, x=1,2,3)$ residues present on the PSi surface are labile, which leads to oxidation and the formation of luminescence quenching defects. The fact that PSi

oxidatively fatigues with exposure to light and chemical treatment has hindered its immediate technological application. Replacement of the silicon hydride bonds with silicon alkyls could impart greater stability to the materials as well as functionalize it for new uses beyond optoelectronics [46].

Insertion of alkenes, alkynes, or unsaturated silicon-carbon bonds into surface Si-H groups yields alkyl, alkenyl, or Si-H termination, respectively. The hydrosilylation is remarkably tolerant of a wide range of chemical functionalities and complementary, which allows for flexibility in choosing specific surface properties. The stereochemistry of the hydrosilylation could be interpreted with FTIR techniques. In this work, enhanced stability with respect to oxidation and hydrosilylation in laboratory, in ambient air conditions is revealed. The effects of functionalization on the intrinsic photoluminescence are also explained. For detection of nitroaromatics, the freshly prepared hydride terminated porous silicon surfaces are modified with several functionalized groups, mostly being hydrophobic. The surface modifications occur in all varieties as follows.

Hydrogen passivation does not provide sufficient long term stabilization, resulting in oxidation even under ambient conditions. Continual exposure of porous silicon to ultraviolet radiation in air will result in rapid decay of photoluminescence efficiency[47]. In order to combat the weaknesses demonstrated by porous silicon, a number of passivation approaches have been considered[48]. Formation of a stable organic overlayer is seen to be a promising strategy with respect to oxidation and chemical stability.

 $2 \ 1$

1.9.3. FT-IR Analysis

The hydrosilylations of alkenes and alkynes takes place as evidenced by the decrease in intensity of the v(Si-H_x) stretch centered around 2100 cm⁻¹ and appearance of new vibrations in the transmission FT-IR spectrum which correspond to the alkyl and alkenyl substitution[49]. The same behaviors are observed to appear with hydrosilylation of methylvinyl silole. Thermal hydrosilylation of alkenes takes longer time compared to that of alkenyl[50, 51]. These hydrosilylation conditions are tolerant of a wide range of functional groups within alkyne or alkenes, as illustrated by the concerned reaction products, as in figures 1.5, 1.6 and 1.7 resectively.

The high surface area network of porous silicon is terminated with Si-H_x (x= 1,2,3) bonds. Because the Si- H_x stretching region around 2000-2100 cm⁻¹ becomes substantially broadened and featureless after hydrosilylation, the individual stretches corresponding to SiH, SiH₂, and SiH₃ can no longer be distinguished and as a result, it has not been determined if the reaction exhibits any selectivity with respect to the Si- H_x functionalities. In all cases, the v(Si-H) centered around 2100 cm⁻¹ diminishes or reduces in intensity, indicating that Si-H groups more or less consumed in the hydrosilylation reaction.

The measurements have been done as offset by some units for clarity. The appearance of a band at 1050-1060 cm⁻¹ in hydrosilylated surfaces indicates a considerable amount of oxidation occured during the course of experiments.

However, a higher peak is observed distinctly in the case of oxidized one. There may be little or no oxidation in the case of freshly prepared H-terminated porous silicon surface.

Functionalization of porous silicon with 1-dodecene yields an alkylterminated substrate supported by appearance of aliphatic C-H features. Hydrosilylation of alkynes as phenylacetylene on porous silicon yields surface bound vinyl groups as revealed by the observation of a strong vibration at 1600 cm^{-1} , indicative of a monosilyl-substituted carbon-carbon double bond v(SiC=C). As shown in figure, the stretch observed at 1595 cm⁻¹ is indeed an olefinic branch and a corresponding v(CH₃) stretch at 2944 cm⁻¹ and v(CH₂) at 2923 and 2854 cm⁻¹ can be observed. Similar cases are observed with the hydrosilylation of monovinyl silole. The difference arises only that v(C-H) stretch is observed at 3080 cm⁻¹. Particularly in the case of aryl alkynes such as phenyl acetylene, the vinyl group overlaps with various v(C=C) aromatic ring modes and thus cannot be distinguished. Other pertinent features observed by FT-IR include the v(C-H) stretches between 2960 and 2850 cm⁻¹ and δ (C-H) methylene and methyl bending modes at 1466 and 1387 cm⁻¹. However the FT-IR profiles for hydrosilylation products are provided for convenience.

1-dodecyl-derivatized PSi: 2944 cm⁻¹ v(CH₃), 2923 and 2854 cm⁻¹ v(CH₂), 2102 cm⁻¹ v(Si-H_x), 1466 cm⁻¹ δ (CH₂), 1378 cm⁻¹ δ (CH₃), 1071 cm⁻¹ v(Si-O), 903 cm⁻¹ δ (SiH₂), 666 cm⁻¹ δ (SiH), and 626 cm⁻¹ δ (SiH₂).

Methylvinyl silole-derivatized PSi: 3070 cm⁻¹ v(CH₃), 2931 and 2881 cm⁻¹

v(CH₂), 2104 cm⁻¹ v(Si-H_x), 1496 cm⁻¹ δ (CH₂), 1459 cm⁻¹ δ (CH₃), 1071 cm⁻¹ v(Si-O), 917 cm⁻¹ δ (SiH₂), 663 cm⁻¹ δ (SiH), and 620 cm⁻¹ δ (SiH₂).

Phenylacetylene-derivatized PSi: $3061 - 3026 \text{ cm}^{-1} \text{v}(\text{CH})$ aromatic, 2104 cm⁻¹ v(Si-H_x), 1595, 1587, and 1566 cm⁻¹ v(C=C) and alkene v(Si=C), 1493 and 1444 cm⁻¹ v(C=C), 1071 cm⁻¹ v(Si-O), 902 cm⁻¹ δ (SiH₂), 662 cm⁻¹ δ (SiH), and 629 cm⁻¹ δ (SiH₂)

.



Figure 1.5. FT-IR spectra of fresh PSi and oxidized PSi.



Figure 1.6. FT-IR spectra of fresh PSi and dodecyl-derivatized PSi.



Figure 1.7. FT-IR spectra of fresh PSi and methylvinyl silole-derivatized PSi.


Figure 1.8. FT-IR spectra of fresh PSi and phenyl ethenyl-derivatized PSi

1.9.4. Photoluminescence Behaviors

The nature of the derivatization with the different surfaces has strong effects on the photoluminescence of porous silicon[52,53]. Probable degradation of the surface resulting from the surface chemistry causes decrease in light emission. As hydrosilylation reaction is assumed to be of very gentle nature, concomitant surface damage appears to be minimal[54]. Thermal hydrosilylation of aliphatic olefins such as 1-dodecene shows a decrease in photoluminescence intensity. But in the case of photo-hydrosilylation the quenching is lower. Thermal hydrosilylation of the conjugated alkyne such as phenylacetylene shows almost total quenching compared to the photoluminescence intensity of fresh porous silicon. But with the same we can observe a considerable amount of photoluminescence intensity in the case of photo-hydrosilylation under white bulb light. It proves that a surface bound alkyne or alkene conjugated to an aromatic ring is an extremely effective quenching agent[52,53].

However, there is observed no such vast differences of quenching in the case of methylvinyl silole hydrosilylated porous silicon among the types of hydrosilylation. Although the chemical nature of the Si-H bonds is not likely to vary from sample to sample, only samples prepared with specific materials and etching conditions emit light. The nature of the silicon–carbon bond quietly affects the photoluminescence of porous silicon. It is due to different modifications on the freshly prepared porous silicon surfaces. It is also assumed that surface chemistry may make a degradation of surface which might be a cause of observed lower intensity. The minimum surface damage occurs, the less intensity is reduced.

silicon surface The oxidized porous possesses reduction а in photoluminescence intensity as well as in wavelength peak compared to that both of fresh one. The thermal hydrosilylation of the conjugated alkyne (phenyl acetylene) shows almost more than 90% reduced intensity in neat condition. However using toluene solvent for the same exhibits slightly increased intensity but that is too considered non-significant as shown in Figure 1.10. But the same hydrosilylated PSi under white light exhibits considerable higher intensity sufficient for quenching observations. It means that a surface-bound alkyne conjugated to an aromatic ring is an extremely effective quenching agent for photoluminescence under thermal conditions. The hydrosilylated PSi derivatized with 1- dodecene and methylvinyl silole maintain their PL intensity even on reflux condition with a lower intensity compared to that of as-prepared hydride

terminated porous surface.



Figure 1.9. Steady-state PL spectra of different functionalized PSi surfaces.



Figure 1.10. PL spectra of phenyl ethenyl-derivatized PSi.

1.9.5. PL and Stability Study



Figure 1.11. Steady-state PL spectra (a) and stability test (b) of fresh PSi in air.

Photoluminescence intensity and emission wavelength are dependent on the type of porous silicon surfaces. If freshly prepared hydrogen terminated porous silicon is left in ambient air or open atmosphere, it gets oxidized gradually and PL intensity is decreased. So it is very essential to save the PSi from being oxidized to protect its PL observation for long term applications. That is why freshly prepared H-terminated PSi just after its formation is surface-derivatized with different functional groups.



Figure 1.12. Stability test of surface-derivatized PSi in air.

1.10. Fluorescence Quenching Studies

The photoluminescent properties of nanocrystalline PSi are of interest for sensor applications. Photoluminescence from porous silicon is quenched in the presence of chemical species. We also observe that surface derivatization can be used to tune the sensor properties of porous silicon by modifying the photoluminescence quenching efficiency. The quenching mechanism is attributed to the electron transfer.

The magnitude of photoluminescence quenching can be measured by expression of photoluminescence intensity in time when various amounts of analytes were introduced into. The quenching mechanism occurs as electron transfer from porous silicon to the lowest triplet state of the molecular quenchers[29]. We can observe a sharp decrease of photoluminescence intensity with gradual introduction of analyte/s and baseline stabilization after passage of a considerable amount of time.

Fluorescence quenching has proved an effective approach in chemical sensing and surface studies[16]. In the present work, fluorescence quenching was expected to occur due to possible electron transfer from surface-derivatized porous silicon to nitroaromatics. In order to examine the role of electron transfer in the quenching process of nitroaromatics to the fluorescence surface, the response of the porous surfaces to a series of nitroaromatics such as DNT, TNT, NB, and PA were investigated. The fluorescence response of the porous films to the vapors of various analytes was ascertained by adjusting the porous films at room temperature upon which a flow of analytes is carried out. Glass wool is placed adjoining the analyte in order to prevent direct contact between analyte and porous film and helps to maintain a constant vapor pressure. The fluorescence spectra were recorded immediately after exposing the porous films to analytes for a specific time. The quenching studies on porous films were performed with excitation wavelengths of 460 and 380 nm and the analyte's equilibrium vapor pressures are assumed to be similar as noted from certain documents[55].

The structures, relative vapor pressures and original vapor pressures of the analytes are given in Figure 1.24.





Figure 1.13. Steady-state PL spectra (a), and quenching plot (b) of fresh PSi with TNT.



Figure 1.14. Quenching plots for PSi with TNT as a function of time.



Figure 1.15. Detection efficiency for PSi with TNT as a function of time.



Figure 1.16. Steady-state PL spectra of freshly prepared H-terminated PSi with

DNT.



Figure 1.17. Quenching plot of freshly prepared H-terminated PSi with DNT.



Figure 1.18. Quenching plots for PSi with DNT as a function of time.



Figure 1.19. Detection efficiency for PSi with DNT as a function of time.



Figure 1.20. Steady-state PL spectra of H-terminated PSi with NB.



Figure 1.21. Quenching plot of freshly prepared H-terminated PSi with NB.



Figure 1.22. Quenching plots for PSi with NB as a function of time.



Figure 1.23. Detection efficiency for PSi with NB as a function of time.

1.10.1. Fluorescence Quenching Measurements

Detection (Quenching) Efficiency: The quenching efficiency was calculated with the following equation;

$$Q(\%) = \frac{Io - I}{Io} \times 100$$

Where Q stands for quenching efficiency, I stands for the fluorescence intensity of porous surface in the presence of saturated vapor of analyte at time t(in minutes), I_o the fluorescence intensity of the porous silicon at time t=0 The evaporation effect of the NACs upon the sensing performance of the porous surfaces was examined. The figures show the plots of the quenching efficiency as a time function for each NAC. It can be observed that (1) it takes hours for the emission of the film to reach equilibrium and (2) the response rate of the film to the all applied NACs follows an order which is just in accordance of the saturated vapor pressure order of the concerned NACs as follows.

Figure 1.24. Decreasing order of vapor pressure of analytes.

The figures illustrate that the plots for DNT and TNT are almost straight lines in the case of all the functionalized porous silicon surfaces but the one for NB is obviously curved up, indicating that the quenching process for the former two NACs may be evaporation controlled. It does mean that the response rate of the porous surfaces to the two NACs is dictated by the evaporation rate of the film. As NB is liquid at room temperature, it is almost impossible to keep the total surface area, *S*, constant during the measurement by simply adding a few drops of it to the porous surface. In the case of PA with its very low vapor pressure compared to that of others, it shows little or no quenching efficiency.



Figure 1.25. Detection efficiencies of fresh PSi to NACs.



Figure 1.26. Detection efficiencies of oxidized PSi to NACs.



Figure 1.27. Detection efficiencies of dodecyl-derivatized PSi to NACs.



Figure 1.28. Detection efficiencies of methylvinylsilole-derivatized PSi to NACs.



Figure 1.29. Detection efficiencies of phenylethenyl-derivatized PSi to NACs.

1.11. Electronic and Structural Effects of Porous Films

Freshly Prepared Hydrogen Terminated Porous Silicon: Porous silicon is a high surface area network (material) of Si nanocrystallites which is produced by an electrochemical etch of single-crystal Si wafers[56]. It consists of a large number of interconnected Si nanocrystallites with a surface that is almost entirely covered with hydrogen atoms[25,39,56,57,58,59,60]. By analogy with molecular compounds containing the Si-H moiety, the hydrogen atoms on the surface of porous Si should behave chemically as H or H species[36].

The nanocrystallites in porous Si exhibit quantum confinement effects and emit visible photoluminescence[61]. Photoluminescence depends upon the presence of surface adsorbates [29,34,62,63]. Molecules capable of acting as energy or charge acceptors can quench the PL of porous silicon at diffusion rates [29,64]. The luminescence of PS was contributed to not only quantum confinement but also surface states[65] which are traps of carriers. Besides this, surface states can act as intermedial energy levels for the charge transfer between interfaces.

Methylvinyl Silole: Silicon-containing π -conjugated compounds, especially silacyclopentadienes (siloles), have emerged as a new class of electroactive materials with intense solid-state fluorescence and/or good electron transport properties in OLEDs[66,67,68,69,70,71,72,73]. Siloles have a relatively low-lying lowest unoccupied molecular orbital (LUMO) level due to the σ^* - π^* conjugation between the σ^* orbital of the two exocyclic Si-C bonds on the ring silicon and the π^* orbital of the butadiene fragment, resulting in a high electron density[66,67,68].

As a result, siloles can serve as efficient electron-transport material.

Phenylacetylene and 1-Dodecene: Conjugation of a phenyl group through either a vinyl[34] or alkenyl[74]unit is highly detrimental to the photoluminescence efficiency. Phenylacetylene upon hydrosilylation yields a styrenyl group that is known as a very effective photoluminescence quencher[52]. During the lightpromoted hydrosilylation reaction, reaction of a small number of phenylacetylene molecules, leading to covalently bonded styrenyl groups, may serve to quench the excitons of the nanocrystallite which block any further hydrosilylation. Their ability to quench the excited state of the porous silicon halts or reduces the reactivity of the sample.

The electronic effects on the Si nanocrystallites, along with the physical proportion of photoluminescent nanocrystallites in a particular sample, should determine the observed hydrosilylation efficiencies. If a substantial fraction of a porous silicon layer is not photoluminescent, then efficiencies will be lower since much of the material cannot undergo hydrosilylation through this mechanism. The decrease of photoluminescence intensity of porous silicon upon functionalization with phenylacetylene happens as it is assumed that this quenching molecule may act as a more efficient non-radiative surface trap than the phenyl species. Aromatic molecules can quench PL from porous silicon by a mechanism involving energy transfer to the molecular triplet states[29]. Neither benzene nor phenylacetylene have accessible energy levels[53] for energy transfer quenching to be a reasonable mechanism.

Oxidized Porous Silicon: After the as-prepared PSi sample received thermal oxidation, as mentioned above, the processed PS sample emitted feeble visible light, and we measured the FTIR spectrum of this processed PS sample. The result is shown in figure 4.5 where we observe that all those peaks related to hydrogen are reduced in intensity, but the 454 cm⁻¹, 800 cm⁻¹, 1090 cm⁻¹ peaks (Si-O-Si asymmetric stretching mode[75] and the 1170 cm⁻¹ peak[76], all related to oxygen, appear.

1.11.1. Order of Detection of Porous Silicon Surfaces



Figure 1.30. Detection of PL of porous surfaces in decreasing order

As the explanations have been mentioned-above, we can arrive at a conclusion that the freshly prepared hydrogen terminated porous silicon surface possesses the highest quenching efficiency. Following this methyl vinyl silole hydrosilylated porous silicon surface comes out to be the second highest flurofore for quenching the analytes. Likewise in the same manner, phenyl acetylene

hydrosilylated porous silicon is the third highest efficient surface for quenching. 1dodecene hydrosilylated porous silicon and oxidized one are the fourth and least efficient surfaces respectively for quenching analytes.

1.12. Adsorption Effects

A study has been made with the evaporation effects for nitroaromatics. When the nitroaromatic compounds were passed through the surface-derivatized porous films for half an hour during experimental period and left in an open atmosphere for a certain time, observations were made whether there exists adsorption of nitroaromatics or not. When surface-derivatized porous silicon was exposed to nitrobenzene in air for an extended time half an hour, the FTIR spectrum showed that the porous Si sample was slightly oxidized as given in figures below. In addition to the certain absorptions at respective wavenumbers, the sample exposed to nitrobenzene displayed a new feature assigned to absorptions of nitrobenzene v(N-O) were detectable at around 1550 and 1360 cm⁻¹ on the surface of derivatized porous silicon. These bands that are associated with nitrobenzene do not disappear after exposure to open atmosphere for 1 hr. Even the adsorptions were found to be disappeared on oxidized sample after 20 hrs



Figure 1.31. Exposure of fresh PSi to nitrobenzene.

These bands will disappear faster if these analyte adsorbed surfaces exposed to the flowing air. Further they do disappear if the samples were washed with ethanol. When the nitrobenzene exposure experiment was carried out in argon and nitrogen instead of air as carrier gases, traces of oxide on the surface of the porous silicon were observed in the FTIR spectrum. This verifies that nitrobenzene is able to oxidize porous surface even in the absence of oxygen (air) in a smaller amount. The same case was applied to other nitroaromatics such as DNT and TNT. However upon exposure to analytes for 1 hr, little or no oxidation was observed. It is assumed that if the porous silicon is exposed to saturated vapors of the concerned analytes for a longer period, absorption bands might be detecteble.

As we have found out that response time and relative photoluminescence quenching of the sensor vary with different carrier gas. It is a surprising factor that the porous silicon sensor using air as carrier gas shows the largest relative absorption change (PL quenching) and the sensor using using Ar as carrier gas the smallest relative absorption change and nitrogen in between.



Figure 1.32. Exposure of phenylethenyl-derivatized PSi to nitrobenzene.

1.13. Mechanism of Quenching of Photoluminescence

Photoluminescence quenching has been observed in a partial reversible manner for all the analytes. The IR spectra clearly verified that the porous silicon surfaces upon exposure to nitroaromatic compounds are oxidized either in the absence or presence of oxygen. The quenching of photoluminescence is related with such type of oxidation. It is assumed that nitroaromatics react with porous silicon surfaces as follows.



Porous Silicon

Scheme 1.9. Proposed mechanism of PL quenching.

The integrated area of the original bands observed with Si-H stretching modes remains generally intact. An assumption is made that in this oxidation mechanism oxygen is inserted into a Si-Si surface bond[77]. Nitroaromatics have been converted to nitroso aromatics that have been shown to act as oxygen atom donors [78]. The quenching of photoluminescence is supposed to arise from a combination of surface oxidation reaction and adsorbed molecules. The more adsorbed molecules, the more quenching of photoluminescence. The quenching of photoluminescence for porous Si can occur due to several processes as follows as .

(i) **Interfacial charge transfer**: This can occur when a molecular electron donor or acceptor atom of the appropriate energy comes in contact with an excited Si nanocrystallite in the porous Si matrix [64,79].

(ii) **Intefacial energy transfer**: This can occur if the molecular quencher has accessible singlet or triplet energy levels[29,80,81,82].

(iii) **Nonradiative surface traps**: Non radiative surface traps can be introduced by a chemical reaction at the porous Si surface that generates mid-gap defects[,34,36,77,83]

(iv) **Dielectric medium effects**: The dielectric constants of the medium surrounding the nanocrystallites in the porous Si modifies the efficiency of geminate recombination [84] which results in a loss of photoluminescence upon immersion of porous Si into any liquid dielectric medium [34,63,84,85].

The earlier studies have proved that quenching of photoluminescence of porous Si by nitroaromatic compounds and the mechanism of quenching is related

with Electron transfer process as follows.



Scheme 1.10. Electron transfer mechanism for PL quenching.

The conduction band of porous Si is negative[57]. Thus intensity of PL depends on the surface of adsorbates[29,34,62,63]. Molecules capable of acting as energy or charge acceptors can quench the PL of porous Si at diffusion controlled rates[29,64] Further the corrosive molecules like NO₂ can quench luminescence by introducing nonradiative defects on the surface of Si nanocrystallites[31,83].

1.14. Conclusions

The porous silicon surfaces with different functional groups have been synthesized and utilized for sensing nitroaromatics as explosives. The quenching of photoluminescence of porous silicon surfaces are measured against the detection of nitroaromatics as analytes.

1.15. References

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Part 2

A New Approach to Synthesis and Photoluminescence of Silicon Nanoparticles

2.1. Introduction

An exciting aspect of the research at the nanoscale results as nanostructures hold the potential to display an enhanced and unexpected reactivity relative to that at the micron scale and bulk phase. Further their formation and interactions may be accompanied by phase transformations not commonly observed in bulk systems[1]. Interest in nanoscale materials increased in recent years with the realization that unique properties may be obtained from otherwise ordinary materials.

Nanoscale materials are being focused, nowadays, as a center of attraction for a great deal of intense scientific research such as biomedical, optical, electronic fields etc. This focus is due to the fundamental differences in properties between nanoscale and macrolevel. The properties of materials change as their size tend to approach the nanoscale. The interesting and sometimes exciting behaviors of nanoparticles are observed, partly, due to the aspects of the surface of the material dominating the properties in lieu of the bulk properties. An investigation of the silicon nanoparticles has also displayed particle size dependent optical and electronic properties. Further they are useful for biologically sensitive materials and applied in optoelectronics^[2]. The prospect of silicon possessing useful optical properties has generated extensive speculation over the possibilities of new applications for silicon. The wide availability of silicon along with its electrical and chemical properties has made this semiconductor the material of choice for many electronic applications[3].

Here an approach has been made for the synthesis of silicon nanoparticles by

improving the solution reduction method. In particular, the use of metal naphthalenides has been reported as precursors to silicon nanoparticles with subsequent surface derivatization with organic ligands. This synthesis covers the reaction of silicon tetrachloride with lithium naphthalenide in tetrahydrofuran as a solvating medium to give rise to chloride capped silicon nanoparticles that can be further terminated by n-butyllithium as a surface-derivatization to give butylcapped silicon nanoparticles. In another attempt, the production of hydrogen terminated silicon nanoparticles is also becoming a hot issue in the area of intense research.

To date very little investigation has been done on the hydrogen terminated silicon nanoparticles. Hydrogen terminated silicon nanoparticle is an attractive starting point for the synthesis of novel modified silicon surfaces. In the present work, hydrogen terminated silicon nanoparticles have been synthesized by the reaction of lithium aluminium hydride with chloride-capped silicon nanoparticle which being produced from silicon tetrachloride with lithium naphthalenide in tetrahydrofuran. After the synthesis, the photoluminescence and stability of both types of silicon nanoparticles have been studied thoroughly.

2.2. Background of Study

Nanoparticles are proving to be of great interest to the scientific community due to their unique physical properties which result mainly from their size. Semiconductor nanoparticles have potential applications in optoelectronic devices such as display devices, optoelectronic sensors, lasers etc. Semiconductor nanoparticles have useful optical and electronic properties that will be required in optoelectronic devices that might be developed for future point of view[1-5]. Due to the potential for industrial applications, interest in the research of this technologically undeveloped area has been great. Many of these unique properties are attributed to quantum confinement effects which occur when the size of the particles becomes comparable to the exciton diameter of the bulk semiconductor material.

Research on silicon nanoparticles started in 1990 after Canham discovered that porous silicon(PSi) can give intense photoluminescence [6]. Elemental silicon is of great technological importance. Single crystal silicon is the basis of the computer revolution while polycrystalline silicon has applications in photovoltaic devices[7]. There has been little advancement in synthetic routes for the production of group IV nanoclusters, despite the large interest in nanostructured Si[3,8]. While bulk crystalline silicon luminesces very weekly, nanocrystalline forms of Si luminesce intensely over a range of wavelengths, with emission occurring primarily in the blue and the red spectral regions[3,8]. This would enable a broad range of optoelectronic applications involving efficient silicon-based emitters and has generated intense worldwide activity in this area[3,8]. Although there is a growing consensus that the luminescent centers involve Si nanoclusters, there remains controversy over the details of the light mechanism. It is assumed

that the red photoluminescence, observed in Si nanoparticles produced by a variety of methods, has been largely attributed to quantum confinement,[3,8,9,10] where as most blue emissions have been ascribed to other sources such as oxide-related defects, molecular species, or impurities[8].

Investigation of the synthesis of silicon nanoparticles by solution routes has been an active area of the research since it was first suggested that the visible luminescence seen in porous silicon could result from quantum confinement of electron-hole pairs[11]. Several different routes are available for the preparation of silicon nanoparticles, including both gas-phase and solution decomposition of silanes[12-15]. the reaction of silicon Zintl salts with silicon halides[16-19] as well as the solution reduction of silicon halides by sodium[20], lithium naphthalenide[21] or hydride reagents[22,23], or reduction of tetraethoxysilane with sodium[24]. Although there has been significant progress in size and shape control of II-IV and III-V semiconductors[25], there has been very little persuit of Si nanoparticles.

Here an approach has been made for the synthesis of silicon nanoparticles by an improvement in the solution reduction method. In particular, the use of metal naphthalenides has been reported as precursors to silicon nanoparticles with subsequent surface derivatization with organic ligands. This synthesis covers the reaction of silicon tetrachloride with lithium naphthalenide in tetrahudrofuran as a solvating medium to give rise to chloride capped silicon nanoparticle that can further be terminated by n-butyllithium and lithium aluminium hydride as source

for surface-derivatization. This route for the solution synthesis of silicon nanoparticles involves the reduction of silicon tetrachloride with lithium naphthalenide and subsequent derivatization of the nanoparticles by means of a surface-derivatized reagent.

The reduction route provides a means of controlling the size of the nanoparticles by controlling the surface–derivatization with the amount of silicon tetrachloride introduced into the synthesis. This provides a nanoparticle capped with chlorine, which is then passivated. Surface-derivatization (passivation) is expected to provide long stability to the nanoparticle[26]. Compared to others, this solution reduction synthetic method is more advantageous in terms of room temperature, expenses and higher yields. As well as the reaction is homogeneous and the intermediate halide capping renders to a large range of surface functionality. Although there have been a large number of papers published on porous silicon, very little research has been done on the chemistry of luminescent Si nanoparticles that are free of a substrate and that have not been derived from.

Information from the literature on silicon wafers and PSi is very helpful in identifying functionalization routes for the free nanoparticles, but chemistry on the free nanoparticles sometimes proceeds much differently than on a bulk surface[27]. The beautiful aspect of this synthesis is that both organic and water-soluble surface-derivatized silicon nanoparticles with the remarkable emission characteristics have been observed.
2.3. Experimental

2.3.1. Materials

Lithium, naphthalene, silicon tetrachloride (99.99 %), n-butyllithium, dichlorodimethylsilane, and lithium aluminium hydride (1 M in THF) were all purchased from Aldrich. Prior to use, the solvent tetrahydrofuran was distilled over Na/benzophenone but all other reagents were used as received without further purification. All sample manipulations were handled via standard inert atmospheric techniques. Glasswares were silonated by reaction for 1hr with a 2 % solution of $(CH_3)_2SiCl_2$ in toluene followed by repeated washes with hexane and methanol and dried overnight at 120 °C.

2.3.2. Syntheses

The lithium naphthalenide was prepared by modification of a literature procedure. 0.9 g of lithium (50 mmol) into small pieces and 3.23 g of naphthalene (25 mmol) were added in 50 mL tetrahydrofuran and stirred vigorously overnight at room temperature. Dark greenish solution was obtained. The lithium naphthalenide solution was cannulated at room temperature to a Schlenck flask containing 1.14 g (6.7 mmol) of silicon tetrachloride in 100 mL of tetrahydrofuran with rapid stirring. It was allowed to stir for about half-an hour. Then 6.4 mL of n-butyllithium (2.5 M in hexane) was added in a single amount. The stirring was continued for overnight. Then the solvent and naphthalene were removed under reduced pressure with heating (if necessary). The residue was extracted with

hexane. The extracted solution was washed with water and the organic portion separated out. Evaporation of the hexane layer followed by heating in an oil bath under vacuum to remove residual naphthalene gave out a viscous oil of silicon nanoparticle with butyl surface-derivatization. The remaining portion was washed with the distilled water, filtered and separated out. The resulting oxidized solution was handled in air. For the production of hydrogen-terminated Si nanoparticles, lithium aluminium hydride (LiAlH₄) solution (2.6 mL) was added via a gastight syringe at 0 °C in place of n-butyl lithium. The mixture was stirred in an ice-bath at 0 °C and allowed to slowly warm up to room temperature overnight. Remaining the processes being the same, the collected hexane layer was clear and colorless. This hexane was removed by evaporation. That gives an oily residue containing Si nanoparticles surface-derivatized with hydrogen which can be further suspended in hexane

2.3.3. Characterization

Photoluminescence spectra were obtained with a Perkin-Elmer LS 55 luminescence spectrophotometer.

2.4. Results and Discussion

2.4.1. Solution Reduction and Surface-derivatization

The nanoparticles were formed according to equations as follows, given in the Scheme 2.1. The reaction involves the reduction of silicon tetrachloride with

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lithium naphthalenide and the subsequent surface-derivatization of the nanoparticle produced with use of an alkyl lithium reagent and contact with water



Scheme 2.3. Synthesis for hydride-capped Si nanoparticles.

2.4.2. Organic-soluble Silicon Nanoparticles

Both for np-Si/Bu and np-Si/H characterizations, no analytical technique can itself verify the crystallinity, size, and surface-derivatization. The observation of photoluminescence suggests that there is occurrence of terminated silicon nanoparticle displaying quantum confinement effects. It does not give details of nanoparticle crystallinity or the size distribution. The identity of the termination source and its relationship to the nanoparticle (relating with structural or crystalline core) remains undefined. The PL data signify only that there are terminated silicon nanoparticles suspended in n-hexane[28]. It is an obvious fact that the quantum size effect in semiconductor nanocrystals is manifested as a blue shift in PL spectrum[29]. It has been shown that this shift is as much a function of the termination and the organization of the nanoparticle surface in the case of silicon and germanium nanocrystals[30].

2.4.3. Water-soluble silicon nanoparticles



Scheme 2.4. Synthesis for hydroxyl-terminated silicon nanoparticles.

Water is reactive to silicon and is capable of oxidizing silicon nanoparticle surfaces. The oxygen is reactive, too, to silicon surfaces. It is obvious that oxidation occurs when silicon and water as well as air come into contact with it. It is probable that a uniform oxide or hydroxide shell forms on the silicon, thereby protecting the crystalline core for a longer time. It is assumed that the nanoparticles appear to be encased in an amorphous material which is able to support nanoparticles. The amorphous material solidifies when the water evaporates. Exposure of silicon with lithium moieties to the air or water may result in significant oxidation[31].

An exposure of chloro-capped silicon nanoparticle to water results in oxide

environments. The reaction of np-Si/Cl, with water to form np-Si/OH suggests that hydroxyl groups have replaced chloro-groups for termination. The loss of chlorogroups in this reaction and the appearance of hydroxyl groups implies that the silicon surface sites are not completely passivated by Cl-groups in the np-Si/Cl, sample.

2.5. Photoluminescence Behaviors

Since the discovery of visible photoluminescence from nanometer sized silicon such as porous silicon, silicon nanoparticles; silicon nanoparticles embedded in other materials at room temperature have attracted much attention in the study of silicon based, light–emitting materials[32]. It is necessary to understand their luminescence processes in order to expose their potential for applications in optoelectronics. However, owing to their low stability and reproducibility, porous silicon devices still seem to be very difficult to use in the industry. Therefore it is important to clarify the stability of the silicon nanoparticles and their surfaces believed to be responsible for blue-luminescence. Pure silicon nanoparticles do not exhibit photoluminescence because they have dangling bonds on their surfaces[33]. PL emission spectra were taken from samples dissolved in n-hexane and water.



Figure 2.1. PL spectra of organic-soluble silicon nanoparticle derived from n-BuLi.

The photoluminescence spectra were measured at room temperature. The present synthesis produces a size distribution of which the photoluminescence spectra are inhomogeneously broadended. One manifestation of quantum confinement in such a system is a monotonic shift of the photoluminescence as the excitation wavelength is changed. This results from the excitations of different sizes of nanoparticles that have different optical transition energies[34]. It has been suggested that the blue-green luminescence is due to a particularly small size of the particles, where strong quantization of the electronic levels occurs, and that the red-orange luminescence is caused by larger particles which are less quantized. The PL of the Si nanocrystals was found to be remarkably stable in terms of the sensitivity of the nanoparticle core to the surface chemistry in the case of porous silicon.

The photoluminescence is considered to be the size dependent, with the larger

particles emitting lower energy light than the smaller particles, regarding with the general concept of quantum confinement effects in silicon. The PL was found to depend on the excitation wavelength yielding the sharpest PL.



Figure 2.2. PL spectra of water-soluble silicon nanoparticle derived from n-BuLi.

The synthesis of Si nanoparticles with two different surfaces allows us to study the effect of the surface on the photoluminescence. In the PL spectra, a strong UV-blue PL ranging from 390 nm to 550 nm is observed for organic-soluble silicon nanoparticle terminated with n-butyl group as shown in Figure 1. The center of the UV-blue peak is located at 446 nm, with an excitation wavelength of 360 nm and shows continuous shift with the increase of excitation wavelength.

Likewise in the same manner, such a strong UV-blue PL, too, ranges from 395 nm to 625 nm for water-soluble silicon nanoparticle as shown in Figure 2. The highest emission spectrum contains a peak centered at about 466 nm, with an excitation wavelength of 370 nm and behaves similarly as before but showing a slight increase in intensity in ending during continuous shift with the increase of excitation wavelength. The highest emission spectra seem to possess the peaks at values significantly.

The PL of the Hydrogen terminated Si nanocrystals was found to be remarkably stable in terms of the sensitivity of the nanoparticle core to the surface chemistry in the case of porous silicon[15].



Figure 2.3. PL spectra of organic-soluble silicon nanoparticle derived from LiAlH₄.



Figure 2.4. PL spectra of water-soluble Si nanoparticles derived from LiAlH₄.

In this case too, the synthesis of Si nanoparticles with two different surfaces allows us to study the effect of the surface on the photoluminescence. In the PL spectra, a strong UV-blue PL ranging from 330 nm to 600 nm is observed for organic-soluble silicon nanoparticle terminated with hydride group as shown in Figure 1. The center of the UV-blue peak is located at 378 nm, with an excitation wavelength of 340 nm and shows continuous shift with the increase of excitation wavelength. This UV-blue PL from these nanocrystallites occur in a different spectral region than that from other blue emitters such as oxidized porous silicon (440-480 nm)[35,36] or silicon carbide (500-520 nm)[37], thus complimenting their blue output performance.

The intensity of the blue PL from these nanoparticles is affected by the cluster size and depends linearly on the excitation power density[38]. It is expected that luminescence from traps in semiconductors will saturate at high excitation powers

due mainly to their lower number density relative to the band edge states of semiconductors. As a result, the observation of a linear dependence of the luminescence intensity as a function of excitation power indicates that saturation does not occur. This suggests that the origin of the luminescence is likely to be from traps, such as oxide or defect sites.

The intensity dependence of the photoluminescence is more consistent with quantum confinement, rather than defects. In the case of water-soluble medium, a distribution of silicon nanoparticles appears. Regarding this, a luminescence, too, ranges from 305 nm to 485 nm together with from 305 nm to 550 nm for water-soluble silicon nanopartices, for which the highest emission spectrum contains a peak centered at 339 nm with an excitation wavelength of 290 nm and another peak centered at 359 nm with an excitation wavelength of 320 nm respectively as shown in Figure 2.4. The peaks centered at 378.5 nm and 359 nm respectively for organic-soluble and water-soluble silicon nanoparticles are significantly greater than the bulk band gap energy, but consistent with what is observed for very small silicon nanoparticles.

2.6. Time-dependence of PL Spectrum

The time dependence behaviors of the PL spectrum for surface derivatized silicon nanoparticles dissolved in n- hexane and water are shown in Figure 2.5.

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Figure 2.5. Time dependence of PL spectrum of organic-soluble Si nanoparticles derived from n-BuLi.



Figure 2.6. Time dependence of PL spectrum of water-soluble silicon nanoparticles derived from n-BuLi.

For the organic-soluble silicon nanoparticle terminated with n-butyl- group as shown in Figure 2.7, the PL intensity is found to be dropped by a difference of around 7% and the peak position to be shifted by about 8 nm toward the blue during 100 hrs just after synthesis. A general trend seems to be that particles with initial emission at longer wavelengths show an increase in PL intensity with time, followed by a decrease in intensity at longer times, while particles with shorter wavelength emission show a monotonic decrease in PL intensity with time. But this uniformity has always not been encountered during the observation of all the samples we prepared (as shown above).

For the water-soluble silicon nanoparticle terminated with hydroxyl-group, the changes tend to be smaller. For the water-soluble sample shown in Figure 2.8, the peak position shifted by almost 7 nm towards the blue and the intensity decreased by almost 3% during 100 hrs. The comparision of the PL from SI nanoparticle samples stored in air at room temperature for different time provides the evidence for the slight increase of intensity in the case of oxidized sample. However the fluctuations may arise; the changes in PL intensity or emission wavelength may be due to slow internal effect of the particles causing a thicker layer and smaller core diameter resulting in self-limiting value[21]. Further it may result from other changes in the state of the particle surface.

In the case of surface-derivatized silicon nanopaticles with hydrogen, the organic-soluble silicon nanoparticles as shown in Figure 2.7, the PL intensity is found to be dropped by a difference of around 6% and the peak position to be

shifted by about 1nm toward the blue during 200 hours (over 1 week) just after synthesis.



Figure 2.7. Time dependence of PL spectrum of organic-soluble silicon nanoparticles derived from LiAlH₄.

For the water-soluble silicon nanoparticle terminated with hydroxyl-group, the changes tend to be larger. For the water-soluble sample shown in Figure 2.8, two prominent concequences arise. The peak position shifted by 1.5 nm towards the red and the intensity decreased by almost 10% occurs for the excitation wavelength 290 nm and as well another peak position shifted by 2.5 nm towards 1red and the intensity increased by almost 7% nm for the excitation wavelength 320 nm during 200 hrs (over 1 week) just after synthesis.



Figure 2.8. Time dependence of PL spectrum of water-soluble silicon nanoparticles derived from LiAlH₄.

The comparision of the PL from Si nanoparticle samples stored in air at room temperature for different time provides the evidence for the slight increase of intensity in the case of oxidized sample. However the fluctuations may arise; the changes in PL intensity or emission wavelength may be due to slow internal effect of the particles causing a thicker layer and smaller core diameter resulting in selflimiting value[39]. Further it may result from other changes in the state of the particle surface.

The mechanism of the photoluminescence considering these factors in the case of such nanoparticles (in both the cases) is not yet strongly discussed and therefore a speculation can only be made regarding the sources of changes in it. The photoluminescence intensities can be compared directly between the two phase nanoparticles. The reason behind this is assumed to be due to the similarities in particle concentration (including other factors may be). Further the change in PL

spectrum with time for the same phase nanoparticle can be observed.

2.7. Physical Appearances

The synthesized and surface-derivatized silicon nanoparticles reveal the photographic images as shown in the Figure 2.9. The organic-soluble Si nanoparticle seems to be colourless but water-soluble Si nanoparticle appears yellow in white light, whereas they emit in the black light appearing blue and green colour, respectively.



Figure 2.9. Photographic image of the photoluminescent Si nanoparticles.

In the case of hydrogen-terminated silicon nanoparticles, when suspended in solvents, both the organic-soluble and water-soluble Si nanoparticle seem to be colourless in white light whereas upon the introduction of UV light source at excitation wavelength of 365 nm, they emit faded blue and no colours, respectively.

2.8. Stability

A very important factor in the ultimate utility of the silicon nanoparticles in applications and investigations of their surface chemistry is the long-term stability of their optical properties. Lack of PL stability significantly hampers applications of silicon nanoparticles. Surface-derivatization (passivation) is expected to provide long stability to the nanoparticle[40]. The surfaces of nanoparticles (nanocrystals) play a key role in virtually every property, from structural transformations to light emission to solubility and ultimately to stability[29]. The stabilization of the particle is usually accomplished by capping or passivating the surface with molecules that are covalently attached to the particle and that have a lyophilic group that interacts favorably with the solvent[41]. Particle formation and passivation (termination) can occur in the same reaction mixture.







Figure 2. 11. Stability of water-soluble Si nanoparticles derived from n-BuLi.

Further the experiments relating with the stability of the photoluminescence and the surface treatment of the particles dissolved in the solvents have to be carried out. It should be emphasized that the changes in PL intensity mentionedabove do not suffer from a significant loss of visible PL from the particles. According to Figures, aging is observed after 1 hour when the particles are left in solution and stored in the dark. The aging of the particles was monitered over 4 days but after aging for 2 days, the stability seems to be constant over-time. The trough in the 2-day-old stability bar in the case of organic-soluble silicon nanoparticles is observed. A similar aging effect was also observed for watersoluble silicon nanoparticles.

According to Figure 2.12 and 2.13, aging is observed after 1 hour when the particles are left in solution and stored in the dark. The aging of the particles was monitered over 1 week but after aging for 2 days, the stability seems to be constant



over time in the case of organic-soluble H-terminated silicon nanoparticles.

Figure 2.12. Stability of organic-soluble Si nanoparticles derived from LiAlH₄.

The trough in the 2-day-old stability bar in the case of organic-soluble silicon nanoparticles is observed. A slight difference for aging effects was observed for water-soluble silicon nanoparticles.





The trough in the 2-day-old stability bar in the case of organic-soluble silicon nanoparticles is observed. A slight difference for aging effects was observed for water-soluble silicon nanoparticles. For excitation wavelength 290 nm, the intensity decreases down slowly up to 5th day and then again increases till the almost original stability is attained. However, a valley is observed in the 2-day-old stability bar. But in the case of excitation wavelength 320 nm, continuous increase and decrease of intensity occurs resulting in overall higher intensity and slight unstability.

Summing up these, an assumption can be made remarkably that the particles may keep growing to a saturated limit at room temperature even after they have been isolated and stored. The fluctuations may be due to non-uniform distribution of the nanoparticles in the respective solvents.

2.9. Conclusions

The surface-derivatization of silicon nanoparticle produced by reaction of the lithium naphthalenide with silicon tetrachloride has been investigated. Hydrogenterminated silicon nanoparticles can be, too, synthesized by reacting lithium naphthalenides with silicon tetrachloride and further with lithium aluminium hydride. The samples studied are the organic and water-soluble silicon nanoparticles. This method is unique in being able to produce in a limited amount of silicon nanoparticles with brighter and visible photoluminescence. We can arrive at a conclusion that n-butyllithium and lithium aluminium hydride serve as

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effective ligands for surface-derivatization for the synthesis of butyl-capped and hydrogen-capped silicon nanoparticles respectively. Probably stable, significantly terminated and photoluminescent silicon nanoparticles can be produced in room temperature as a bench reaction. Summing up, the Si nanoparticles have been investigated in order to understand the role of the surface in the UV-blue photoluminescence.

2.10. References

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Part 3

Synthesis and Photoluminescence of Silole Derivatives

3.1. 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 spirosilafluorene 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-1silafluorene have been produced. The starting material for all the silafluorenes and spirosilafluorene is regarded the same. The spiro-linked molecules compared to the corresponding non-spiro linked parent compounds exhibit greater morphological stability and more fluorescence.

3.2. Background of Study

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 obital 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).

3.3. Results and Discussion

3.3.1. Synthesis and Characterization

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

3.1) 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 obromophenyllithium (2) as an intermediate leading to couple with further with odibromobenzene 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 organosilicon 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 3.2). But latter

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step at very cooled condition (i.e. liquid nitrogen freezing temperature at -196°C) gives 1,1-dichloro-1-silafluorene.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.



Scheme 3.1. Synthesis of 2,2'-dibromobiphenyl.



Scheme 3.2. Synthesis of 9.9'-spiro-9-silabiluorene.

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 3.3) with 70% yield and on the other hand with one equivalent of dichloro dimethyl silane gives to 1,1-dimethyl-1-silafluorene (scheme 3.4).

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].



Scheme 3.3. Synthesis of 1,1-dichloro-1-silafluorene.



Scheme 3.4. Synthesis of 1,1-dimethyl-1-silafluorene.

3.3.2. Optical Properties

The photoluminescence of symmetric spirosilabifluorene 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 3.1. Upon excitation of 315 nm, symmetric

spirosilabifluorene however shows the fluorescence emission centered at 365 nm. The photoluminescence of 1,1-dichloro-1-silafluorene was measured in tetrahydrofuran at a concentration of 1 X 10^{-6} M at room temperature as shown in Figure 3.2. 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 figure 3.3.



Figure 3.1. Photoluminescence of 9,9'-spiro-9-silabifluorene.



Figure 3.2. Photoluminescence of 1,1-dichloro-1-silafluorene.



Figure 3.3. Photoluminescence of 1,1-dimethyl-1-silafluorene.

3.4. Experimentals

3.4.1. 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 measurements were carried out with conventional methods.

3.4.2. 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.

3.4.3. Syntheses

(i) 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)

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(ii) 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 spirosilabifluorene 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).

(iii) 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).

(iv) 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).

3.5. Conclusion

The syntheses of 9,9'-spiro-9-silabifluorene as well as 1,1-dichloro-1silafluorene 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.

3.6. References

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