# Synthesis and Properties of Boron/Silicon Bimetallic Copolymers

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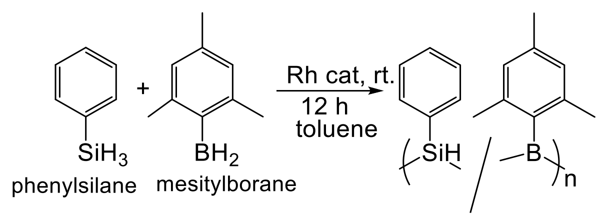
**Background:** Organosilicon polymers and organoboron polymers have been widely investigated because of their unique electronic states and characteristics. However, there has been few studies on polymers including both elements in the main chain. It appears to be an attractive approach to design such a novel bimetallic copolymers whose properties are unknown. Keeping this in mind we have synthesized different type of silicon/boron bimetallic polymers in order to use them as chemosensors, polymer support for electrolytes, self-healing anti-corrosion coating, emitter in OLED and so forth.

**Aim**: (i) Synthesis of boron/silicon bimetallic copolymers with different functionalities

(ii) Study their possible applications.

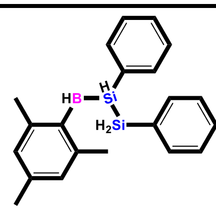
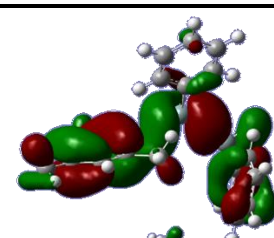
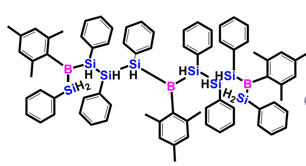
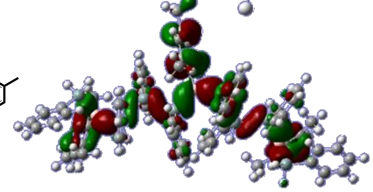
**Results and Discussion:**

In the chapter 2, a novel σ-p conjugated copolymer of phenylsilane and mesitylborane was synthesized by the dehydrocoupling polymerization using rhodium catalyst (**Scheme1**). Change in electronic states due to the incorporation of boron moiety was determined both by DFT calculations (**Table 1**) and experiments. The obtained colorless polymers were characterized by $^1$H-NMR and $^{11}$B-NMR spectra. Incorporation of boron was confirmed by $^{11}$B-NMR, while the Si/B ratio was calculated by $^1$H-NMR integration ratios. GPC analysis showed the $M_n$ of the polymer as 1200-2900 g/mol. Copolymers showed high sensitivity towards fluoride



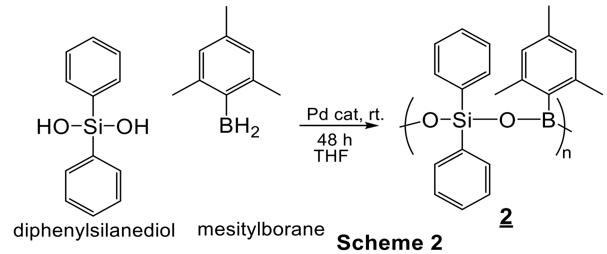

**Scheme 1** **1**

**Table 1: HOMO and Band Gap Energies of Models.**

| Chemical Structure | HOMO | $E_{gap}$ (eV) |
|---|---|---|
|  |  | 4.10 |
|  |  | 3.60 |

ions both optically and electrochemically exhibiting "turn on" type of sensing mechanism.

In chapter 3, synthesis of highly alternating poly(borosiloxane) by dehydrocoupling polymerization was successfully carried out (**Scheme 2**). The polymer sequence structure was understood by various model reactions. This particular polymer was examined for various applications and found to be a *multipurpose* material.




**Scheme 2**

A solid state sensing experiment was designed to examine the affinity of the polymer towards fluoride ions and it was found to be highly sensitive ($10^{-10}$ M of fluoride anion) (**Fig. 1**, **Fig. 2**). Detection of such low concentration was possible by the synergistic contributions of both, the solid state electrochemical sensing measurements and the Si-O back-bonding in the polymer chain exposing boron atom in a suitable conformation for reaction with fluoride. The kind of sensing behavior being presented here, is unprecedented under these conditions to the best of our knowledge which will open a new window for the development of fluoride anion sensing methods and materials.

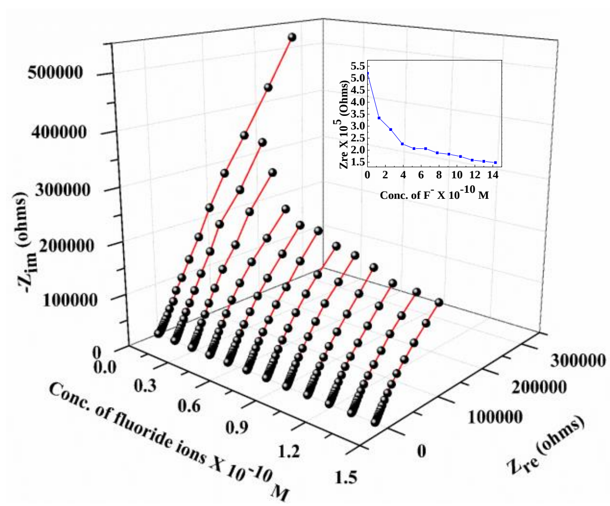



**Fig. 1: Electrochemical Impedance Analysis of 1 with Titration of Fluoride Ions. Supporting Electrolyte: Disodium Hydrogen Phosphate, RE: Ag/AgCl, WE: GC, CE: Pt..**

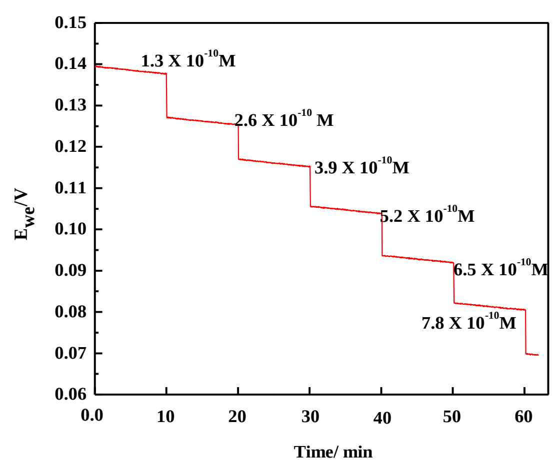
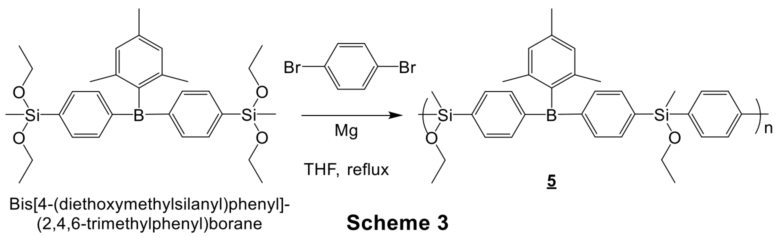



**Fig. 2: Open Circuit Potential Measurement of 1 with Titration of Fluoride Ions. Supporting Electrolyte: Disodium Hydrogen Phosphate, RE: Ag/AgCl, WE: GC, CE: Pt.**

Secondly, the self-healing behavior of poly(borosiloxane) under damage induced condition was achieved by heating to 45 $^oC$. A reptile motion of the polymer was believed to be the mechanism for self-healing and thus was confirmed by SEM micrographs. The polymer coat behaved as a remarkable corrosion protectant to the metal surface. The self-healing property was also observed by monitoring electrochemical impedance measurements and depolarization studies. Good protection was observed after self-healing in samples which were subjected to scratch-heal test. This proved that the healing process was complete in all the facets.

Also, novel ion-gel electrolytes were prepared by doping the synthesized poly(borosiloxane) with low viscous ionic liquid and lithium salts. The ionic conductivity of the prepared samples was in the range of $10^{-5}$-$10^{-3}$ $Scm^{-1}$. Also, the lithium transference number was found to be in range of 0.23-0.40. The samples prepared by doping with LiFSI showed relatively enhanced ionic conductivity as well as lithium ion transference number than samples with LiTFSI because of better interaction of borane with FSI anions.

In chapter 4, poly(silylene/phenylene/borane) ultraviolet emitter via thermally activated delayed fluorescence was successfully synthesized (**Scheme 3**).




**Scheme 3**

The largely separated HOMO and LUMO were observed in DFT calculations with smaller $\Delta E_{ST}$. The molecule was successfully designed to have large band gap to get photoluminescence (PL) emission in ultraviolet range (**Fig. 3**). The quenching of PL was observed with dissolved oxygen, which confirmed the involvement of triplet excitons in PL. Prediction of triplet and singlet energies at room temperature provided a strong evidence of RISC by thermal activation. Thus prepared material is first example of solution processable ultraviolet emitter via TADF and can provide valuable dimension to the design of OLED emitters.

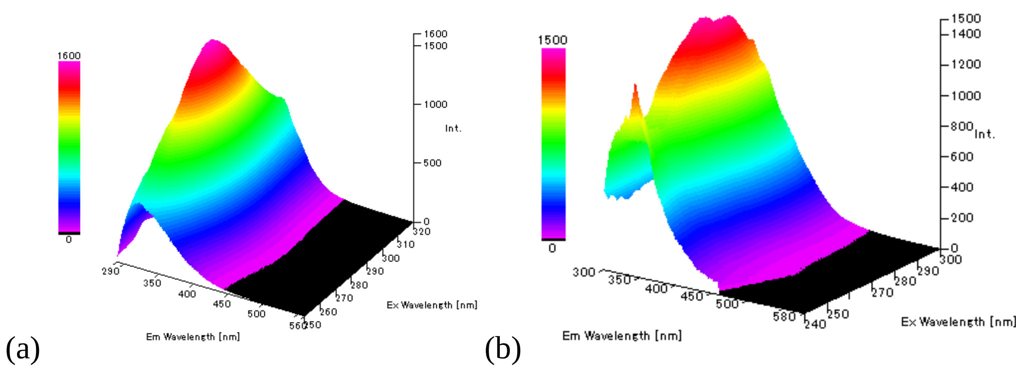



**Fig. 3: Excitation Wavelength Dependence of Photoluminescence of <u>5</u> (a) Acetonitrile (b) in THF ($10^{-5}$ M).**

**Table of Contents:**



**A) Publication (Peer Reviewed):**

**1)** Noriyoshi Matsumi, Yoshiyuki Toyota, Prerna Joshi, **Puhup Puneet**, Raman Vedarajan, and Toshihiro Takekawa. "Boric Ester-Type Molten Salt via Dehydrocoupling Reaction." ***Int. J. Mol. Sci.***, 15, **2014**, 21080-21089.

**2)** **Puhup Puneet**, Raman Vedarajan, Noriyoshi Matsumi, "σ-p Conjugated Copolymers via Dehydrocoupling Polymerization of Phenylsilane and Mesitylborane", ***Polymer Chemistry***, 7, **2016**, 4182.

**B) Manuscript (In Preparation):**

**1)** **Puhup Puneet**, Raman Vedarajan, Noriyoshi Matsumi, "Alternating Poly(borosiloxane) For Solid State Ultrasensitivity Towards Fluoride Ions in Aqueous Media", (Submitted, Under Review).

**3)** **Puhup Puneet**, Raman Vedarajan, Noriyoshi Matsumi, "Self-Healing Properties of Alternating Poly(borosiloxane) as smart coating for Corrosion Protection of Metal Surfaces".

**4)** **Puhup Puneet**, Prerna Joshi, Raman Vedarajan, Noriyoshi Matsumi, "Ion Conductive Properties of Ion-Gels with Poly(borosiloxane) Polymer Support"

**5)** **Puhup Puneet**, Raman Vedarajan, Noriyoshi Matsumi, "Synthesis of Organoborane/Ionic Liquid Block Copolymer by ATRP for Selective Cation Transport.