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論文題目	Synthesis and Properties of Boron/Silicon Bimetallic Copolymers
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論文の内容の要旨

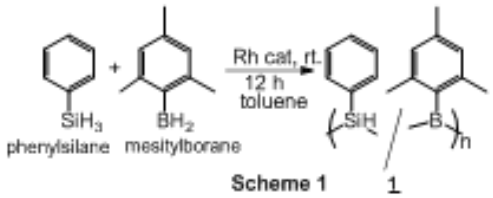
Background: Organosilicon polymers and organoboron polymers have been widely investigated because of their unique electronic states and characteristics. However, there has been few studies on polymers including both elements in the main chain. It appears to be an attractive approach to design such a 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 (**Schemel**). 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

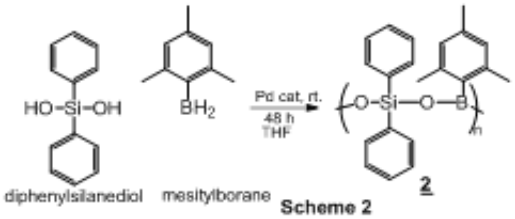
Table 1: HOMO and Band Gap Energies of Models.

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.

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.



Scheme 2

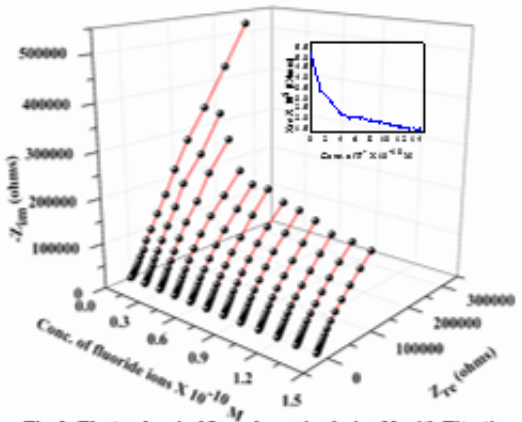


Fig. 1: Electrochemical Impedance Analysis of 1 with Titration of Fluoride Ions. Supporting Electrolyte: Disodium Hydrogen Phosphate, RE: Ag/AgCl, WE: GC, CE: Pt.

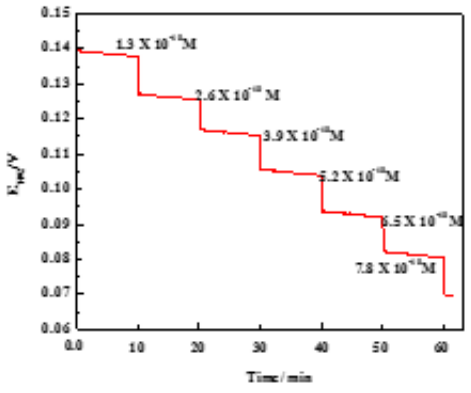


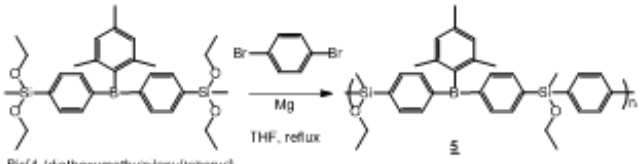
Fig. 2: Open Circuit Potential Measurement of 1 with Titration of Fluoride Ions. Supporting Electrolyte: Disodium Hydrogen Phosphate, RE: Ag/AgCl, WE: GC, CE: Pt.

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 ΔE_{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.

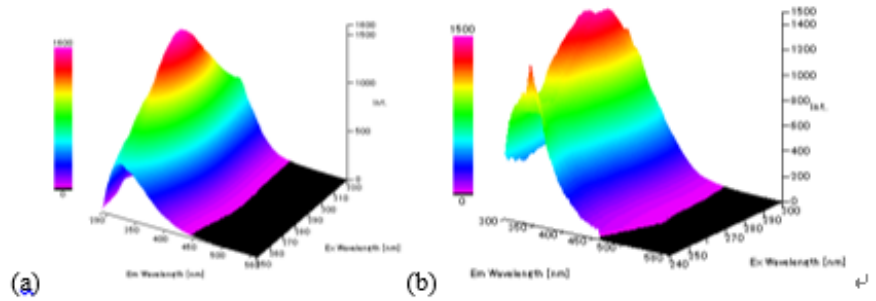


Fig. 3: Excitation Wavelength Dependence of Photoluminescence of 5 (a) Acetonitrile (b) in THF (10^{-5} M).

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.

論文審査の結果の要旨

本論文では、ホウ素とケイ素の両元素を同時に高分子主鎖に有する新規な無機高分子材料を３種類合成し、それらの機能材料としての諸特性を詳細に検討した。

一般にホウ素やケイ素を主鎖に有する無機高分子にはそれらのユニークな電子状態により様々な光・電子的機能を示す材料が多く見られる。一方で、ホウ素とケイ素の両元素を同時に高分子主鎖に導入する研究は世界的にも未だ限られた事例しか知られておらず、従来にない特性を有した新奇高分子を創出する上で有効なアプローチである。

まず、メシチルボランとフェニルシランとをロジウム触媒の存在下で脱水素カップリング重合させることにより、ポリシラン主鎖にホウ素を導入した共重合体を得ることに成功した。この材料はσ-p 共役と呼ぶべき従来にない共役モードによる新たなカテゴリーの共役系高分子と見なすことができ、学術的に興味深い。また、DFT 計算においてもσ-p 共役モードによる共役長の拡張が示唆された。さらに、本高分子材料はμM オーダーのフッ化物イオン存在下において発光を示し、turn-on 型のフッ化物イオンセンサーとして機能することが明らかとなった。

さらに、メシチルボランとジフェニルシランジオールとの脱水素カップリング重合により、ポリ（ボロシロキサン）の合成に成功した。ケイ酸ガラスにホウ酸構造が導入されたケイホウ酸ガラスは一般的な材料であるが、この構造に対応した一次元高分子材料はこれまで知られていなかった。この材料は水に対しても安定性が高く、DFT 計算により Si-O 部位の逆電子供与が隣接 B-O 部位の電子状態に顕著に影響していることが示された。得られた材料はフッ化物イオンセンシング能、自己修復能を示すほか、リチウムイオン２次電池用のイオンゲル電解質の支持高分子としても有用であることが分かった。特に、本材料のフッ化物イオンセンシング能(~10^{-10} M)は世界最高値を示している。

一方、ジグリニャール試薬を経た重縮合により合成したポリ（フェニレン/シラン/ボラン）は高い量子収率で紫外光発光を示すことが見出され、近年注目されている TADF (Thermally Activated Delayed Fluorescence)による発光を示していることが発光の時間減衰挙動などから示唆された。本メカニズムに基づいた紫外光発光材料はこれまで知られておらず、発光デバイス分野における今後の応用展開が期待される。

以上、本論文は、機能性無機高分子材料の新たな設計コンセプトを与えるものであり、とりわけ学術的に貢献するところが大きい。よって博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。