จุฬาลงกรณ์มหาวิทยาลัย
ทุนวิจัย
กองทุนรัชดาภิเษกสมโภช

รายงานผลการวิจัย
เรื่อง

วัสดุสกัดไอออนโลหะประเภทใหม่จากซิลิกาที่ปรับผิวโครงสร้างด้วยอนุพันธ์ไซลิลเบนซอกซาซีนโดยสมบัติสารหลัก-สารรอง

โดย

สุวบุญ จิรชาญชัย

สิงหาคม ๒๕๔๔

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บทคัดย่อ

ไซลิลเบนซอกซาซีนที่มีหมู่เคมีบนวงแหวนเบนซีนต่างๆกันได้ถูกเตรียมขึ้น โดยการใช้อะมิโนไซเลนเป็นอามีนปฐมภูมิในการสังเคราะห์ อนุพันธ์ไซลิลเบนซอกซาซีนที่มีหมู่เคมีที่เกะกะมากกว่าแสดงความสามารถในการสกัดไอออนที่ต่ำกว่าทั้งนี้เป็นผลจากความยากในการรวมตัวของโมเลกุลที่มีหมู่เคมีที่เกะกะ ทำให้เกิดการต้านกันระหว่างสายโซ่อัลคิลขนาดยาวของไซเลน การปรับผิวซิลิกาด้วยเบนซอกซาซีนประสบความสำเร็จจากการใช้อนุพันธ์ไซลิลเบนซอกซาซีน ซิลิกาที่ได้รับการปรับผิวด้วยหมู่ไซลิลเบนซอกซาซีนที่มีหมู่เกะกะในโครงสร้างแสดงผลการสกัดไอออนที่สูงทั้งนี้เนื่องจากโครงสร้างในการก่อตัวที่หลวม ทำให้ได้ช่องว่างในการสำหรับบรรจุสารรองมากขึ้น

Project Title : A Novel Ion Extraction Material derived from Silica Surface Modified Silylbenzoxazine Derivatives via Host-Guest Properties
Name of the Investigators : Suwabun Chirachanchai
Year : August, 2001

Abstract

Silylbenzoxazine derivatives with different bulky group on benzene ring are synthesized employing aminosilane as a primary amine. The silylbenzoxazine derivatives with more bulky group exhibit low ion extraction percentage due to the difficulty of molecular assembly formation as a result of the bulky group repulsion combining with the long alkyl chain of silane. Silica surface modified benzoxazines are successfully achieved via silylbenzoxazine derivatives and show the ion extraction property for various alkali and alkaline earth metal ions. When silane is coupled onto silica, the benzoxazine shows different ion extraction ability from that of silylbenzoxazine. The silica surface modified silylbenzoxazines with bulky groups exhibit high ion extraction percentage which may be due to the loose packing structure of the molecular assembly inducing the high amount of cavity for guest.

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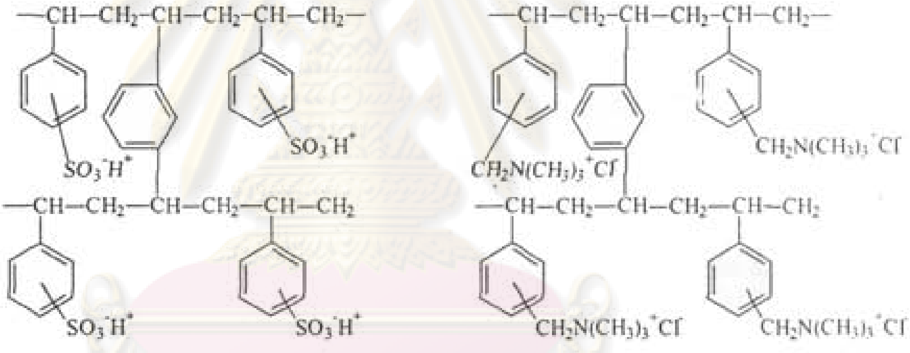
CHAPTER 1

Introduction

1. From Separation Chemistry to Supramolecular Chemistry

Separations of chemical species and extractions of metal ions are concerned to be important for the industries and global environment. In the past decades, ion separation by using ion exchange resin is one of the most practical purification methods. Conventionally, as shown in Figure 1, ion exchange resin can be prepared from the synthetic polymer containing active functional groups such as sulfonic, carboxylic, and phenolic or amino group, etc. This provides ionic interaction property with metal ion to the resin.



(a) (b)

Figure 1. Examples of conventional ion exchange resin, a) cationic resin, and b) anionic resin.

The ion exchange resin also has the advantage about recycle uses because the basic concept of reversible chemical reaction between a solid (ion exchanger) and a fluid containing various types of ions. However, traditional ion exchange resin has reached its own limit for the sensitivity and selectivity when dealing with the mixtures of similar ions or molecules.

Recently, the understanding of supramolecular chemistry at the molecular level has increased rapidly due to the advanced technology of analytical instrumentation.

The concept of supramolecular chemistry contributes the guideline of molecular recognition and is concerned to be an extended area for separation technology.

2. Supramolecular Chemistry

Originally, supramolecules can be claimed to the natural system when a specific molecule or a group of molecules forms a molecular asset to interact with another species of molecule or a group of molecules or ion species[1]. The ideal structure of supramolecules can be referred to the nucleic acid base pairing system[2]. This gives the double helix of DNA and RNA systems where the supramolecules are formed via hydrogen bonding and $\pi-\pi$ stacking interaction between purine and pyrimidine rings. Thus, supramolecules are always called as host-guest or inclusion compounds. The inclusion or host-guest compound is defined as a molecular assembly of host concave and guest convex stabilized under secondary forces[3], such as hydrogen bonding, van der Waals, dipole-dipole interaction, polar or nonpolar attractive force, and π-π stacking[4].

Artificial inclusion compounds have received much attention under the approach of a synthetic host compound that can provide a specific interaction to accept another molecule or ion species as guests. In the present era, it comes to the point that we design a particular molecule satisfying the conditions to form the host-guest compound, so-called the molecular architecture research. The extension of the research is to find the new molecules under the concept of supramolecular chemistry by imitating the bio-system or natural supramolecules, so called biomimetic chemistry. The development of biomimetic chemistry enables us to obtain the unique functions in the new host molecules. In this way, we can expect the materials for advanced practical applications such as drug delivery system and separation process. Host-guest phenomena of urea and thiourea were first reported as the honeycomb structure by Schlenk[5].

In 1956, Clasen *et al.*[6] proved the concept of inclusion polymerization by using urea and thiourea as host molecules for butadiene monomer. Pedersen reported the interaction of crown ether derivatives with alkali and alkaline earth metal ions which becomes one of the most potential works for practical application since then. Up to now, several works clarified the interaction of hosts with neutral moleculest[7], or monomer species[8] or ionic species[9]. The applications of artificial host-guest were then proposed as ultra-high purifications[10], microspheres[11], polymer prodrugs[12] when the guest molecule is neutral species, or waste water treatment[13], ion catalyst[14], when the guest molecule is ionic species, and stereoregular polymer synthesis[15] when guest molecule is monomer species.

3. Types of Host Compounds

The types of host compounds in either artificial or natural system can be categorized into two main types, i.e., macrocyclic and noncyclic types[16]. Macrocyclic host molecules are defined as a group of molecules bonded covalently to form a cyclic ring with a space to entrap guest molecules. Noncyclic host molecules are a group of molecules aligned in a specific manner to form an assembly giving a channel or layer for guest. The unique feature of macrocyclic is the fixed cyclic structure with hydrophilic or hydrophobic or ionic ring, while that of the noncyclic one is the flexible structure based on the hydrogen bonding and van der Waals forces.

The known structures of artificial host compounds for macrocyclic type can be raised as nonactin, enniatin, valinomycin and enterobactin, while for noncyclic types can be raised as DNA, RNA helices[17]. Macrocyclic artificial host-guest compounds are referred to crown ether, cyclodextrin, and calixarenes, as the first, second, and third host generation, respectively. For noncyclic types, the well-known hosts are cholic acid and its derivatives, and acetylenic alcohol derivatives.

4. Types of Guest Compounds

In general, types of guests, can be neutral species, reactive neutral species or monomer, and ion species. Crown ether is known for the ion dipole interaction to form inclusion complex with metals depending on the polyether ring[18], e.g., 14-crown-4, 15-crown-5 and 18-crown-6 with cavity diameter for guest in the range of 1.2~ 1.5, 1.7~ 2.2 and 2.6~ 3.2 angstrom, respectively. Up to now, many reports clarified that crown ether can form complex with alkali, alkaline-earth metals, heavy metals and so on. Cyclodextrin is reported for the inclusion phenomena related to the size of the cyclic structure[19], i.e., α-cyclodextrin for benzene and phenol, β-cyclodextrin for naphthalene, 1-anilino-8-naphthene-sulphonate and γ-cyclodextrin for anthracene, 1-aniline-8-naphthalene-sulphonate[20]. Calixarenes are known to interact with either ion species or neutral molecules. Calix-4, -5, and -6-arenes and their major derivatives are known to form complexes with metal ions such as lithium, sodium, potassium and so on. Sone *et al.*[21] reported that calixarenes interact with benzene, acetone, dioxane, dichloromethane and 1,2-dichloroethane in the ratio of 1:1, 1:1, 2.1, 2.1, 2.1, respectively. Miyata *et al.*[22] reported that cholic acid and its derivatives entrapped alcohol derivatives, phenol derivatives and vinyl monomers mostly in a ratio of 1:1, 1:2, or 2:1.

5. Clarification of Inclusion Compound

There are many techniques that can be used to clarify the host guest compound, depending on the nature of guest species, i.e., ionic and neutral species. In the case of ions as guest species, the host guest interaction can be identified whether it is in liquid or solid state.

UV/Vis can be applied to clarify the ion interaction ability. Smid[23] reported that UV spectra clarifies the changing of host and guest about electron surroundings as can be observed from the peak shifting.

NMR technique is good for quantitative analysis on the host guest ratio. Cram and Ho[24] noted that the chemical shift of picrate proton is around at 8.8 ppm via ^{1}H-NMR. Arbuini *et al.*[25] studied cone conformation of p-t-butylcalix[4]arenes to entrap with K^+.

Thermogravimetry Analysis (TGA) is one of the direct methods to clarify host-guest stability and ratio. When the thermal energy is applied to the host-guest compound, at some particular temperature, guest instability will appear and will release from the host molecule. As a result, guest releasing temperature and amount of guest can be confirmed by TGA. Miyata et al. applied TGA to evaluate host-guest ratios.

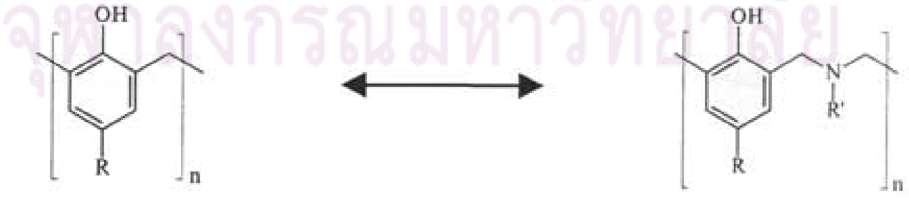
The development of soft and hardware make the single crystal X-ray analysis become the most informative and reliable data to determine host-guest in terms of structure, ratio, involved secondary forces and molecular stabilization. However, the technique requires a complete host guest crystal with the least defect, hence, the crystal preparation, especially when it comes to polymer host compound, is the main problem to apply this technique. Miyata et al.[22a] succeeded in clarification the movement of cholic acid host channel related to the size of the guest.

Powder X-ray Diffraction (XRD) is applied to simplify the single crystal X-ray analysis technique. A series of XRD patterns help us clarify the host structure, host-guest structure and the changing of host channel when guests are varied[22b].

Mass spectroscopy is another method that gives the information about host-guest complexation and the molecular assembly when the host and the guest form a cluster. Leize *et al.* noted that electrospray mass spectrometry exhibited the metal complexes between their compound entrapped with Cu^{2+}. Shiina and Kinumaki[26] reported the complexation by using mass spectrometry and showed the differences in fragmentation between $[M+H]^+$ and $[M+Li]^+$.

6. Benzoxazine: A Novel Host Compound

The expectation for benzoxazine as a host compound is reasonable when we compare to that of calixarenes, one of well-known host compounds (Figure 2).



Calix[n]arenes

Benzoxazine oligomer

Figure 2. Resemble structures of calix[n]arenes and the open ring benzoxazine oligomer.

The repeating unit of benzoxazine consists of the hydrophilic hydroxyl group at one side while the hydrophobic benzene ring at the other. There are lone pair electrons at oxygen in the hydroxyl group and nitrogen in the tertiary amine linkage at each monomer unit, which is partially similar to the calixarenes. By varying the functional groups, R and R', we can control the hydrophobicity of benzoxazines.

Chirachanchai *et al.*[27] reported that Bisphenol-A based benzoxazine monomer and its oligomer act as ionophore and these benzoxazine compounds can interact with ion metals, alkali and alkaline earth metal ions. The solubility parameter of the organic phase at 0.34 provides significant ion extraction abilities for ionophore and the concentration of ionophore can control the ion extraction ability. Phongtamrug *et al.*[28] reported that benzoxazine monomer forms assembly to entrap alkali and alkaline earth metal ions via its inclusion phenomena. Ion extraction ability is depending on the functional group of benzoxazine monomer. Techakamolsuk *et al.*[29] demonstrated that benzoxazine dimer interacts with alkali and alkaline earth metal ions. The ion extraction ability of the dimer is significant when the structure is modified to be ester derivatives. This might relate to the decrease of intramolecular hydrogen bonding.

7. Molecular Design of the Benzoxazine to be Ion Extraction Resin

Based on the ion interaction ability of benzoxazine, it is an interesting theme to apply benzoxazine as an ion extraction material. In this case, the material can be achieved by either curing benzoxazine monomer directly or coupling with a stable material, such as silica.

It is well known that a silane coupling agent is an important binder used to reinforce the bonding between silica and matrix resin. Silane coupling agents are monomeric species, R-Si(OR′)$_3$, where R is a reactive group with a polymer matrix and (OR′) is a hydrolyzable ester group. Ishida reported the chemistry of silane coupling agent including the application of various silanes for composite materials.

Ernst *et al.*[30] used ^{29}Si-NMR spectroscopy to quantify the anchoring of 3-chloropropyltrimethoxysilane and 3-aminopropyltriethoxysilane to the surface of silica gel particle and reported three different types of surface bonds, i.e., covalent linkages between the organosilane moiety by one, two, or three silanol groups.

8. Aminoalkoxysilane as an Amine in Benzoxazine Preparation

Ishida *et al.*[31] proposed glass fiber reinforced polybenzoxazine composite by using aminoalkoxysilane coupling agent as an amine in the method of benzoxazine synthesis. It is reported that the silane is successfully coupled onto benzoxazine resin and promoting the adhesion between glass fiber and polymer resin to obtain the composite. However, the reaction of silane with benzoxazine produces the water molecule by-product, which causes the hydrolysis of the alkoxysilane. If the alkoxysilane is hydrolyzed, the silane oligomer will be formed and the gelation may occur. In order to avoid these problems, the water molecule is separated from the product by using the nonpolar solvent.

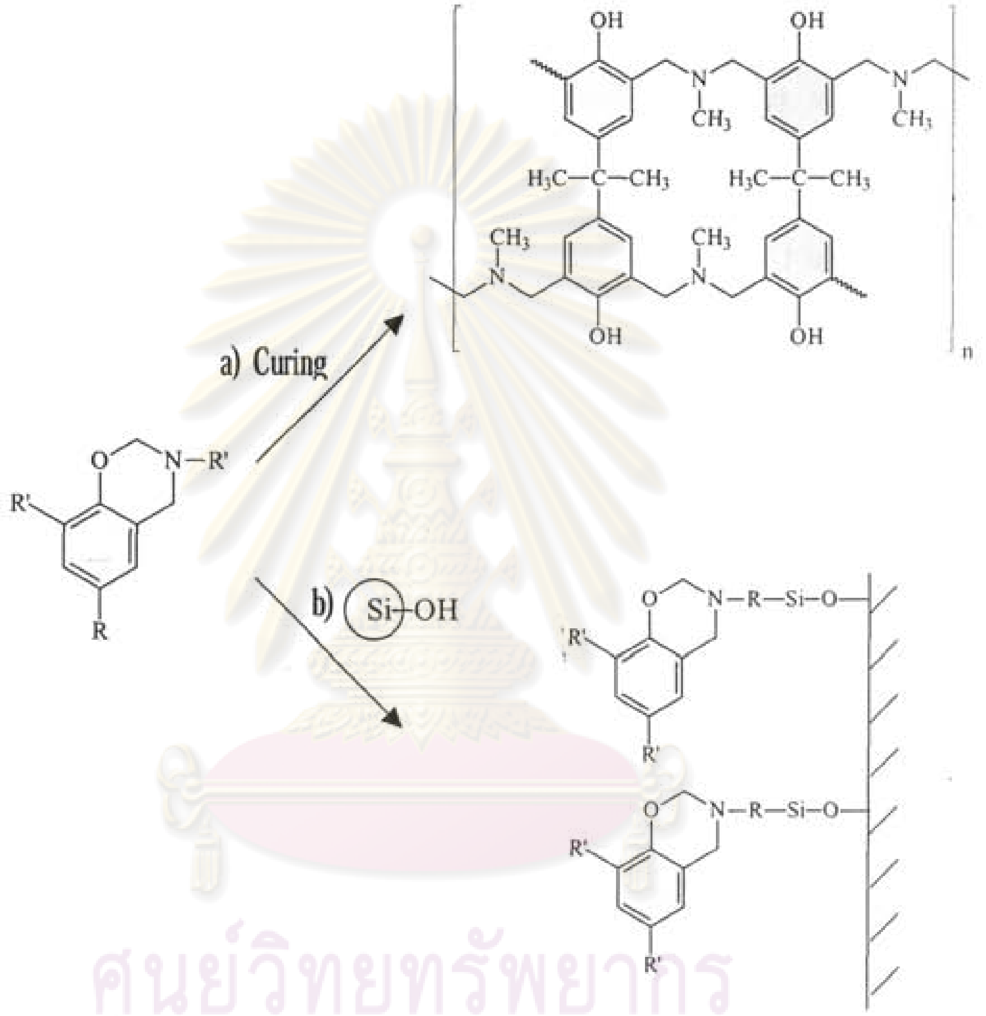
9. Points of Interest of the Present Project

In order to apply benzoxazine as a material for ion extraction, we proposed two strategies, as shown in Scheme II. In our previous work[27], we reported the cured polybenzoxazine to obtain the benzoxazine resin. The present work proposed an application benzoxazines based on the previous results about preparation of silyl benzoxazines and the ion interaction properties of benzoxazines. By coupling silyl benzoxazines onto silica, it is expected that the silica resin perform as ion extraction materials.

The present work is, thus, divided into two parts. The first part concentrates on the preparation of silyl benzoxazines and silica coupled silyl benzoxazines. The second part deals with the ion interaction ability of silica resin.

Here, silylbenzoxazines are synthesized employing the method of benzoxazine synthesis with the use of aminosilane as the primary amine. The obtained resins are applied as a stationary phase in the chromatographic separation system to determine the ability of alkali and alkaline earth cation extraction.

Scheme I. Two strategies to apply benzoxazine as ion extraction material.



CHAPTER 2

Experimental

1. Materials

Chemical reagents were purchased from the companies as follows, and were used without further purification. Paraformaldehyde, *p*-cresol and phenol were purchased from SIGMA (USA). 3-Aminopropyltriethoxysilane, sodium sulfates anhydrous, 2,4-dimethyl phenol, and lithium chloride were the products of Fluka chemicals (Buchs, Switzerland). Chloroform and diethyl ether were purchased from J.T. Baker Inc. (Phillipsburg, USA). Picric acid, magnisium chloride, potassium chloride, sodium hydroxide and sodium chloride were obtained from Ajax chemicals (Australia). Barium chloride and calcium chloride were purchased from E. Merck (Germany). All solvents were used as received and stocked over 4 Å molecular sieve before use.

2. Instruments and Equipment

Fourier Transform Infrared Spectrophotometer (FT-IR)

Fourier transform infrared (FT-IR) spectra were taken from Bruker Equinox 55 spectrophotometer with 16 scans at a resolution of 4 cm^{-1} in the frequency range of 4000-400 cm^{-1}. Both techniques on ZnSe plate and KBr pellet were used.

Proton Nuclear Magnetic Resonance Spectrometer (^{1}H-NMR)

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained from Fourier Transform NMR spectrometer ACF 200 MHz of Bruker, Switzerland. Sample was dissolved in deuterated chloroform with tetramethylsilane as an internal standard.

Vortex Mixer

Vigorous shaking of the organic-aqueous mixture was performed by Vortex mixer (GENIE-2, Scientific Industries).

Ultraviolet-Visible Spectrophotometer

Percent extraction of picrate metal salt was determined by Ultraviolet-Visible Spectrophotometry, Perkin Elmer Lambda-16 UV-VIS spectrophotometer.

Atomic Absorption Spectrophotometer

Ion concentration in aqueous phase was determined by an atomic absorption spectrometer Varian SpectrAA-300. The hollow cathode lamps used were sodium cathode lamp for sodium, potassium cathode lamp for potassium, magnesium cathode lamp for magnesium, barium cathode lamp for barium, and calcium cathode lamp for calcium. Ion solution standard was prepared according to the analytical method of Varian.

Elemental Analysis

The percent elements were obtained from PE 2400 Series II CHNS/O Analyzer with combustion temperature at 975 °C, reduction temperature at 500 °C and vial receptacle for 1000 runs. The sample was put in tin foil and weighed approximately for 1-2 mg and analyzed under air atmosphere with O_2 as a combustion gas and He gas as a carrier gas.

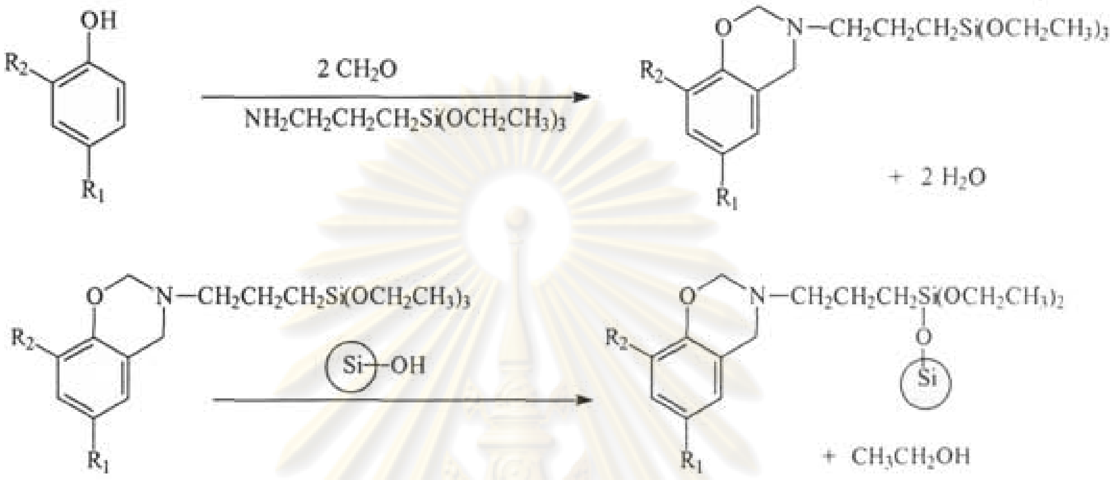
3. Preparation of Silylbenzoxazine Derivatives

Preparation of silylbenzoxazines is shown in Scheme II.

Synthesis of 3-triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine **1**

A portion of paraformaldehyde (6.3063 g, 0.2 mole) in 25 mL of chloroform was measured into a 100 mL three neck flask, with continuous stirring. 3-aminopropyl triethoxysilane (22.137 g, 0.1 mole) in 10 mL of chloroform was then added to the paraformaldehyde solution, of which was heated to 85°C. The mixture was allowed reacting for 10 minutes. Phenol (9.411 g, 0.1 mole) in 25 mL of chloroform was further added into the reaction to proceed for 3 hrs.

Scheme II Preparation of silylbenzoxazine derivatives.



When R_1 : -H and R_2 : -H for **1**

R_1 : $-CH_3$ and R_2 : -H for **2**

R_1 : $-CH_3$ and R_2 : $-CH_3$ for **3**

The obtained solution was evaporated to remove the solvent and then dried over sodium sulphate anhydrous. The crude product was then purified by vacuum distillation to remove unreacted starting materials to obtain a colorless liquid at room temperature.

Synthesis of 3-triethoxysilyl-n-propyl-3,4-dihydro-6-methyl-2H-1,3 benzoxazine **2** and 3-triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine **3**

Similarly, **2** and **3** were prepared as the procedure of **1** with *p*-cresol and 2,4-dimethyl phenol as a starting material, respectively.

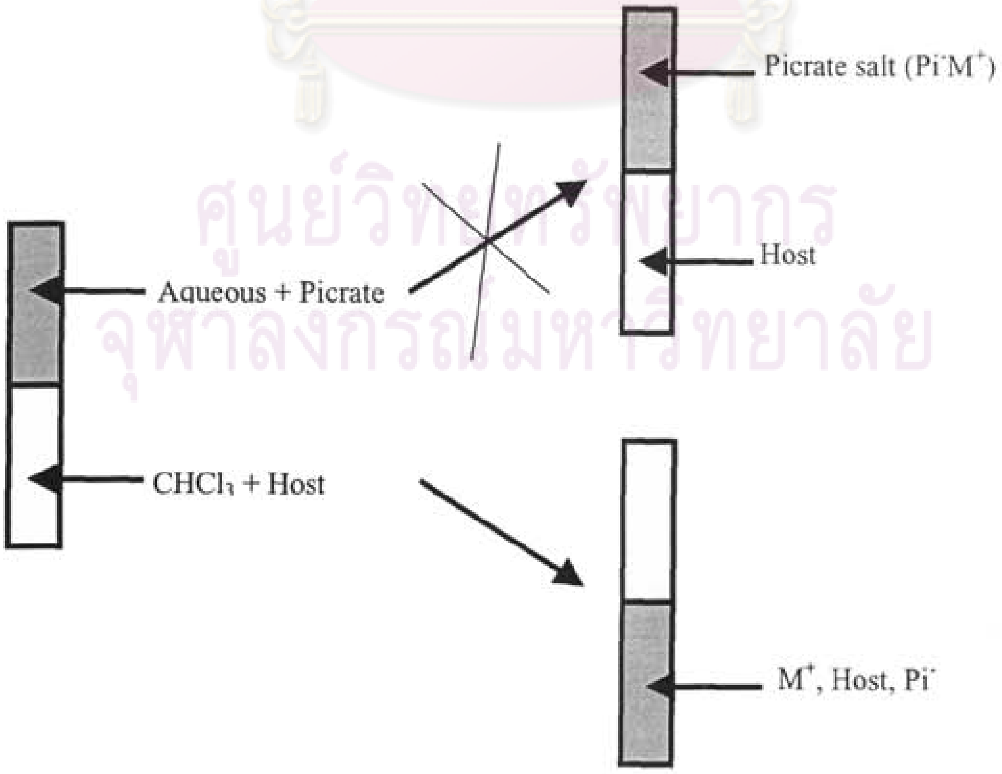
Preparation of Silica Coupled with 3-triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine **4**, 3-triethoxysilyl-n-propyl-3,4-dihydro-6-methyl- 2H-1,3-benzoxazine **5** and 3-triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine **6**

3-Triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine (8 mmol, 3 g) was stirred with silica (1 g) and heated to 200°C without solvent for 3 hrs to obtain yellow silica particles. The product was washed thoroughly with chloroform to exclude the unreacted silylbenzoxazine and THF to eliminate the physisorbed silane on silica, followed by drying in vacuo at room temperature for 3 hrs to obtain a light yellow powder. Similarly, **5** and **6** were prepared as the procedure of **4**.

4. Ion Extraction Studies

Ion extraction property was studied using Pedersen's technique (Scheme III) for all silylbenzoxazines, **1-3**. Chloride salts of lithium, sodium, potassium, magnesium, calcium, and barium ions are used as metal ions. 7×10^{-5}M of picric acid and 0.1M of ion salts were dissolved in deionized water so that the UV absorbance at 354 nm becomes one absorbance unit. Benzoxazine solution was prepared by dissolving each monomer, **1-3**, in chloroform to obtain concentrations of 7×10^{-3}M, 7×10^{-2} M, and 7×10^{-1}M.

Scheme III Pedersen's technique applying for evaluation of ion extraction properties.



Ion extraction was studied as follows; 5 mL of aqueous alkali or alkaline earth picrate salt solution and 5 mL of benzoxazine solution were mixed vigorously for 1 minute. The mixture was left at room temperature till the aqueous phase and organic phase were completely separated. The aqueous phase was taken to determine the metal ion concentration by atomic absorption to quantify the amount of the picrate ion.

The concentration of silylbenzoxazine in chloroform phase was varied to clarify the capability of benzoxazine as a host compound for ion extraction.

CHAPTER 3

Results and Discussion

In order to obtain silica surface modified benzoxazine, amino silane is considered as an effective coupling agent because amino group is required in the preparation of benzoxazine while siloxane bonds are necessary for coupling onto silica surface.

1. Characterization of Silylbenzoxazine Derivatives

Phenol, *p*-cresol and 2,4-dimethylphenol were used as starting materials and reacted with 3-aminopropyltriethoxysilane to obtain different silylbenzoxazine derivatives. The obtained silylbenzoxazine derivatives can be confirmed by FT-IR as follows. Theoretically, the asymmetric Si-O-C stretching modes of the ethoxy group appear at 1104 cm^{-1} and 1080 cm^{-1}. The ethoxy group shows two strong bands at 1168 cm^{-1} and 958 cm^{-1}.

It is important to pay caution that aminosilane can be readily hydrolyzed by water. In this method, the water produced during the synthesis will be separated from the product phase by using chloroform as a solvent. Since the benzoxazine monomer is not soluble in water, the alkoxy groups of the silane will remain unhydrolyzed. Thus, there are no bands related to the siloxane mode in the region between 1130 cm^{-1} and 1000 cm^{-1} in the product. The ^{1}H-NMR spectrum and TLC suggest that the product is not either dimer or oligomer. The products were characterized as follows.

Structural Characterization of 3-triethoxysilyl-n-propyl-3,4- dihydro-2H-1,3 benzoxazine **1**

FT-IR (KBr, cm^{-1}): 2975 (CH_3:stretching), 2928 (CH_2:stretching), 2886 (CH_3:stretching), 1489 (oxazine), 1240-1020 (C-N-C:stretching), 1227 (C-O-C:stretching), 1168, 958 ($-OCH_2CH_3$), 1104, 1080 (Si-O-C: stretching), 956 ($Si-OC_2H_5$)

^{1}H-NMR (in $CDCl_3$, at 25°C, ppm): 0.63 (2H, t, C-4), 1.19 (3H, t, C-6), 1.65(2H, m, C-3), 2.73 (2H, t, C-2), 3.77 (2H, q, C-5), 3.95 (2H, s, C-7), 4.83 (1H, s, C-1), 6.76 (1H, d, C-9), 6.90 (1H, d, C-10), 7.04 (1H, d, C-8), 7.08 (1H, d, C-11)

TLC: R_f (5%MeOH : $CHCl_3$) = 0.8

Yield = 89.7%

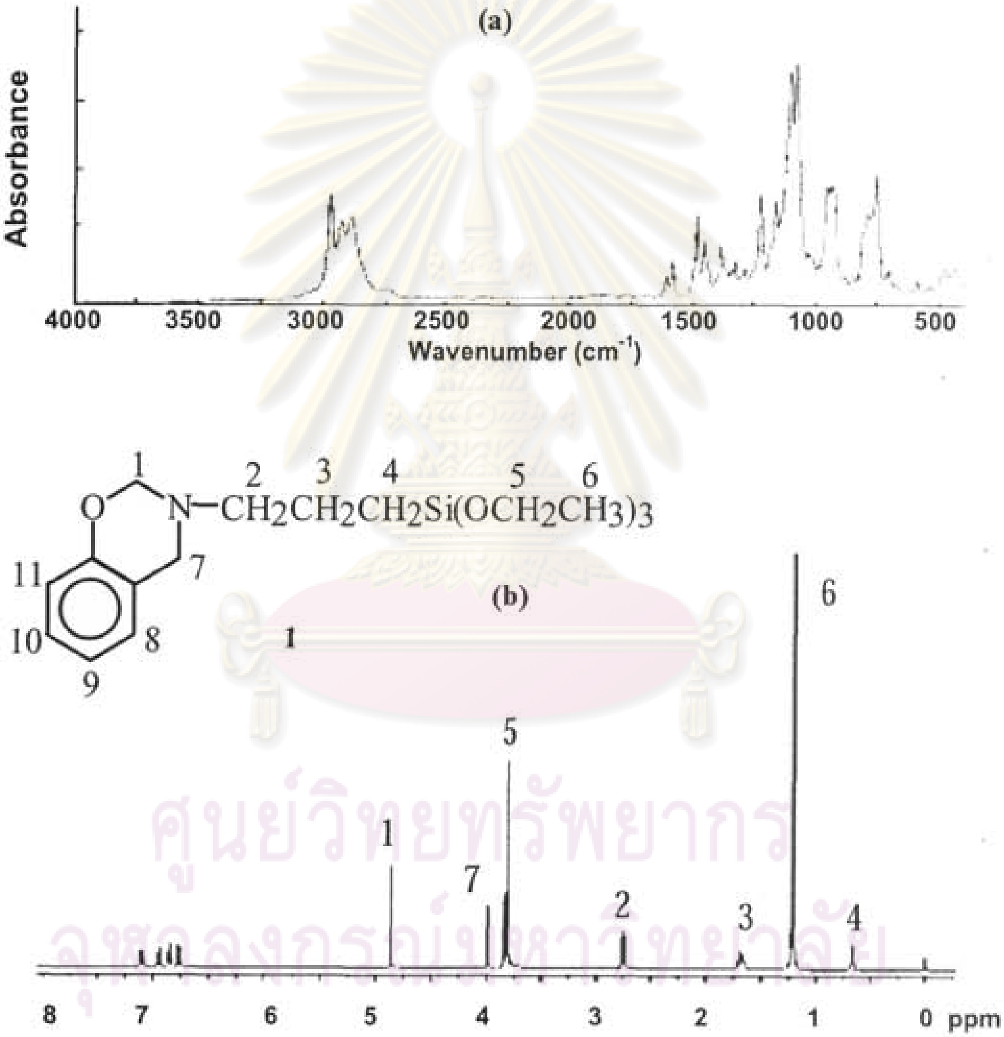


Figure 3. FT-IR (a) and ^{1}H-NMR (b) of **1**.

Structural Characterization of 3-triethoxysilyl-n-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine **2**

FT-IR (KBr, cm^{-1}): 2975 (CH_3:stretching), 2928 (CH_2:stretching), 2886 (CH_3:stretching), 1502 (oxazine), 1240-1020 (C-N-C:stretching), 1228 (C-O-C:stretching), 1168, 958 ($-OCH_2CH_3$), 1104, 1080 (Si-O-C:stretching), 956 ($Si-OC_2H_5$), 820, 855 (1,2,4 substituted)

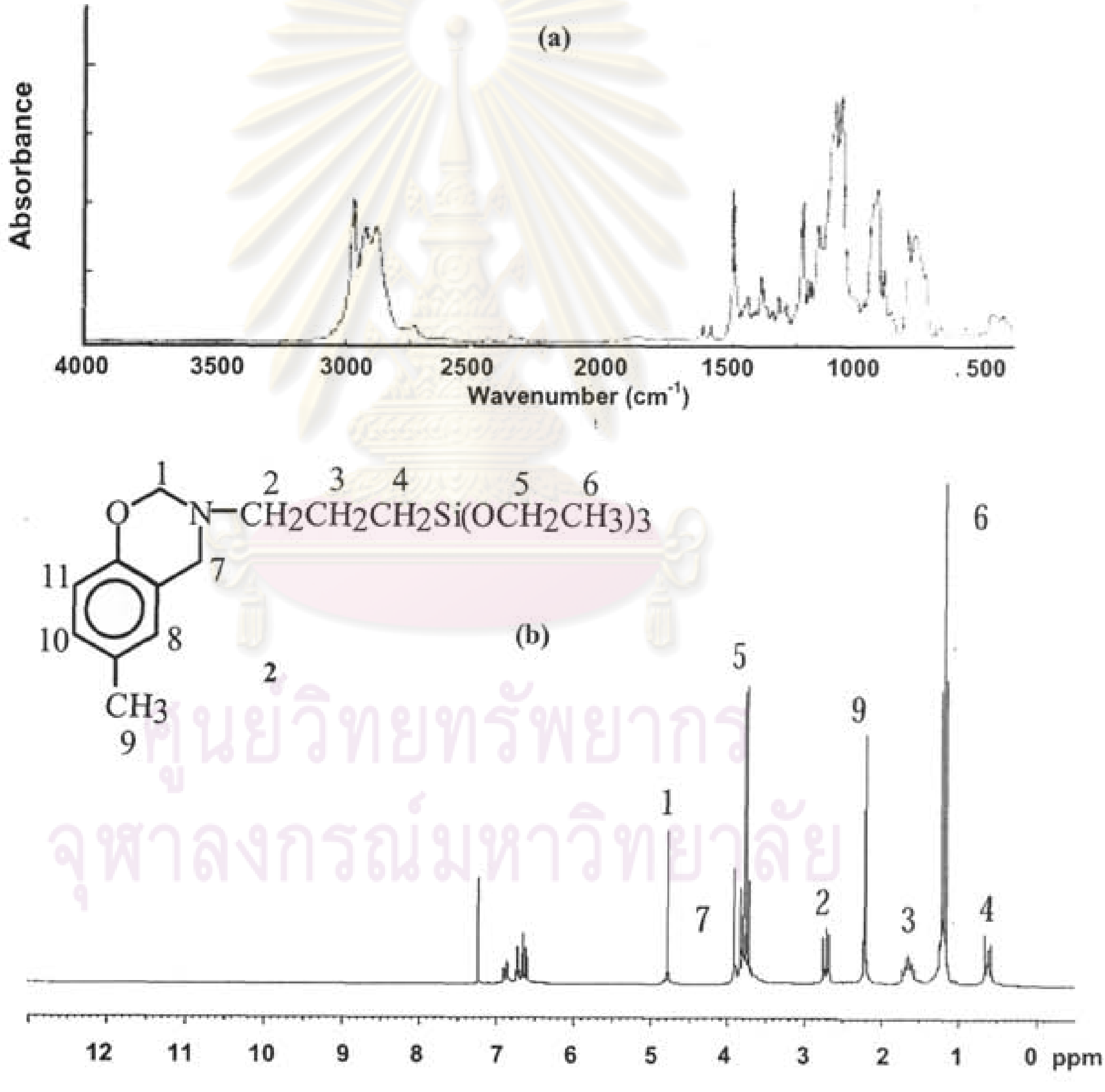


Figure 4. FT-IR (a) and ^1H-NMR (b) of **2**.

^{1}H-NMR (in $CDCl_3$, at 25°C, ppm): 0.65 (2H, t, C-4), 1.21 (3H, t, C-6), 1.67(2H, m, C-3), 2.22 (3H, s, C-9), 2.73 (2H, t, C-2), 3.82 (2H, q, C-5), 3.93 (2H, s, C-7), 4.82 (1H, s, C-1), 6.66 (1H, d, C-10), 6.79 (1H, s, C-8), 6.91 (1H, d, C-11)

TLC: R_f (5%MeOH : $CHCl_3$) = 0.9

Yield = 87.6%

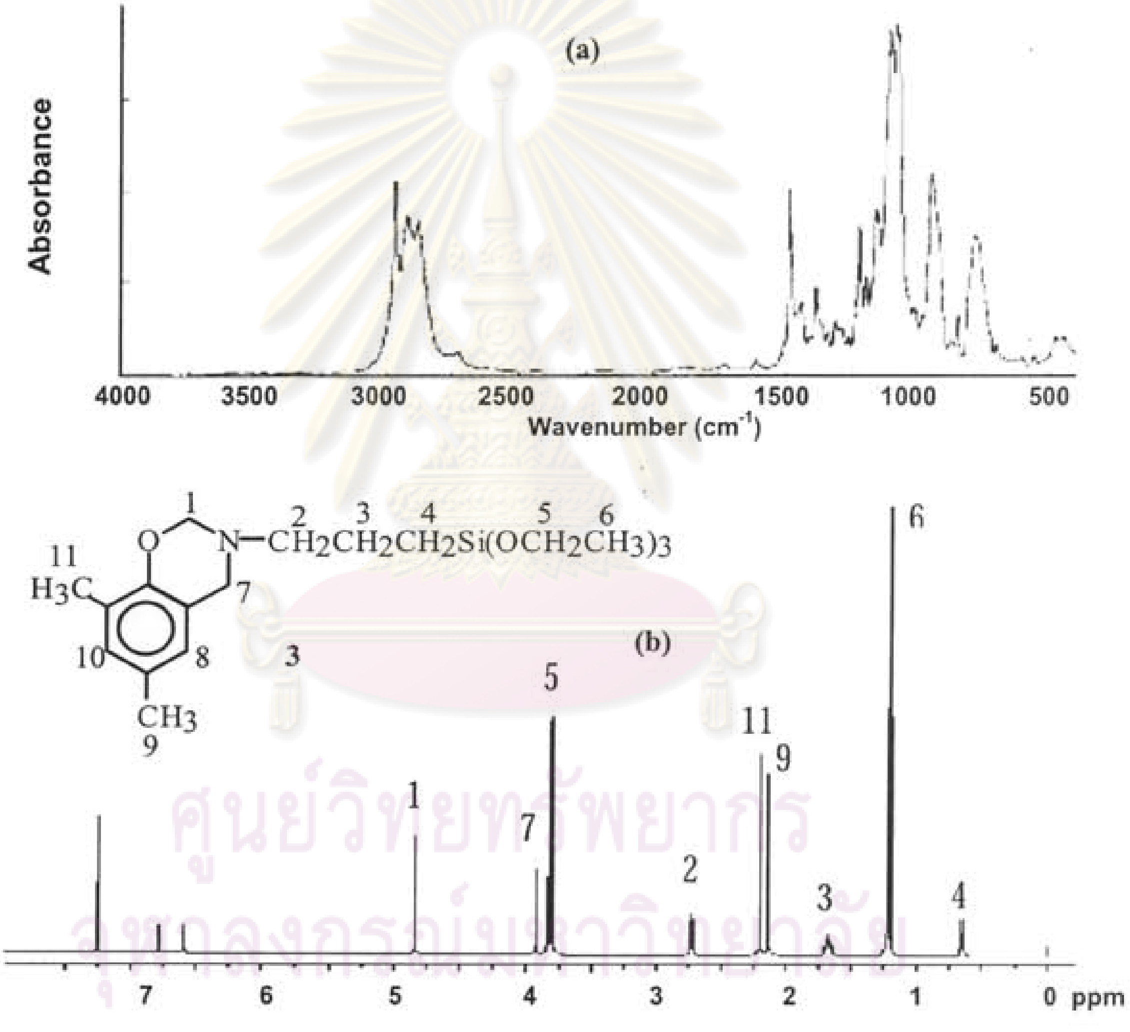


Figure 5. FT-IR (a) and ^{1}H-NMR (b) of 3.

Structural Characterization of 3-triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine 3

FT-IR (KBr, cm^{-1}): 2975 (CH_3:stretching), 2928 (CH_2:stretching), 2886 (CH_3:stretching), 1486 (oxazine), 1240-1020 (C-N-C:stretching), 1228 (C-O-C:stretching), 1168, 958 ($-OCH_2CH_3$), 1104, 1080 (Si-O-C: stretching), 956 ($Si-OC_2H_5$), 868 (1,2,3,5 substituted)

^{1}H-NMR (in $CDCl_3$, at 25°C, ppm): 0.65 (2H, t, C-4), 1.21 (3H, t, C-6), 1.67 (2H, m, C-3), 2.22 (3H, s, C-9), 2.27 (1H, dd, C-11), 2.73 (2H, t, C-2), 3.82 (2H, q, C-5), 3.93 (2H, s, C-7), 4.82 (1H, s, C-1), 6.58 (1H, d, C-10), 6.79 (1H, s, C-8)

TLC: R_f (5%MeOH : $CHCl_3$) = 0.95

Yield = 85.8%

2. Characterization of Benzoxazine Monomer Coupling with Silica

For the adsorption of the silane coupling agent on silica surfaces, any organotrialkoxysilane may condense with one, two, or three silanol groups, to form one, two, or three surface bonds. Usually, silica is added to the aqueous solution of the silane coupling agent to obtain the modified silica. In this work, silylbenzoxazine monomer which has silanol functional group reacts with the silica surface in the solvent free system to avoid the impurities and moisture.

Structural Characterization of Silica Coupled with 3-triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine 4

FT-IR (KBr, cm^{-1}): 2975 (CH_3:stretching), 2928 (CH_2:stretching), 2886 (CH_3:stretching), 1489 (oxazine), 1228 (C-O-C:stretching), 1130-1000 (Si-O-C:stretching).

Anal. calcd. (assuming all alkoxy groups are hydrolyzed and all the silanol groups are coupled with the silica surface): C, 38.94%; H, 4.13%; N, 4.13%.

Found: C, 37.24%; H, 4.41%; N, 4.44%.

Structural Characterization of Silica Coupled with 3-triethoxysilyl-n-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine(5)

FT-IR (KBr, cm^{-1}): 2975 (CH$_3$:stretching), 2928 (CH$_2$:stretching), 2886 (CH$_3$:stretching), 1503 (oxazine), 1228 (C-O-C:stretching), 1130-1000 (Si-O-C:stretching).

Anal. calcd. (assuming all alkoxy groups are hydrolyzed and all the silanol groups are coupled with the silica surface): C, 40.79%; H, 4.53%; N, 3.97%.

Found: C, 37.52%; H, 5.18%; N, 4.98%.

Structural Characterization of Silica Coupled with 3- triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine(6)

FT-IR (KBr, cm^{-1}): 2975 (CH$_3$:stretching), 2928 (CH$_2$:stretching), 2886 (CH$_3$:stretching). 1490 (oxazine), 1228 (C-O-C:stretching), 1130-1000 (Si-O-C:stretching).

Anal. calcd. (assuming all alkoxy groups are hydrolyzed and all the silanol groups are coupled with the silica surface): C, 42.51%; H, 4.9%; N, 3.81%.

Found: C, 38.42%; H, 4.07%; N, 3.86%.

As shown in Figure 6, spectral subtraction of silica reduces the contribution of the silica and emphasizes the spectral feature of the surface species. Here, the benzoxazine bands at 1504, 1491, and 1489 cm^{-1} are found, indicating that the coupling procedure with benzoxazine ring is successful. The spectra show that the bands due to ethoxy group, i.e., 2975, 2928, 1390, and 956 cm^{-1} disappear or decrease in intensity, whereas the bands near 1050 and 770 cm^{-1} appear due to the formation of Si-O-Si linkages. These indicate that the silylbenzoxazine derivatives are coupled onto the silica surface. Thus, the amino silane coupling agent used as an amine in the benzoxazine preparation provides the possibility to be used as a silylbenzoxazine for modifying silica surface.

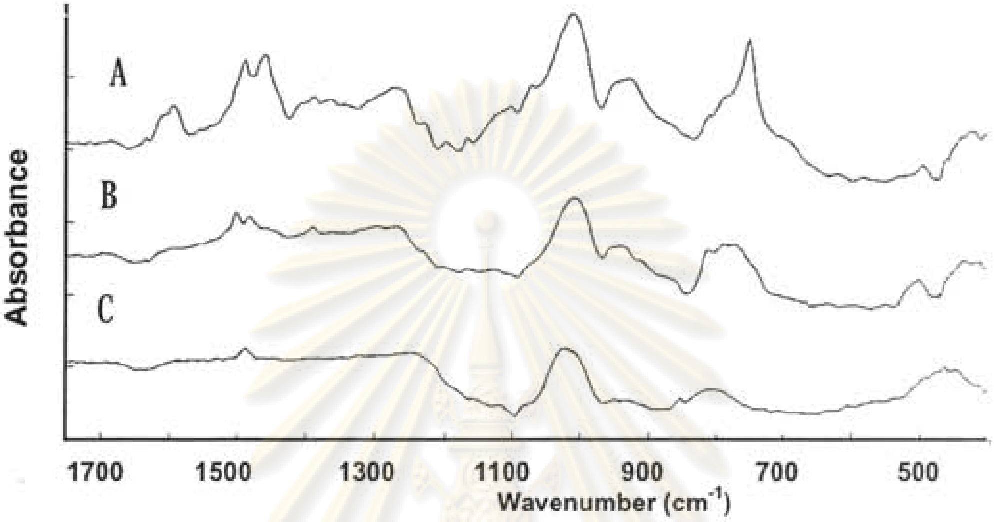


Figure 6. FT-IR spectra of, A) 3-triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine **1**, B) 3-triethoxysilyl-n-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine **2**, and C) 3-triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine **3** on the silica surface with the contribution of the silica exclusion.

On the assumption of all triethoxysilanes coupling onto silica surface at a monolayer coverage, the carbon content (%C) can be calculated to be 38.5-42.5% for the three surface-treated silica, **4-6**. Based on the elemental analysis results, it is found that the carbon percentage is slightly deviate from the calculation data in each product. This indicates that almost all ethoxysilanes are successfully coupled onto silica and, further, the majority of the ethoxy groups are hydrolyzed.

3. Ion Extraction Studies

Pedersen's technique is applied to study the ion extraction property in liquid/liquid system. As shown in Scheme III, normally, picric acid can form picrate salt with metal ions in aqueous phase due to its very large acidity constant. The picrate salt will be presented in aqueous phase and gives the yellow color to the phase while the organic phase is colorless. If the benzoxazine provides a structure as a host molecule and acts as an ionophore, when benzoxazine is added to the system, the picrate salt will be shifted to the organic phase as soon as the host-guest compound is formed. Thus, ion extraction can be investigated by determining the changing of picrate concentration in aqueous phase either using UV-Vis spectrophotometry at the absorption wavelength of the picrate or atomic absorption at the emission spectroscopy of metal picrate.

4. Ion Extraction Behavior of Silylbenzoxazine Derivatives

As shown in Figures 7, 8, and 9, when the monomer concentration is increased, the percentage of ion extraction increases for all types of metal ions.

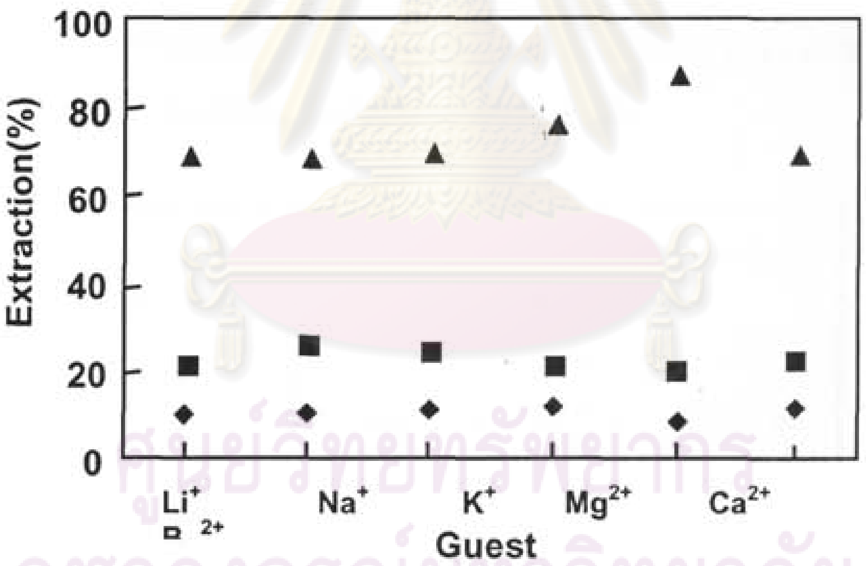


Figure 7. Extraction percentage of metal picrate at $[M^+][Pic^-] = 7\times10^{-5}$M by silylbenzoxazine **1**, when the concentration is varied at ◆) 0.007M, ■) 0.07M, and ▲) 0.7M.

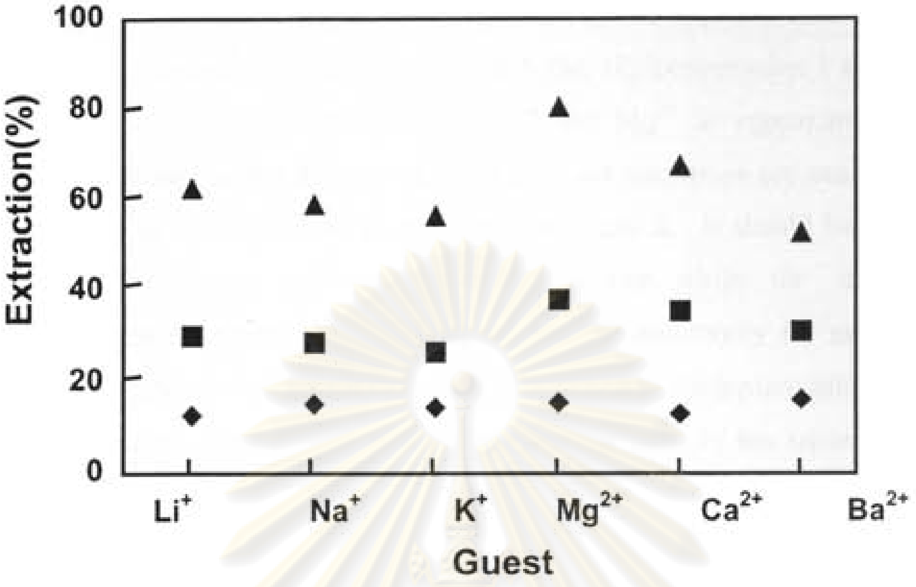


Figure 8. Extraction percentage of metal picrate at $[M^+][Pic^-] = 7x10^{-5}M$ by silylbenzoxazine **2**, when the concentration is varied at ◆) 0.007M, ■) 0.07M, and ▲) 0.7M.

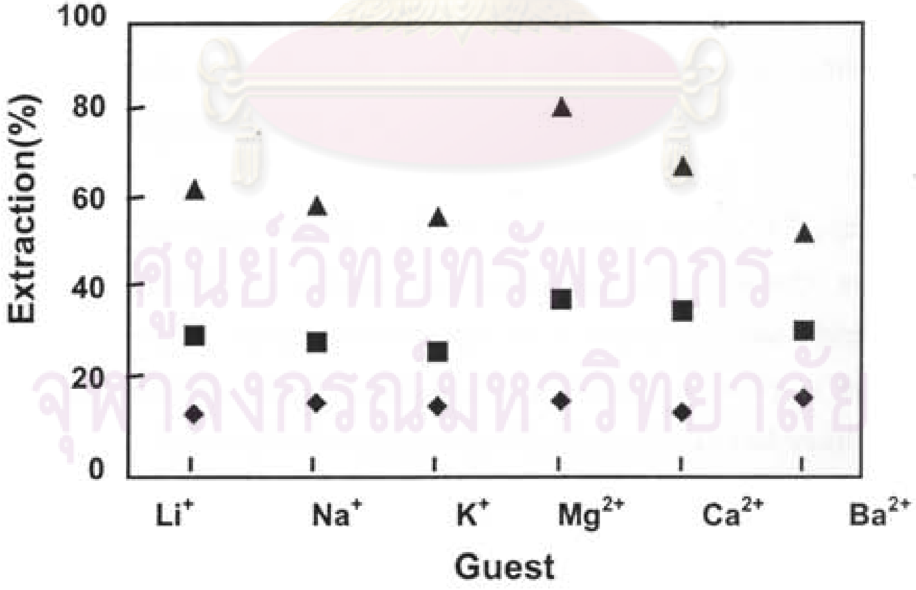


Figure 9. Extraction percentage of metal picrate at $[M^+][Pic^-] = 7x10^{-5}M$ by silylbenzoxazine **3**, when the concentration is varied at ◆) 0.007M, ■) 0.07M, and ▲) 0.7M.

Thus, the ability for ion entrapment of silylbenzoxazine depends on the monomer concentration. Considering each monomer at 0.7M, silylbenzoxazine **1** shows slight selectivity for Ca^{2+} while silylbenzoxazine **2** for Mg^{2+} at approximately 80%. However, silylbenzoxazine **3** does not show high ion extraction percentage and the ion selectivity is not significant as compared to **1** and **2**. It should be noted that silylbenzoxazine shows the ion interaction ability while the structure of silylbenzoxazine monomer unit itself cannot provide any cavity for metal guests. Thus, the ion interaction may be acheived by gathering silylbenzoxazine unit as a host compound to construct the cavity for guest, as seen in the reported case of pseudocyclic calixarene[32].

However, difference in silylbenzoxazine **1-3** is the presence of methyl substituent group and its location on the benzoxazine ring. The difference in ion extraction behavior can be considered as a result of the preferred assembly structure to form a host. In the case of **3**, which has two methyl groups and a long chain alkyl of N-substitution group, the molecular assembly may be difficult to form because of the steric hindrance by the bulky groups. As a result, the ion extraction percentage of **3** is low. In contrast, **1** can form the assembly by the stacking conformation to allow the metal ion entrapping in the cavity.

Although it further requires other analytical studies such as, 2D-NMR, single crystal X-ray crystallography to support the assumption, we tentatively propose the schematic structures. As shown in Figure 10, it is expected that when the bulky group of benzoxazine ring is enhanced, the molecular assembly of benzoxazine becomes loose. As a result, the host guest interaction is weak and metal ion cannot be entrapped efficiently.

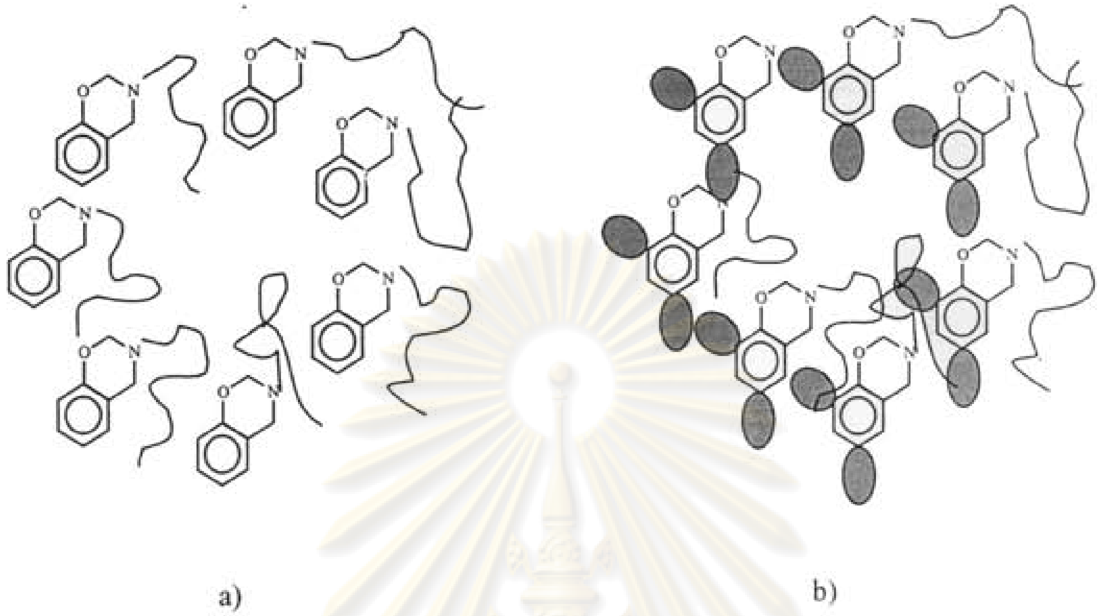


Figure 10. Schematic draws for silylbenzoxazine derivatives, a) compound **1**, and b) compound **3**.

5. Ion Extraction Behavior of the Silylbenzoxazine-modified Silica Surface

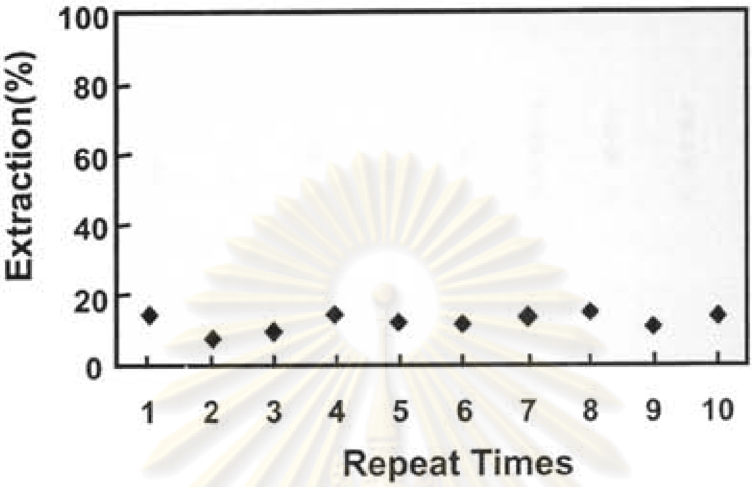


Figure 11. Extraction percentage of metal picrate at $[M^+][Pic^-] = 7x10^{-5}$ M by pure silica.

The ion extraction of pure silica and benzoxazine coupled silica, **4-6**, for alkali and alkaline earth metal ions were determined by atomic absorption spectroscopy. The surface-treated silica was packed in the column and column chromatography was used to study the ion extraction.

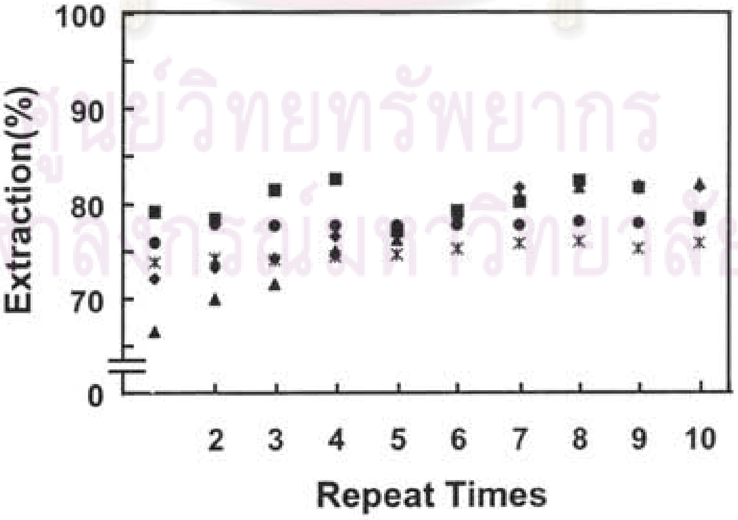


Figure 12. Extraction percentage of metal picrate at $[M^+][Pic^-] = 7x10^{-5}$M by **4** for for Na^+ (●), K^+ (◆), Mg^{2+} (■), Ca^{2+} (▲) and Ba^{2+} (✱).

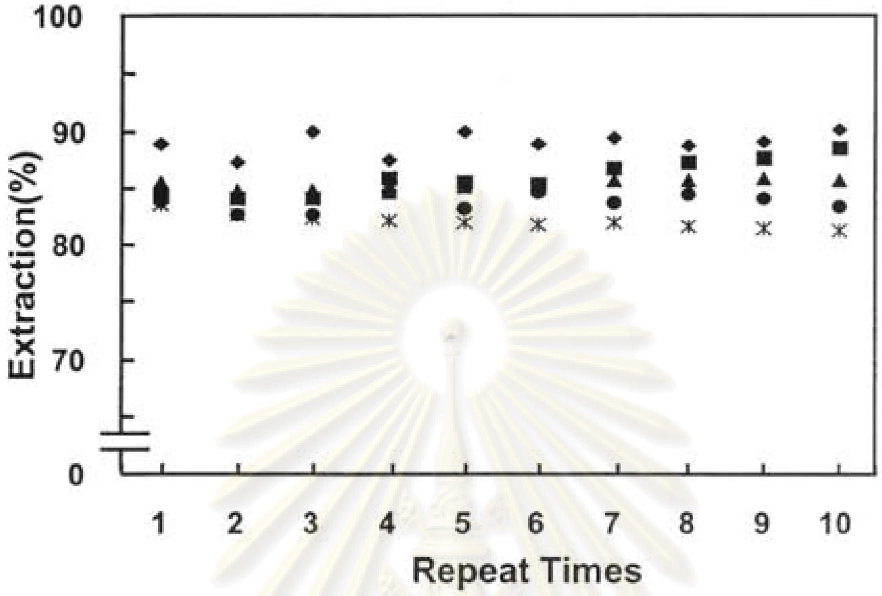


Figure 13. Extraction percentage of metal picrate at $[M^+][Pic^-] = 7x10^{-5}M$ by **5** for Na^+ (●), K^+ (◆), Mg^{2+} (■), Ca^{2+} (▲) and Ba^{2+} (∗).

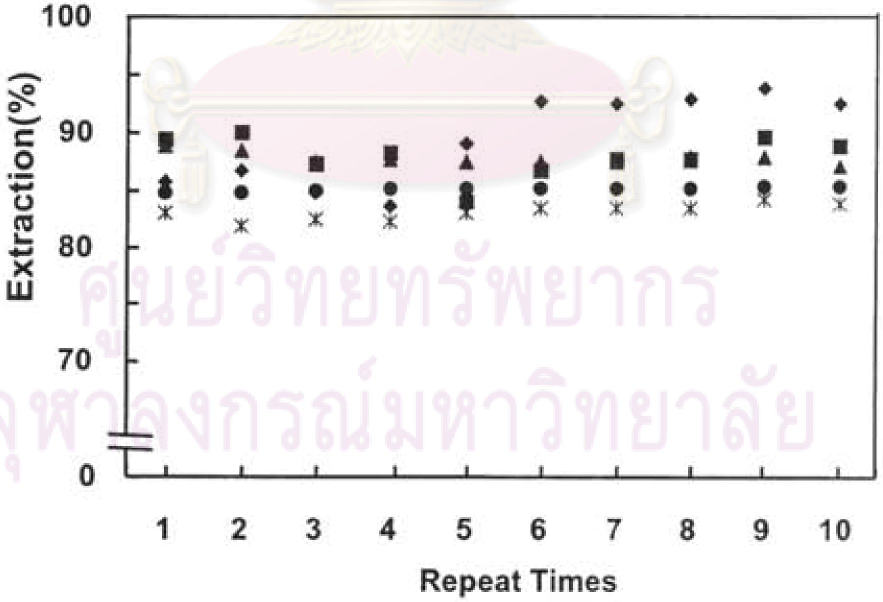
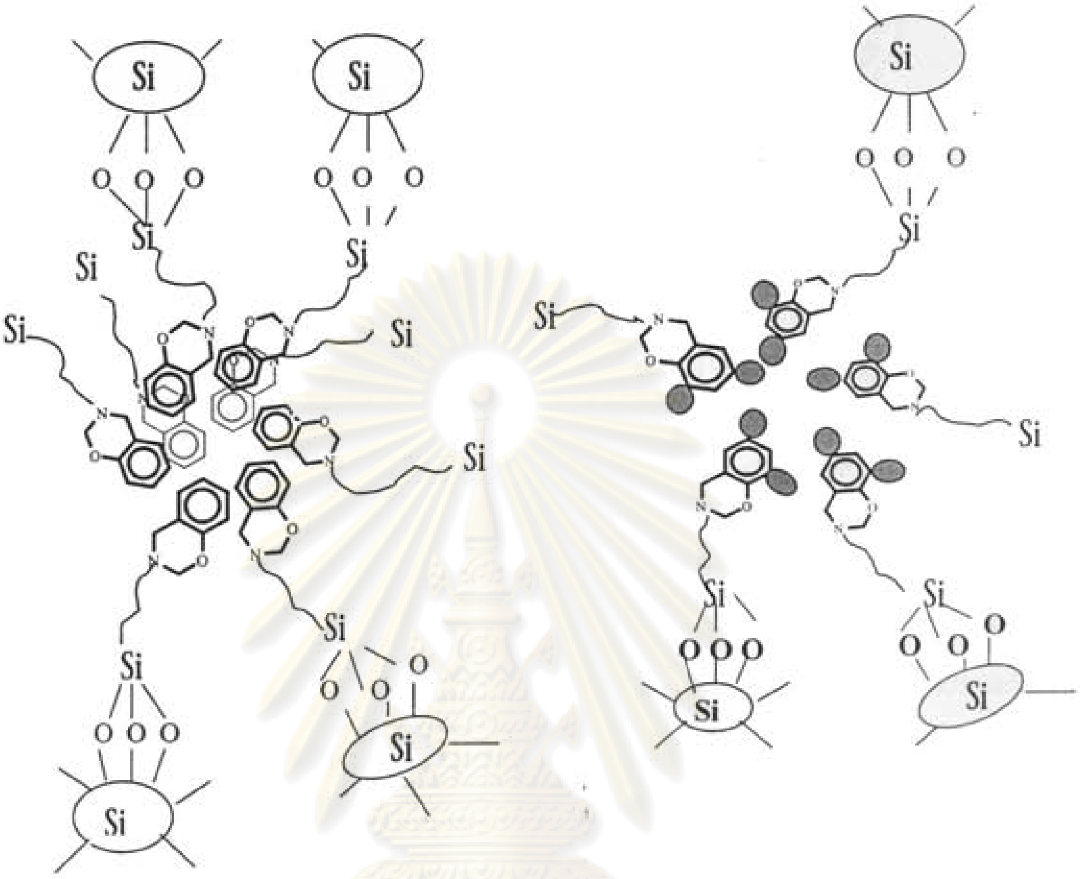


Figure 14. Extraction percentage of metal picrate at $[M^+][Pic^-] = 7x10^{-5}M$ by **6** for for Na^+ (●), K^+ (◆), Mg^{2+} (■), Ca^{2+} (▲) and Ba^{2+} (∗).

Figure 11 shows that, in the case of pure silica, little picrate metal ion is observed even if the silica is used for the adsorption process many times. However, Figures 12-14 show silylbenzoxazine derivatives coupled silica (**4-6**) for 80 to nearly 100 percent of ion extraction. Here, it should be noted that the first to fifth repeating time, the extraction percentage is not stable. This may be due to the effect of the dry surface, which makes the ion interaction in solvent poor. After the adsorption process was repeated more than five times, the constant extraction percentage is obtained. Considering the effect of the silylbenzoxazine structure, the compound **4** with less bulky group shows the ion extraction ability around 65-83% while the compound **5** with one methyl group shows 80-90%. The compound **6** with two methyl groups shows the highest ion extraction percentage at 82-95%.

Unexpectedly, the results are in contrast to that of silylbenzoxazine without silica. In the present case, a propyl group exits as a spacer between silica and benzoxazine to promote the mobility of the benzoxazine group. Phongtamrug *et al.* reported that the monomer with bulky group exhibits high ion extraction percentage. The bulky structure of the benzoxazine on the silica surface packs loosely and provides cavity for the metal guests.

In the present work, in order to explain these behaviors, the proposed structure is shown in Figure 15. The silica surface modified with silylbenzoxazine without bulky group, **4**, the silica surface interaction should be strong owing to the silanol group of silica surface together with the stacking conformation of benzoxazine monomer. This high packing structure induces the less amount of cavity for metal ion guests. As a result, low ion extraction behavior is observed. As a result, the ability of ion extraction of silica surface modified benzoxazine is in the order of **6>5>4**.



a)

b)

Figure 15. Schematic draws for silylbenzoxazine derivatives, a) compound **4**, and b) compound **6**.

CHAPTER 4

Conclusions

Application of aminoalkoxysilane as an alkylamine in the preparation of benzoxazine compound proved to be a successful key to prepare silylbenzoxazine precursor. In the present work, three types of silylbenzoxazines with different benzene ring were synthesized successfully as characterized by ^{1}H-NMR, FT-IR. Although the main purpose of the project is to explore the ion extraction ability of silica surface modified benzoxazines, it is an important issue to study whether silylbenzoxazines shows the metal ion interaction property of silylbenzoxazines before coupling onto the silica surface. At present, we found that silylbenzoxazines shows ion interaction ability as quantitative analysis by UV and AA instrumentation. The results from both analysis methods suggested that silylbenzoxazine derivatives interact with metal ion under the condition of host concentration and the structures of silylbenzoxazine itself. The higher the concentration, the more ion extraction ability was found. The less bulky benzene ring gives higher ion extraction percentage as compared to the high bulky one.

CHAPTER 5

Future Aspects and Work Extended

The present work clarifies that silyl benzoxazine monomer can be successfully coupled onto silica. The benzoxazine monomer functions as a host to entrap various metal ions. However, the interaction between benzoxazine monomer and metal ion is operated under individual benzoxazine molecule, thus, to enhance the guest entrapment, we proposed the oligo-silylbenzoxazine coupled silica. The work should challenge from the studies on the preparation of oligobenzoxazine linked with silane functional group followed by coupling reaction onto silica surface. The various designs of oligobenzoxazine molecules should bring a novel type of ion extraction resin with high selectivity as well as high sensivity.

Those strategies have been considered starting from studying the synthesis of controlled structure oligobenzoxazines. However, the reaction conditions are more complicated than expected. There we found two important phenomena related to the unique reaction of benzoxazines. Oligobenzoxazines cannot be polymerized as theoretical propose by Ishida et al. but it gives a self-terminated reaction to be dimer (in preparation). Moreover, when using dimer for another step of oligomerization, the dimer gives an incomplete reaction to be an asymmetric structure, so called monooxazine (Laobuthee, A., Chirachanchai, S., Ishida, H., and Tashiro, K., Asymmetric Mono-oxazine: An Inevitable Product from Mannich Reaction of Benzoxazine Dimers, *J. Am. Chem. Soc.*, in press).

The two phenomena were discovered when we extended the present work to coupling oligomer onto silica surface. The analytical results (NMR, 2D-NMR, FT-IR) implied that we obtained monooxazine dimer coupling onto silica rather than simple dimer or trimer. At present, we are focusing on those reactions and potential application based on the silylmonooxazine benzoxazine dimers we obtained.

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Presentation in Conferences, The Abstracts

1. International Conference on Composite Interfaces, Case Western Reserve University, Cleveland, Ohio, USA, October 11-14, 2000.
2. Second International Conference on Silica, Silica 2001, Mulhouse, France, September 3-6, 2001.

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General Information

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On-Site Registration - Wine & Cheese Reception
Wyndham Cleveland Hotel
4:00pm

Silica Surface Modified with Benzoxazine-functional Silane

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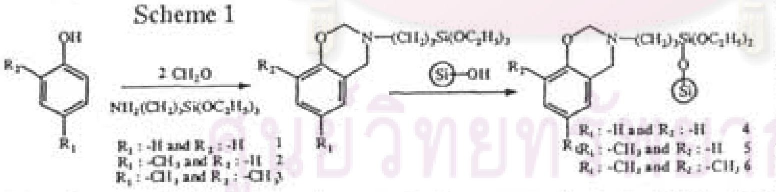
Introduction

Ion separation process by using ion exchange resin has been one of the most practical purification methods. Conventionally, ion exchange resin can be obtained by incorporating active functional groups, such as sulfonic, carboxylic, and phenolic or amino group, etc., which provide the site for the ionic specific interaction property with metal ion, into polymer structure. Inclusion compounds have received much attention owing to its specific properties induced from host and guest species. An understanding of supramolecular structures at the molecular level contributes the theory of molecular recognition which is considered to be an extended area of separation process, as seen in the cases of calixarenes and crown ether. Recently, we focused on the molecular design of benzoxazine based on the resemble structure to calixarenes and demonstrated the potential ion recognition property for various types of metal ions[1]. The present work concerns on the practical applications of benzoxazine derivatives as an ion extraction material. The uniqueness of the study is the preparation of benzoxazine-functional silane and coupling onto high surface area silica to obtain benzoxazine-functional silica powder. The study is extended to the ion extraction ability.

Experimental

A series of silylbenzoxazine monomers with different bulky groups at ortho and para positions on the oxazine ring are prepared from phenol derivatives and 3-aminopropyltriethoxysilane. The coupling reaction of silylbenzoxazine onto silica was achieved by heating to 200°C without solvent for 3 h (Scheme 1). The product was washed throughly with chloroform and THF. The characterizations were done by FTIR, NMR, and EA. Ion extraction property was studied by Pedersen's technique. Chloride salts of lithium, sodium, potassium, magnesium, calcium, and barium ions are used as metal ions. 7×10^{-5}M of picric acid and 0.1M of ion salts were dissolved in deionized water. Six mL of picrate ion solution was shaken with 5 g of each silica-silylbenzoxazine, for 3 minutes in a column at room temperature. The solution was drained and the procedure was repeated 10 times with fresh picrate ion solution. Ion extraction was evaluated by the change of picrate concentration in the aqueous phase observed by UV/Vis and AA.

Scheme 1



Results and Discussions

Figure 1 shows the FTIR spectra of various benzoxazine-functional silanes. The asymmetric Si-O-C stretching modes of the ethoxy group appear at 1104 and 1080 cm^{-1}.

The ethoxy group shows two strong bands at 1168 cm^{-1} and 958 cm^{-1}. Spectral subtraction reduces the contribution of the silica and emphasizes the spectral feature of the surface species. Here, the benzoxazine bands at 1504, 1491, and 1489 cm^{-1} were found, indicating that the coupling procedure with benzoxazine ring was successful. The subtracted spectra between the silylbenzoxazine derivatives treated silica were identified. The difference spectrum showed that the bands due to ethoxy group, i.e., 2975, 2928, 1390, and 956 cm^{-1} disappear or decrease in intensity, whereas the bands near 1050 and 770 cm^{-1} appear due to the formation of Si-O-Si linkages. These indicated that the silylbenzoxazine derivatives were coupled onto the silica surface.

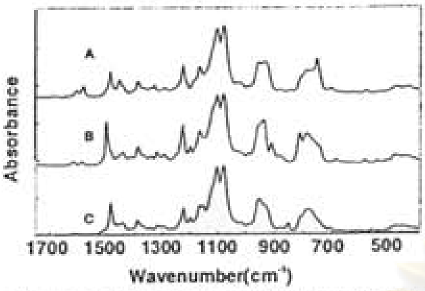


Figure 1. FTIR spectra of, A) 3-triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine **1**, B) 3-triethoxysilyl-n-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine **2**, and C) 3- triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine **3**.

In the case of ion extraction study of pure silica, little amount of picrate metal ion is observed even if the silica is used for the adsorption process many times. However, silylbenzoxazine derivatives coupled silica show 80 to nearly 100 percent of ion extraction. At the first to fifth repeating time, the extraction percentage is not stable. This may be due to the effect of the dry surface, which makes the poor ion interaction. After the adsorption process was repeated more than five times, the constant extraction percentage is obtained. Considering the effect of the silylbenzoxazine structure, the compound **4** with less bulky group shows the ion extraction ability around 65-83% (Figure 2) while the compound **5** with one methyl group shows 80-90%. The compound **6** with two methyl groups shows the highest ion extraction percentage at 82-95%.

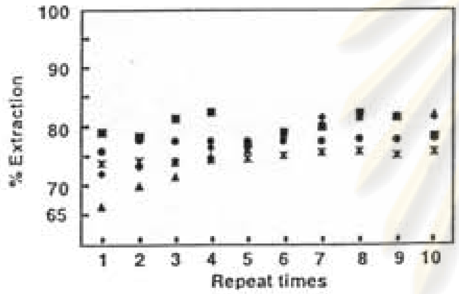


Figure 2. Extraction percentage of metal picrate (7x10^{-5} M) by 4 for Na$^+$(◆), K$^+$(■), Mg^{2+}(▲), Ca^{2+}(●), and Ba^{2+}(✻).

Conclusions

Silica surface modified benzoxazines were successfully achieved via silylbenzoxazine derivatives and showed the ion extraction property for various alkali and alkaline earth metal ions. The silica surface modified with benzoxazine derivatives with bulky groups exhibited high ion extraction percentage which might be due to the loose packing structure of the molecular assembly inducing the high amount of cavity for guest.

Acknowledgements

The present work was supported by Ratchadapisaeksomphot Endownment, Chulalongkorn University in the year of 1999 and the Hitachi Scholarship Foundation.

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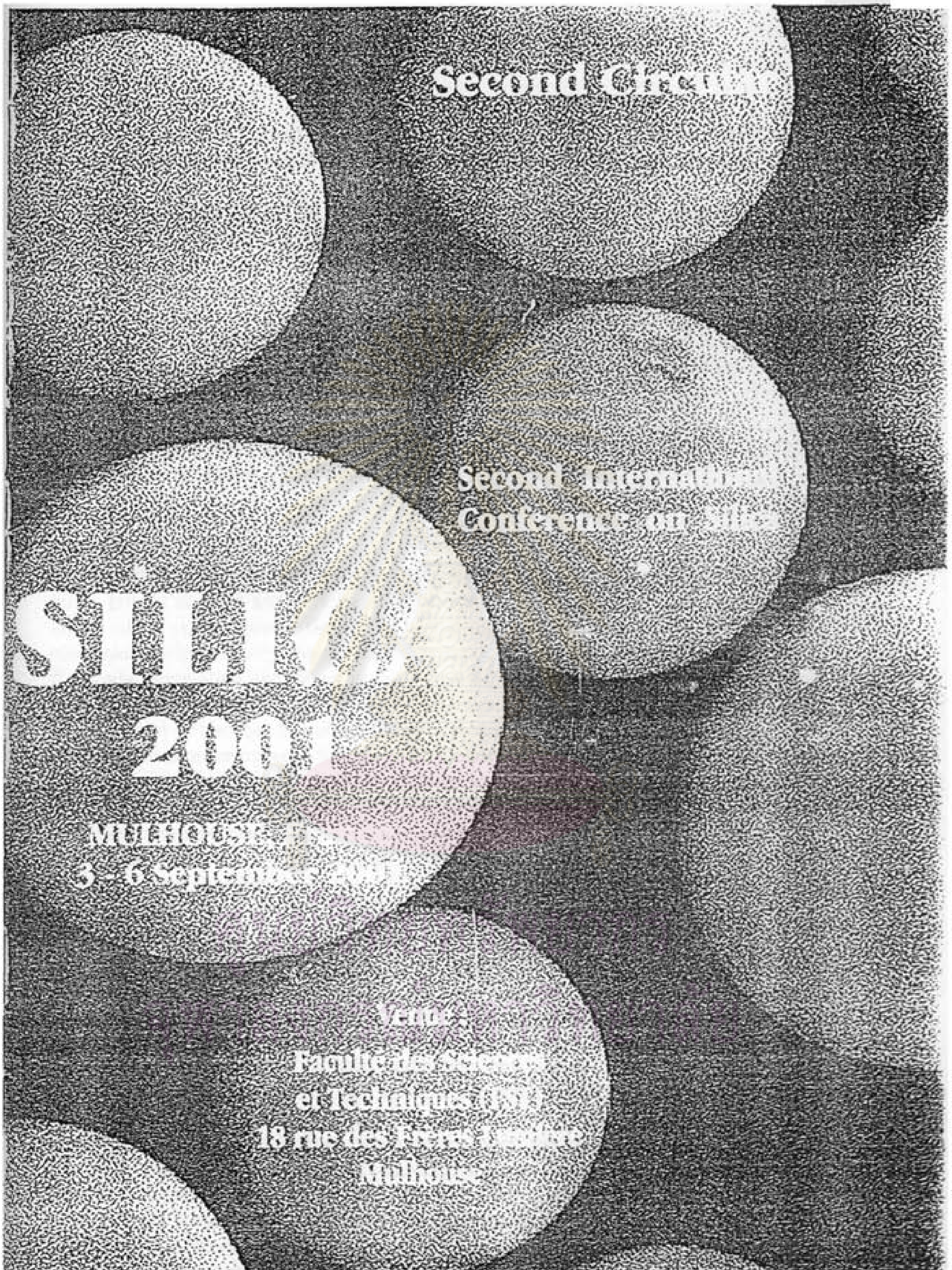

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A NOVEL ION EXTRACTION MATERIAL DERIVED FROM BENZOXAZINE MONOMER AND DIMER COUPLING ONTO SILICA SURFACE

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Keywords: Benzoxazine-functional Silane, Ion Extraction Material, Silica Surface, Silane Coupling Agents, Picrate Salts

ABSTRACT

Silica surface modified with silylbenzoxazine monomers and dimers having different bulky groups at ortho and para positions on the oxazine ring are synthesized by using amino silane as an amine in the step of benzoxazine preparation. FT-IR, ^{1}H-NMR and elemental analysis clarify the successful benzoxazine-functional silane precursors and the products coupling onto silica surface. The ion extraction studies of various picrate metal ions are carried out by Pedersen's technique via column chromatography. The metal picrate extraction by fumed silica is around 15%, while by surface modified benzoxazine monomers are 75-90%. The monomers with disubstituted at ortho and para position on phenol ring give significant ion extraction ability. In the case of benzoxazine dimer, the coupling reaction is proceeded via a unique asymmetric-structured monooxazine pathway as confirmed from the 2D-^{1}H-NMR and FTIR. The percent ion extraction by benzoxazine dimer in basic condition is higher than that in acid and neutral conditions.

INTRODUCTION

Separations of chemical species and extractions of metal ions are important for industries and global environment. In the past decades, ion separation by using ion exchange resin has been one of the most practical purification methods. Conventionally, ion exchange resin can be synthesized by incorporating active functional groups, such as sulfonic, carboxylic, and phenolic or amino group, etc., which provide the site for the ionic specific interaction property with metal ion into polymer structure. However, traditional ion exchange resin[1] has reached its own limit for the sensitivity and selectivity when dealing with the separation of ion mixtures. Recent understanding of host-guest compound at the molecular level contributes to the theory of molecular recognition. Host-guest compound is, thus, considered to be an extended area for separation processes, including ion separation, as seen in the cases of calixarenes and crown ethers[2].

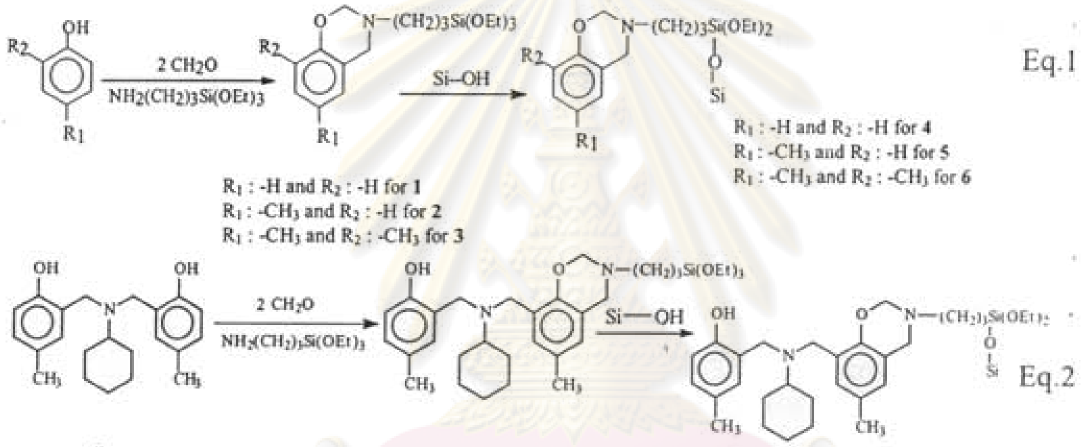
Recently, our group has proposed the structure of oligobenzoxazine to be one of the inclusion compounds[3] according to its repeating unit, which resembles to that of calixarenes. The property of benzoxazine as a host compound was clarified for the ion interaction ability with alkali and alkaline earth metals.

The present work, thus, aims to study on the application of benzoxazine by functionalizing silica surface with benzoxazine monomer and dimer. The target of this work is also to clarify the ion interaction ability in order to establish a novel ion extraction resin.

EXPERIMENTAL

Preparation of Silica coupled with 3-triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine **4**, 3-triethoxysilyl-n-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine **5** and 3-triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine **6**

The general method of silylbenzoxazine synthesis is shown in Scheme I (Eq. 1). The precursors for **4, 5** and **6** were prepared as reported by Chirachanchai et al[4]. Compound **4** (8 mmol, 3 g) was mixed with silica (1 g) and stirred at 200°C without solvent for 3 hrs to obtain yellow silica particles. The product was washed thoroughly with chloroform and THF, followed by drying in vacuo at room temperature for 3 hrs to obtain a light yellow powder. Similarly, **5** and **6** were prepared as **4**.



7 **8** **9**

Preparation of N,N-bis(5-methyl-2-hydroxybenzyl) cyclohexylamine **7**, 3,4-dihydro-3-triethoxysilyl-n-propyl-6-methyl-8-[(2'-hydroxy-5'-methylbenzyl)cyclohexylaminomethyl]-2H-1,3-benzoxazine **8**, Silica coupled with 3,4-dihydro-3-triethoxysilyl-n-propyl-6-methyl-8-[(2'-hydroxy-5'-methylbenzyl) cyclohexylaminomethyl]-2H-1,3-benzoxazine **9**

Compound **7** was prepared according to Laobuthee *et al* [5] and used as a precursor to prepare the compound **8** (Scheme I, Eq.2). Paraformaldehyde 0.60g (20 mmol) in $CHCl_3$ 5 mL was mixed with 3-aminopropyltriethoxysilane 2.22 g (10 mmol) and stirred for 10 minutes at 40°C, followed by adding **7** (3.39 g in 20 mL $CHCl_3$). The reaction was refluxed continuously for 6 h. The solvent was removed and the crude product was purified by a column packed with silica gel using mobile phase $CHCl_3$: CH_3OH (19:1, v / v) to obtain the yellowish viscous product **8**. Compound **8**, 4.5 g (7.7 mmol) was mixed with 1 g fumed silica in 5 mL of xylene. The mixture was refluxed under N_2 for overnight to obtain yellowish silica. The product obtained was washed thoroughly by xylene, ethanol, THF, and ether, followed by drying under reduced pressure at 40°C for

2h to obtain **9**.

Ion Extraction Studies

The ion extractions of compounds **4-6** were determined by using picrate salts of lithium, sodium, potassium, magnesium, calcium, and barium at the concentration of 7×10^{-5}M. Six mL of picrate solution was shaken with 5 g of each **4**, **5** and **6** for 3 minutes in a column at room temperature. Ion extraction percentage was evaluated by the change of picrate concentration in the aqueous phase using atomic absorption spectrophotometry. The procedure was repeated for 10 times. In the case of compound **9**, zinc, cadmium, manganese, and lead were used as metal ions at the concentration of 1×10^{-4} M in various buffer solutions. The buffers used were pH 3.4 (formic acid / sodium formate buffer), pH 4.6 and 5.1 (acetic acid /sodium acetate buffer), pH 7.01 and 8.1 (KH_2PO_4 /K_2HPO_4 buffer), pH 9.0, 10.0, and 10.9 (ammonium hydroxide /ammonium chloride buffer). Twelve mL of buffer ion solution was mixed with 0.05 g of **9**. After shaking for a minute at room temperature, the aqueous phase was taken to determine the ion concentration by atomic absorption spectrophotometry.

RESULTS AND DISCUSSIONS

FTIR results of the products **4-6** showed the asymmetric Si-O-C stretching modes of the ethoxy group appear at 1104 and 1080 cm^{-1}. The ethoxy group was confirmed from two strong bands at 1168 and 958 cm^{-1}. By using the subtraction technique, the benzoxazine bands were confirmed at 1504, 1491, and 1489 cm^{-1} indicating the successful coupling reaction.

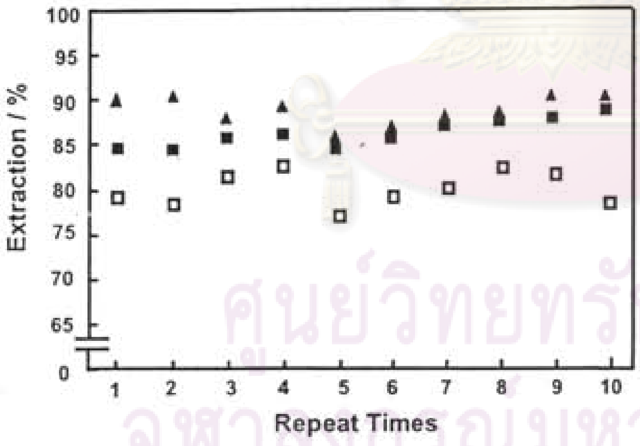


Fig. 1. Extraction percentage of Mg^{2+} by **4** (□), **5** (■), and **6** (▲).

The ion extractions of **4-6** for alkali and alkaline earth metal ions were compared with that of pure silica. Pure silica shows a low picrate ion extraction (20%) while **4-6** show above 65-90% (Fig. 1). Compounds **5** (with a methyl group at para position of phenol unit) and **6** (with methyl group at both ortho and para positions of phenol unit) were found to exhibit more significant extraction percentage than **4** (without any substitution group). The extraction behavior might be based on the fact that the bulky structure of the silylbenzoxazine (i.e., **5** and **6**) leads to the loose packing structure and induces cavity for metal guests.

FTIR of precursor **9** showed the intramolecular hydrogen bonding observed from the broad peak from 3100~3300 cm^{-1} and the oxazine peak at 1503 cm^{-1}. The benzoxazine dimer was confirmed by 1498 cm^{-1} belonging to -C-N-. The silane group was also confirmed from the sharp peaks at 1104~1080 cm^{-1} for Si-O-C and 916 cm^{-1} for Si-OC_2H_5. 2D-NMR and FTIR implied the unique structure of the monooxazine[6] coupling on the silica (Scheme I, Eq.2). The coupling of the precursor onto Si to obtain **9** was

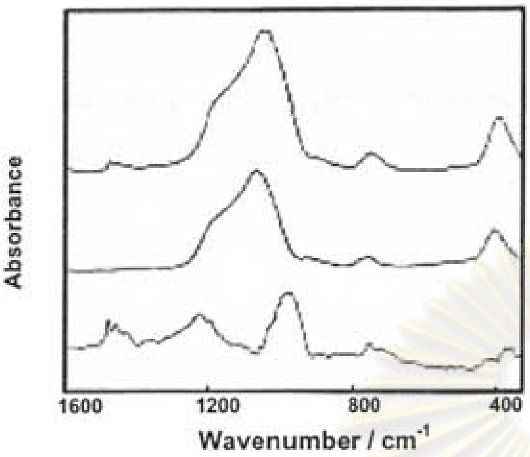


Fig. 2. DRIFT FTIR spectrum of **3** (top); pure fumed silica (middle); and peak subtraction of **3** and pure fumed silica (bottom).

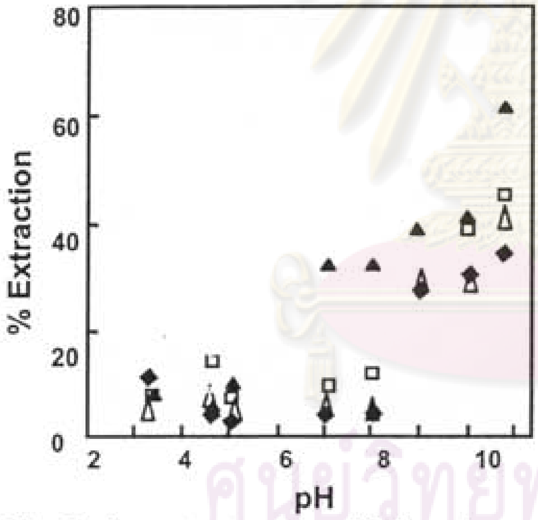


Fig. 3. Percent extraction of **9** in various pH values; (▲) for Pb^{2+}, (Δ) for Cd^{2+}, (□) for Zn^{2+}, and (◆) for Mn^{2+}.

confirmed by DRIFT FT-IR peak subtraction technique. Figure 2 (bottom) shows the peak of Si-O-Si at 1030 cm^{-1}, including the monooxazine peak at 1503 cm^{-1} and the open ring of benzoxazine at 1489 cm^{-1}.

The ion extraction ability of **9** was studied comparing with that of pure silica. Pure silica gives ion extraction for 10% while **9** in acidic conditions show less than 20% and in basic conditions exhibit even at 70% for Pb^{2+} (Figure 3). The ion extraction selectivity was found to be $Pb^{2+}>Cd^{2+}\sim Zn^{2+}\sim Mn^{2+}$.

CONCLUSIONS

Silylbenzoxazine derivatives with different bulky group on benzene ring are synthesized employing aminoalkylsilane as a primary amine. The silica surface modified with benzoxazine monomers exhibits the extraction ability depending on the structure of monomer. The benzoxazine dimer coupling onto silica resin is achieved by using a molecular design hinted from our previous studies about monooxazine-typed benzoxazine dimer. The ion extraction ability of benzoxazine dimer depends on pH and exhibits selectivity among the studied ions.

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Publication

1. Chirachanchai, S., Yoswathananont, N., Laobuthee, A., and Ishida, H. *Composite Interfaces*. In press.

Interfaces

March 9, 2001

Dr. Suwabun Chirachanchai
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Bangkok 10330 Thailand

Dear Dr. Suwabun:

I am happy to inform you that your paper (MS #123-ICCI-VIII-122200) entitled, "Silica Surface Modified with Benzoxazine -functional Silane" has been accepted for publication in Composite Interfaces. You shall hear from the publisher in due course regarding the galley proof.

Thank you very much for your fine contribution to Composite Interfaces, I look forward to your submission in the near future.

Sincerely,

Hatsuo Ishida
Professor of Macromolecular Science & Engineering
Editor-in-Chief, Composite Interfaces

HI/bjd

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Silica surface modified with benzoxazine-functional silane

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Abstract—Silica surface modified with silylbenzoxazine monomers having different bulky groups at ortho and para positions on the oxazine ring, i.e. 3-triethoxysilyl-*n*-propyl-3,4-dihydro-2H-1,3-benzoxazine coupled with silica (**4**), 3-triethoxysilyl-*n*-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine coupled with silica (**5**), and 3-triethoxysilyl-*n*-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine coupled with silica (**6**) are synthesized to obtain a series of ion extraction resins. Fourier transform infrared spectroscopy (FT-IR) and elemental analysis support the successful coupling of benzoxazine-functional silane onto silica surface. The ion extraction studies of various alkali and alkaline earth metal ions from aqueous phase via the surface treated silica column chromatography shows the significant ion extraction ability of (**6**) compared to those of (**4**) and (**5**).

Keywords: Benzoxazine; silane; silica; surface modification; FT-IR.

1. INTRODUCTION

Ion separation is considered as an essential process for product synthesis, pollution control, and purification. Ion exchange resin is a practical material for various separation processes due to the simple procedure and cost performance. This can be done under the concept of a reversible chemical reaction between solid (ion exchanger) and fluid containing various types of ion [1]. Traditionally, the resin is developed from a synthetic polymer containing active functional groups, such as sulfonic, carboxylic, phenolic, or amino groups, that create in the resin a specific interaction with certain metal ions. Though ion exchange resin has been widely used for over three decades, the ultra-high selectivity of a specific ion is still the major goal for development.

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For the past three decades, interaction at the molecular level under the concept of formation of an inclusion compound has become a direction to develop materials used for separation processes. Thus, ultra-high selective ion extraction may be expected from such an inclusion compound. The inclusion compounds, such as calixarenes [2], cyclodextrin [3], crown ether [4], and their derivatives are known as host–guest compounds that induce ion interaction phenomena and neutral molecule entrapment. Due to advanced structural analyses, an understanding of the molecular recognition at molecular level is now more precise and this provides us with the possibility of designing specific molecules as practical inclusion compounds. The applications of inclusion compound have received much attention as material not only for separation processes [5] but also as optical and chemical sensors [6], interfacial catalysts [7], and medical agents [8].

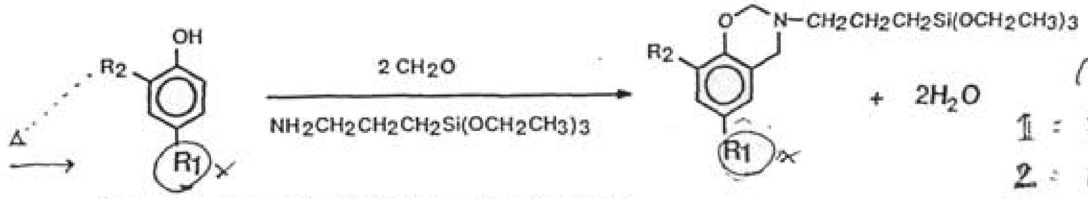
Polybenzoxazine is known as a polymer with a repeating unit of azamethylene phenol obtained from the ring opening polymerization of benzoxazine monomers. Ishida *et al.* have focused on polybenzoxazines and proposed a series of derivatives to be a novel class of phenolic materials which exhibit a superb balance of mechanical and thermal properties [9, 10]. Polybenzoxazine is also attractive from the point of view of preparation since there is no catalyst required in synthesis procedures, no by-product formed during the curing reaction, and various derivatives can be designed. By considering the repeating unit of polybenzoxazine, our group has proposed it as calixarene with azamethylene linkage. In previous work, we studied the preparation of benzoxazine oligomers and clarified the inclusion phenomena involving a metal ion [11]. Our preliminary work demonstrated that oligobenzoxazines show high ion extraction ability towards alkaline, alkaline metal and transition metal ions.

The present work is, thus, an initial step to study the practical application of benzoxazine derivatives as an ion extraction material. The uniqueness of this study is the preparation of benzoxazine-functional silane and its coupling onto a high surface area silica to obtain benzoxazine-functional silica resin. The model study for ion extraction is done by chromatographic column using the benzoxazine coupled silica as a material in stationary phase to separate alkali and alkaline-earth cations.

2. EXPERIMENTAL

2.1. Materials

Paraformaldehyde, *p*-cresol (99%) and phenol were purchased from Sigma (USA). 3-Aminopropyltriethoxysilane (99%), anhydrous sodium sulfate, 2,4-dimethyl phenol (97%), lithium chloride, and silica gel (particle size = 0.063–0.2000 mm) were the products of Fluka chemicals (Buchs, Switzerland). Chloroform was purchased from J.T. Baker Inc. (Phillipsburg, USA). Picric acid, magnesium chloride, potassium chloride, sodium hydroxide and sodium chloride were obtained from Ajax chemicals (Australia). Barium chloride and calcium chloride were purchased from



Scheme 1. Preparation of silylbenzoxazine derivative.

(insert this below the equation

1 : R_1 : H and R_2 : H
2 : R_1: H and R_2 : CH_3
3 : R_1: CH_3 and R_2: CH_3

E. Merck (Germany). All solvents were used as received and stocked with 0.4 nm molecular sieve before use.

2.2. Synthesis of silylbenzoxazine

The general method of synthesis of silylbenzoxazine is shown in Scheme 1.

2.3. Synthesis of 3-triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine(**1**)

Phenol, paraformaldehyde and 3-aminopropyltriethoxysilane were mixed in 1 : 2 : 1 mole ratio and refluxed in chloroform at 85°C for 3 h as reported previously by Ishida *et al.* [12]

× 3-Triethoxysilyl-*n*-propyl-3,4-dihydro-2H-1,3-benzoxazine(**1**)

T-IR FTIR (KBr, cm^{-1}): 2975 (CH_3: stretching), 2928 (CH_2: stretching), 2886 (CH_3: stretching), 1489 (oxazine), 1240-1020 (C–N–C: stretching), 1227 (C–O–C: stretching), 1168, 958 ($-OCH_2CH_3$), 1104, 1080 (Si–O–C: stretching), 956 ($Si-OC_2H_5$).

^{1}H-NMR (in $CDCl_3$, at 25°C, ppm): 0.63 (2H, t, C-4), 1.19 (3H, t, C-6), 1.65(2H, m, C-3), 2.73 (2H, t, C-2), 3.77 (2H, q, C-5), 3.95 (2H, s, C-7), 4.83 (1H, s, C-1), 6.76 (1H, d, C-9), 6.90 (1H, d, C-10), 7.04 (1H, d, C-8), 7.08 (1H, d, C-11). } please change as attached paper

TLC: R_f (5%MeOH: $CHCl_3$) = 0.8.
Yield = 89.7%. a space

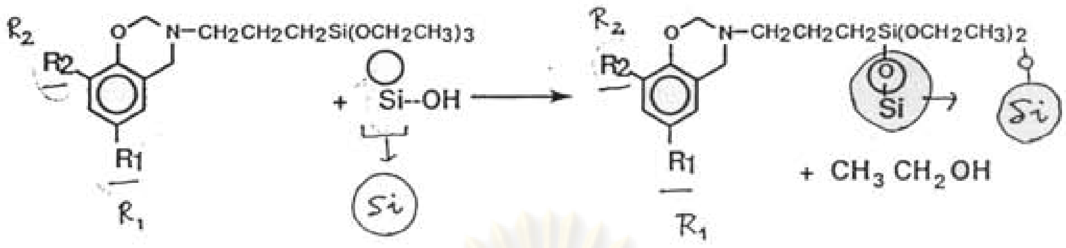
2.4. Synthesis of 3-triethoxysilyl-n-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine(2) *and 3-triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine*(**3**)

Similarly, (2) and (3) were prepared as the procedure of (1) with *p*-cresol and 2,4-dimethyl phenol as starting materials, respectively.

3-Triethoxysilyl-*n*-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine(2)

FTIR (KBr, cm^{-1}): 2975 (CH_3: stretching), 2928 (CH_2: stretching), 2886 (CH_3: stretching), 1502 (oxazine), 1240-1020 (C–N–C: stretching), 1228 (C–O–C: stretching), 1168, 958 ($-OCH_2CH_3$), 1104, 1080 (Si–O–C: stretching), 956 ($Si-OC_2H_5$), 820, 855(1, 2, 4: substituted).

^{1}H-NMR (in $CDCl_3$, at 25°C, ppm): 0.65 (2H, t, C-4), 1.21 (3H, t, C-6), 1.67(2H, m, C-3), 2.22 (3H, s, C-9), 2.73 (2H, t, C-2), 3.82 (2H, q, C-5), 3.93 (2H, s, C-7), 4.82 (1H, s, C-1) 6.66 (1H, d, C-10) 6.79 (1H, s, C-8) 6.91 (1H, d, C-11).



4 = R_1: -H and R_2: -H

5 = R_1: -CH_3 and R_2: -H

6 = R_1: -CH_3 and R_2: -CH_3

Scheme 2. Preparation of benzoxazine monomer coupled with silica.

TLC: R_f (5%MeOH : $CHCl_3$) = 0.9.

Yield = 87.6%.

3-Triethoxysilyl-*n*-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine(**3**)

FTIR (KBr, cm^{-1}): 2975 (CH_3: stretching), 2928 (CH_2: stretching), 2886 (CH_3: stretching), 1486 (oxazine), 1240-1020 (C−N−C: stretching), 1228 (C−O−C: stretching), 1168, 958 (−OCH_2CH_3), 1104, 1080 (Si−O−C: stretching), 956 (Si−OC_2H_5), 868(1, 2, 3, 5 substituted).

^{1}H-NMR (in $CDCl_3$, at 25°C, ppm): 0.65 (2H, t, C-4), 1.21 (3H, t, C-6), 1.67 (2H, m, C-3), 2.22 (3H, s, C-9), 2.27 (1H, dd, C-11), 2.73 (2H, t, C-2), 3.82 (2H, q, C-5), 3.93 (2H, s, C-7), 4.82 (1H, s, C-1), 6.58 (1H, d, C-10), 6.79 (1H, s, C-8).

TLC: R_f (5%MeOH : $CHCl_3$) = 0.95.

Yield = 85.8%.

2.5. Preparation of benzoxazine monomer coupled with silica

The general method of preparation of benzoxazine monomer coupling with silica is shown in Scheme 2.

*2.6. Preparation of silica coupled with 3-triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine(**4**), 3-triethoxysilyl-n-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine(**5**) and 3-triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine(**6**)*

3-Triethoxysilyl-*n*-propyl-3,4-dihydro-2H-1,3-benzoxazine (8 mmol, 3 g) was stirred with silica (1 g) and heated to 200°C without solvent for 3 h to obtain yellow silica particles. The product was washed thoroughly with chloroform to exclude the unreacted silylbenzoxazine and THF to eliminate the physisorbed silane on silica, followed by drying *in vacuo* at room temperature for 3 h to obtain a light yellow powder.

Similarly, (**5**) and (**6**) were prepared as (**4**).

× 3-Triethoxysilyl-*n*-propyl-3,4-dihydro-2H-1,3-benzoxazine coupled silica (**4**).

T-IR FTIR (KBr, cm^{-1}): 2975 (CH_3: stretching), 2928 (CH_2: stretching), 2886 (CH_3: stretching), 1489 (oxazine), 1228 (C−O−C: stretching), 1130-1000 (Si−O−C: stretching).

Anal. calcd. (Assuming all alkoxy groups are hydrolyzed and the silanol groups are coupled with the silica surface): C, 38.94%; H, 4.13%; N, 4.13%. Found: C, 37.24%; H, 4.41%; N, 4.44%.

× 3-Triethoxysilyl-*n*-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine coupled silica (**5**).

T-IR FTIR (KBr, cm^{-1}): 2975 (CH_3: stretching), 2928 (CH_2: stretching), 2886 (CH_3: stretching), 1503 (oxazine), 1228 (C−O−C: stretching), 1130-1000 (Si−O−C: stretching).

Anal. calcd. (Assuming all alkoxy groups are hydrolyzed and the silanol groups are coupled with the silica surface): C, 40.79%; H, 4.53%; N, 3.97%. Found: C, 37.52%; H, 5.18%; N, 4.98%.

× 3-Triethoxysilyl-*n*-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine coupled silica (**6**).

FT-IR FTIR (KBr, cm^{-1}): 2975 (CH_3: stretching), 2928 (CH_2: stretching), 2886 (CH_3: stretching), 1490 (oxazine), 1228 (C−O−C: stretching), 1130-1000 (Si−O−C: stretching).

Anal. calcd. (Assuming all alkoxy groups are hydrolyzed and the silanol groups are coupled with the silica surface): C, 42.51%; H, 4.9%; N, 3.81%. Found: C, 38.42%; H, 4.07%; N, 3.86%. 4.90%

2.7. *Characterization*

FT-IR

Fourier transform infrared (FTIR) spectra were taken on a Bruker Equinox 55 spectrophotometer with 16 scans at a resolution of 4 cm^{-1} in the frequency range of 4000–400 cm^{-1}. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained from a Fourier Transform NMR spectrometer ACF 200 MHz of Bruker, Switzerland. The sample was dissolved in deuterated chloroform with tetramethylsilane as an internal standard. The percent elements were obtained from PE 2400 Series II CHNS/O Analyzer. Vortex mixer (GENIE-2, Scientific Industries) was used in the procedure of ion extraction. Percent extraction of picrate metal salt was determined by UV spectra obtained from a Perkin-Elmer Lambda-16 Spectrophotometer. Ion concentration in aqueous phase was determined by an atomic absorption spectrometer, Varian SpectrAA-300.

2.8. *Ion extraction studies*

The ion extraction property was studied by using Pedersen's technique [13] for silylbenzoxazine, (**1**)–(**3**), and silica surface modified with benzoxazine-functional silanes, (**4**)–(**6**). Chloride salts of lithium, sodium, potassium, magnesium, calcium, and barium ions are used as metal ions. 7 × 10^{-5} M of picric acid and 0.1 M of ion salts [11] were dissolved in deionized water so that the UV absorbance at 354 nm becomes one absorbance unit. Benzoxazine solution was prepared by dissolving each monomer, **(1)**–**(3)**, in chloroform to obtain concentrations of 7×10^{-3} M, 7×10^{-2} M, and 7×10^{-1} M.

Ion extraction was studied as follows. Five ml of aqueous alkali or alkaline earth picrate salt solution and 5 ml of benzoxazine solution were mixed vigorously for 1 min. The mixture was left at room temperature till the aqueous phase and organic phase were completely separated. The aqueous phase was taken to determine the metal ion concentration by ultraviolet-visible spectrophotometer at 354 nm, i.e. the wavelength of maximum absorption of the picrate ion.

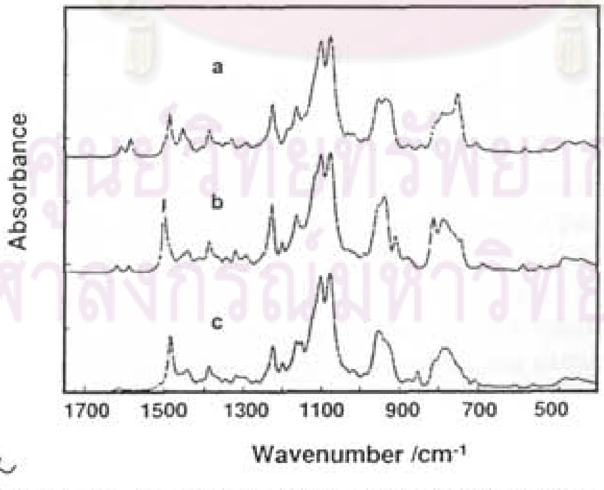
The ion extraction ability of benzoxazine monomers coupled with silica was determined as follows. Six ml of picrate ion solution was shaken with 5 g of benzoxazine-treated silica ((**4**)–(**6**)) for 3 min in a column at room temperature. The solution was drained and the procedure was repeated 10 times with fresh picrate ion solution. Ion extraction was evaluated by the change of picrate concentration in the aqueous phase observed by ultraviolet-visible and atomic absorption spectrophotometry.

3. RESULTS AND DISCUSSION

3.1. Synthesis of silylbenzoxazine

FT-IR

Figure 1 shows the FTIR spectra of various benzoxazine-functional silanes. The asymmetric Si–O–C stretching modes of the ethoxy group appear at 1104 cm^{-1} and 1080 cm^{-1}. The ethoxy group shows two strong bands at 1168 cm^{-1} and 958 cm^{-1}. It should be noted that aminosilanes are readily hydrolyzed by water.



FT-IR

Figure 1. FTIR spectra of: (a) 3-triethoxysilyl-*n*-propyl-3,4-dihydro-2H-1,3-benzoxazine (1), (b) 3-triethoxysilyl-*n*-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine (2), and (c) 3-triethoxysilyl-*n*-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine (3).

In this method, the water molecules produced during the synthesis were excluded from the product phase by using chloroform as a solvent. Since the benzoxazine monomer is not soluble in water, the alkoxy groups of the silane will remain unhydrolyzed. Thus, the product did not show the bands related to the siloxane mode in the region between 1130 cm^{-1} and 1000 cm^{-1}.

The structures of (1), (2) and (3) were characterized by ^{1}H-NMR as shown in Fig. 2. The ^{1}H-NMR spectrum confirms that the product is not either dimer or oligomer.

3.2. *Preparation of silica surface modified with benzoxazine* (4), (5) *and* (6)

As shown in Fig. 3, the spectral subtraction technique reduces the large contribution of the silica to the spectra and emphasizes the spectral feature of the surface species. Here, the benzoxazine bands at 1504, 1491, and 1489 cm^{-1} are clarified, indicating that the coupling procedure with benzoxazine ring is successful. The subtracted spectra between the silylbenzoxazine derivatives treated silica (Fig. 4) shows that the bands belonging to the ethoxy group, i.e. 2975, 2928, 1390, and 956 cm^{-1} have disappeared or are decreased in intensity, whereas the bands near 1050 and 770 cm^{-1} have appeared, implying the formation of Si$-$O$-$Si linkages. These indicate that the silylbenzoxazine derivatives are coupled onto the silica surface. Thus, the amino silane coupling agent used as an amine in the benzoxazine preparation provides the possibility to obtain silylbenzoxazines.

On the assumption of all triethoxysilanes coupling onto the silica surface, the carbon content (%C) can be calculated to be 38.5–42.5% for the three types of surface-treated silica ((4)–(6)). Based on the elemental analysis results, the carbon percentage of each product is close to that of the calculation. This indicates that almost all ethoxysilanes are successfully coupled onto silica.

3.3. *Ion extraction behavior of the silylbenzoxazine-modified silica surface*

The ion extraction Figs. of pure silica and benzoxazine coupled silica, (4)–(6), for alkali and alkaline earth metal ions were determined by atomic absorption spectroscopy, as shown in Figs 5, 6, 7, and 8. The surface-treated silica was packed in a column and column chromatography was used to study the ion extraction. Figure 5 shows that, in the case of pure silica, little picrate metal ion is observed even if the silica is used for the adsorption process many times. However, silylbenzoxazine derivatives → Figs. coupled silica, (4)–(6), show 80 to nearly 100 percent ion extraction (Fig. 6–8). Here, it should be noted that for the first to fifth repeating time, the extraction percentage is not stable. This may be due to the effect of the dry surface, which makes the ion interaction in solvent poor. After the adsorption process was repeated more than five times, a constant extraction percentage is obtained. Considering the effect of the silylbenzoxazine structure, the compound (4) with less bulky group shows ion extraction ability around 65–83% while the compound (5) with one

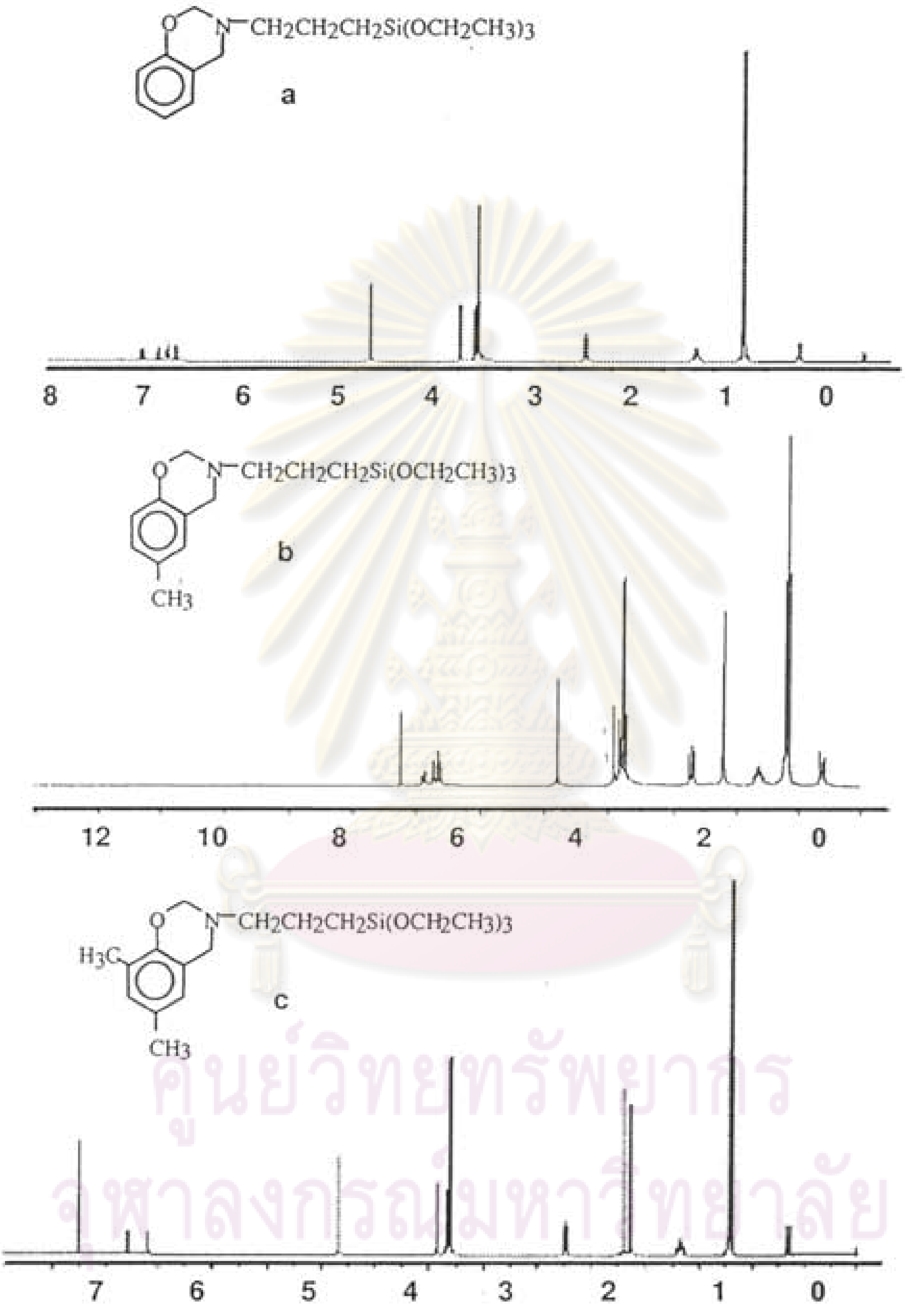
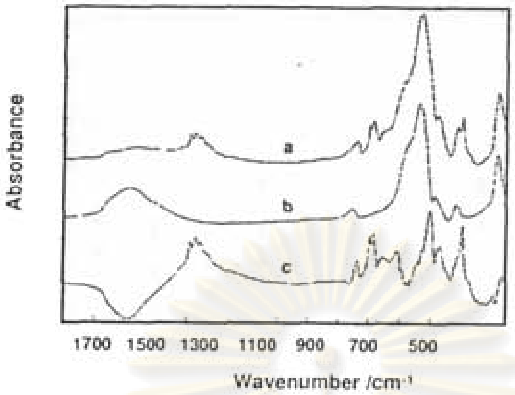
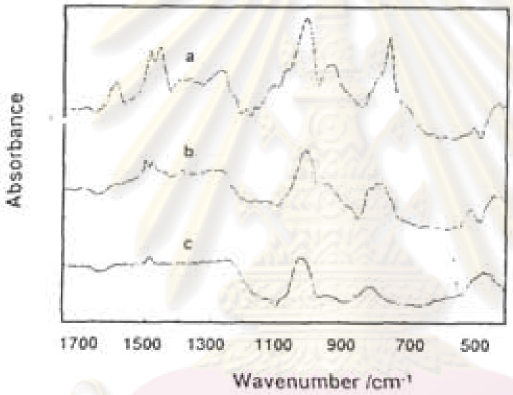


Figure 2. ^{1}H-NMR spectra of: (a) 3-triethoxysilyl-*n*-propyl-3,4-dihydro-2H-1,3-benzoxazine (**1**), (b) 3-triethoxysilyl-*n*-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine (**2**), and (c) 3-triethoxysilyl-*n*-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine (**3**).



FT-IR

Figure 3. FTIR spectra of: (a) 3-triethoxysilyl-*n*-propyl-3,4-dihydro-2H-1,3-benzoxazine coupled silica (4), (b) silica, and (c) a)-b) subtraction.



FT-IR

Figure 4. FTIR spectra of: (a) 3-triethoxysilyl-*n*-propyl-3,4-dihydro-2H-1,3-benzoxazine (1), (b) 3-triethoxysilyl-*n*-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine (2), and (c) 3-triethoxysilyl-*n*-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine (3) on the silica surface with the contribution of the silica exclusion.

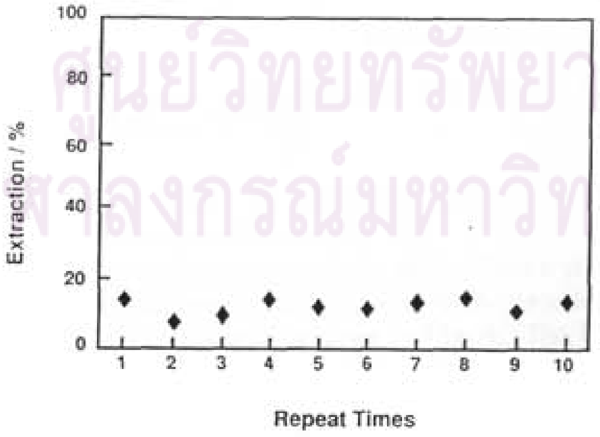


Figure 5. Extraction percentage of metal picrate at $[M^+][Pic^-] = 7 \times 10^{-5}$ M by pure silica.

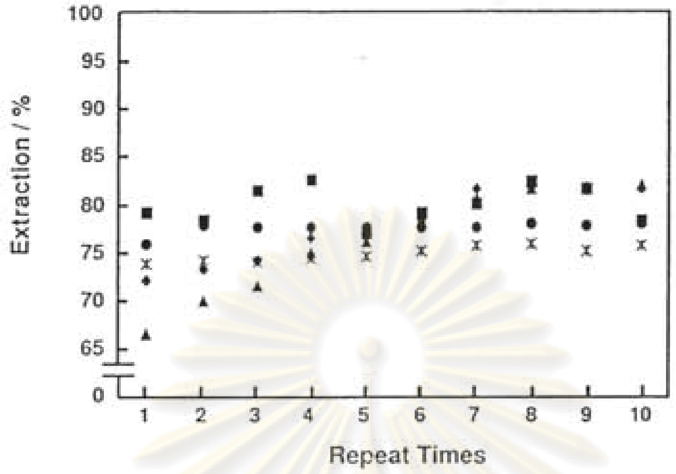


Figure 6. Extraction percentage of metal picrate at $[M^+][Pic^-] = 7 \times 10^{-5}$ M by (**4**) for Na^+ (◆), K^+ (■), Mg^{2+} (▲), Ca^{2+} (●), and Ba^{2+} (×).

↘✱ ×

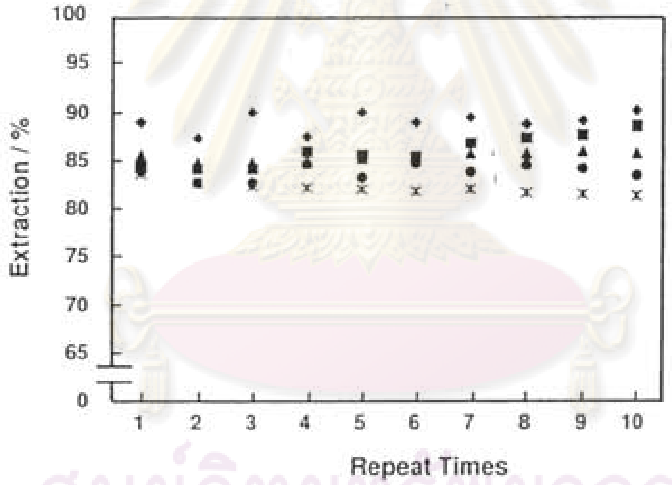


Figure 7. Extraction percentage of metal picrate at $[M^+][Pic^-] = 7 \times 10^{-5}$ M by (**5**) for Na^+ (◆), K^+ (■), Mg^{2+} (▲), Ca^{2+} (●), and Ba^{2+} (×).

✱ ×

methyl group shows 80–90%. The compound (**6**) with two methyl groups shows the highest ion extraction percentage at 82–95%.

The extraction behavior might come from the fact that a propyl group exists as a spacer between silica and benzoxazine to promote the mobility of the benzoxazine group, as shown in the schematic drawing in Fig. 9. The bulky structure of the benzoxazines on the silica surface makes them pack loosely and provides cavities for the metal guests. In the silica coupled with silylbenzoxazine without bulky group (**4**), the interaction on silica surface should be strong due to the silanol group combining with the stacking conformation of benzoxazine monomer. This high

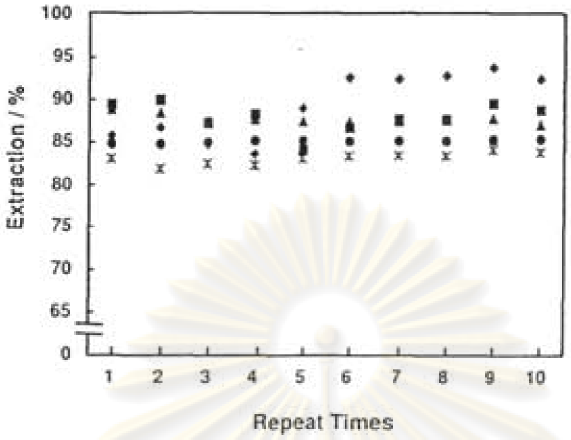


Figure 8. Extraction percentage of metal picrate at $[M^+][Pic^-] = 7 \times 10^{-5}$ M by (**6**) for Na^+ (◆), K^+ (■), Mg^{2+} (▲), Ca^{2+} (●), and Ba^{2+} (×).

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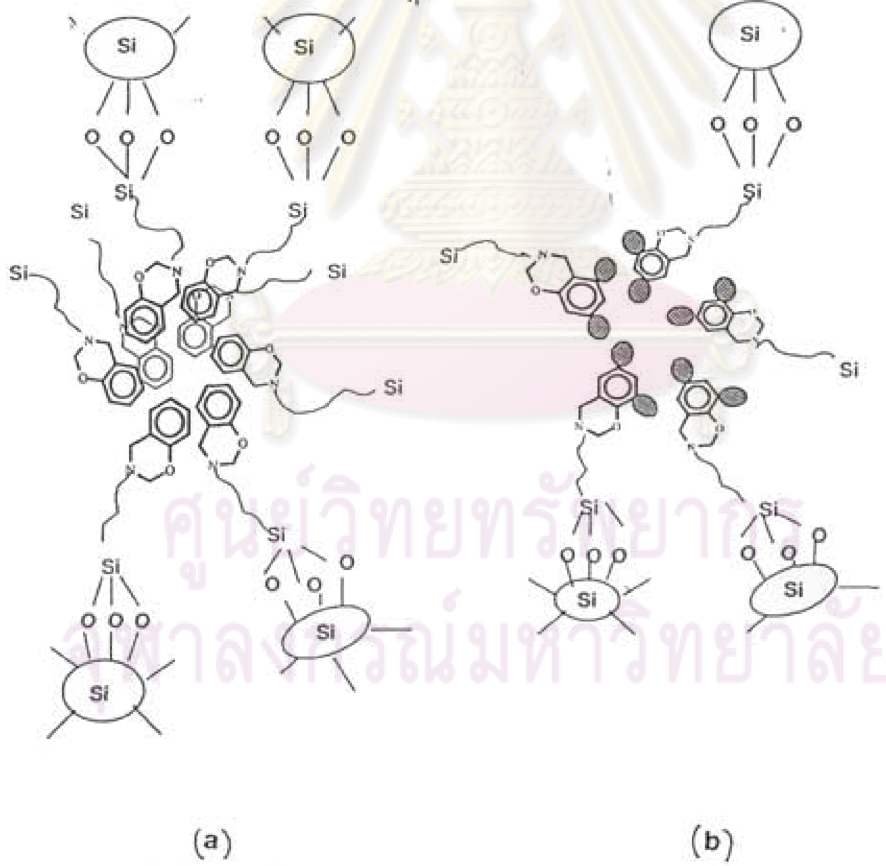

Figure 9. Schematic diagram of silica surface modified with benzoxazine: (a) compound (**4**), and (b) compound (**6**).

packing structure induces fewer cavities for metal ion guests. As a result, low ion extraction behavior is observed. As a result, the ability of ion extraction of silica surface modified benzoxazine is in the order (6) > (5) > (4).

4. CONCLUSIONS

Silylbenzoxazine derivatives with different bulky groups on the benzene ring are synthesized employing aminosilane as a primary amine. Silica surface modified benzoxazines are successfully achieved via silylbenzoxazine derivatives and show the ion extraction property for various alkali and alkaline earth metal ions. When the silane is coupled onto silica, the benzoxazine shows different ion extraction ability from that of silylbenzoxazine. The silica surface modified with benzoxazine derivatives with a bulky group exhibits high extraction, which may be due to the loose packing structure of the molecular assembly inducing a high amount of cavity for guest atoms.

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