

## CHAPTER IV

### RESULTS AND DISCUSSION

In order to obtain silica surface modified benzoxazine, amino silane can be 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.

#### 4.1 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 products were characterized as follows.

##### 4.1.1 Structural Characterization of 3-triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine(1)

FTIR (KBr,  $\text{cm}^{-1}$ ): 2975 ( $\text{CH}_3$ :stretching), 2928 ( $\text{CH}_2$ :stretching), 2886 ( $\text{CH}_3$ :stretching), 1489 (oxazine), 1240-1020 (C-N-C:stretching), 1227 (C-O-C:stretching), 1168, 958 ( $-\text{OCH}_2\text{CH}_3$ ), 1104, 1080 (Si-O-C: stretching), 956 (Si- $\text{OC}_2\text{H}_5$ ).

$^1\text{H-NMR}$  (in  $\text{CDCl}_3$ , at  $25^\circ\text{C}$ , 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 :  $\text{CHCl}_3$ ) = 0.8.

Yield = 89.7%.

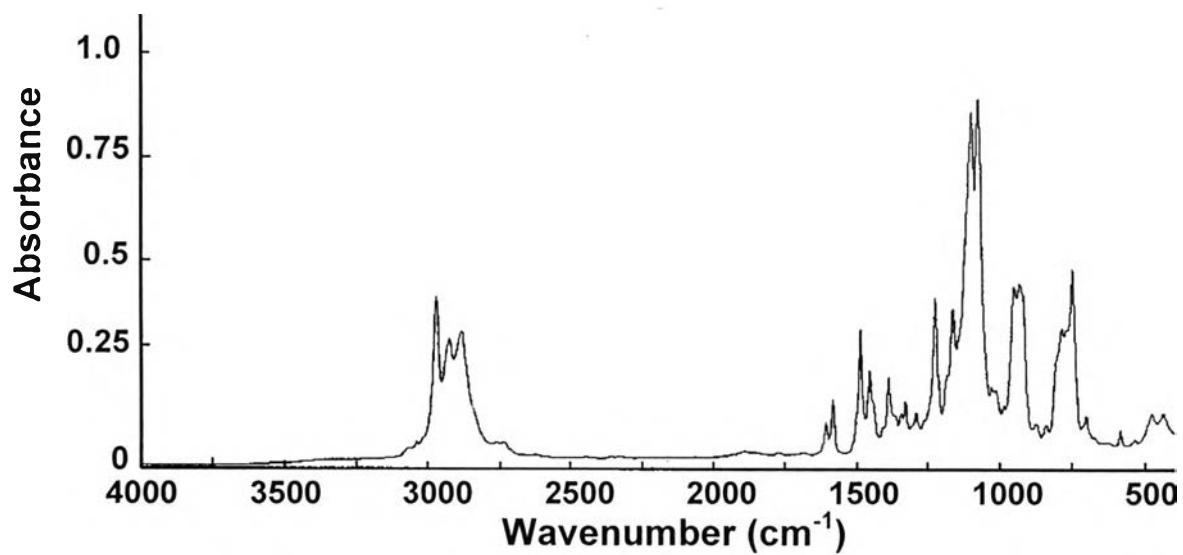


Figure 4.1 FTIR spectrum of (**1**).

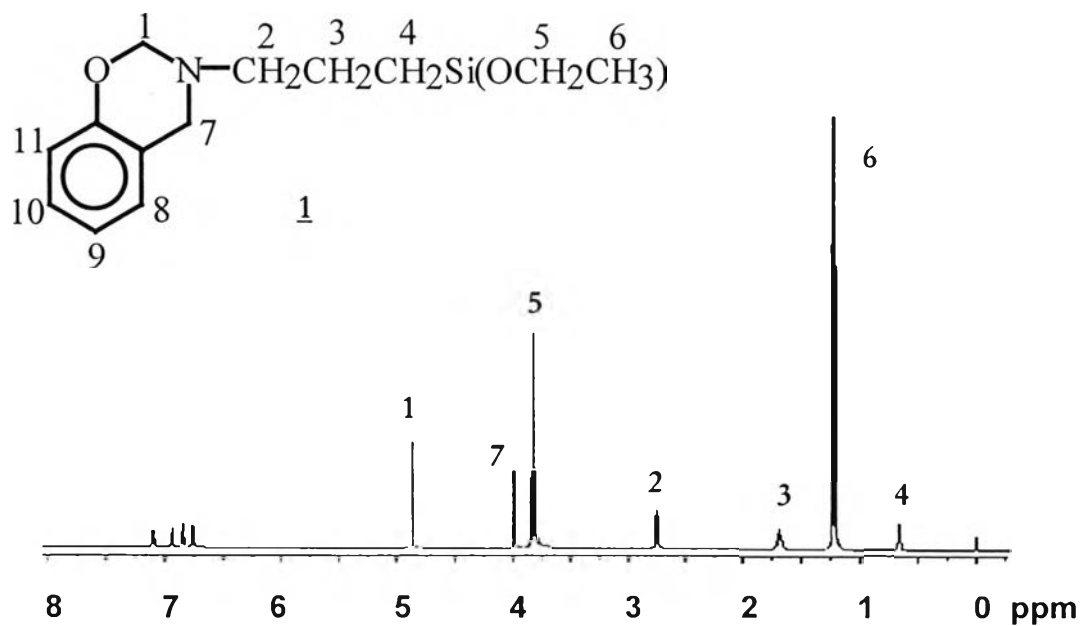


Figure 4.2  $^1\text{H-NMR}$  spectrum of (**1**).

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

FTIR (KBr,  $\text{cm}^{-1}$ ): 2975 ( $\text{CH}_3$ :stretching), 2928 ( $\text{CH}_2$ :stretching), 2886 ( $\text{CH}_3$ :stretching), 1502 (oxazine), 1240-1020 (C-N-C:stretching), 1228 (C-O-C:stretching), 1168, 958 ( $-\text{OCH}_2\text{CH}_3$ ), 1104, 1080 (Si-O-C:stretching), 956 (Si- $\text{OC}_2\text{H}_5$ ), 820, 855 (1,2,4 substituted).

$^1\text{H-NMR}$  (in  $\text{CDCl}_3$ , at  $25^\circ\text{C}$ , 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 :  $\text{CHCl}_3$ ) = 0.9.

Yield = 87.6%.

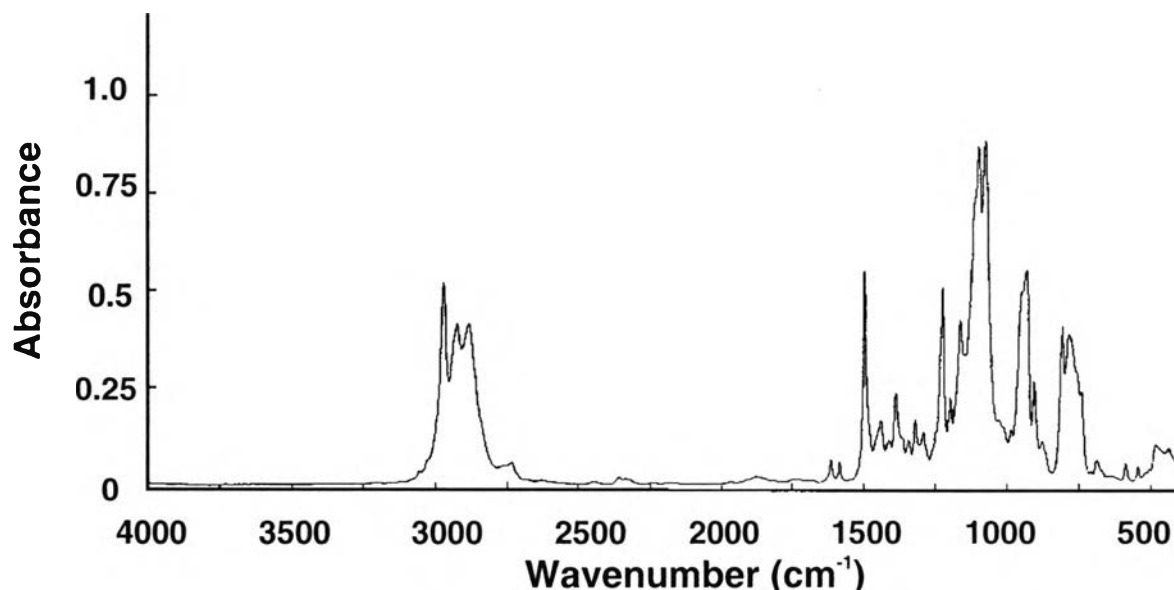


Figure 4.3 FTIR spectrum of (2).

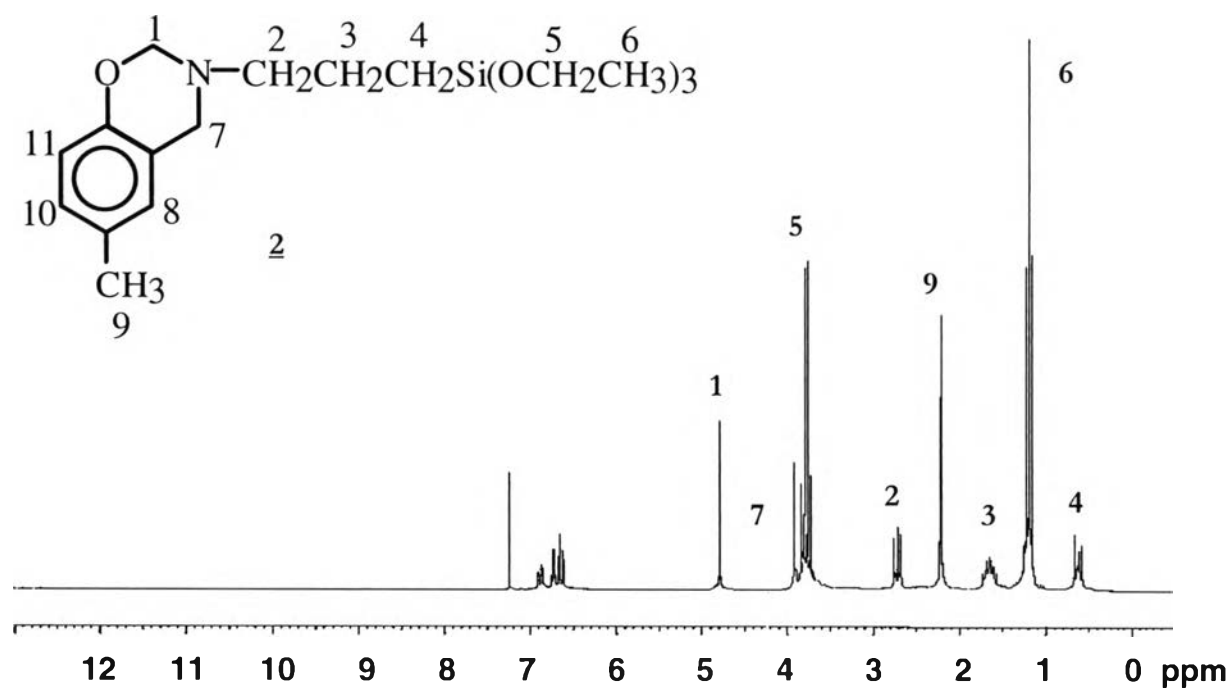


Figure 4.4  $^1\text{H-NMR}$  spectrum of (2).

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

FTIR (KBr,  $\text{cm}^{-1}$ ): 2975 ( $\text{CH}_3$ :stretching), 2928 ( $\text{CH}_2$ :stretching), 2886 ( $\text{CH}_3$ :stretching), 1486 (oxazine), 1240-1020 (C-N-C:stretching), 1228 (C-O-C:stretching), 1168, 958 ( $-\text{OCH}_2\text{CH}_3$ ), 1104, 1080 (Si-O-C: stretching), 956 (Si- $\text{OC}_2\text{H}_5$ ), 868 (1,2,3,5 substituted).

$^1\text{H-NMR}$  (in  $\text{CDCl}_3$ , at  $25^\circ\text{C}$ , 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 :  $\text{CHCl}_3$ ) = 0.95.

Yield = 85.8%.

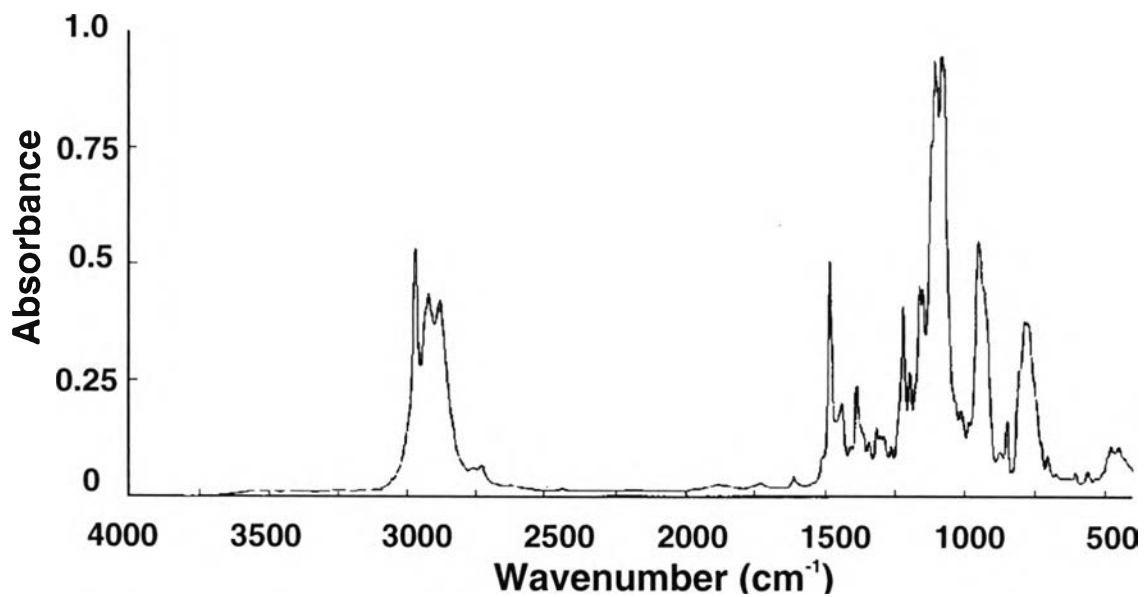


Figure 4.5 FTIR spectrum of (3).

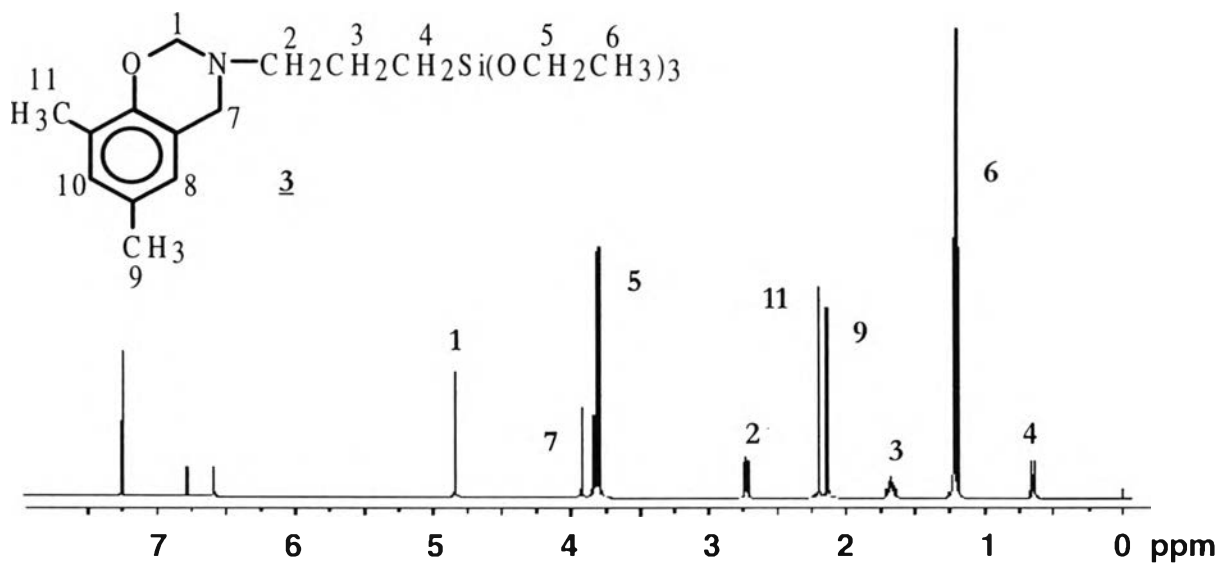


Figure 4.6  $^1\text{H-NMR}$  spectrum of (3).

Silylbenzoxazine derivatives can be confirmed as follows. The asymmetric Si-O-C stretching modes of the ethoxy group appear at  $1104\text{ cm}^{-1}$  and  $1080\text{ cm}^{-1}$ . The ethoxy group shows two strong bands at  $1168\text{ cm}^{-1}$  and  $958\text{ cm}^{-1}$ . It should be noted that aminosilane can be readily hydrolyzed by water. In this method, the water produced during the synthesis is 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  $1130\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$  in the product.

The  $^1\text{H-NMR}$  spectrum confirms that the product is not either dimer or oligomer.

## 4.2 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.

### 4.2.1 Structural Characterization of Silica Coupled with 3-

#### triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine(4)

FTIR (KBr,  $\text{cm}^{-1}$ ): 2975 ( $\text{CH}_3$ :stretching), 2928 ( $\text{CH}_2$ :stretching), 2886 ( $\text{CH}_3$ :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%.

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

FTIR (KBr,  $\text{cm}^{-1}$ ): 2975 ( $\text{CH}_3$ :stretching), 2928 ( $\text{CH}_2$ :stretching), 2886 ( $\text{CH}_3$ :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%.

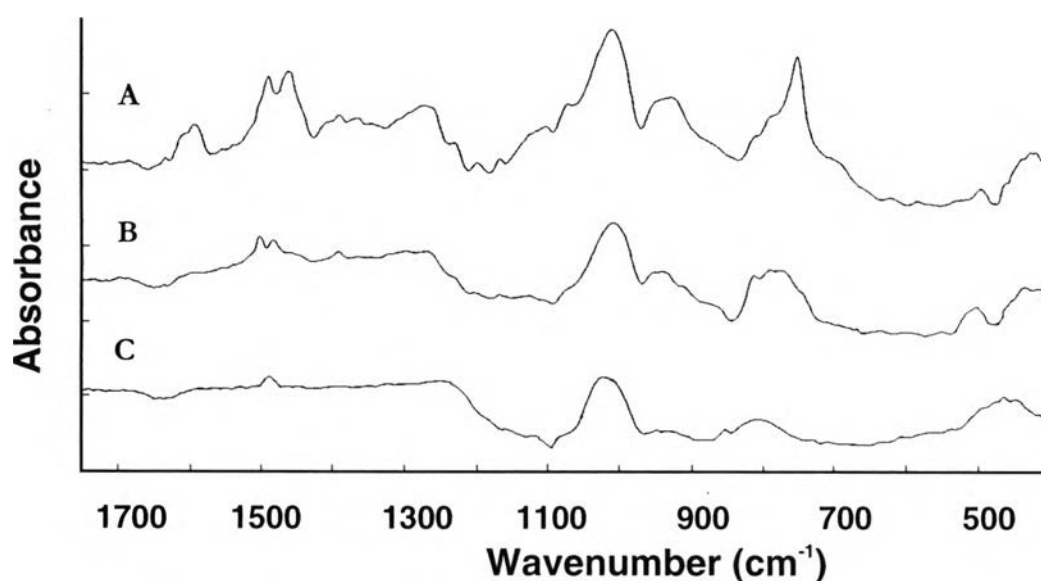
4.2.3 Structural Characterization of Silica Coupled with 3-triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine(6)

FTIR (KBr,  $\text{cm}^{-1}$ ): 2975 ( $\text{CH}_3$ :stretching), 2928 ( $\text{CH}_2$ :stretching), 2886 ( $\text{CH}_3$ :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 4.7, 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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  disappear or decrease in intensity, whereas the bands near 1050 and

$770\text{ cm}^{-1}$  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 4.7** 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.

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.

### 4.3 Ion Extraction Study

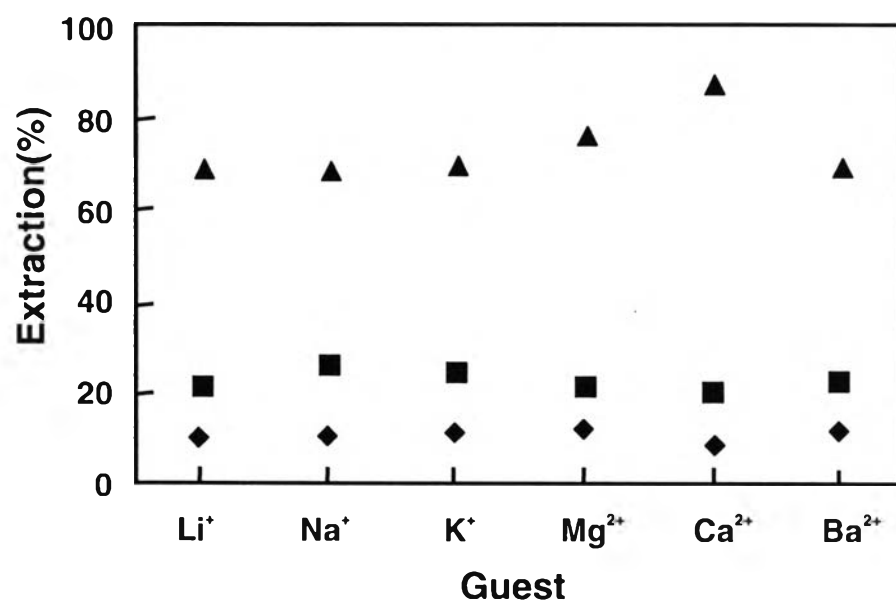
Pedersen's technique is applied to study the ion extraction property in liquid/liquid system. Normally, picric acid can form picrate salt with metal ions in aqueous phase due to its very large acidity constant. The picrate salt will be presented in aqueous phase and gives the yellow color to the phase 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 using UV-Vis spectrophotometry at the absorption wavelength of the picrate.

In order to propose silylbenzoxazine coupled onto silica as an ion extraction material, ion extraction property of each treated silica was studied using Pedersen's technique for alkali and alkali earth metal ions.

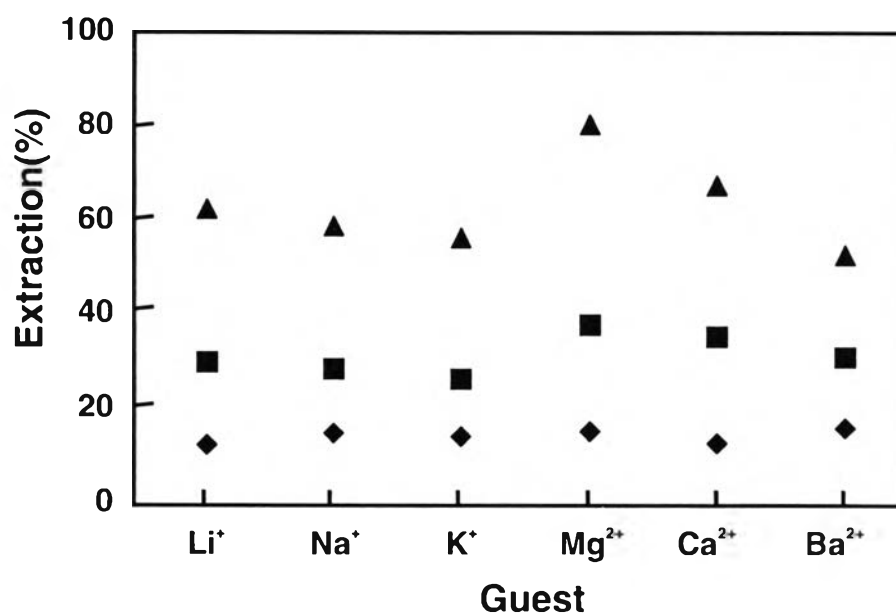
#### 4.3.1 Ion Extraction Behavior of Silylbenzoxazine Derivatives

The concentration of silylbenzoxazine in chloroform phase was varied to clarify the capability of benzoxazine as a host compound for ion extraction. Ultraviolet-visible spectrophotometry was used to determine the picrate salt in aqueous phase at the equilibrium state.

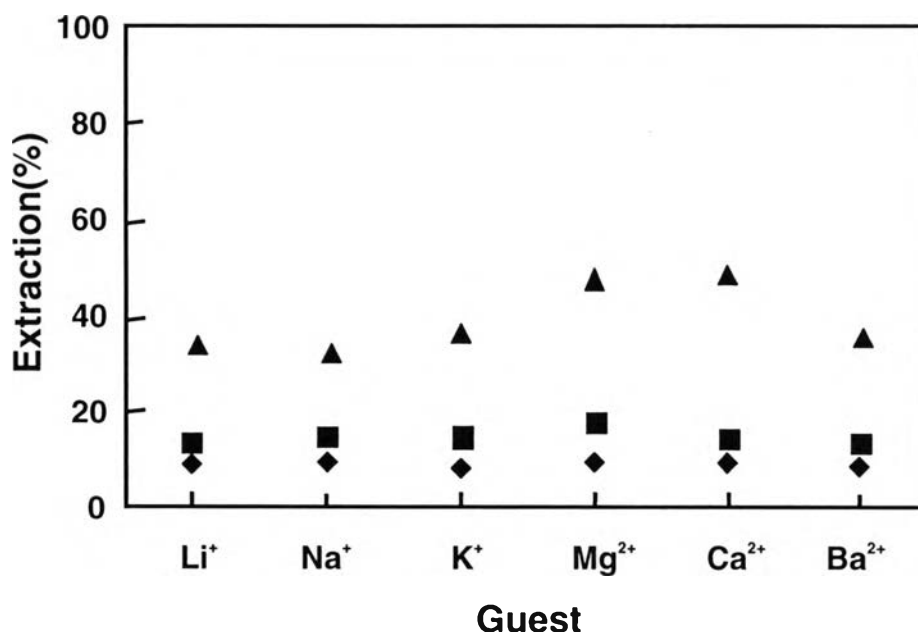




**Figure 4.8** Extraction percentage of metal picrate at  $[M^+][Pic^-] = 7 \times 10^{-5} M$  by silylbenzoxazine (**1**), when the concentration is varied at  $\blacklozenge$ ) 0.007M,  $\blacksquare$ ) 0.07M, and  $\blacktriangle$ ) 0.7M.



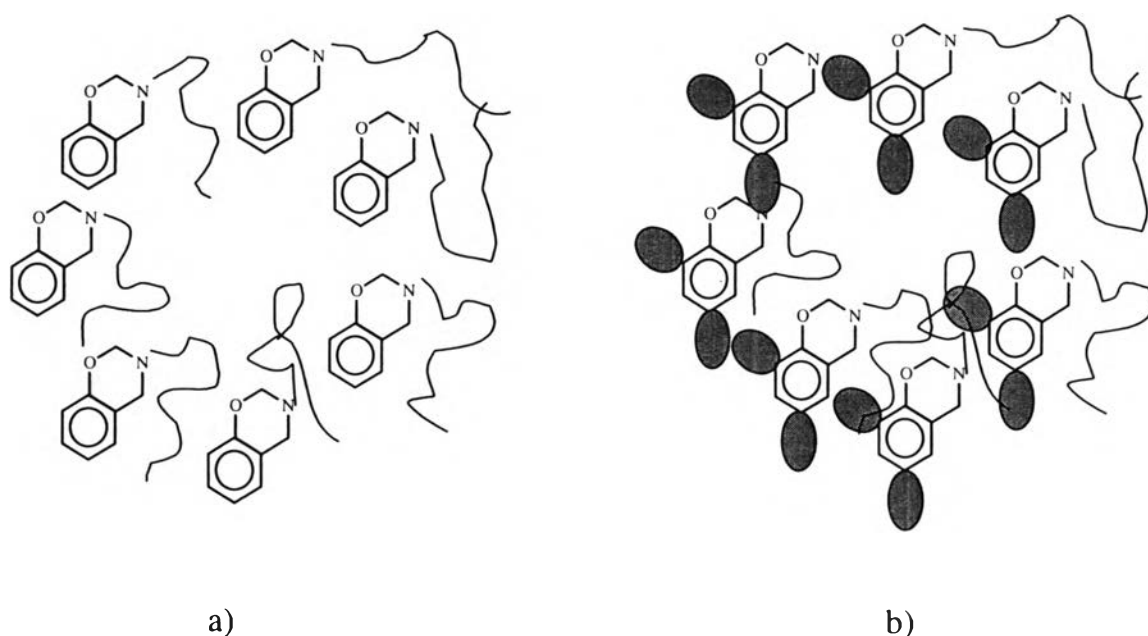
**Figure 4.9** Extraction percentage of metal picrate at  $[M^+][Pic^-] = 7 \times 10^{-5} M$  by silylbenzoxazine (**2**), when the concentration is varied at  $\blacklozenge$ ) 0.007M,  $\blacksquare$ ) 0.07M, and  $\blacktriangle$ ) 0.7M.



**Figure 4.10** Extraction percentage of metal picrate at  $[M^+][Pic^-] = 7 \times 10^{-5} M$  by silylbenzoxazine (**3**), when the concentration is varied at  $\blacklozenge$ ) 0.007M,  $\blacksquare$ ) 0.07M, and  $\blacktriangle$ ) 0.7M.

As shown in Figures 4.8, 4.9, and 4.10, when the monomer concentration is increased, the percentage of ion extraction increases for all types of metal ions. 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 achieved by gathering silylbenzoxazine unit as a host compound to construct the cavity for guest, as seen in the reported case of pseudocyclic calixarene (Yamagishi *et al.*, 1996). However, difference in silylbenzoxazine (**1**)-(b>3) is

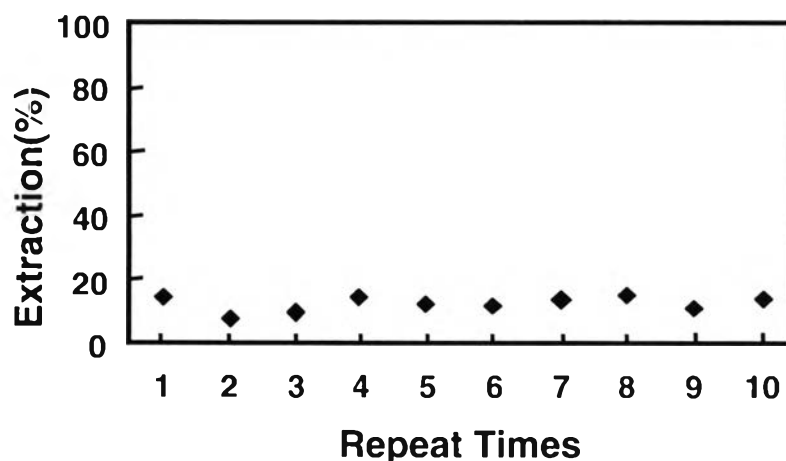
the presence of methyl substituent group and its location on the benzoxazine ring. The difference in ion extraction behavior can be considered as a result of the preferred assembly structure to form a host as shown schematically in Figure 4.11. In the case of **(3)**, which has two methyl groups and 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 structure as schematically shown in Figure 4.11.



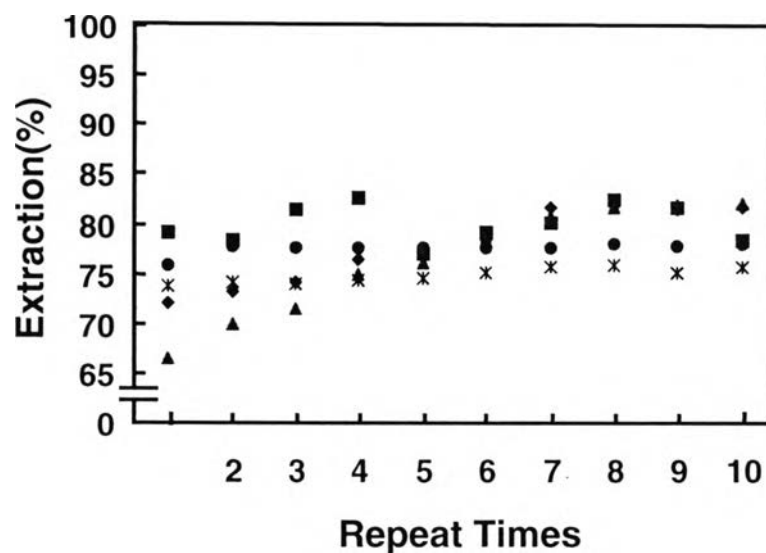
**Figure 4.11** Schematic draw for silylbenzoxazine derivatives, a) compound **(1)**, and b) compound **(3)**.

#### 4.3.2 Ion Extraction Behavior of the Silylbenzoxazine-modified Silica Surface

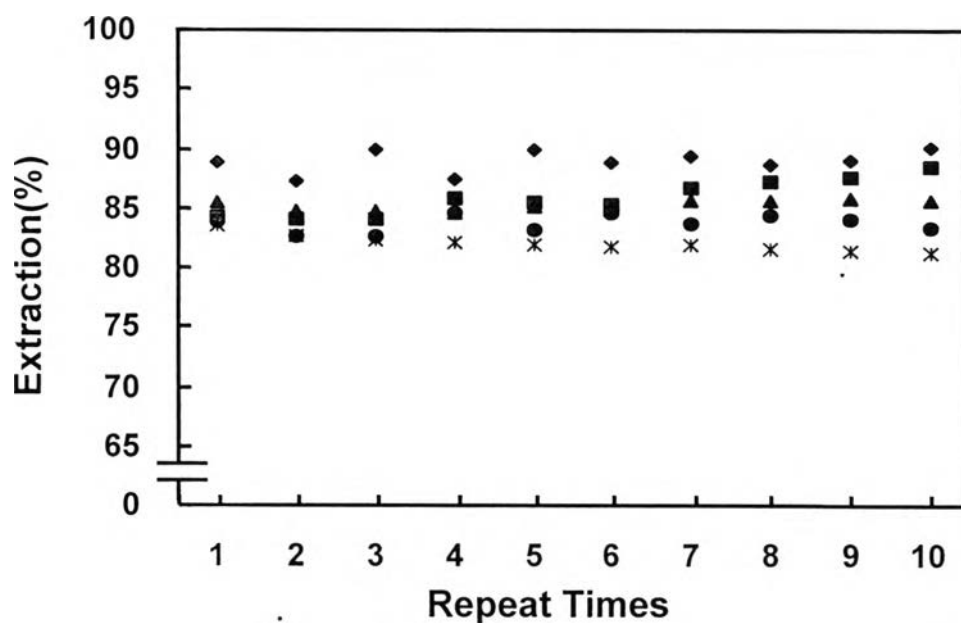
The ion extraction of pure silica and benzoxazine coupled silica, (4)-(6), for alkali and alkaline earth metal ions were determined by atomic absorption spectroscopy. The surface-treated silica was packed in the column and column chromatography was used to study the ion extraction.



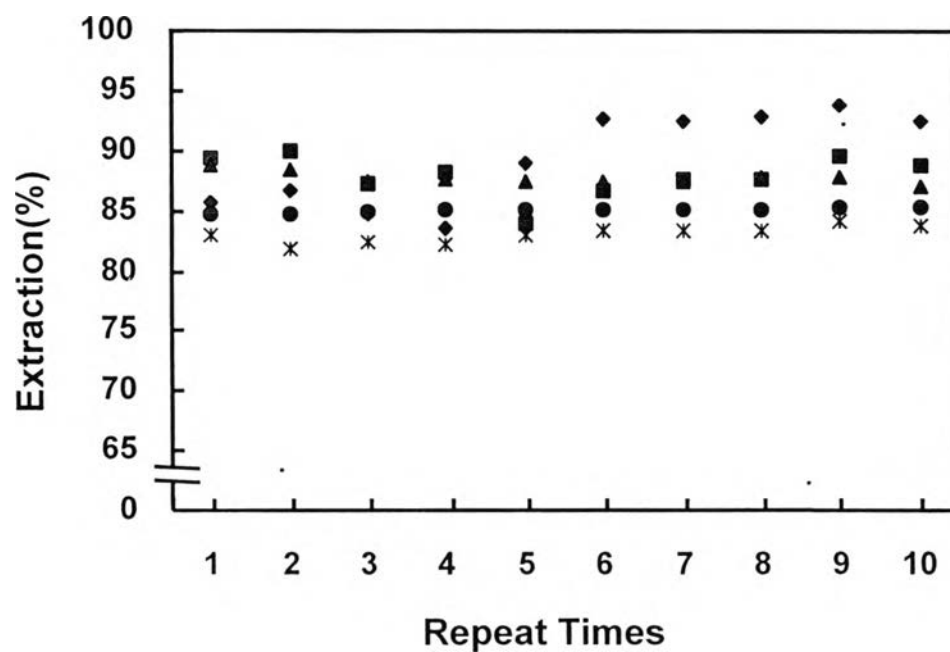
**Figure 4.12** Extraction percentage of metal picrate at  $[M^+][Pic^-] = 7 \times 10^{-5} M$  by pure silica.



**Figure 4.13** Extraction percentage of metal picrate at  $[M^+][Pic^-] = 7 \times 10^{-5} M$  by (4) for  $Na^+$  (◆),  $K^+$  (■),  $Mg^{2+}$  (▲),  $Ca^{2+}$  (●) and  $Ba^{2+}$  (χ).



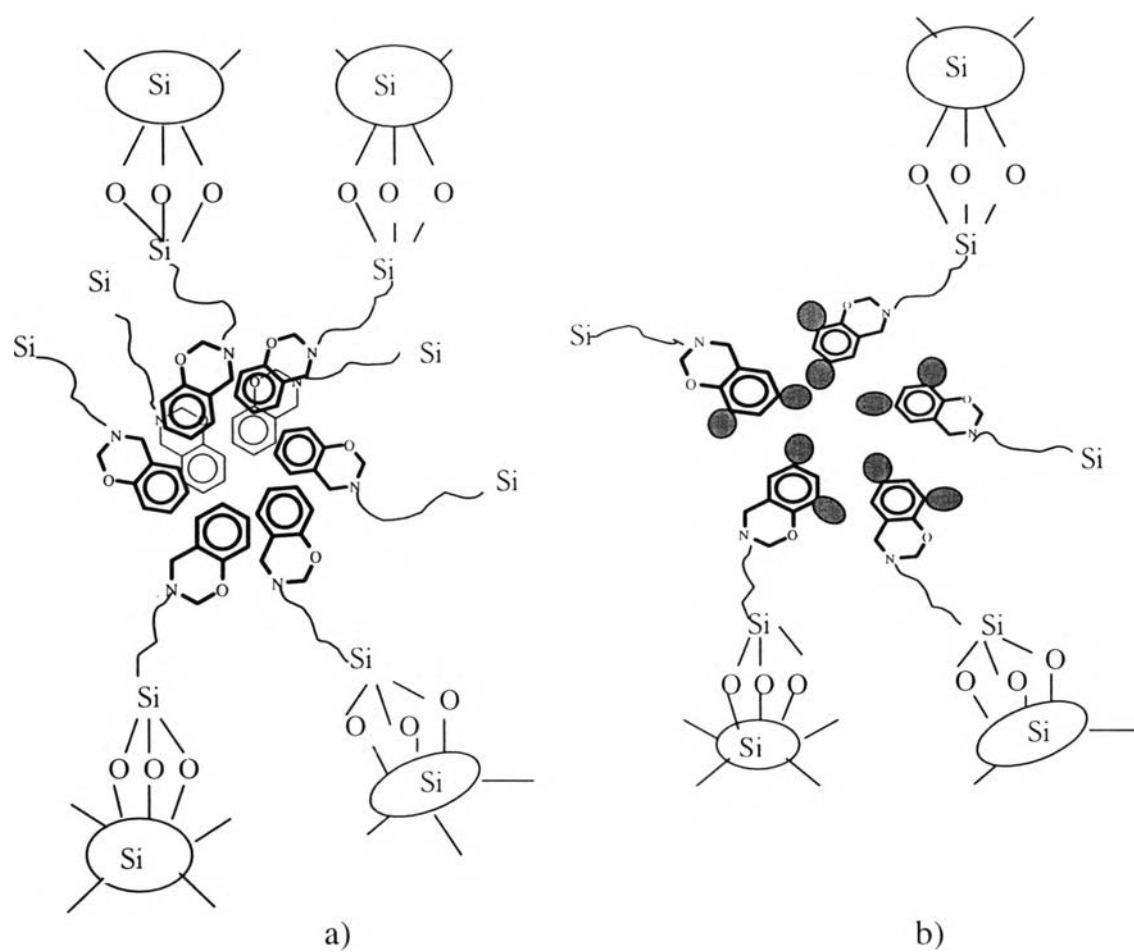
**Figure 4.14** Extraction percentage of metal picrate at  $[M^+][Pic^-] = 7 \times 10^{-5} M$  by (5) for  $Na^+$  (◆),  $K^+$  (■),  $Mg^{2+}$  (▲),  $Ca^{2+}$  (●) and  $Ba^{2+}$  (×).



**Figure 4.15** Extraction percentage of metal picrate at  $[M^+][Pic^-] = 7 \times 10^{-5} M$  by (6) for  $Na^+$  (◆),  $K^+$  (■),  $Mg^{2+}$  (▲),  $Ca^{2+}$  (●) and  $Ba^{2+}$  (×).

Figure 4.12 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, as shown in Figures 4.13, 4.14, and 4.15, silylbenzoxazine derivatives coupled silica, (4)-(6), show 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 exists 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 4.16. The silica surface modified with silylbenzoxazine without bulky group (compound 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).



**Figure 4.16** Schematic draw for silica surface modified benzoxazine derivatives, a) compound (4), and b) compound (6).