CHAPTER III
EXPERIMENTAL

3.1 Materials

Hydroquinone monomethyl ether, propylamine (w/w 40 %), hydroiodic acid (55-58 %), and anhydrous sodium sulfate were purchased from Fluka Chemicals (Buchs, Switzerland). Chloroform, dichloromethane, and isopropanol were the products of Lab-scan (Thailand). Methanol, and tetrahydrofuran were purchased from J.T. Baker (USA.). Picric acid, sodium hydroxide, and potassium hydroxide were obtained from Ajax Chemicals (Australia). Diethyl ether was from Scharlau (Barcelona, Spain), and paraformaldehyde was used without further purification from E. Merck (Germany). Deuterated chloroform was from Euriso-top (France).

3.2 Instruments

3.2.1 Fourier Transform Infrared Spectrophotometer (FTIR)

FTIR spectra were obtained from a Bruker Equinox 55 spectrometer with 32 scans at a resolution of 4 cm^{-1} in frequency range of 4,000-400 cm^{-1}. Crude and liquid samples were measured by casting on ZnSe cell. Powder samples were measured by pressing with KBr into a pellet.

3.2.2 Fourier Transform Nuclear Magnetic Resonance Spectrometer (FT-NMR)

Fourier transform ^{1}H-NMR spectrometer (ACF 200 MHz of Bruker Switzerland) was used to study the structure of the prepared compounds.

3.2.3 Ultraviolet-Visible Spectrophotometer (UV-Vis)

Picrate metal ion concentration in aqueous phase was determined by a Perkin-Elmer Lamda-16 ultraviolet-visible spectrophotometer.

3.2.4 Mass Spectrometer (MS)

Mass spectra of benzoxazine monomer and dimer were obtained using a VG Autospec model 7070E from Fison Instruments with VG data system. Samples were run in the positive fast atomic bombardment ($FAB\text{-}MS^+$) mode using glycerol as the matrix. Cesium gun was used as an initiator and cesium iodide (CsI) was used as a reference.

For cyclic oligobenzoxazine, mass sprectrum was determined by Bruker Polymer TOF mass spectrometer under the courtesy of the National Metal Materials Technology Center.

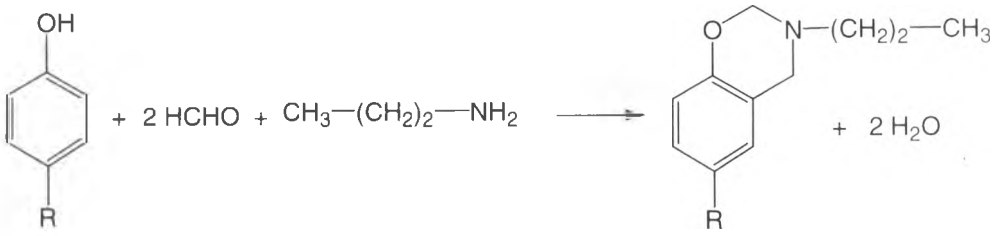
3.2.5 Vortex Mixer

A GENIE-2 Scientific Industries vortex mixer was applied for shaking the mixture of host in organic phase and metal in aqueous solution.

3.3 Methodology

3.3.1 Preparation of Benzoxazine Monomer; 3, 4-dihydro-6-methoxy -3-propyl-2H-1,3-benzoxazine,**1**, 3,4-dihydro-6-methyl-3-propyl -2H-1,3-benzoxazine, **2** (Scheme 3.1)

3,4-dihydro-6-methoxy-3-propyl-2H-1,3-benzoxazine **1**, and 3,4-dihydro-6-methyl-3-propyl-2H-1,3-benzoxazine **2** were prepared from the reaction of paraformaldehyde and propylamine with hydroquinone monomethyl ether and p-cresol, respectively, as reported by Ishida *et al.*



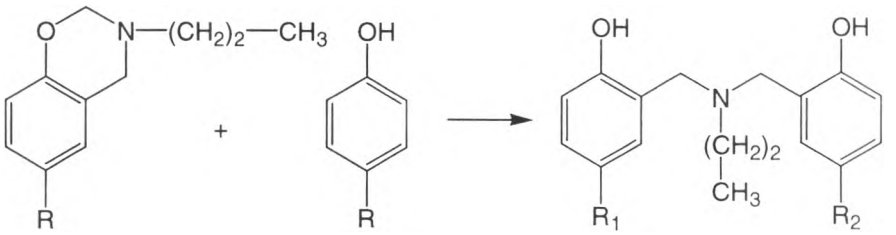
R: OCH_3 for **1**

CH_3 for **2**

Scheme 3.1 Preparation of benzoxazine monomers **1**, and **2**.

3.3.2 Preparation of Benzoxazine Dimer; N,N-bis (5-methoxy-2-hydroxybenzyl) propylamine, **3**, N,N-bis (5-methyl-2-hydroxybenzyl) propylamine, **4** (Scheme 3.2)

The obtained monomers **1**, and **2** were reacted with hydroquinone monomethyl ether, and p-cresol to prepare N,N-bis (5-methoxy-2-hydroxybenzyl) propylamine **3**, and N,N-bis (5-methyl-2-hydroxybenzyl) propylamine **4**, respectively, as reported by Laobuthee *et al.*



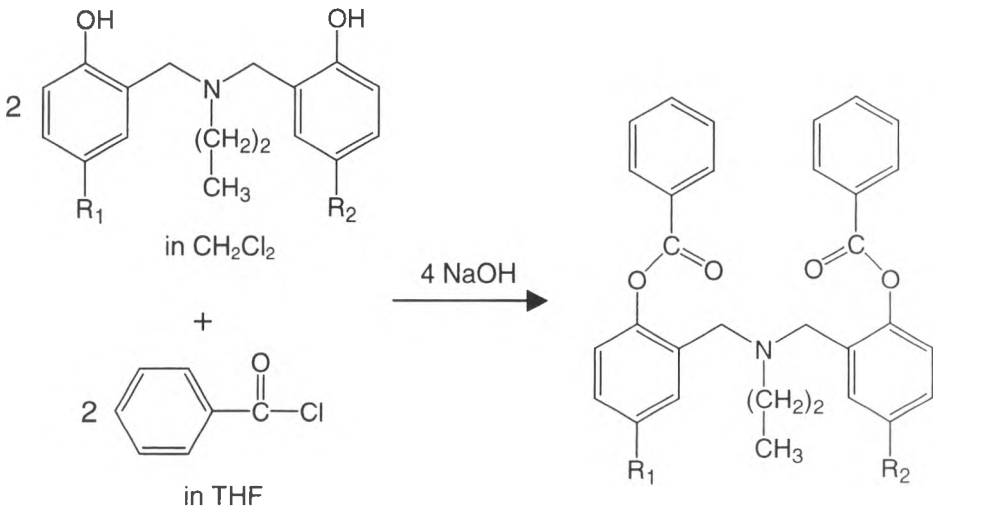
R_1, R_2: OCH_3 for **3**

CH_3 for **4**

Scheme 3.2 Preparation of benzoxazine dimers **3**, and **4**.

3.3.3 Preparation of Esterified Dimer; N,N-bis (5-methoxy-2-benzoylbenzyl) propylamine, **5**, N,N-bis (5-methyl-2-benzoylbenzyl) propylamine, **6** (Scheme 3.3)

Benzoxazine dimers **3** (5 mmol) was dissolved in dichloromethane (50 mL), followed by adding sodium hydroxide (20 mmol) in water (50 mL). The mixture was stirred vigorously and benzoyl chloride (10 mmol) in dichloromethane (50 mL) was slowly added. The reaction was performed at room temperature for 8 h and the completion of reaction was confirmed by TLC. The solution obtained was then washed with water to remove unreacted benzoyl chloride. Anhydrous sodium sulfate was added and was left overnight. The solvent was removed to obtain a white powder of N,N-bis (5-methoxy-2-benzoylbenzyl) propylamine benzoxazine **5**. N,N-bis (5-methyl-2-benzoylbenzyl) propylamine benzoxazine **6** was prepared similar to **5** but using **4** as a starting precursor.



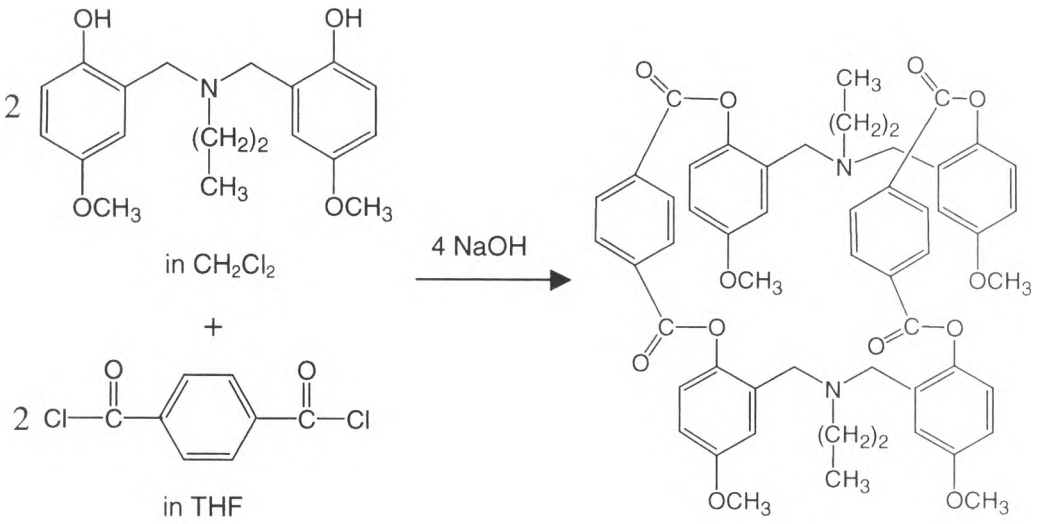
R_1, R_2: OCH_3 for **5**

CH_3 for **6**

Scheme 3.3 Preparation of esterified dimers **5**, and **6**.

3.3.4 Preparation of Cyclic Oligobenzoxazine, **7** (Scheme 3.4)

Benzoxazine dimer **3** (2 mmol) was dissolved in dichloromethane (100 mL), followed by adding sodium hydroxide (8 mmol) in water (15 mL). The mixture was vigorously stirred for 20 min. A solution of terephthaloyl chloride (2 mmol) in tetrahydrofuran (50 mL) was added dropwise for 1 h. The reaction was proceeded at room temperature for 8 h. Dichloromethane phase was collected and extracted with water for 6 times. Anhydrous sodium sulfate was added and left overnight. The solvent was removed and the white precipitate was obtained. The precipitation was collected and recrystallized in dichloromethane.



Scheme 3.4 Preparation of cyclic oligobenzoxazine **7**.

3.3.5 Preparation of Metal Picrate Solution

Sodium and potassium picrates were prepared by recrystallization of picric acid with NaOH and KOH, respectively, in methanol. The metal picrate was dissolved in aqueous solution at concentration $7x10^{-5}$ M and used as a metal picrate solution.

3.3.6 Study on Ion Extraction Ability

Five mL of ionophore in organic solution and 5 mL of ion solution were mixed vigorously for 2 min at room temperature. Ion concentration in aqueous phase was determined by UV-Vis spectrophotometer.