CHAPTER III
EXPERIMENTAL

3.1 Materials

Paraformaldehyde, 2,4-dimethylphenol and cupric acetate monohydrate were purchased from Fluka, Switzerland. Sodiumhydroxide and isopropanol were obtained from Carlo Erba, Italy. Ethylenediamine and copper (II) sulfate pentahydrate were purchased from Sigma-Aldrich, Germany. Copper (II) perchlorate hexahydrate was obtained from Aldrich, Germany. Cupric chloride dehydrate was received from Shimakyu's Pure Chemical, Japan. Chloroform, acetonitrile, diethylether, methanol, and *t*-butanol were provided from Labscan, Ireland. Deuterated chloroform, deuterated dimethylsulfoxide and deuterated acetonitrile were obtained from Aldrich, Germany. All chemicals were used as received.

3.2 Instruments and Equipment

Fourier transform infrared spectra (FTIR) were recorded by a Nicolet Nexus 670 FT-IR spectrometer in the range 4000-400 cm^{-1}. ^1H NMR was obtained from a Bruker ultrashield plus 500 MHz NMR spectrometer. Mass spectroscopy was analyzed by a Bruker a micrOTOF II electrospray ionization mass spectrometer (ESI-MS) and a Bruker Autoflex III Matrix-assisted laser desorption/ionization-time of flight mass spectrometer (MALDI-TOF MS). Particles size was measured by a Malvern zetasizer (nano-ZS). Specific viscosity was evaluated by a CANNON ubbelohde 50 B582 with a constant temperature bath CANNON CT1000. Absorption of compounds and kinetic of reaction were gained from a Shimadzu UV-Vis spectrophotometer (UV-1800). Morphology of supramolecular polymers was captured by a Hitachi H-7650 transmission electron microscope (TEM) and a Hitachi S-4800 ultra-high resolution cold field emission scanning electron microscope (FE-SEM).

3.3 Methodology

Bifunctional Benzoxazine Derivatives

Compound **1** was prepared as reported elsewhere (Laobuthee *et al*, 2001). In brief, 2,4-dimethylphenol (12.207 g, 100 mmol), paraformaldehyde (6.302 g, 210 mmol) and ethylenediamine (3.343 ml, 50 mmol) in chloroform (15 ml) were stirred at 70°C until the light yellow viscous solution was obtained. The crude product was washed by 1 M sodium hydroxide and water several times and recrystallized in a mixed solvent of chloroform and methanol (1:1 v/v). The white crystals were dried to yield 86%.

Compound **2** was accomplished by ring opening reaction as reported previously (Laobuthee *et al.*, 2001). In brief, 2,4-dimethylphenol (12.207 g, 100 mmol), was added into **1** (17.600 g, 50 mmol) in chloroform (15 ml) and allowed stirring at 120°C until the yellow viscous solution was obtained. The crude product was further purified in a mixed solvent of chloroform and methanol (1:1 v/v). The white crystals were dried to yield **2** for 80%.

Compound **3** was prepared as reported elsewhere (Laobuthee *et al*, 2001). In brief, 2,4-dimethylphenol (12.207 g, 100 mmol), paraformaldehyde (6.302 g, 210 mmol) and hexamethylenediamine (3.343 ml, 50 mmol) in chloroform (15 ml) were stirred at 70°C until the light yellow viscous solution was obtained. The crude product was washed by 1 M sodium hydroxide and water several times and recrystallized in a mixed solvent of chloroform and methanol (1:1 v/v). The white crystals were dried to yield 80%.

Compound **4** was accomplished by ring opening reaction as reported previously (Laobuthee *et al.*, 2001). In brief, 2,4-dimethylphenol (12.207 g, 100 mmol), was added into **1** (17.600 g, 50 mmol) in chloroform (15 ml) and allowed stirring at 120°C until the yellow viscous solution was obtained. The crude product was further purified in a mixed solvent of chloroform and methanol (1:1 v/v). The white crystals were dried to yield **4** for 87%.

Preparation of Metallo-supramolecular System

A solution containing 29.85 mg (0.05 mmol) of **2** in DMSO (1 ml) was mixed with a stoichiometric amount of 18.53 mg (0.05 mmol) of copper (II) perchlorate

hexahydrate in DMSO (1 ml). Other copper salts, i. e., cupric acetate monohydrate, copper (II) sulfate pentahydrate and cupric chloride dehydrate were used to prepare the complex with **2** in similar procedures. Compound **4** was also used to prepare similar complexation with the copper salts. The mixture was then left for 3 days before characterization.

Scheme 3.1 Synthesis of bifunctional benzoxazine derivatives.