CHAPTER IV
CONTROLABLE SUPRAMOLECULAR POLYMER FORMATION BASED ON HYDROGEN BOND NETWORK AND METAL-LIGAND BINDING AS A MODEL COMPOUND OF BENZOXZAZINE

Abstract

A novel benzoxazine-based hydrogen bond network and metallo-supramolecular polymers are proposed. By using N,N-bis(2-hydroxybenzyl)alkylamine derivative as a terminated chain, supramolecular polymer can be growth. Poly(dimethylsiloxane)-based benzoxazine dimer terminated prepared by the ring opening reaction of poly(dimethylsiloxane) diamine-based benzoxazine monomer are good example for showing ability of benzoxazine dimer terminated moiety as a precursor of supramolecular polymer via hydrogen bonding and metal ion complexation.

Keywords: Supramolecular polymer, Benzoxazine, Hydrogen bond network.

4.1 Introduction

Supramolecular polymers are polymeric arrangement of monomer molecules, linked together by reversible and highly directional secondary interaction such as hydrogen bond. In recent years, a unique molecular assembly which develops to supramolecular polymers[1] under weak reversible noncovalent interactions[2] is accepted as a novel model for advanced functional materials. Self-assembly can be controlled by molecular interactions, stoichiometric ratios, and binding kinetics of supramolecular motif.[3] Various noncovalent interactions, such as van der Waals (especially, hydrophobic interactions)[4, 5], π–π stacking[6-9], hydrogen bonding[10-14] and metal–ligand interations[15-18] are known to induce supramolecular polymers. Dynamic nature of supramolecular polymers, therefore, relies on their molecular responsiveness under external conditions, such as monomer concentrations, temperatures, and pressures, which are not possible in the case of traditional covalent polymers.[1, 3, 19]

For the past few years, our group has focused on *N,N*-bis(2-hydroxyalkylbenzyl)alkylamines and demonstrated their advantages of simple preparation and high reaction yield.[20, 21] These derivatives can be obtained by a single ring opening reaction of benzoxazine derivatives with phenol compounds. The single crystallography analysis points out that the derivatives are in a unique structure with inter- and intramolecular hydrogen bond networks to provide asymmetric compounds.[21] Our work also extended to the supramolecular chemistry of *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine by showing how these derivatives can form self-assembly through hydrogen bond[22] and also can be host molecules to accept various guest species such as alkali, alkaline earth, and transition metal ions.[23] It is important to note that, as identified by single crystal analysis, benzoxazine dimers show inter- and intramolecular hydrogen bonds between two dimers and at the same time, benzoxazine dimers perform host-guest complexation with metal ions. This come to our viewpoint to study how we can further develop benzoxazine dimers as supramolecular polymers based on the above mentioned unique molecular structure.

Herein, we focus on the use of diamine prepolymer in preparing benzoxazine dimer terminated which ease of synthesis and characterization. We firstly report the formation of supramolecular polymer through hydrogen bond network and metal ligand binding after adding metal guest, at the same time with controllable polymer to be branch or linear type depending on metal ions.

4.2 Experimental Section

4.2.1 Materials

Poly(dimethylsiloxane), bis(3-aminopropyl) terminated, M_w 2 500 g/mol, ethylenediamine, hexaethylenediamine, Europium(III) nitrate pentahydrate and copper (II) perchlorate hexahydrate were purchased from Aldrich, Germany. Paraformaldehyde, 2,4-dimethylphenol were purchased from Fluka, Switzerland. Sodiumhydroxide and were obtained from Carlo Erba, Italy. Chloroform, acetronitrile, and toluene were provided from Labscan, Ireland. All chemicals were used without further purification.

4.2.2 Synthesis of Diamine-based Benzoxazines

4.2.2.1 Synthesis of 6,6',6'',6'''-(ethane-1,2-diylbis(azanetriyl))tetrakis (methylene)tetrakis(2,4-dimethylphenol) (C2)

1,2-bis(6,8-dimethyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)ethane was simply prepared similar to our previous report. In brief, 2,4-dimethylphenol (1.22g, 10 mmol), paraformaldehyde (0.63 g, 21 mmol) and ethylenediamine (0.33 ml, 5 mmol) in chloroform (5 ml) were stirred in the opened-bath at 70°C until the white solid was obtained. Then followed by ring-opening reaction by adding 2,4-dimethylphenol (1.22 g, 10 mmol) in chloroform (5 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 C2 for 82%.

^{1}H NMR (500 MHz, DMSO): δ 2.05 (12H, s), 2.11 (12H, s), 2.85 (4H, t), 3.62 (8H, s), 6.63 (4H, s), 6.76 (4H, s), 9.29 (4H, br). ESI-MS: m/z 596.8.

4.2.2.2 Synthesis of 6,6',6'',6'''-(hexane-1,6-diylbis(azanetriyl))tetrakis (methylene)tetrakis(2,4-dimethylphenol) (C6)

The preparation of C6 was similar to C2, C6 was prepared from 2,4-dimethylphenol (1.22 g, 10 mmol), paraformaldehyde (0.63 g, 21 mmol) and hexamethylenediamine (0.58 g, 5 mmol) in chloroform (5 ml), after the white solid was obtained, followed by ring-opening reaction by adding 2,4-dimethylphenol (1.22 g, 10 mmol) in chloroform (5 ml) and allowed stirring at 120°C until the yellow viscous solution was obtained. The crude product was further purified with the same procedure as C2 to obtain white crystals were dried to yield C6 for 92%.

^{1}H NMR (500 MHz, DMSO): δ 1.04 (4H, *m*) 1.43 (4H, *m*), 2.08 (12H, *s*), 2.13 (12H, *s*), 2.33 (4H, *t*), 3.57 (8H, *s*), 6.70 (4H, *s*), 6.77 (4H, *s*), 9.49 (4H, *br*). ESI-MS: *m/z* 652.9.

4.2.2.3 Synthesis of Benzoxazine Dimer-terminated Poly (dimethylsiloxane) (PDS-Bz)

PDS-Bz, bis(6,6'-(propylazanediyl)bis(methylene) bis(2,4-dimethylphenol)) terminated was synthesized from Poly(dimethylsiloxane), bis(3-aminopropyl) terminated, formaldehyde and 2,4-dimethylphenol by refluxing in toluene at about 110°C for 12 hours. The crude product was washed by 1 M sodiumhydroxide and water several times and removing solvent to obtain yellow viscous compound (PDS-mBz). PDS-Bz was accomplished by ring opening reaction of PDS-mBz and 2,4-dimethylphenol refluxing in toluene for 12 hours. The crude product of PDS-Bz was further purified by washing by 1 M sodiumhydroxide and water several times and removing solvent to obtain yellow viscous compound (PDS-Bz).

4.2.3 Preparation of Supramolecular System of Metal Complexation

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 C2 in similar procedures. C6 was also used to prepare similar complexation with the copper salts. The mixture was then left for 3 days before characterization.

4.2.4 Preparation of Metallosupramolecular Polymer

A solution containing 150 mg (0.05 mmol) of PDS-Bz in mixed chloroform and acetronitrile (1:1) was added with a stoichiometric amount of 18.53 mg (0.05 mmol) of copper (II) perchlorate hexahydrate in mixed chloroform and acetronitrile (1:1). Europiumnitrate pentahydrate was used to prepare the complex with PDS-Bz in similar procedures but different in a stoicheometric ratio. The mixture was then left for 3 days before characterization.

4.2.5 Instruments and Characterization

The infrared spectra were recorded with 32 scan at resolution 2 cm^{-1} on a Thermo Nicolet Nexus 670 in the frequency range of 4000–400 cm^{-1} equipped with deuterated triglycinesulfate (DTGS) detector. The temperature dependence FTIR spectra were collected using an in-house temperature controller attachment. ^{1}H NMR spectra were recorded on a Bruker Ultrashield Plus NMR spectrometer operating at Larmor frequencies of 500.13 MHz. For spin-lattice relaxation time (T_1) measurements, T_1 value was evaluated from inversion recovery (π–τ–$\pi/2$) measurements at controlled temperature. Mass spectroscopy was analyzed by a Bruker micrOTOF II electrospray ionization mass spectrometer (ESI-MS). The particle sizes of the molecular assembly were determined at 25°C by a Malvern Zetasizer Nano Series with a detection angle of 173. The single crystals were obtained from recrystallization in DMSO. Specific$_e$ 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). The compounds were dissolved in DMSO as defined concentration, a drop of which was dispersed on an amorphous carbon film supported by a Cu grid for transmission electron microscopy. A Hitachi H-7650 transmission electron microscope (TEM) operating at an accelerating voltage of 200 kV and equipped with a double tilt holder was used for imaging and electron diffraction.

4.3 Results and Discussion

As monoamine based benzoxazine dimers (*N,N*-Bis(2-hydroxybenzyl)alkylamine derivatives) are stabilized under hydrogen bond networks and copper (II) ion complexation as evidenced from single-crystal x-ray analyses in the previous report[21, 24, 25] it is possible that diamine based benzoxazine dimers C4, and C6 perform supramolecular polymer via hydrogen bond network and also metal-ligand binding due to two positions of the structure play the role as molecular motif for continuously growing as the polymer chains.

Two compounds of dimer-based benzoxazines with methylene segmental length $-(CH_2)_n-$ with n = 2 and 6 were synthesized as a molecular motif to proof the concept of supramolecular polymer under hydrogen bond and metal-ligand complexation as shown in Scheme 4.1.

Scheme 4.1 Designed and synthesized model compounds.

C2: n = 1
C6: n = 2
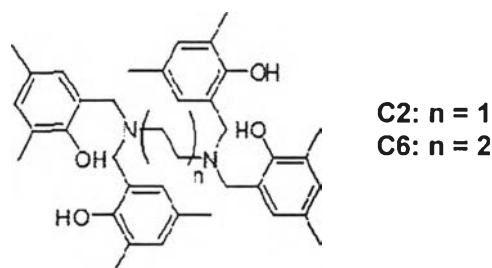
4.3.1 Self-assembly through hydrogen bond network and possibility to be supramolecular polymer

The self-assembly through hydrogen bond of C2 and C6 were by observing spin-lattice relaxation (T_1 relaxation). T_1 relaxation is a process of energy exchange between individual nuclear spins and the surrounding liquid or solid lattice. When molecules form interaction with each other, the interaction induces some changes to the T_1 relaxation time of the molecule. As bound sites have a shorter relaxation time than the unbound sites,[26, 27] the T_1 value is useful to evaluate how the molecule is under a specific network. For supramolecular polymer, when the concentration increases, the molecular weight will be increased and this brings an increase of T_1 value. Here, by simply varying the concentrations of C2, and C6

follow by observing T_1 value of each proton, we are able to apply T_1 values to trace how the molecules are packed and initiate supramolecular polymer. To investigate this in detail, the hydroxyl protons at about 9.56 ppm were focused (Figure 4.1 (a)), and it was found that the T_1 value at this position significantly changes with the concentration. In the case of C2, the value gradually decreased as the concentration increased, as it did for those of C6, but more rapidly. This suggests that C2 and C6 might be in a tight environment where hydroxyl group play the important role in forming intermolecular hydrogen network resulting in the self-assembly. It should be noted that hydrogen bond network of C2 might be initiated in the different way with C6 which shown in slightly decrease of T_1 value comparing to C6. In addition, the 0.001 M of C2 and C6 solution were further investigated. The T_1 values of hydroxyl proton were observed at different temperature. The T_1 values increase as temperature increased, implying that the energy can destroy the intermolecular hydrogen bond affect the higher T_1 values (Figure 4.1b).
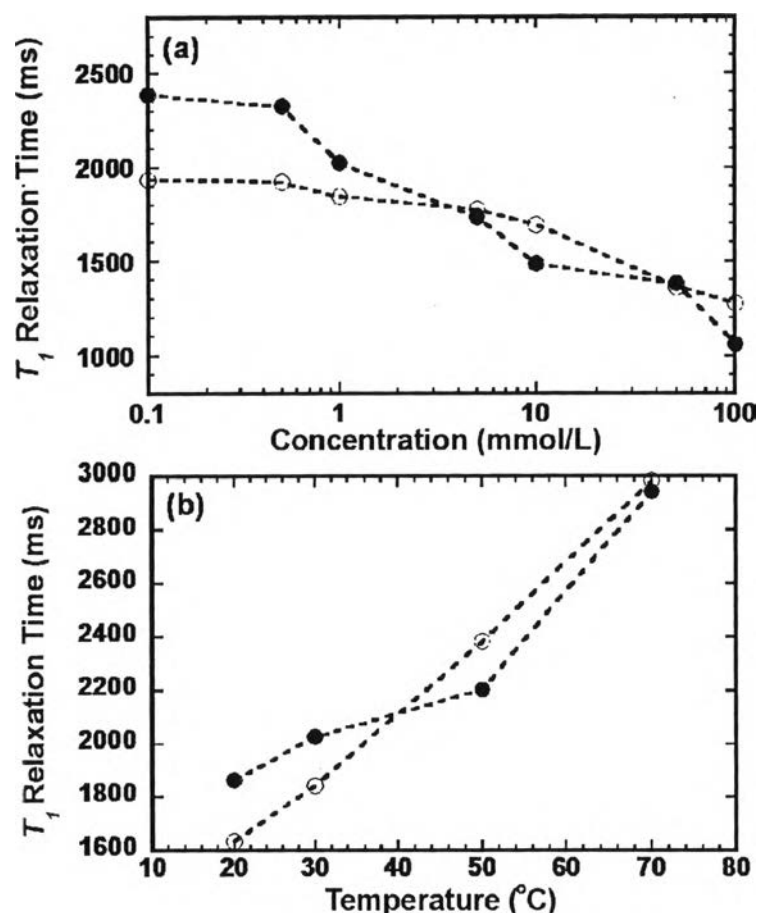
Figure 4.1 Spin-lattice relaxation time (T_1) of C2 (O) and C6 (●) under varying (a) concentration and (b) temperature.

To clarify how the hydrogen bond networks form in the structures, the crystal lattices were investigated using X-ray single crystal structure analyses. Here, the single crystals were grown slowly from the DMSO solutions. As shown in Figure 2 (a), the C2 crystal is in the triclinic system (P$\bar{1}$) with not only the intramolecular hydrogen bonds between N1 and O1 atoms, but also the intermolecular hydrogen bonds between O1 and O2 atoms with the distance of 2.84 Å. The molecules are in the extending, or stretching, structure. Figure 3B (a) illustrate the packing structures of C2 by emphasizing the hydrogen bonds and tilting of the molecules. For C6, the crystal structure is monoclinic (C2/c) with the

intermolecular hydrogen bonds between O1 and O2 atoms along the c-axial direction (Figure 2 (b)). It is important to note that the crystal structures of C2 and C6 in the different connected molecular packing implies the possibility of supramolecular polymer formation.
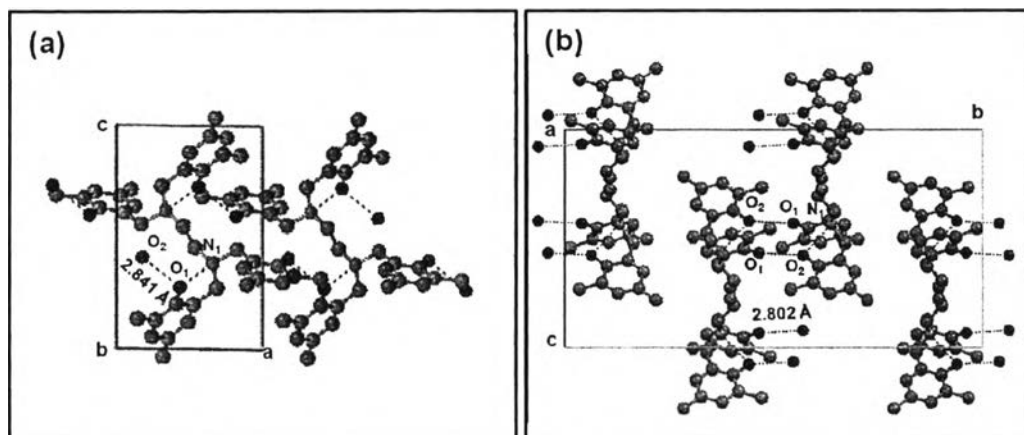

Figure 4.2 Crystal structures of (a) C2 and (b) C6.

To trace the self-assembly morphology, all derivatives were dissolved in DMSO with concentrations 0.001 M before naturally dried and the developed morphologies were observed by TEM. Figure 4.3(a) shows the spherical shape of C2 and (b) the dendrite of C6.
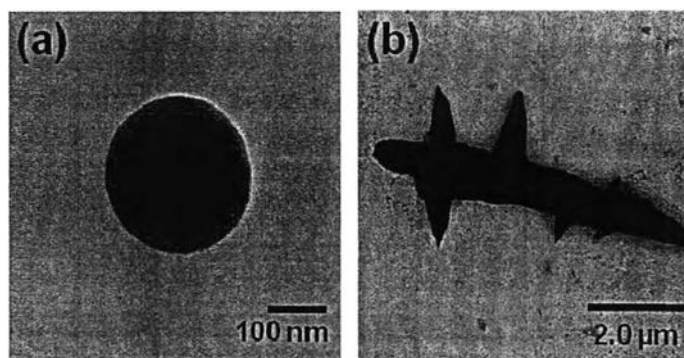
Figure 4.3 TEM images of (a) **C2** and (b) **C6** at concentration 0.001 M.

4.3.2 Self-assembly through metal-ligand complexation and possibility to be supramolecular polymer

The previous report shows that (*N,N*-Bis(2-hydroxybenzyl)alkylamine derivatives can form complex with copper (II) ions.[25, 28, 29] Diamine based benzoxazine dimers C2, and C6 were studied based on the complexation with copper (II) perchlorate ($Cu(ClO_4)_2$) in DMSO solvent. It is clear that when C2 and C6 formed the complex with copper, two new peaks at 313 nm, and 353 nm were observed showing the complexation.

To find the optimum condition for metallosupramolecular polymer, ratios of copper salts were varied, i.e., $CuCl_2$, $CuSO_4$, $Cu(ClO_4)_2$ and C_4H_6CuO in DMSO solvent. Figure 4.4 (a) is the plot of each complex related to the molar ratios. It is clear that C2 forms the complex with all copper salts as seen from the highest absorbance at 1:1 molar ratio which implies the host-guest complexation between C2 and copper ion is 1:1. Moreover, this ratio can be implied that metallosupramolecular polymers are formed.

In the case of C6, the host-guest complexation is different from that of C2. As indicated in Figure 4.4 (b), the host-guest ratio is depending on the type of ligand of metal ion. Only $C6/CuSO_4$; the host-guest ratio is 1:1, whereas both of $C6/CuCl_2$ and $C6/Cu(ClO_4)_2$; the host-guest ratio are 5:1 and that of $C6/C_4H_6CuO$; the host guest ratio is 1:2. It is not clear to us about the non-integral host guest ratio.
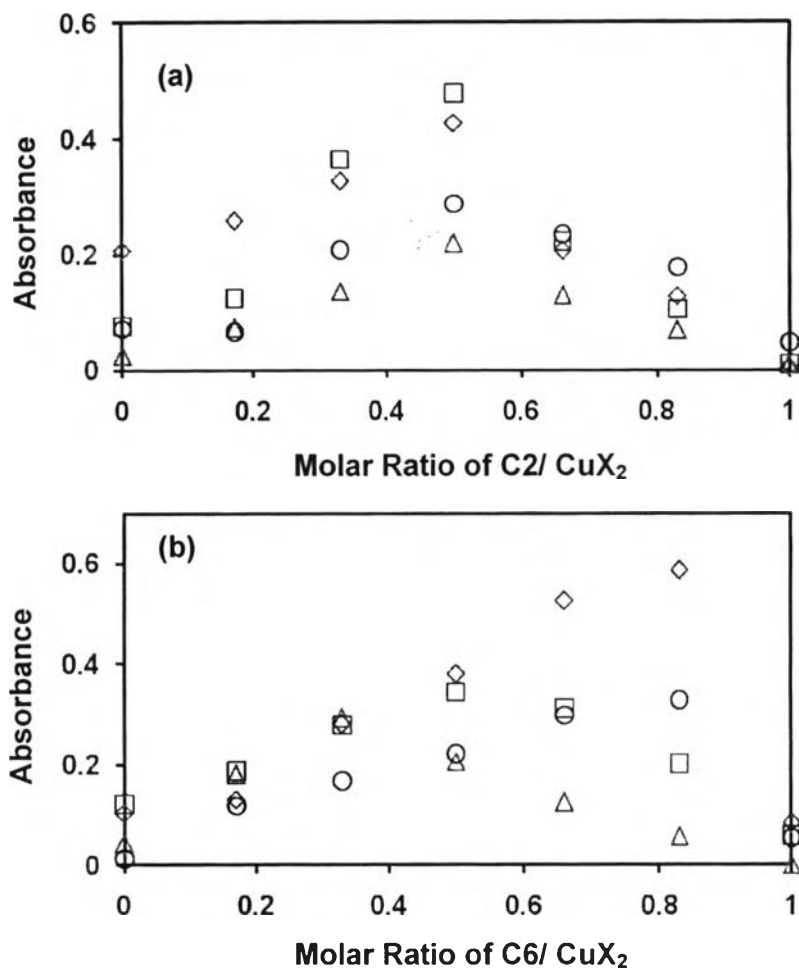
Figure 4.4 (a) UV spectra of CuX_2: C2 at different molar ratios in DMSO, and (b) UV spectra of CuX_2: C4 at different molar ratios in DMSO ($\Diamond$: $CuCl_2$, $\bigcirc$: $Cu(ClO_4)_2$, $\square$: $CuSO_4$, and $\triangle$: $C_4H_6CuO_2$).

Specific viscosity and molecular assembly size (particle size) are other information to confirm the supramolecular polymer formation. Beck, J. B. *et al.* reported an increase in viscosity related to the host-guest formation of 2,6-Bis(1'-methylbenzimidazolyl)pyridine-terminated monomers with metal ions system.[15] Figure 4.5 shows the specific viscosity of C2 after complexation with various types of copper salts. It is clear that all complexes show an increase in viscosity related to the amount of C2. Although it is expected to see the highest viscosity at 1:1 host-

guest ratio, only C2/Cu(ClO₄)₂ shows the highest viscosity at 1:1 ratio whereas other complexes are fluctuated.
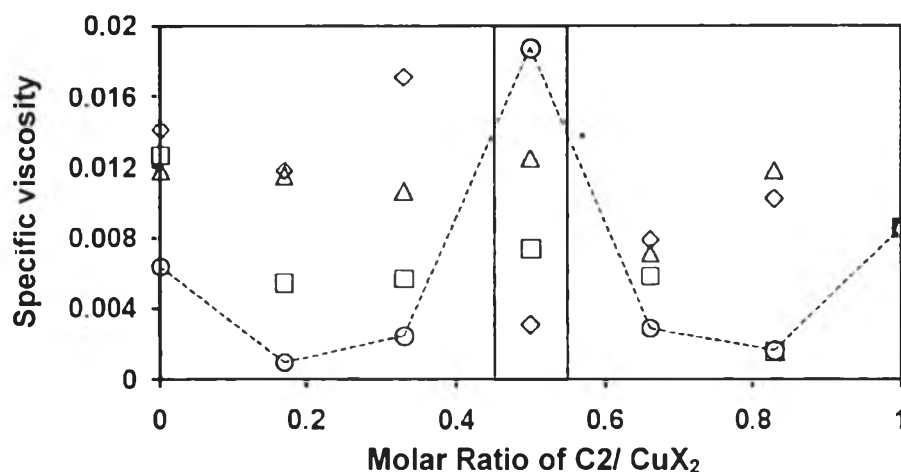

Figure 4.5 Specific viscosity of CuX₂: C2 at different molar ratios in DMSO (◇: CuCl₂, ○: Cu(ClO₄)₂, □: CuSO₄, and △: C₄H₆CuO₂).

Figure 4.6 shows the particle sizes of C2 and C6 after complexation with Cu(ClO₄)₂. It is clear that the particle size of 2/Cu(ClO₄)₂ becomes as high as 380 nm when the host-guest ratio is 1:1. This implies that 2/Cu(ClO₄)₂ might form a stable metallo-supramolecular polymer.

As C2 and Cu(ClO₄)₂ might be a good model to show the formation of supramolecular system as evidenced from the saturation of hyperchromic effect at 313 nm for 1:1 molar ratio (Figure 4.7). The metallo-supramolecules formation evaluated from the repeating units of supramolecular polymer was studied by using ^{1}H NMR end-group analysis. At 1:1 molar ratio, 0.005 M concentration, the end-group analysis by ^{1}H NMR confirms the repeating unit to be 4 as shown in the calculation (Figure 4.8).
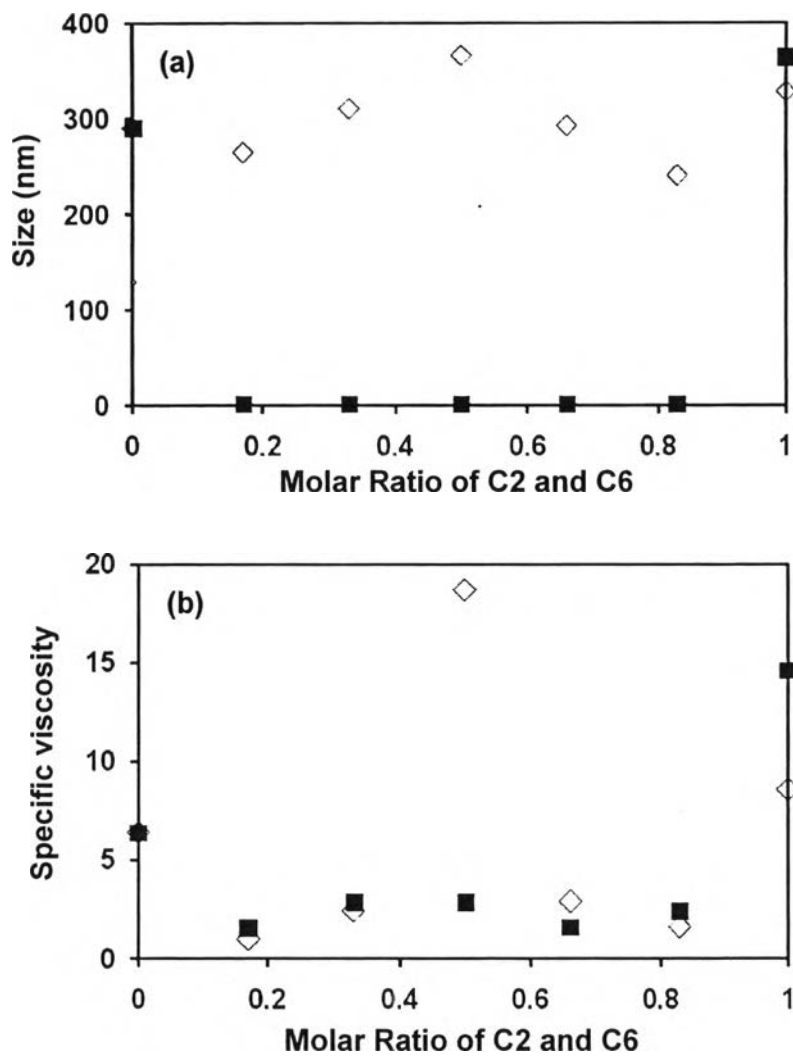
Figure 4.6 (a) Size of $Cu(ClO_4)_2$: **C2** ($\Diamond$, nm) and $Cu(ClO_4)_2$: **C6** ($\blacksquare$, nm) at different molar ratios in DMSO, and (b) specific viscosity of $Cu(ClO_4)_2$: **C2** ($\Diamond$) and $Cu(ClO_4)_2$: **C6** ($\blacksquare$) at different molar ratios in DMSO.
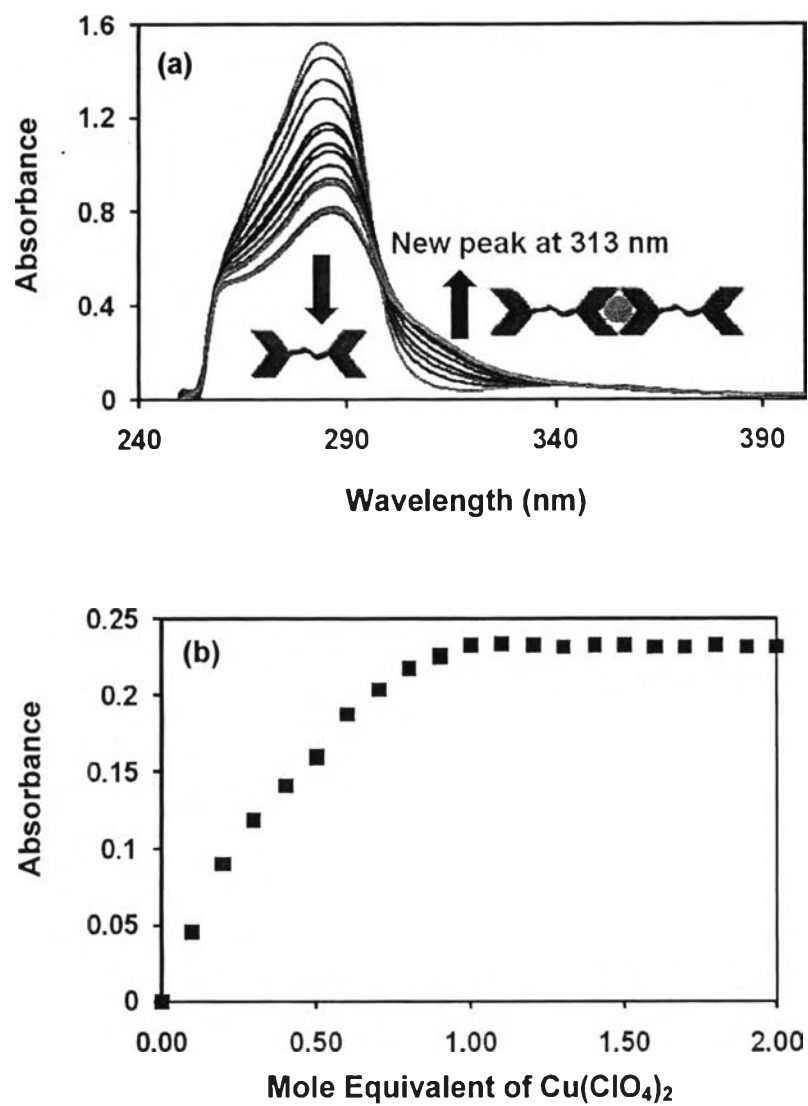
Figure 4.7 (a) UV spectra of $Cu(ClO_4)_2$: C2 at different molar ratios in DMSO, and (b) the absorbance at 313 nm obtained from each molar ratio.
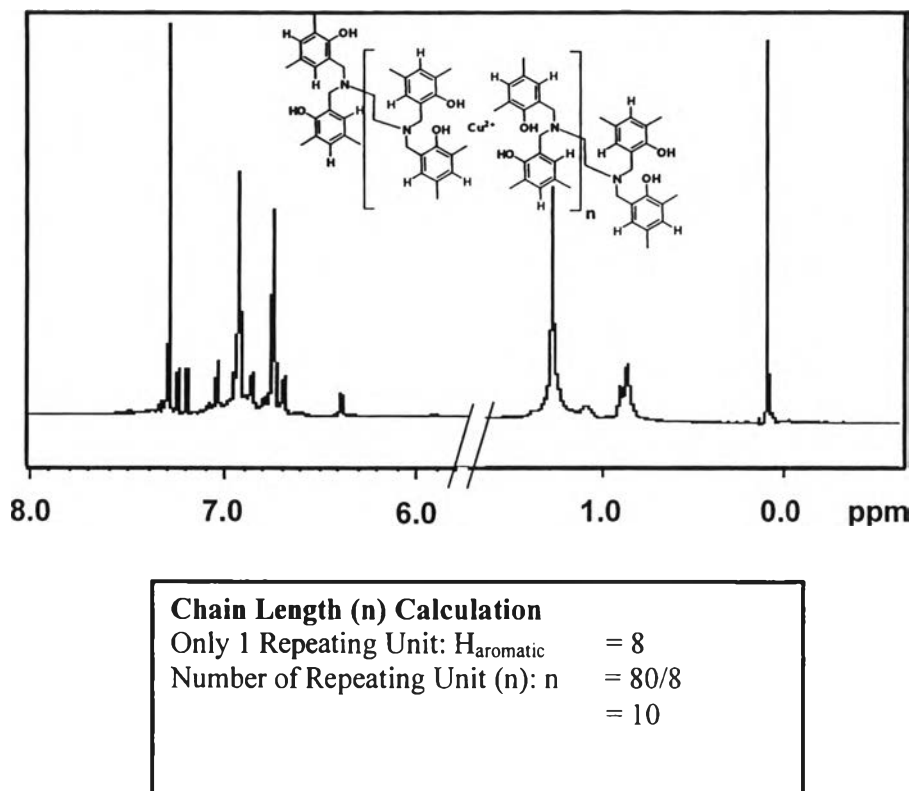
Chain Length (n) Calculation
Only 1 Repeating Unit: $H_{aromatic}$ $= 8$
Number of Repeating Unit (n): n $= 80/8$
$= 10$

Figure 4.8 ^{1}H NMR of $[2 \cdot Cu(ClO_4)_2]_n$ and integral ratio for chain length calculation.

4.3.3 Morphology of Metallo-supramolecular Self-assembly of C2

It comes to our question whether the supramolecular structured C2 and Cu^{2+} brings any changes in morphology. The morphology was clarified by using and TEM. The spherical shape was observed from starting material, C2. Surprisingly, after adding an equivalence of $Cu(ClO_4)_2$, 2 shows the needle-like shape morphology (Figure 4.9a, and b) which indicates the chains developed from C2.
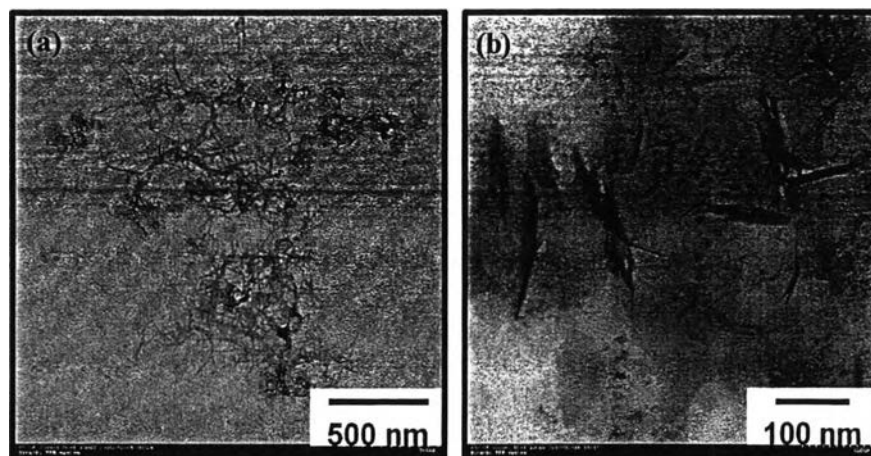
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Figure 4.9 TEM micrographs of C2 and Cu²⁺ at; a) 10 k and b) 30 k at 30 k.

4.3.4 Self Assembly and Solution Properties of the Supramolecular Polymer.

From the results, we found that the unit of (*N,N*-Bis(2-hydroxybenzyl)alkylamine derivatives) can act as the supramolecular motif to perform supramolecular polymer through hydrogen bonding and metal-ligand complexation. To study the supramolecular formation, the monomer C2 and C6 were changed to be macromonomer PDS-Bz. The creation of supramolecular polymer PDS-Bz via hydrogen bond network and metal-ligand binding was studied.

Figure 4.10 shows the image of PDS compared to PDS-Bz, the viscosity of PDS-Bz is higher which can be observed by naked eyes whereas PDS is a droplet of liquid polymer.
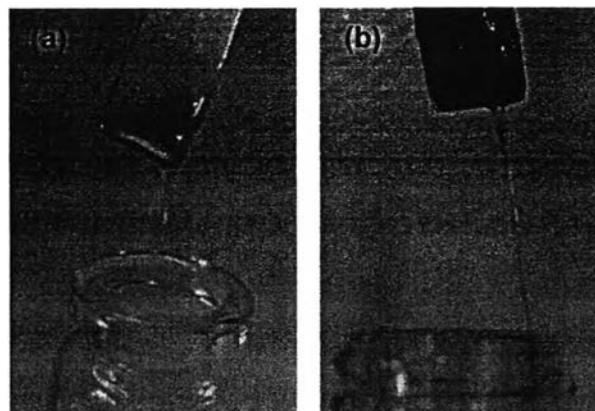
Figure 4.10 Photo of (a) PDS and (b) PDS-Bz.

From the Figure 4.5, $Cu(ClO_4)_2$ is the suitable metal compound to form metallosupramolecular polymer. PDS-Bz was used as a macromonomer to initiate metallosupramolecular polymer by adding $Cu(ClO_4)_2$. Figure 4.11 shows evidence of $Cu(ClO_4)_2$ complexation from the saturation of hypochromic effect at 386 nm for 1:1 molar ratio. It might be implied that metallosupramolecular polymer of PDS-Bz and Cu^{2+} is possible as a linear chain.
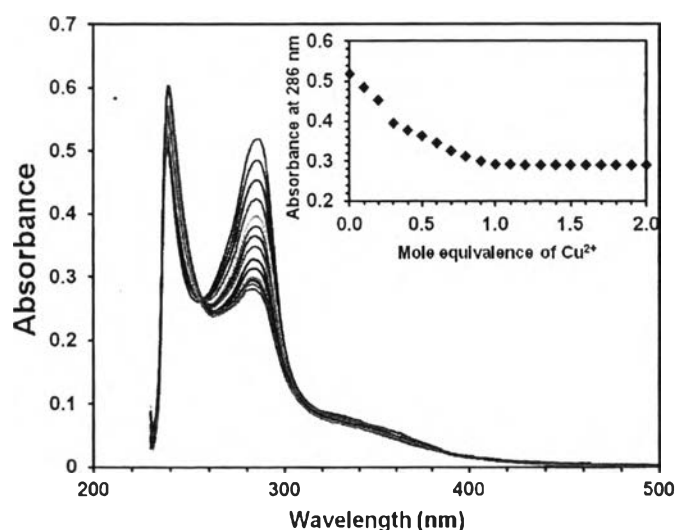

Figure 4.11 UV spectra of $Cu(ClO_4)_2$: PDS-Bz at different molar ratios in 1:1 $CHCl_3/CH_3CN$ with absorbance at 286 nm obtained from each molar ratio.

Metallo-supramolecular polymer in solution system can also be evaluated by particle size. Figure 4.12 shows semi-logarithmic plot of particle size related to the concentration of the metal complex of PDS-Bz. An increase in size of the supramolecular polymer as a function of concentration was verified by dynamic light scattering (DLS) technique to find a gradual increase in specific viscosity with an increase in complex $[PDS-Bz\cdot Cu(ClO_4)_2]_n$ concentration. However, PDS-Bz also shows the increasing in size compared to the PDS, suggesting that after terminated modification PDS-Bz can form supramolecular polymer through hydrogen bond and also mital-ligand binding.
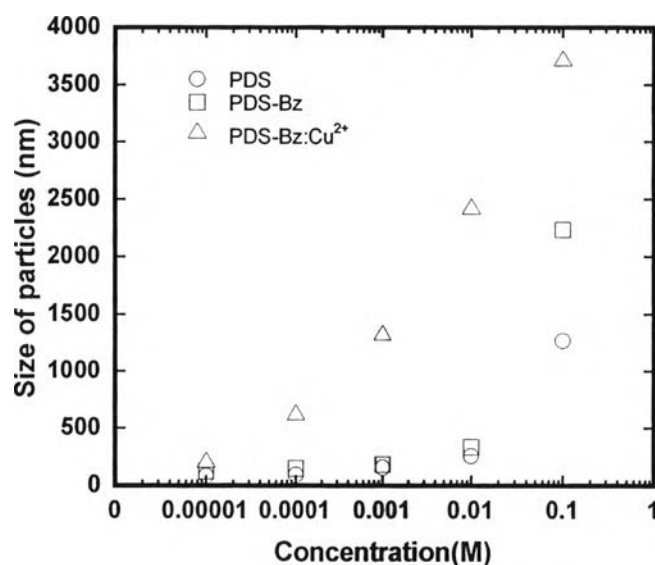

Figure 4.12 Particle size related to the concentration of PDS (O), PDS-Bz (□), and PDS-Bz:Cu^{2+} at 303 K.
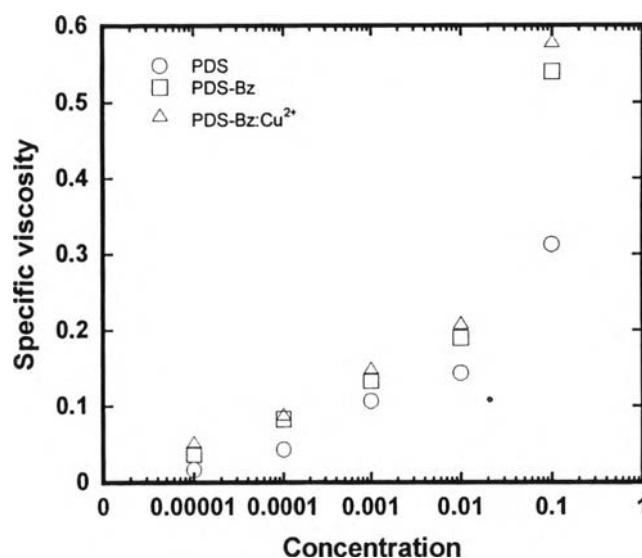
Figure 4.13 Specific viscosity related to the concentration of PDS (O), PDS-Bz (□), and PDS-Bz:Cu^{2+} at 303 K.

In our case, Figure 4.13 is a semi logarithm plot of specific viscosity obtained from ubbelohde viscosity measurement. It should be noted that the specific viscosities PDS is less than that of PDS-Bz and PDS-Bz:Cu^{2+} which all specific viscosity are increased as the concentration increased which slope around 1. So it is possible to say that PDS-Bz and PDS-Bz:Cu^{2+} form supramolecular polymer cause higher molecular weight thought hydrogen bonding and metal-ligand binding, respectively.

4.4 Conclusions

Structurally, diamine based benzoxazine dimers are unique as each unit contains four hydroxyl groups belonging to two phenols and two lone pair electrons belonging to two nitrogen atoms to possibly form the continuous framework of supramolecular polymer. The present work showed C2 and C6 which are different in terms of methylene chain length for two and four, respectively, as model supramolecular polymers. The studies indicated that C2 tended to be metallosupramolecular polymer whereas C6 tended to be hydrogen bonding supramolecular polymer. For C2, the complexation with copper (II) ions at an equimolar ratio led to metallosupramolecular polymer with the repeat unit for ≈10 and the morphology was fibrillar pattern. In the case of C6, the hydrogen bonded

supramolecular structure could be clearly identified by the shift of hydroxyl protons and the morphologies of C2 largely depended on the concentration to develop to be spheres. However, we can prove that benzoxazine dimer derivatives can be terminated moiety for supramolecular polymer building block. We confirmed this concept by using poly(dimethylsiloxane) terminated by benzoxazine dimer (PDS-Bz) and the supramolecular polymer via hydrogen bond and metal-ligand binding.

4.5 Acknowledgement

4.6 References

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