



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Supramolecular Chemistry

Supramolecular chemistry is termed as the chemistry of molecular assemblies and of the intermolecular bond, as “chemistry beyond the molecule” (Lehn 1995). Supramolecules consist of many simple subunits, each designed to perform a specific task. Ideal supramolecules found in natural system are DNA, RNA, enzyme, etc. (Ball, 1994).

For the past decades, developments of instruments lead to precise information of natural supramolecular formation and network which enables us to understand and imitate the natural phenomena by designing simple molecules feasible for two- and/or three-dimensional structure. For example, Lehn *et al.* (1988) proposed double-stranded “helicates”, which are the complex of Cu(I) with tris(bipyridine) (Figure 2.1). Catenanes and rotaxanes were carried out by donor-acceptor interactions between bipyridinium ions and both benzocrowns and naphthalenocrowns (Ortholand *et al.*, 1989). This leads to the development of synthetic supramolecules for many applications such as catalysts in biological systems, transporting agents in phase separation systems, building blocks in supramolecular system, molecular devices and machines, and molecular switches (Gokel, 1999).

Considering the components of supramolecular system,, which are the host and the guest molecules, one may realize how they are bound under the lock and key structure under intermolecular forces, including hydrogen bonding (Fu *et al.*, 1992) but not covalent bonds (Scheme 2.1) (Pederson, 1967; Lehn, 1995)., The examples of well-known host molecules are crown ethers (Pederson, 1967), cyclodextrins (Chankvetadze *et al.*, 1996), calixarenes (Böhmer, 1995), and their various derivatives (Scheme 2.2). The possible guest species are cations, anions or neutral molecules (Pederson, 1967; Lehn, 1995; Tuemmler *et al.*, 1977)

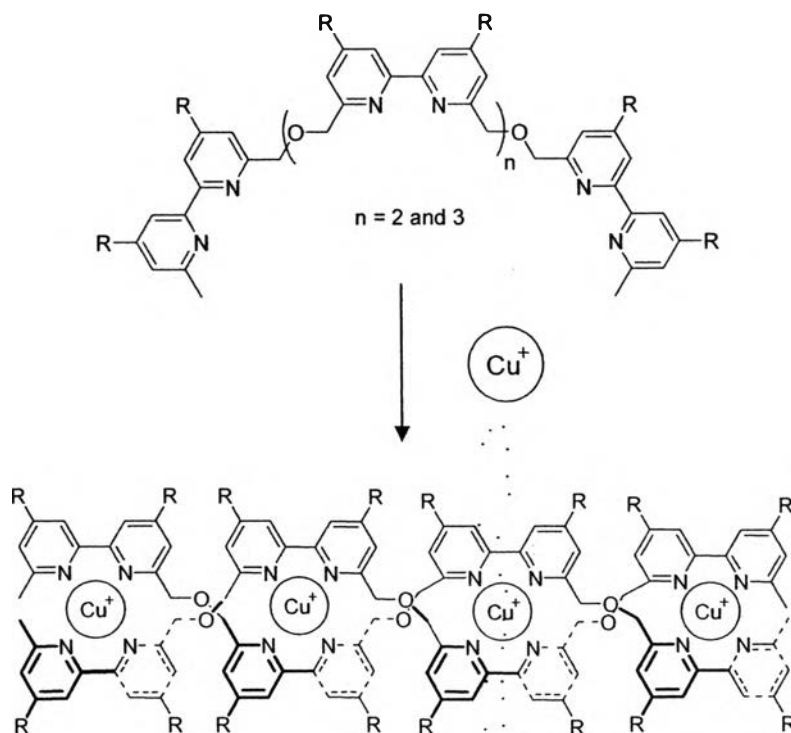
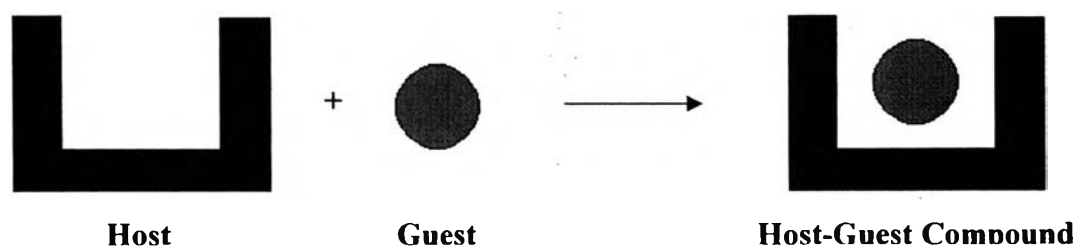


Figure 2.1 Schematic representation of the double-stranded “helicite”, resulting from the complexation of Cu(I) with oligobipyridine (Lehn *et al.*, 1988).

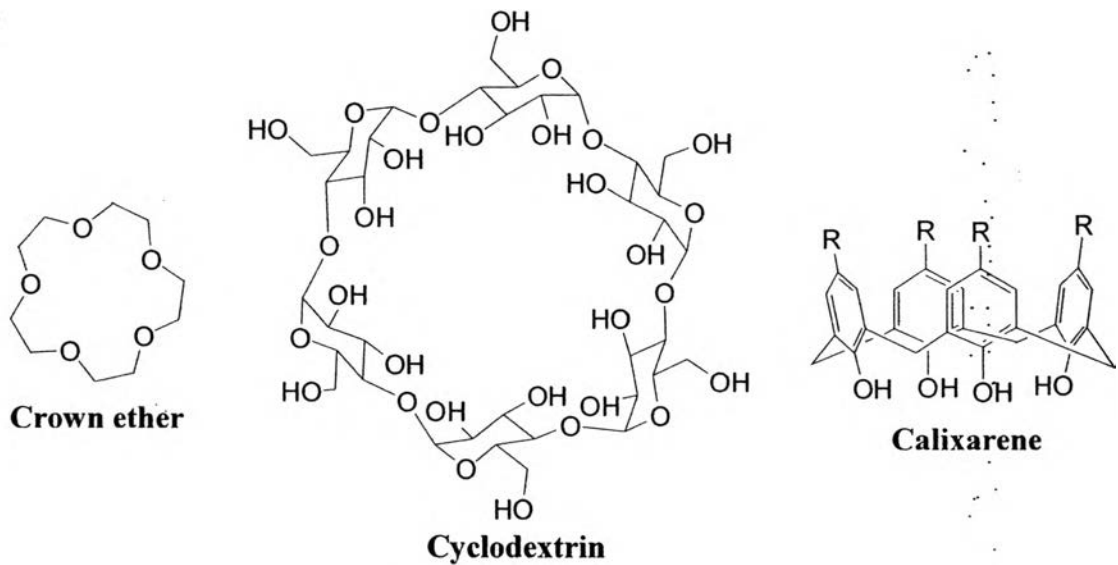
Scheme 2.1 Model of host-guest compound.



2.2 Supramolecular Polymers and Supramolecular Polymerization

Supramolecular polymers are defined as polymers which their monomeric units are connected to each other via secondary interactions (Brunsveld *et al.*, 2001) resulting in polymer structures under specific condition (Fox *et al.*, 2009). The formation is absolutely different from conventional polymers which each monomeric unit is bound together by covalent bond (Scheme 2.3). Normally, supramolecular

polymerizations are initiated from self-assembly of monomer to develop polymeric structures in main-chain by reversible/ dynamic noncovalent interactions. However, such main-chain supramolecular polymers are existed under an equilibrium process between monomeric, oligomeric, and polymeric species.



For example, a monomer (A-A) which contains self-complementary binding units will, under the suitable conditions, naturally, self-assemble into a linear supramolecular polymer chain $(A-A)_n$ as governed by the thermodynamics of the system. As an assembly also possesses a few irreversible termination processes, and the degree of polymerization (DP) is controlled by monomer concentration, binding constant, and assembly mechanism (Figure 2.2).

Scheme 2.3 Conventional polymer and supramolecular polymer.

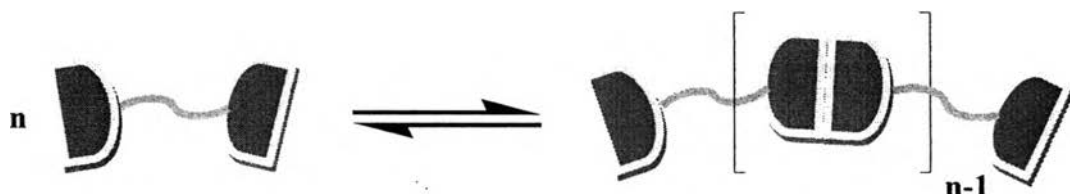
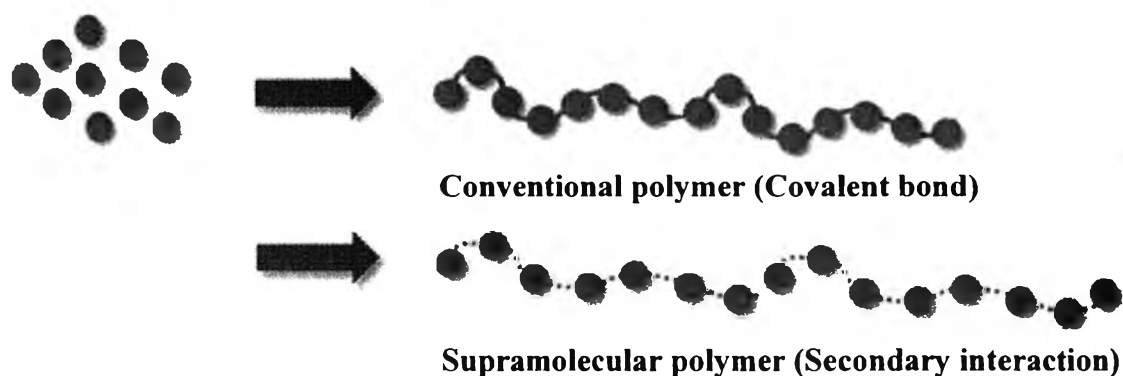


Figure 2.2 Formation of main-chain supramolecular polymer under the dynamic and kinetic equilibria.

A directional complementary couple (A–B) or a self-complementary unit (A–A) is possible to form many types of polymer structures, including linear homo- and copolymers, cross-linked networks and even branched structures (Lehn, 2000). For supramolecular polymers, which are formed by the reversible association of bifunctional monomers, the average degree of polymerization (DP) is determined by the strength of the end group interaction (Martin, 1996). The degree of polymerization is obviously dependent on the concentration of the solution and the association constant (Figure 2.3) (Brunsveld *et al.*, 2001).

Polymerization reactions involving covalent bond formation mostly occur under kinetic control because the potential barrier for the backward reaction (depolymerization) is often much larger than for the forward reaction. As a result, dilution (or heating) of the macromolecule will not result in a decrease of the molecular weight, in other words, the degree of conversion. This situation is very

much different in supramolecular polymerizations where, due to reversibility, the extent of reaction is directly coupled to thermodynamic forces such as concentration, temperature, and pressure. On the thermodynamic aspect of supramolecular polymerization processes, a single ditopic monomer is capable to form a supramolecular polymer via noncovalent association of its end groups. It is important to realize that the same phenomena can occur for supramolecular polymerizations involving two structurally different monomers, although in such a case the Gibbs free energy as a function of conversion is also dependent on the stoichiometric ratio of the two monomers. Three major mechanisms are isodesmic, ring-chain, and cooperation growth (Figure 2.4) (De Greef *et al.*, 2009).

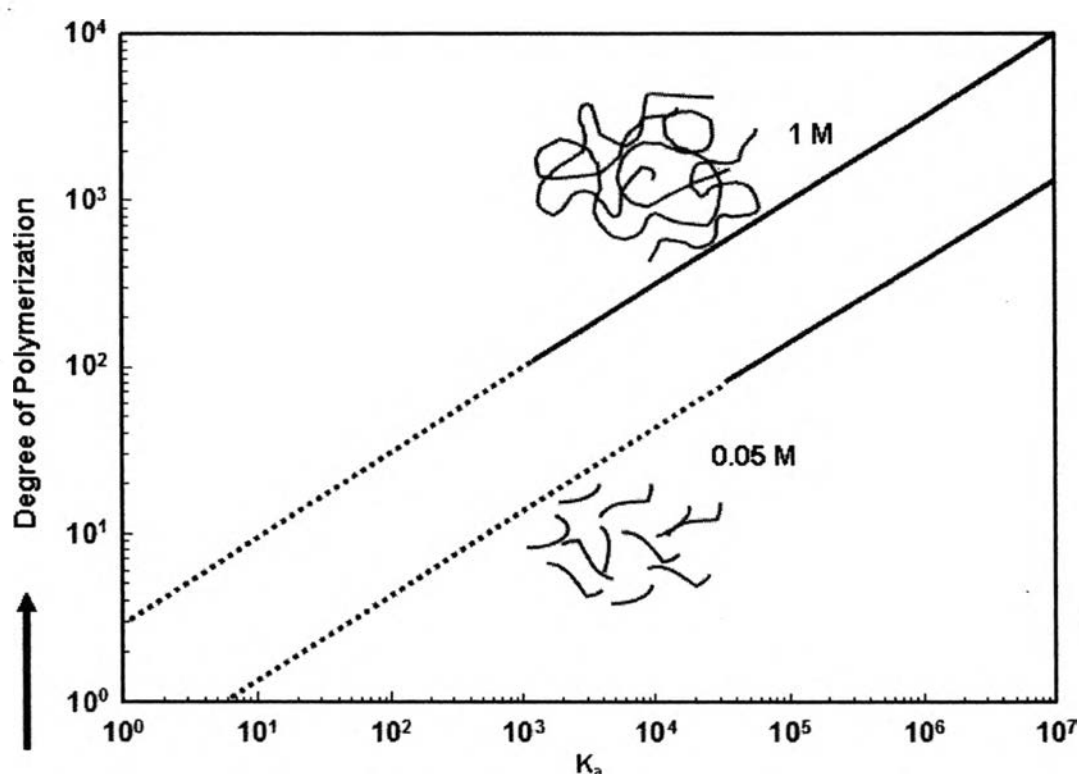


Figure 2.3 Theoretical plot of the degree of supramolecular polymerization versus association constant, K_a (M^{-1}) at two different concentrations.

Functional supramolecular polymers are different from commodity and/or engineering polymers. The polymerization of commodity and/or engineering

polymers is based on the polymerization through bulk, suspension, micelles, etc. in an elevated temperature, whereas that of the supramolecular polymer proceeds as the molecular assembly established. The molecular assembly may bring unique properties and functions as compared to those known for macromolecules. The control over mechanism of supramolecular polymer formation, the variety of self-assembling units, and the stability of the structures offers an enormous range of properties of these supramolecular polymers. This not only yields unique processing capabilities of responsive materials but also creates approaches to construct functional materials. The three distinctive areas application areas are (1) general functions based on excellent mechanical properties with a unique ease in processing, (2) electronic functions based on π -conjugated repeating units leading to supramolecular electronics, and (3) biomedical functions in regenerative medicine of biologically active supramolecular polymers (De Greef *et al.*, 2009).

2.2.1 Supramolecular Polymer based on Hydrogen Bonding

Although hydrogen bond between neutral organic molecules is not among the strongest noncovalent interaction, it holds a prominent place in supramolecular structure because of their directionality and versatility (Krische and Lehn, 2000). The relationship between the degree of polymerization and the strength of the noncovalent interaction between monomers in a supramolecular polymer (Figure 2.3) implies that cooperativity is required to obtain significant degrees of polymerization. Hence, either multiple-hydrogen bonds or a single hydrogen bond should be supported by additional forces (Sherrington *et al.*, 2001).

The strength of hydrogen bonds effects to a particular arrangement. The strength of single hydrogen bonds basically depends on the nature of donor and acceptor but it is influenced to a large extent by the solvent. The strength between multiple hydrogen bonding units obviously depends on the same factors, as well as on the number of hydrogen bonds. It has also been shown that the particular arrangement of neighbouring donor (D) and acceptor (A) sites is an additional factor which significantly affects the strength of the complexation. Figure 2.5 shows the examples of hydrogen bond units whereas complexes between the common ADA-DAD (1-2) motif exhibit an association constant of around 10^2 M^{-1} in chloroform,

this value is around 10^4 M^{-1} in complexes with a DAA-DDA (3-4) motif, while AAA and DDD arrays (5-6) exhibit association constants exceeding 10^5 M^{-1} .

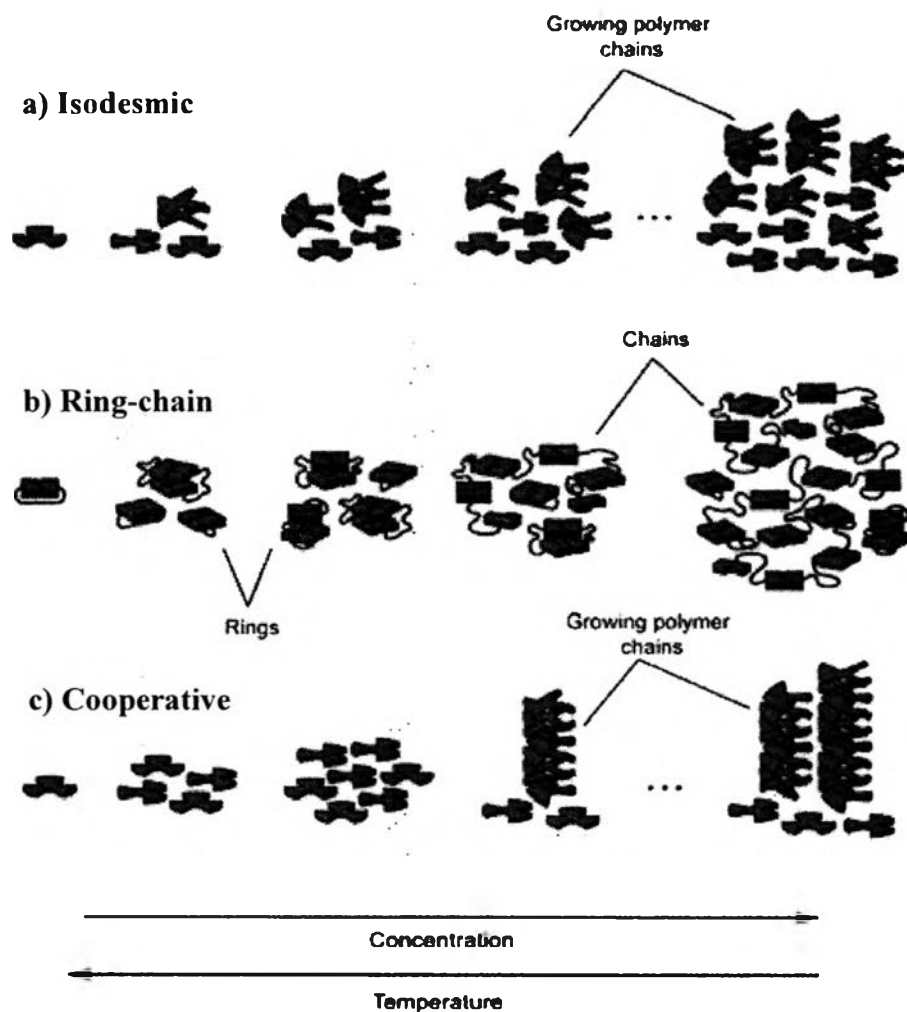


Figure 2.4 Schematic representation of three growth mechanisms by which a monomer can be polymerized into a supramolecular polymer: (a) isodesmic supramolecular polymerization; (b) ring-chain mediated supramolecular polymerization; and (c) cooperative supramolecular polymerization (De Greef *et al.*, 2009).

2.2.2 Supramolecular Polymer based on π -Conjugated System

The π -conjugated systems built up from repeating units can roughly be divided into oligomers and polymers. The self-assembly of these systems has mainly

been approached from both a material and a supramolecular chemistry. Self-assembly of π -conjugated oligomers has been achieved through supramolecular design rules. For example, the relation between intermolecular interactions and optical properties of substituted ter- and quarterthiophenes or tetrathienylenevinylene has been studied by UV-vis and fluorescence spectroscopy in linear and branched alkane or PMMA matrices (DiCesare *et al.*, 1999). These results showed that aggregates of oligothiophenes display a blue shifted absorption spectrum with respect to the molecularly dissolved state. Fréchet *et al.* synthesized triblock systems by symmetrically substituting undeca- and heptadecathiophene cores (**7**, **8**) with oligo(benzyl ether) dendrons. In such a way, monodisperse macromolecular architectures obtained were similar to dendritically substituted oligothiénylenevinylene (Jestin *et al.*, 1998) and oligoimides (Miller *et al.*, 1999).

Janssen *et al.* showed TEM images of the self-assembly of **8** into uniform nanoaggregates in size (20 nm) and shape (rod-like) in dichloromethane at low temperatures (Figure 2.6). Detailed analysis of the self-assembly in solution indicated a temperature-induced aggregation in which an intrachain planarization preceded the intermolecular π - π stacking. The favourable interactions led to an interchain delocalization of the photo-excited singlet, triplet, and charged states. Quantitative analysis of the aggregation process showed that the supramolecular aggregates were relatively small involving five to six molecules (Apperloo *et al.*, 2000). The apparent size limitation of the aggregates was ascribed to steric constraints imparted by the dendritic wedges (Lee *et al.*, 2002).

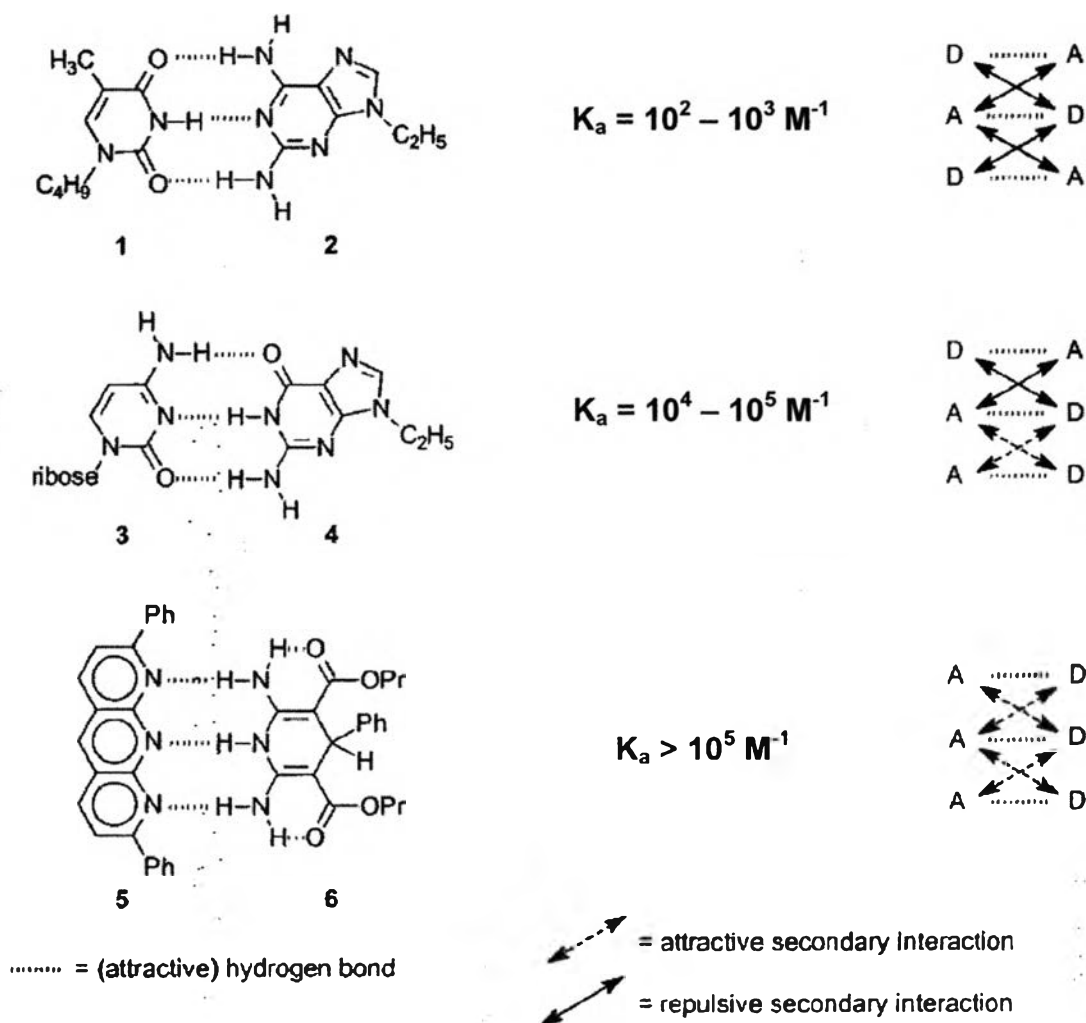


Figure 2.5 Stability of complexes with different hydrogen-bonding motifs (Brunsveld *et al.*, 2001).

2.2.3 Supramolecular Polymer based on Metal-ligand Binding

Metal ion and ligand binding is another type of interaction based on dipole-dipole interaction. Craig *et al.* recently developed a supramolecular motif, pyridine/metallopincers, in which the exchange rates could be varied without significantly changing the binding constant. The work demonstrated an important role of the binding rate on the properties of a supramolecular system. Rowan *et al.* focused on how the assembly influenced the solid state and the consequent physical properties, for example on the film materials. Metallo-supramolecular polymers (MSPs) which has a core consisting of a “soft” unit, such as poly(tetrahydrofuran) or poly(ethylene

backbone of the MSP. This phase segregation results in physical crosslink (Figure 2.7a) within the films and potentially leads to elastomeric properties. In 2005, Beck et al. synthesize Mebip₂, a system utilizing the Mebip₂·Zn^{II} motif (Figure 2.7(b)). X-ray (WAXD) and DMTA data were consistent with a presence of cross-linking phase

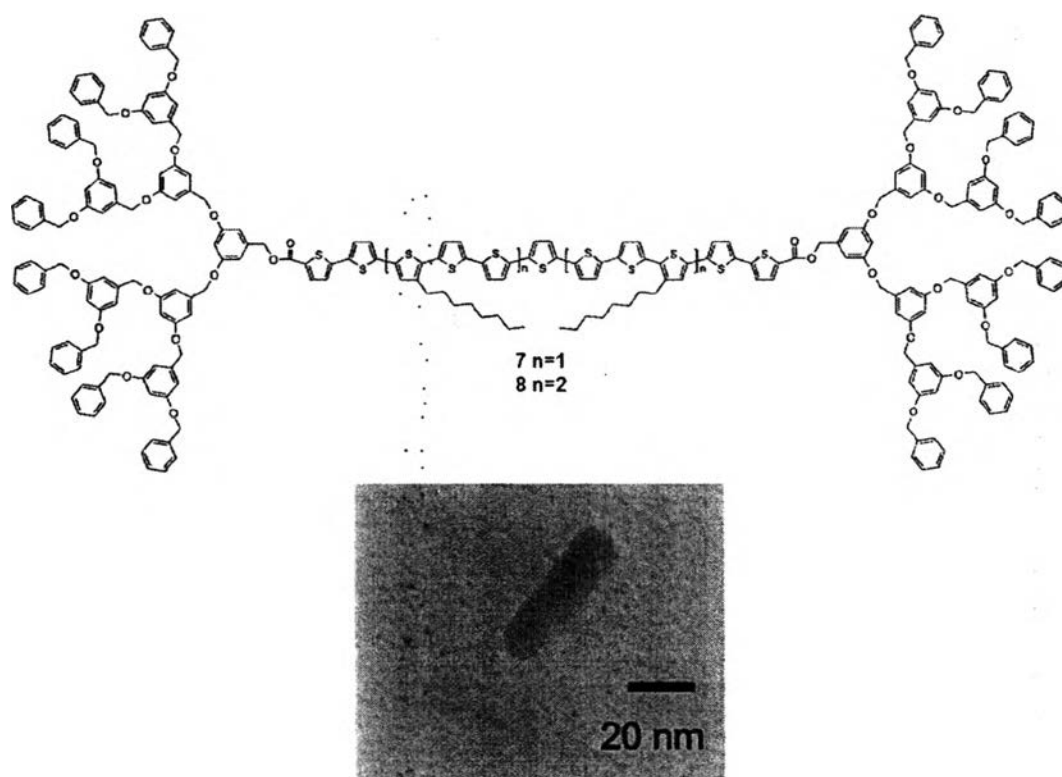


Figure 2.6 Dendritically substituted thiophenes that aggregate into nanorods as imaged by TEM. (Apperloo *et al.*, 2001).

(lamellar morphology) which was further backed up by the elastomeric behavior exhibited by these films at room temperature. This demonstrated that the physical properties could be influenced by phase segregation of a main-chain supramolecular polymer, i.e., in this case through physical cross-linking by the “hard” supramolecular motif.

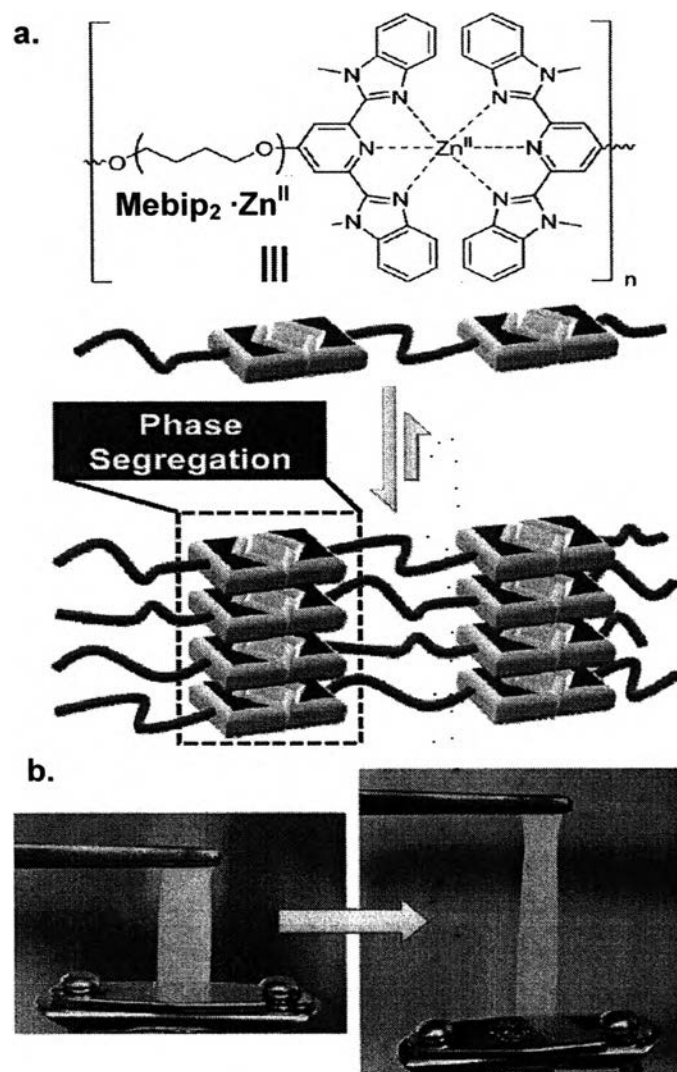
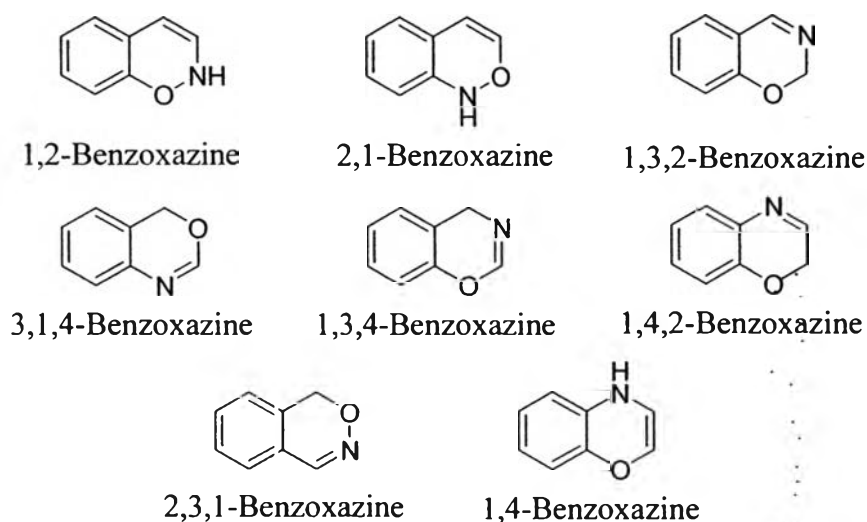


Figure 2.7 (a) Structure of metallo-supramolecular polymer Mebip₂ · Zn^{II} and the proposed AB multiblock-like phase segregation present in the solid state, and (b) elastic nature of the metallo-supramolecular polymer Mebip₂ · Zn(ClO₄)₂ (Fox *et al.*, 2009).

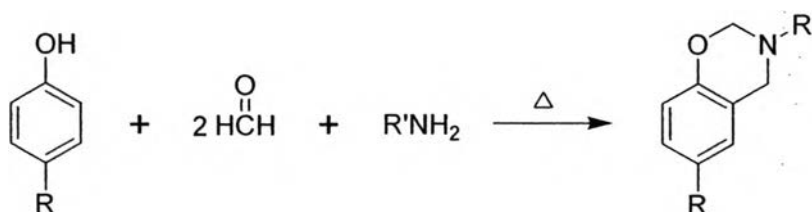
2.3 Benzoxazines

2.3.1 Structures and Chemistry of Benzoxazine derivatives

Benzoxazine is a heterocyclic compound, which consist of benzene ring and oxazine ring. There are 8 isomers, which are different at methylene position and substituted hydrogen atom position (Scheme 2.4).

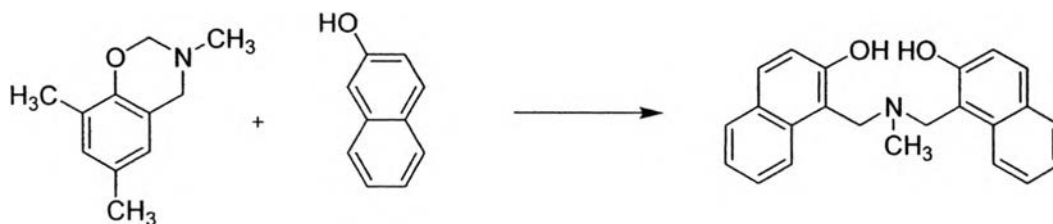
Scheme 2.4 Isomers of benzoxazine.

In 1964 Burke *et al.* reported the preparation of benzoxazine derivative (3,4-dihydro-1,3-2*H*-benzoxazines) by using one step of Mannich reaction between phenol derivative, formaldehyde and amine derivative (Scheme 2.5).

Scheme 2.5 Preparation of benzoxazine.

In 1965 Burke *et al.* reported on the preparation of *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine derivatives via a single ring opening of benzoxazine. For example, *N,N*-bis(2-hydroxy-1-naphthylmethyl)methylamine was carried out by the ring opening reaction of 2,3-dihydro-2-methyl-1*H*-naphth-(1,2-*e*)-1,3-oxazine with 2-naphthol (Scheme 2.6).

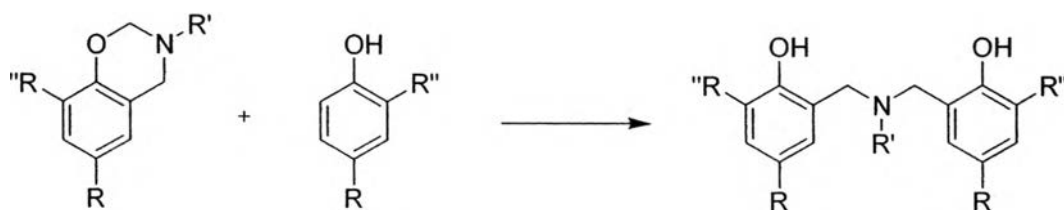
Scheme 2.6 Ring opening reaction of 2,3-dihydro-2-methyl-1H-naphth-(1,2-e)-1,3-oxazine with 2-naphthol.



In the case of para-substituted phenol based benzoxazines, linear polymer should be obtained. However, Riess *et al.* (1985) found that the polymerization proceeded with a limit of four to six repeat units. At that time, the involved factors and the mechanisms controlling the polymerization were not clarified.

Our group demonstrated that benzoxazine ring opening reaction terminates at the very first step. This leads to a quantitative amount (yield 80%-90%) of a benzoxazine dimers, *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine derivatives (Scheme 2.6) (Laobuthee *et al.*, 2001, 2003; Phongtamrug *et al.*, 2004, 2005, 2006). Considering the structure of these derivatives, the single crystallography analyses pointed out the unique structure under inter- and intramolecular hydrogen bonds network (Figure 2.8). Our group also demonstrated the effect of the inter- and intramolecular hydrogen bond in controlling the reaction resulting in an asymmetric structure (Laobuthee *et al.*, 2001) as shown in Scheme 2.7.

Scheme 2.7 Single ring opening reaction of benzoxazines with phenol derivatives.



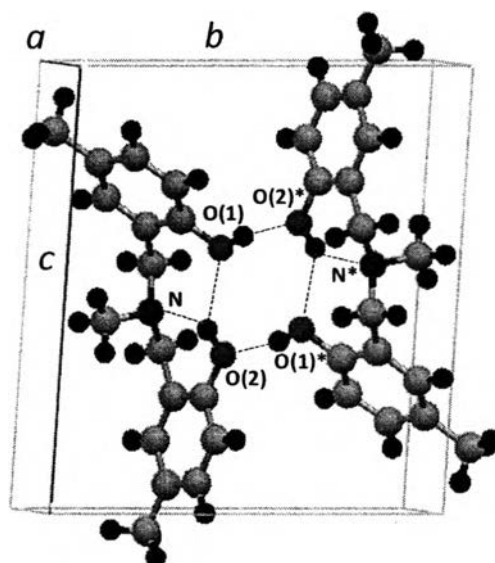


Figure 2.8 Crystal structure of *N,N*-bis(5-methyl-2-hydroxybenzyl)methylamine.

2.3.2 Inclusion Phenomena of *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine and Its Derivatives

According to the repeat unit of *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine which is resemble to that of calixarene, it is expected to see the molecules perform as a host compound to accept various kinds of guest species. In the past, we succeeded in showing an inclusion phenomena of *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine derivatives with alkaline picrate salts (Laobuthee *et al.*, 2003). We demonstrated the copper ion binding properties of the derivatives under the double-oxygen-bridged dimeric system through X-ray single crystal analysis result (Phongtamrug *et al.*, 2006) (Figure 2.9). We also proposed the existence of multi-guest species, i.e., ion and neutral molecules, in a single host-guest framework (Phongtamrug *et al.*, 2005, 2006).

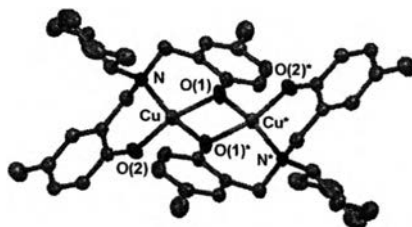


Figure 2.9 Crystal structure of copper ion binding with *N,N*-bis(5-cyclohexyl-2-hydroxybenzyl)cyclohexylamine.

2.4 Points of the Present Work

In the past, our group succeeded in preparing *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine and its derivatives in high yield (80-90%) via simple reaction condition. We also clarified the supramolecular structure of *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine derivatives, this brings us to modify this derivative to be diamine-linked benzoxazine derivatives and study on supramolecular polymer of these benzoxazines.

The present work has the aims to clarify about (i) the supramolecular chemistry of diamine-linked benzoxazine dimers derivatives, (ii) the supramolecular polymers via hydrogen bond network and metal-ligand binding of diamine-linked benzoxazine dimmers, and (iii) the development of morphology of these supramolecular polymer systems.