

## CHAPTER II

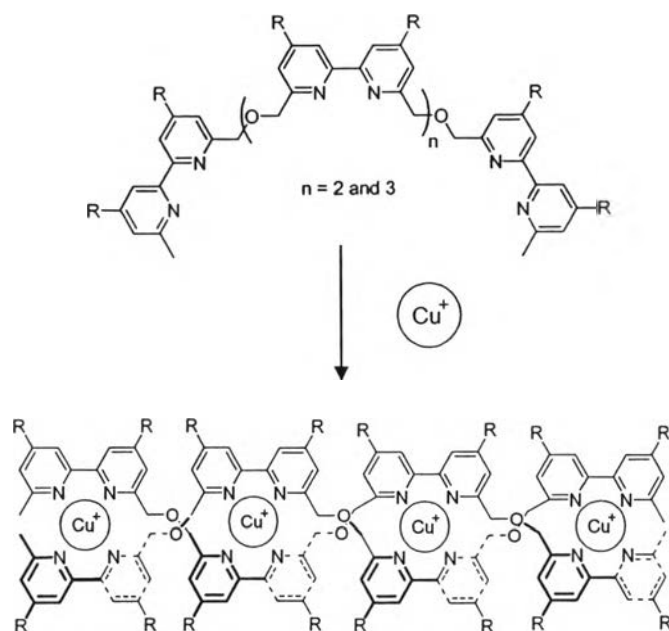
### LITERATURE REVIEW

#### 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).

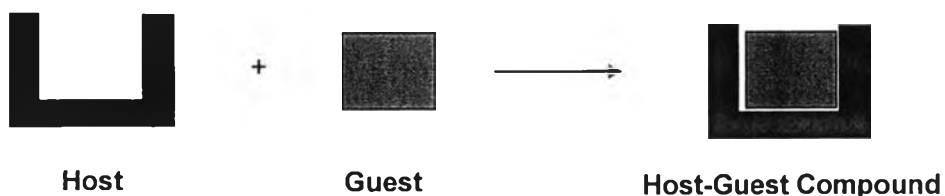
For the past decades, developments of instruments lead to precise information of natural supramolecular formation and network which enables us to understand and imitate the natural phenomena by designing simple molecules feasible for two- and/or three-dimensional structure. For example, Lehn *et al.* (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).

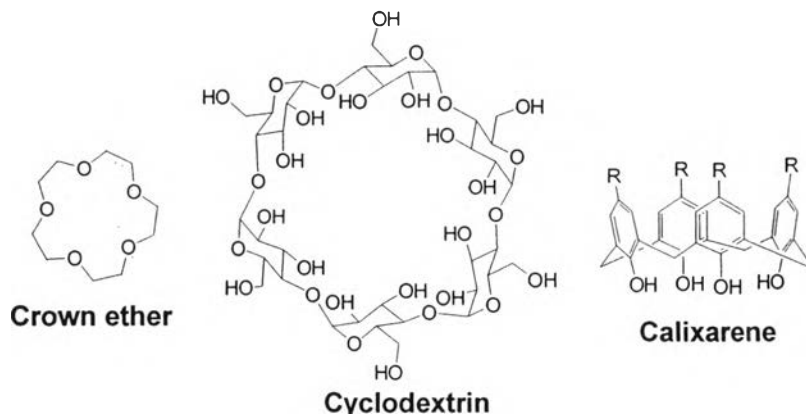


**Figure 2.1** Schematic representation of the double-stranded “helicite”, resulting from the complexation of Cu(I) with oligobipyridine (Lehn *et al.*, 1988).

**Scheme 2.1** Model of host-guest compound.



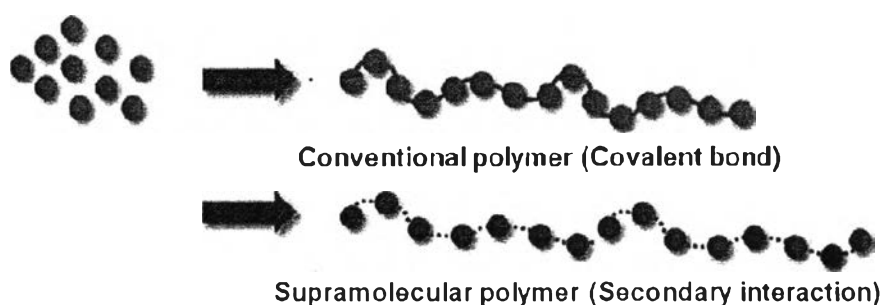
**Scheme 2.2** Examples of well-known host molecules.



## 2.2 Supramolecular Polymers and Supramolecular Polymerization

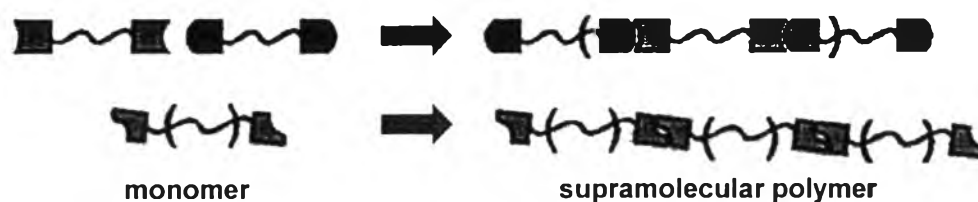
Supramolecular polymers are defined as polymers which their monomeric units are connected to each other via secondary interactions (Brunsveld *et al.*, 2001) resulting in polymer structures under specific condition (Fox *et al.*, 2009). The formation is absolutely different from conventional polymers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



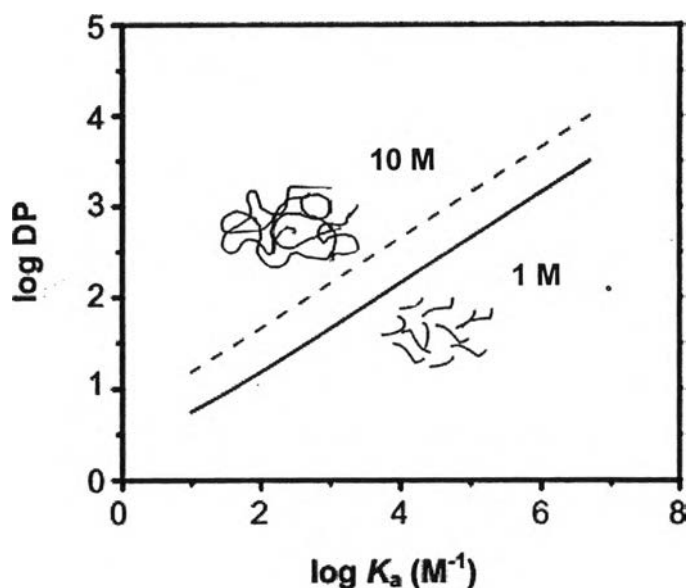
A directional complementary couple (A–B) or a self-complementary unit (A–A) is possible to form many types of polymer structures, including linear homo- and copolymers, cross-linked networks and even branched structures (Lehn, 2000). For supramolecular polymers, which are formed by the reversible association 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).



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

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).



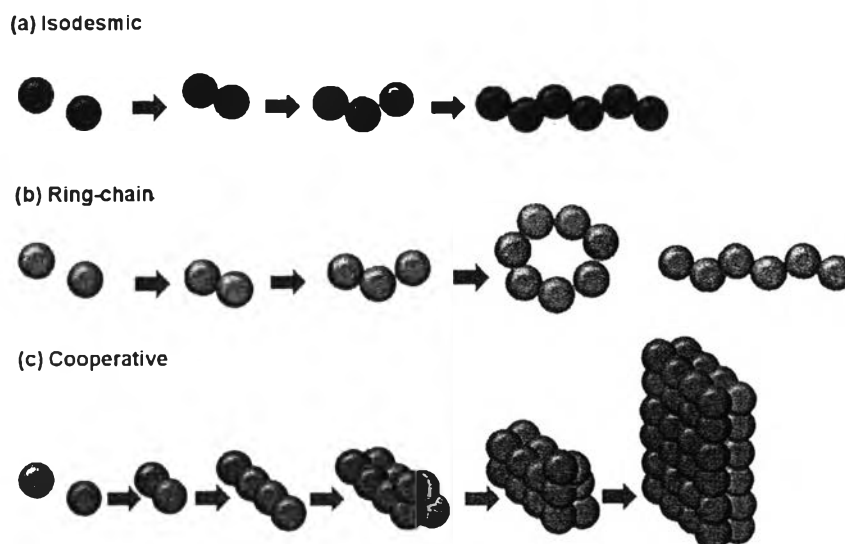
**Figure 2.3** Theoretical plot of the degree of supramolecular polymerization versus association constant,  $K_a$  ( $M^{-1}$ ) at two different concentrations.

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 yields not only 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  $\pi$ -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 a single hydrogen bonds or multiple 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  $10^2 \text{ M}^{-1}$  in chloroform, this value is around  $10^4 \text{ M}^{-1}$  in complexes with a DAA-DDA (3-4) motif, while AAA and DDD arrays (5-6) exhibit association constants exceeding  $10^5 \text{ M}^{-1}$  (De Greef *et al.*, 2009).



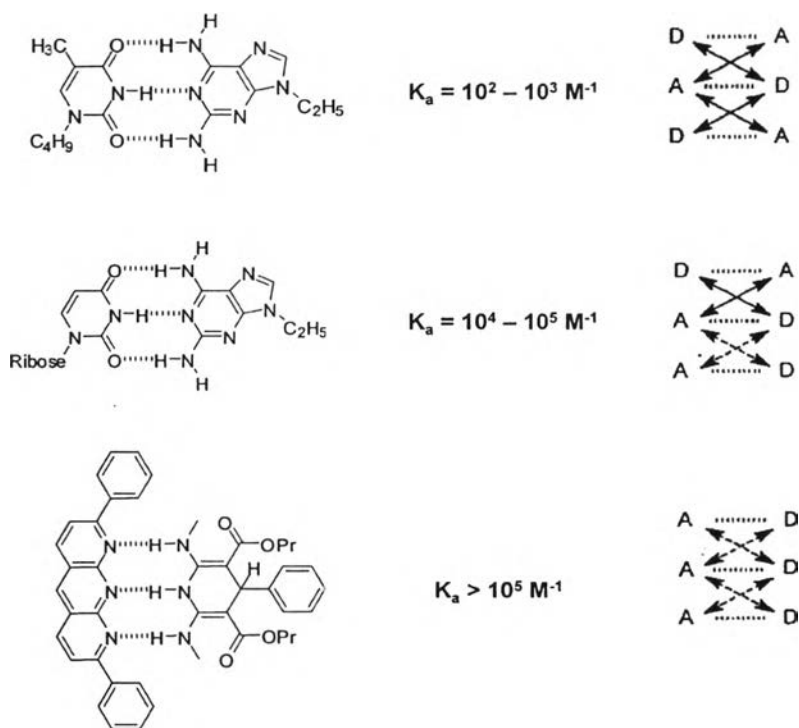
**Figure 2.4** Schematic representation of the three growth mechanisms by which a monomer can be polymerized into a supramolecular polymer: (a) isodesmic supramolecular polymerization; (b) ring-chain mediated supramolecular polymerization; and (c) cooperative supramolecular polymerization (De Greef *et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

### 2.2.2 Supramolecular Polymer based on $\pi$ -Conjugated System

The  $\pi$ -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  $\pi$ -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 (DiCe'sare *et al.*, 1999). These results showed that aggregates of oligothiophenes display a blue shifted absorption spectrum with respect to the molecularly dissolved state. Fre'chet *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

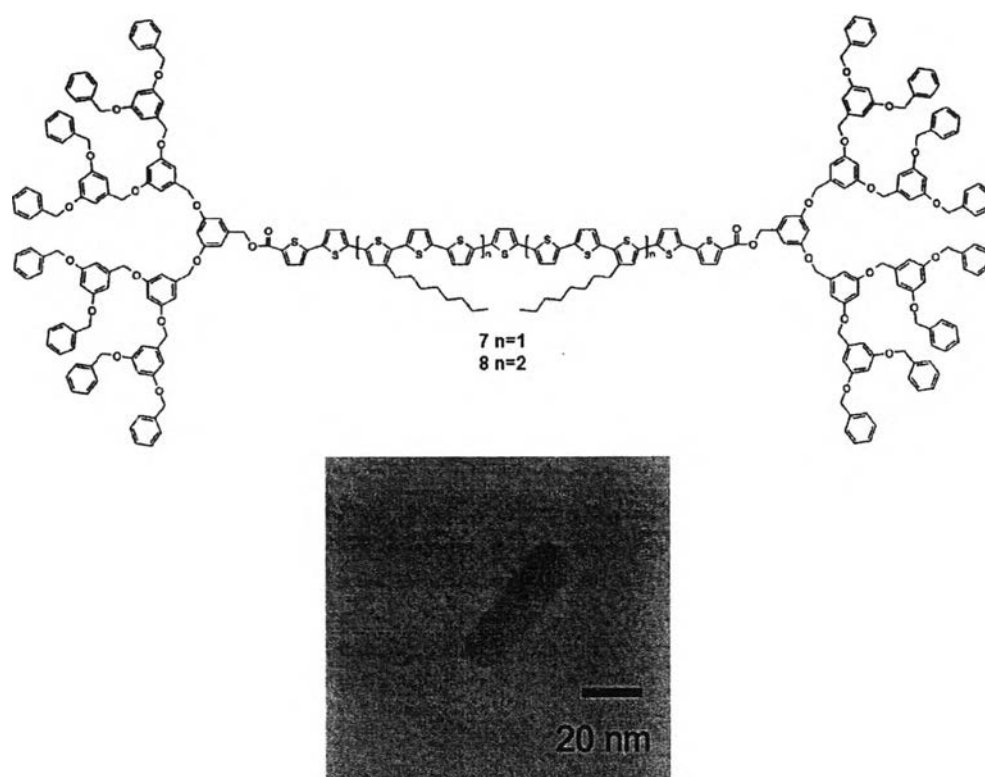
architectures obtained were similar to dendritically substituted oligothiénylenevinylene (Jestin *et al.*, 1998) and oligoimides (Miller *et al.*, 1999).

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  $\pi$ - $\pi$  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).



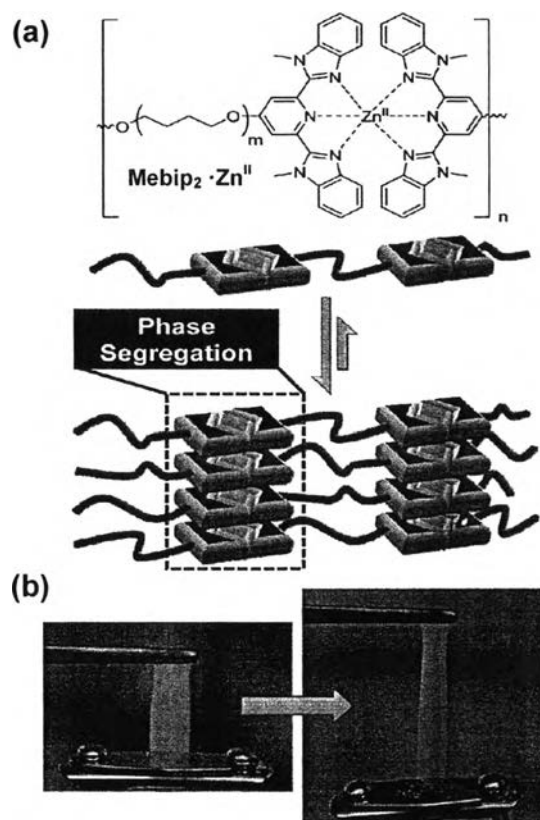


**Figure 2.6** Dendritically substituted thiophenes that aggregate into nanorods as imaged by TEM. (Apperloo *et al.*, 2001).

### 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. It generally consist of two complementary self-assembly components, a multiple-ligand containing organic component and metal ion so called metallosupramolecular polymer. It has received a growing amount of attention, in part, as these materials are known to display stimuli-responsive properties and have been used in many different applications ranging from organic light-emitting diodes (OLEDs) to sensor. 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. Metallosupramolecular 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 Mebip<sub>2</sub>, a system utilizing the Mebip<sub>2</sub>·Zn<sup>II</sup> motif (Figure 2.7b). X-ray (WAXS) and DMTA data were consistent with a presence of cross-linking phase (lamellar morphology) which was further backed up by the elastomeric behaviour 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.



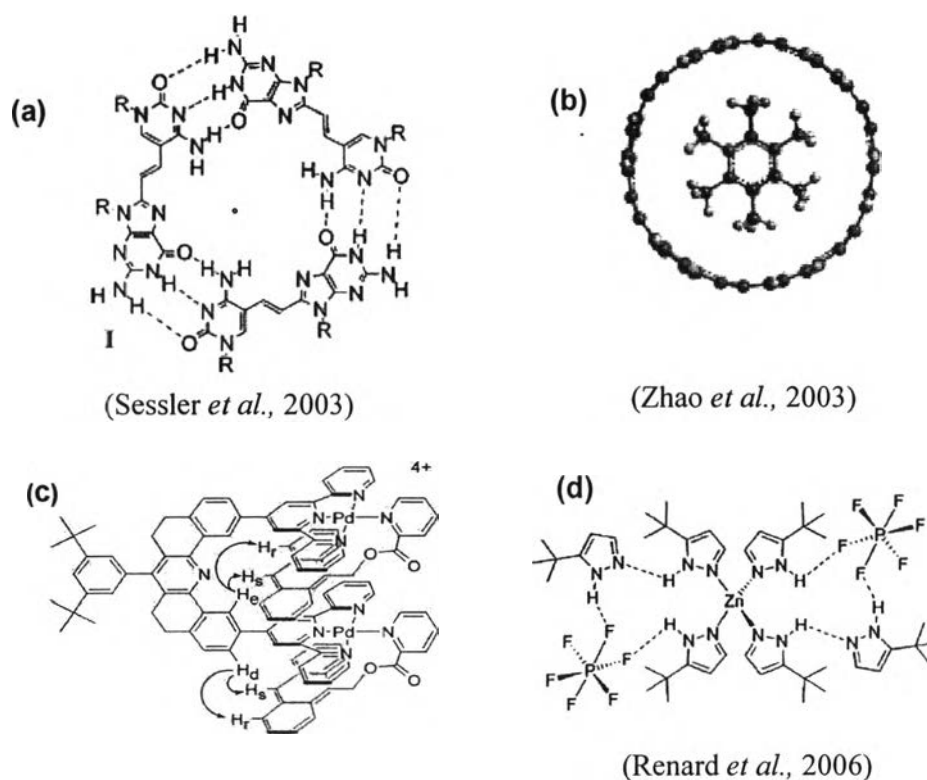
**Figure 2.7** (a) Structure of metallo-supramolecular polymer Mebip<sub>2</sub>·Zn<sup>II</sup> and the proposed AB multiblock-like phase segregation present in the solid state, and (b)

elastic nature of the metallo-supramolecular polymer  $\text{Mebip}_2 \cdot \text{Zn}(\text{ClO}_4)_2$  (Fox *et al.*, 2009).

### 2.3 Molecular Self-assembly

Molecular self-assembly is a versatile tool to construct higher order structures under specific noncovalent interaction i.e., hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces,  $\pi$ - $\pi$  interactions, and/or electrostatic effects (Figure 2.8) (Lehn 1988). Based on those specific interactions, various self-assembly structures have been continuously developed, such as deoxycholic acid (Sada *et al.*, 2001), calixarenes (Corbellini *et al.*, 2005) and rotaxanes (Bissell *et al.* 1994). Apart from those small molecules, self-assembly in polymeric materials has been reported. Mostly, amphiphilic structure is dealt with spontaneous self-assembly in polymer. Amphiphilic structure consists of hydrophilic (water-loving) parts and lipophilic (oil-loving) parts which separately organized into an ordered structure to minimize interaction energy with two different environments (Rotello and Thayumanavan 2008). Amphiphilic polymers, such as block copolymer, graft polymer, as well as dendrimer are known to form self-assembly structure in micelle structure in solution with selective solvents or micro- or nano-phase separation in solid state.

Numerous applications from biological therapies to novel materials and electronic devices based on self-assembly concept have been reported. Gene therapy is one of the good and high performance examples which the self-assembly approach for binding the mutant gene in individual strand forms a double-helical structure through hydrogen bonding is effective.



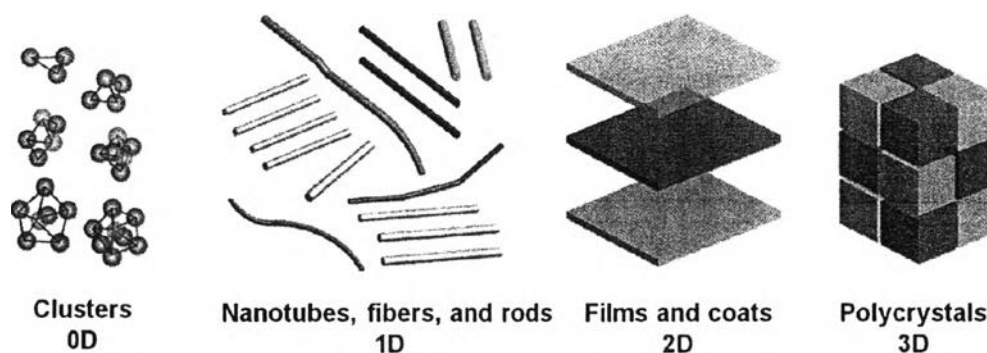
**Figure 2.8** Typical examples of supramolecular structure via: (A) hydrogen bonding (B) van der Waals forces, (C)  $\pi$ - $\pi$  interactions and (D) metal coordination.

On the molecular scale, the accurate and controlled application of intermolecular forces can lead to new and previously unachievable nanostructures. This is why molecular self-assembly is a highly topical and promising field of research in nanotechnology today.

## 2.4 Nanostructures

Nanostructures are assemblies of bonded atoms that have dimensions in the range of 1-100 nm. In describing nanostructures, it is necessary to differentiate between the numbers of dimensions on the nanoscale. The main types of nanostructured materials based on the dimensions of their structural elements are:

zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) nanomaterials. Zero-dimensional nanomaterials include nanocluster materials and nanodispersions, i.e. materials in which nanoparticles are isolated from each other. One-dimensional nanomaterials are nanofibre (nanorod) and nanotubular materials with fibre (rod, tube) length from 100 nm to tens of microns. Two-dimensional nanomaterials are films (coatings) with nanometer thickness. Structural elements in 0D, 1D and 2D nanomaterials can be distributed in a liquid or solid macroscopic matrix or be applied on a substrate. Three-dimensional nanomaterials include powders, fibrous, multilayer and polycrystalline materials in which the 0D, 1D and 2D structural elements are in close contact with each other and form interfaces. An important type of three-dimensional nanostructured materials is a compact or consolidated (bulk) polycrystal with nanosize grains, whose entire volume is filled with those nanograins, free surface of the grains is practically absent, and there are only grain interfaces. The formation of such interfaces and "disappearance" of the nanoparticle (nanograin) surface is the fundamental difference between three-dimensional compact nanomaterials and nanocrystalline powders with various degrees of agglomeration that consist of particles of the same size as the compact nanostructured materials.

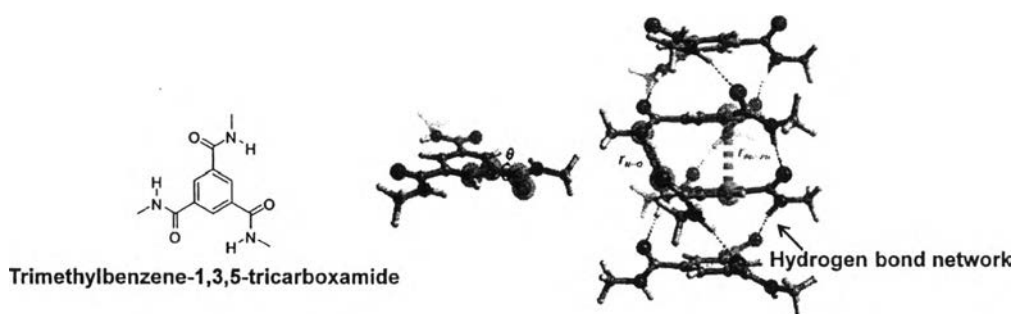


**Figure 2.9** Types of nanocrystalline materials by size of their structural elements: 0D (zero-dimensional) clusters; 1D (one-dimensional) nanotubes, fibers and rods; 2D (two-dimensional) films and coats; 3D (three-dimensional) polycrystals. (Gusev 2004)

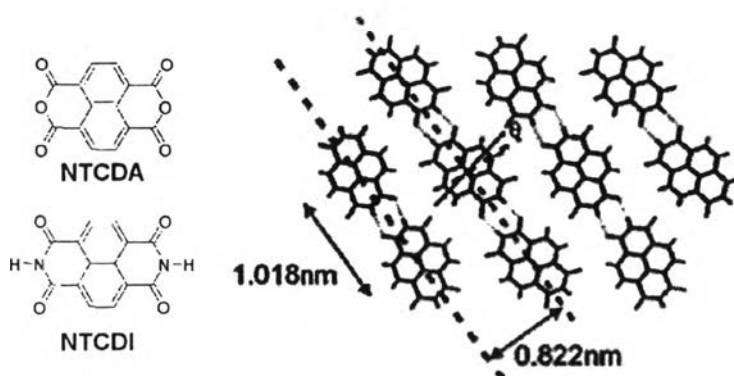
## 2.5 Secondary Interactions and Supramolecular Structures

### 2.5.1 Hydrogen Bond and Supramolecular Structures

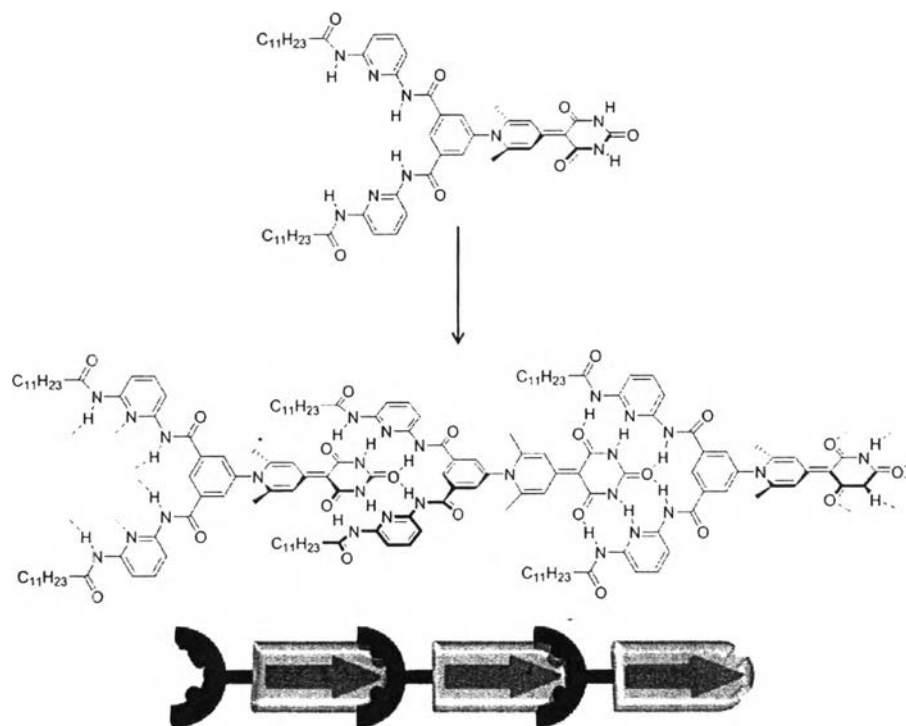
As mentioned above, supramolecular assemblies established by directional intermolecular interactions such as hydrogen bond. Hydrogen bond has provided promising strategies to control the relative molecular arrangement in the development of molecular nanomaterials. For examples, Filot and co-workers proposed a compound derivatives and its mechanism for hydrogen bond growing which is trialkylbenzene-1,3,5-tricarboxamides. The compound can be self-assembly to threefold amide type hydrogen bond as shown in Figure 2.10. D. L. Keeling et al reported that the mixture of naphthalene tetracarboxylic dianhydride (NTCDA) and naphthalene tetracarboxylic diimide (NTCDI) shows the nanostructure of supramolecular structure as shown in Figure 2.11. In some cases that hydrogen bond is strong enough and the direction favour to grow as a chain, it also can be supramolecular polymer, for example Schmidt proposed the orientation of merocyanine dye which can be supramolecular polymer through head-to-tail hydrogen bonding orientation due to it contains *N*-alkyl-substituted barbiturate acceptor moiety and dihydropyridone heterocycles forming directional hydrogen bonding as shown in Figure 2.12.



**Figure 2.10** Structure of trimethylbenzene-1,3,5-tricarboxamides and its hydrogen bond network.

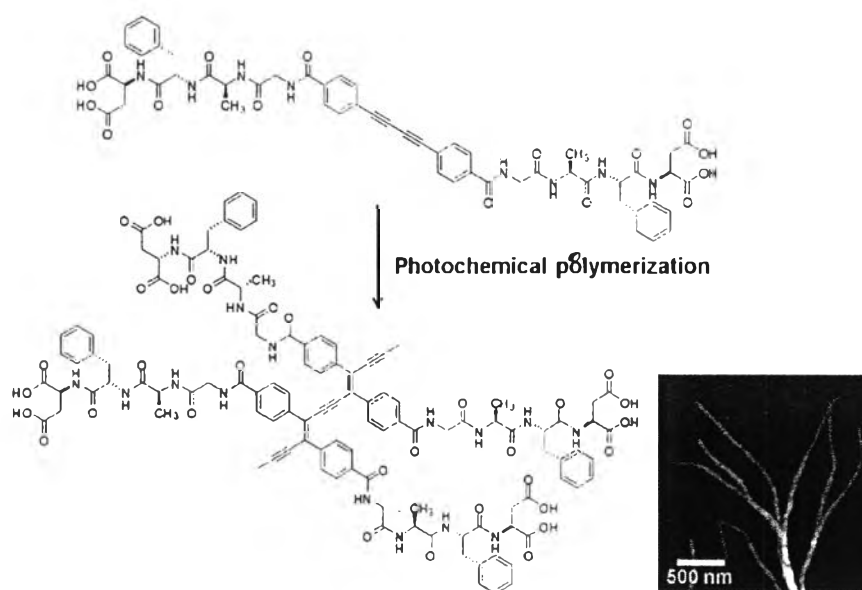


**Figure 2.11** Structures of naphthalene tetracarboxylic dianhydride (NTCDA) and naphthalene tetracarboxylic diimide (NTCDI) and hydrogen bond pattern in the crystal lattice.



**Figure 2.12** Supramolecular polymer structures of merocyanine through the hydrogen bond.

On the other hands, hydrogen bond also plays the role on packing structure, which is a key factor for topochemical polymerization. In this book, the diacetylene photopolymerization is focused. As the preparation of polydiacetylene (PDAs) requires the assembly of diacetylene monomers in an appropriate arrangement to favor 1,4-addition polymerization. The minimum requirements are the translational period ( $d$ ) must be in range of 4.7 to 5.2 Å and the tilt angle ( $\gamma$ ) between the diacetylene rod and  $d$  must be close to  $45^\circ$ , then the initiation step can be created. However, there are few reports of successful case of topochemical polymerization when the aryl groups were attached both end of butadiyne. This reaction might be difficult due to the bulkiness of phenyl group to endure significant conformational change within the crystal. The preform diacetylene structure by hydrogen bond framework is considered. From the idea, in 2012, Tovar group reported that diacetylene-peptide could be successfully photopolymerized to be polydiacetylene and self-assembly as 1D nanostructure as shown in Figure 2.13. Besides, the systematic variation of diarylbutadiyne derivative photopolymerization is studied in terms of substituted group, substituted position, and preforming structure by hydrogen bond.

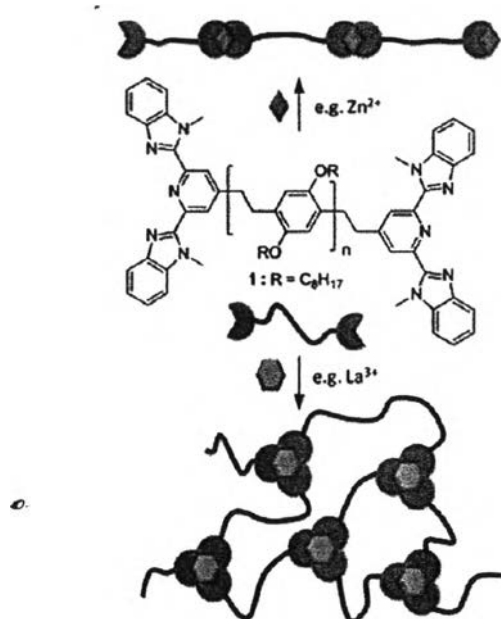


**Figure 2.13** Structure of diacetylene monomer and resulting PDA with AFM images of PDA nanostructures derived from peptide.



### 2.5.2 Metal-ligand Binding and Supramolecular Structures

The metal-ligand coordination is one of the secondary interactions which widely used to produce nanomaterials in term of self-assembly and supramolecular polymer. Supramolecular metal complexes are interesting candidates due to dynamic metal–ligand interactions serve a reversibility property, as the combination of transition metal ions with, e.g., terpyridine ligands offers the possibility to create versatile “switchable” binding motifs. For examples, Burnworth et. al. proposed the self-assembly polymerization of ditopic monomers via metal-ligand binding as a facile route for preparation. They use poly(p-xylylene) based on 2,6-bis(1'-methylbenzimidazolyl)pyridine end capped telechelic oligomers with a p-xylylene core and difference metal salts as shown in Figure 2.14.



**Figure 2.14** Metallosupramolecular polymerization of ditopic telechelic oligomers with either transition or lanthanide metal ions.

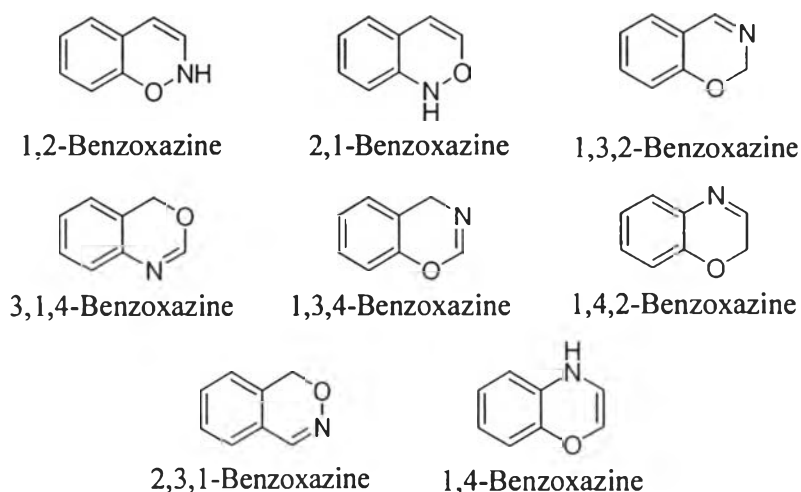
From literatures, benzoxazine dimer is considered for development of self-assembly and supramolecular polymer. At the same time with, diacetylene is simply modified, consisting of hydrogen bond framework for topochemical polymerization.

## 2.6 Benzoxazines

### 2.6.1 Structures and Chemistry of Benzoxazine Derivatives

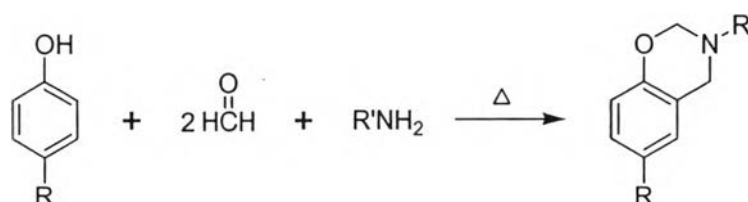
Benzoxazine is a heterocyclic compound, which consist of benzene ring and oxazine ring. There are 8 isomers, which are different at methylene position and substituted hydrogen atom position (Scheme 2.4).

Scheme 2.4 Isomers of benzoxazine.



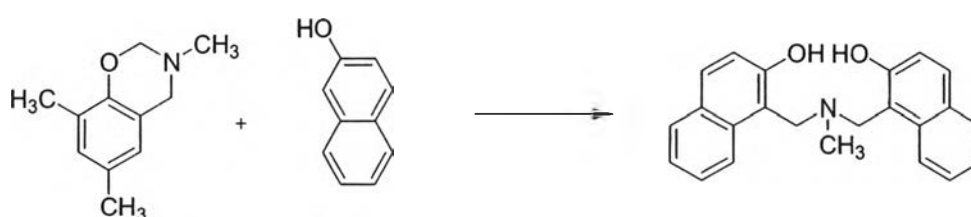
In 1964, Burke *et al.* reported the preparation of benzoxazine derivative (3,4-dihydro-1,3-2*H*-benzoxazines) by using one step of Mannich reaction between phenol derivative, formaldehyde and amine derivative (Scheme 2.5).

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-1H-naphth-(1,2-e)-1,3-oxazine with 2-naphthol (Scheme 2.6).

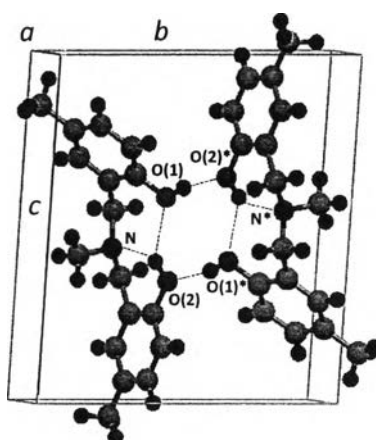
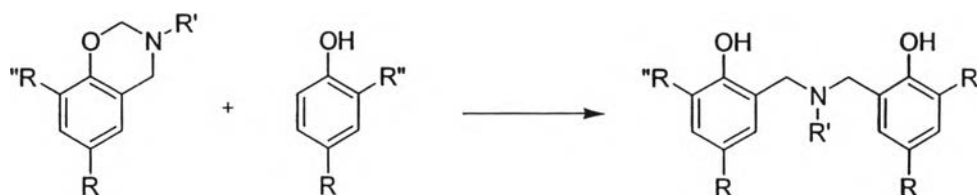
**Scheme 2.6** Ring opening reaction of 2,3-dihydro-2-methyl-1H-naphth-(1,2-e)-1,3-oxazine with 2-naphthol.



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.

Chirachanchai and coworkers 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 2.10). Benzoxazine dimer derivatives are demonstrated about 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.

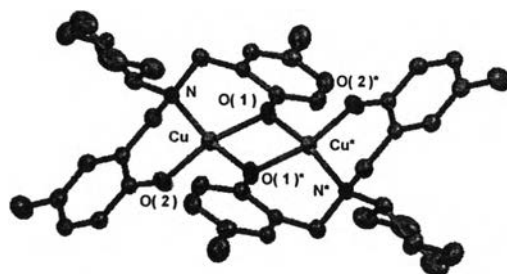


**Figure 2.15** Crystal structure of *N,N*-bis(5-methyl-2-hydroxybenzyl)cyclohexylamine.

### 2.6.2 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, Laobuthee *et al.* succeeded in showing an inclusion phenomena of *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine derivatives with alkaline picrate salts. They also demonstrated that the copper ion binding properties of the derivatives under the double-oxygen-bridged dimeric system through X-ray single crystal analysis result

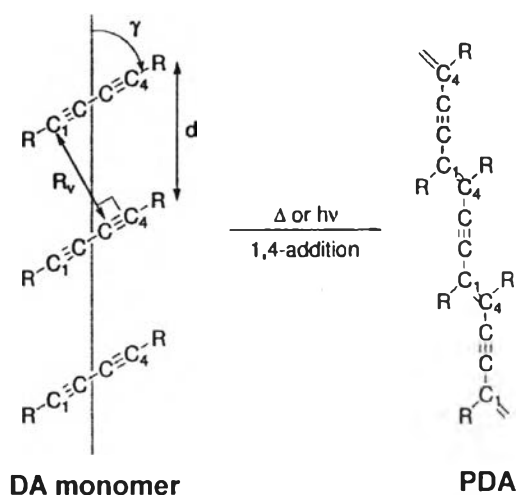
(Phongtumrug *et al.*, 2006) (Figure 2.11). They also proposed the existence of multi-guest species, i.e., ion and neutral molecules, in a single host-guest framework (Phongtumrug *et al.*, 2005, 2006).



**Figure 2.16** Crystal structure of copper ion binding with *N,N*-bis(5-cyclohexyl-2-hydroxybenzyl)cyclohexylamine.

## 2.7 Diacetylenes and Polydiacetylene (PDAs)

PDAs are known as a conductive polymer which can be polymerized in solid state, topochemically polymerized, such as in form of mono-layer film or crystal via UV- or  $\gamma$ - irradiation. (Wegner 1969) It results in a highly ordered orientation of ene-yne conjugated back bone of obtained PDAs. However, a preorganization of diacetylene monomer in closed-packing structure under a repeat distance  $\sim 5$  Å and an orientation angle  $\sim 45^\circ$  is required. (Lauher *et al.*, 2008) Thus, alternatively, polymerization by thermal treatment in solid (Chance *et al.*, 1978) or melt (Fomina *et al.*, 1995) state has been reported. Due to the conjugated back bone of PDAs, it shows unique electrical and optical properties which are promising in various applications, especially, for sensor materials.



**Figure 2.17** Typical preorganization of DA monomer for topochemical polymerization. (Lauher *et al.*, 2008).

The preparation of PDAs requires the assembly of diacetylene monomers in an appropriate arrangement to favour 1,4-addition polymerization which the minimum requirement as mentioned above (translational period ( $d$ ) must be in range of 4.7 to 5.2 Å and the tilt angle ( $\gamma$ ) between the diacetylene rod and  $d$  must be close to 45°), then the initiation step can be created. Because the topochemical polymerization results in a change of the atomic coordinates inside the crystal, the nature of the substituent directly attached to the butadiyne unit has a significant impact on the polymerization process. In fact, the substituents should be able to accommodate structure changing within the crystal lattice, and this is why almost of the topochemical polymerizations of butadiyne reported only on derivatives bearing of flexible alkyl chain directly attached to the butadiyne moiety. To the best of our knowledge, there are very few reports of successful case of topochemical polymerization when the aryl groups were attached both end of butadiyne. This reaction might be difficult due to the bulkiness of phenyl group to endure significant conformational change within the crystal. For example, Diegelmann and co-workers reported the successful case of polydiacetylene-peptide which contain

diarylbutadiyne in structures and can be polymerized under the UV light and formed 1D nanostructure.

## 2.8 Points of Study

Based on the above mentioned supramolecular chemistry, secondary interaction potentially plays an important role as thermodynamic driving force for self-assembly, especially in supramolecular polymer development. Creating self-assembled structures based on multiple interactions has been widely reported, however, the difficult synthesis and characterization to follow phenomena are considered. Herein, we propose a simple approach to initiate the unique self-assembly based on secondary interaction. In Chapter III, the self-assembly formation ability of diamine-based benzoxazine derivatives with varied concentration and solvent polarity are proposed, resulting in nanostructures. In addition, hydrogen bonding direction formation is controlled by alkyl chain length produce the tunable morphologies. As there has been no report on the supramolecular polymer which holds together by both hydrogen bond and metal-ligand binding, In Chapter IV, we focus on the use of diamine prepolymer for preparing benzoxazine dimer terminated, function as a binding site for supramolecular polymer. In this work, we firstly report the formation of supramolecular polymer through both hydrogen bond network and metal ligand binding. In Chapter V, we demonstrate remarkable formation of PDAs derived from topochemical reaction of diarylbutadiynes by using hydrogen bond network arrangement as a preform structure. This is the first time proposed the role of hydrogen bond network and also position of substituent group on the aryl units as the systematic study.