

CHAPTER I

INTRODUCTION

For the past decades, weak interactions or secondary forces have much attention due to dynamic and reversible performance until the specific word is created and called supramolecular chemistry which has been described as “chemistry beyond the molecule” (Lehn 2007). The concept of supramolecular chemistry is used for defining arrangement and organizing molecular structures through the intermolecular forces such as hydrogen bond, metal complexation, π - π stacking, and hydrophobic van der Waals which play an important role in the conformation, assembly, or behaviour of a system, so called molecular assembly.

Currently, many exquisite supramolecular systems have been reported by synergistic interplays of multiple secondary interactions to finely tune nanostructure assemblies. The challenge on supramolecular research is about how to design unique molecules under specific requirements of supramolecular structures in terms of molecular assembly shapes, sizes, and properties. When the molecular self-assembly form a continuous molecular interaction, a noncovalent bonded polymer, so called supramolecular polymer can be developed. Therefore, supramolecular polymer can be defined as a polymeric system which further extends the molecules and holds together via noncovalent interactions. It is important to note that the key point of supramolecular polymer structure is the terminal group as they play the role as binding site via secondary interactions. From the publications, hydrogen bond and metal-ligand binding are commonly used for supramolecular polymer formation. However, the supramolecular polymer created by both hydrogen bond and metal complexation has rarely seen.

In this work, two model cases which are benzoxazines and diacetylenes are studied. For the past decade, our group developed benzoxazine derivatives which simply produced by Mannich reaction of phenols, formaldehyde, and amines. The supramolecular networks of benzoxazine dimers based on their inter- and intramolecular hydrogen bonds at the phenol rings and aza linkage is clarified. Currently, development of benzoxazine dimers to satisfy the multiple weak

interaction of the formation of benzoxazines with diamine is one of the choices. In addition, by simply varying the alkyl chain lengths of the diamines, the benzoxazine dimers with different hydrophobic chains can be obtained. As diamine-based benzoxazine dimer has the hydrophobic chains as well as the hydrogen bond networks, it comes to our question whether the length of hydrophobic chain can control the hydrogen bond direction and induce supramolecular structures and at that time, how it possible that the molecular self-assembly express the tunable morphologies.

Up to the present, although several supramolecular polymers are reported, most of them focus on only one specific interaction such as hydrogen bond, π - π stacking or metal-ligand binding. In the previous work, we proposed that benzoxazine dimer can form complexation with copper (II) ions. To the best of our knowledge, there is no report about a supramolecular motif offers the feasible structure to form both hydrogen bond and metal ion complexation creating supramolecular polymers. It is our goal to prepare and demonstrate the supramolecular system via the simple methods for the concept of molecular self-assembly.

In the case study of diacetylene, polydiacetylenes (PDAs) are the unique linear conjugated polymers derived from the topochemical polymerization of diacetylene monomer by solid-state polymerization during UV, X-ray, γ -ray, and electron beam radiation. PDAs have attracted great interest for their electronic and optical properties for many potential applications such as light emitting diodes (OLEDs), Langmuir-Blodjet film and sensors. However, the preparation of PDAs requires the assembly of diacetylene monomers in an appropriate arrangement to favour 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 (γ) 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 substituent 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. Preparation of polydiacetylene containing diarylbutadiyne is quite complicate, due to the secret behind how the diacetylene monomer can be topochemical polymerized especially in term of packing structure. However, in 2012, Tovar group reported that diacetylene-peptide could be successfully photopolymerized to be polydiacetylene and self-assembly as 1D nanostructure. From this propose, we think about preformation of the structure which easily generated by hydrogen bond network, resulting in molecular self-assembly. The systematic variation for diarylbutadiyne derivative photopolymerization is studied in terms of substituted group, substituted position, and preforming structure by hydrogen bond.