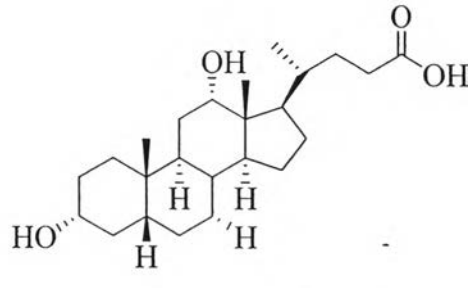
CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Supramolecular Chemistry

Supramolecular chemistry is the chemistry that focuses on the molecular assemblies, based on noncovalent interactions or secondary forces between hosts and guests such as van der Waals, dipole-dipole, π-π stacking, and hydrogen bond. The unique structure of supramolecules provides interaction between host molecules and guest molecules leading to inclusion phenomena (Steed *et al.*, 2009).

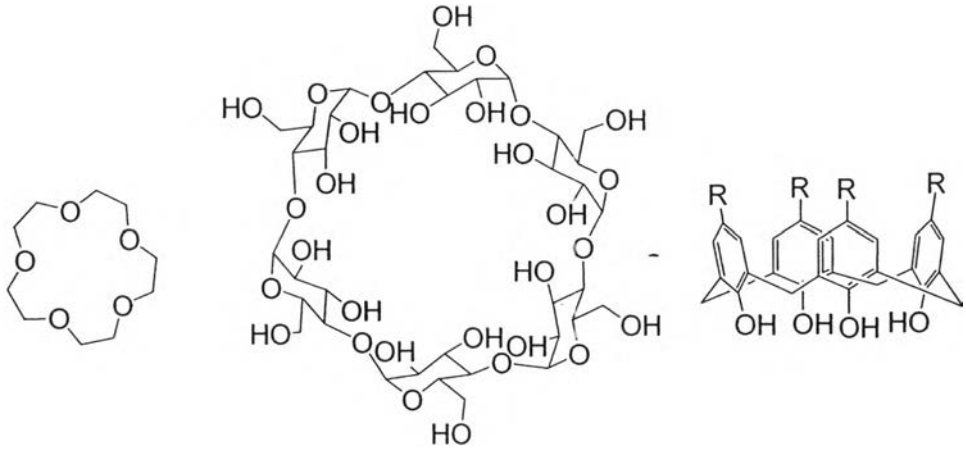
Generally, the structure of the host molecules can be acyclic structure such as cholic acid (M. Miyata *et al.*, 2004) (Figure 2.1a), cyclic structure such as crown ether (G.W. Gokel *et al.*, 2004), cyclodextrin (J. Szejtli *et al.*, 2004), and calixarenes (C.D. Gutsche *et al.*, 2004) (Figure 2.1b) and hierarchical structure such as molecular necklace (Figure 2.1c).

(a) Acyclic structure



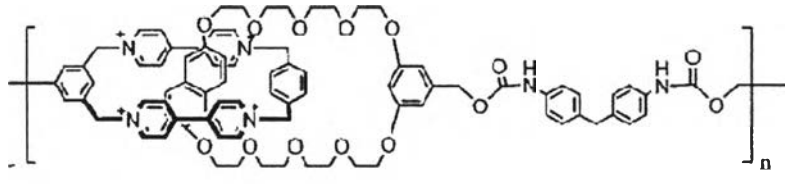
Cholic acid

(b) Cyclic structure



18-Crown-6 α-Cyclodextrin Calix[4]arene

(c) Hierarchical structure



Molecular necklace

Figure 2.1 The structures of (a) acyclic structure, (b) cyclic structure and (c) hierarchical structure

2.2. Molecular Necklace

Molecular necklace is one of supramolecular structure based on connected macrocycles. There are many works reported about the mechanism of molecular necklace formation. For example, rotaxanes is the well-known molecular necklace consisting of dumbbell shaped molecule formed through a macrocycle via molecular interlocking as shown in Figure 2.2 (Loeb, S. J. *et al.*, 2000).

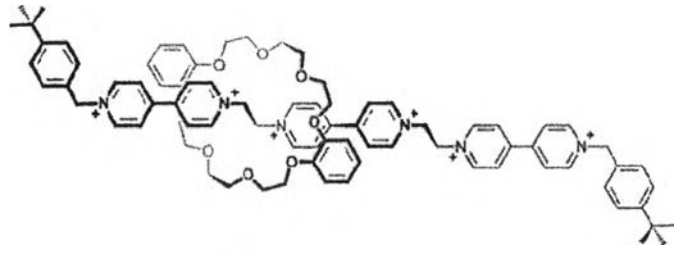


Figure 2.2 The structure of rotaxanes.

Another example is "pearl-necklace-like" molecule reported by Yang, S., *et al.* (2010). It was formed by aggregation of micelle polystyrene-block-poly(ethylene oxide) (PS-*b*-PEO) associated with poly(acrylic acid) (PAA). The hydrogen-bonding between the PEO blocks and PAA chains is the key of molecular necklace formation (Figure 2.3).

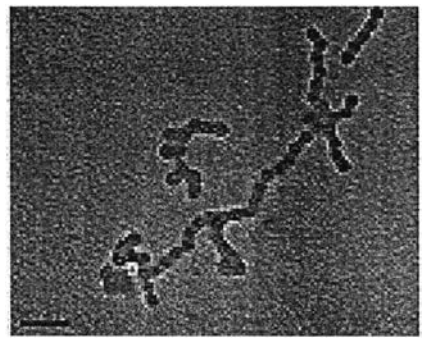


Figure 2.3 The pearl-necklace-like" morphology of micelle PS-*b*-PEO associated PAA.

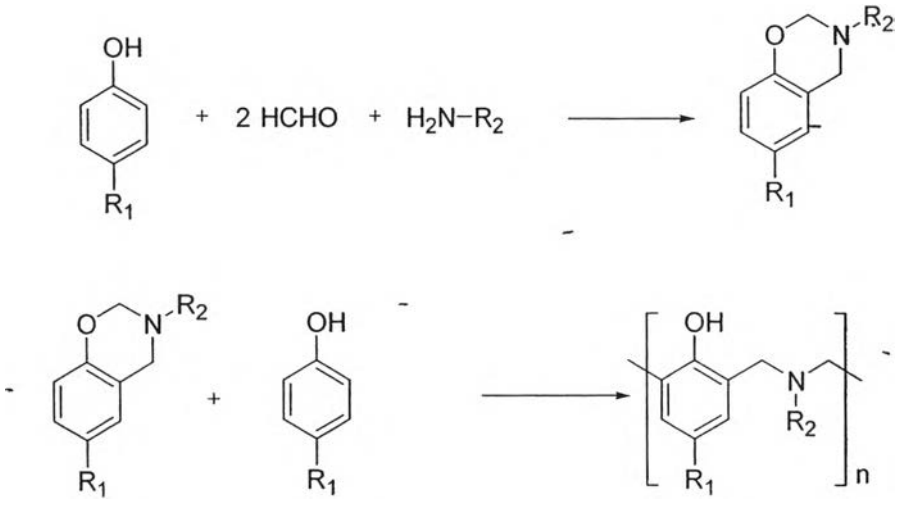
2.3 Benzoxazines

2.3.1 Benzoxazine Chemistry

Benzoxazines are heterocyclic molecules derived from reaction of a phenolic derivative, formaldehyde, and a primary amine to form benzoxazine monomers. Ring opening polymerization of benzoxazine monomers is achieved by at-

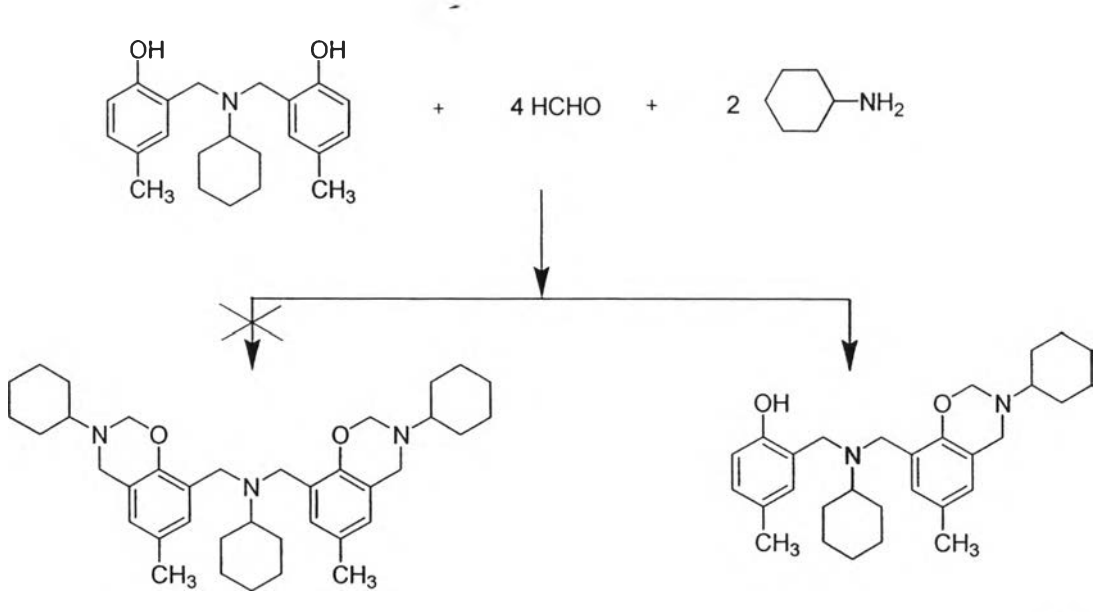
tacking new phenolic molecules to obtain benzoxazine resins (Scheme 2.1) (Ishida *et al.*, 2011).

Scheme 2.1



Laobuthee *et al.* (2001) reported that the reaction of benzoxazine dimer via the Mannich reaction resulted in only mono-oxazine (Scheme 2.2). This is due to the strong inter- and intramolecular hydrogen bonding between nitrogen atoms and hydroxyl groups as shown in Figure 2.4.

Scheme 2.2



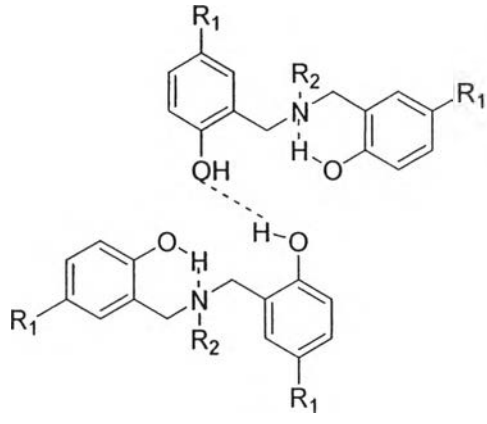
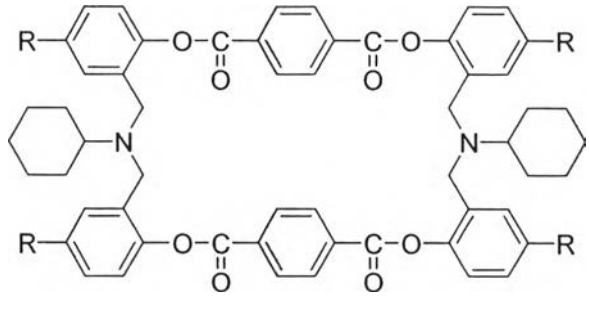


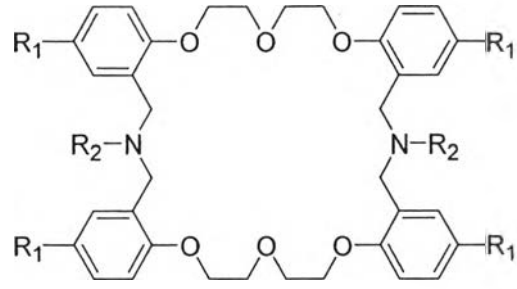
Figure 2.4 Inter- and intramolecular molecular hydrogen bonding.

2.3.2 Development of Supramolecule Benzoxazine

In 2003, Laobuthee *et al.* succeeded in synthesis of [2+2] macrocyclic dimers via esterification and etherification by using the reaction of *p*-substituted phenol-based benzoxazine dimers react with diacid chloride or ditosylated glycol, without specific catalyst and further complicated purification (Figure 2.5). These macrocyclic benzoxazine dimers derivatives showed inclusion phenomena with transition metals that related to structure and cavity sizes of the macrocycles. The inclusion phenomena were confirmed by Pedersen's technique.



(a)



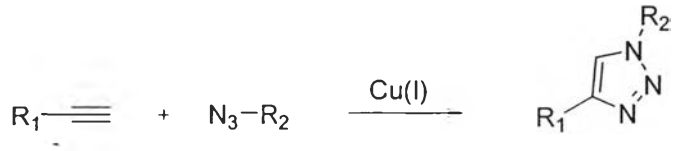
(b)

Figure 2.5 [2+2] macrocyclic dimer via (a) esterification (b) etherification.

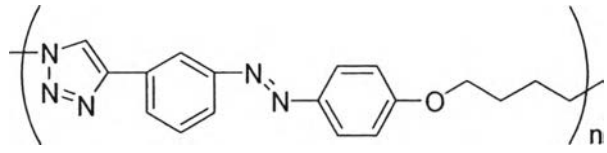
2.4 Click Chemistry

Click chemistry is a term applied to chemical synthesis tailored to generate substances quickly and reliably linking small units together. Click chemistry have received much attention due to its high efficiency, quantitative yields and selectivity under mild reaction conditions. The reaction of azide wtih terminal alkyne via copper(I) is one of the examples of click chemistry, which give 1,2,3-triazole as a product (Kolb *et al.*, 2001) as shown in Scheme 2.3.

Scheme 2.3



Xue *et al.* (2009) reported that a novel main chain azobenzene polymer, PEAPA, which was successfully synthesized by a step-growth polymerization via 1,3-dipolarcycloaddition reactions (''Click'' chemistry) (Figure 2.8), This novel method provided a high efficiency way to prepared a main chain azobenzene polymer and also showed a good thermal stability and crystallinity, due to the introduction of the triazole ring in the polymer backbone



PEAPA

Figure 2.6 The structure of novel main chain azobenzene polymer, PEAPA.

2.5 Points of the Present Work

In the past, our group succeeded in preparing macrocyclic monomer base on benzoxazine via esterification of *N*,*N*-bis(2-hydroxy-5-ethylbenzyl)cyclohexylamine with terephthaloyl dichloride. This leads to our motivation on the idea how to decorate this macrocyclic monomer to be the necklace molecule

The present work, we propose molecular decoration of a macrocyclic benzoxazine to be molecular necklace by using esterification of benzoxazine dimers to obtain macrocyclic benzoxazine, followed by Click chemistry to link macrocyclic benzoxazine with triazole linkage (Scheme 2.4).

Scheme 2.4