LIGHT RESPONSIVE WITH METALLO-, AND HYDROGEN BONDED BENZOXAZINE DIMER-BASED SUPRAMOLECULAR STRUCTURE

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ABSTRACT

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The present work focuses on multi-responsive molecule based on supramolecular chemistry of benzoxazine dimer as a benzoxazine supramolecular crosslinker, fluorescent labelling benzoxazine conjugated with rotaxane system and benzoxazine pendant group block copolymer. The use of azobenzene derivatives in benzoxazine synthesis provides light responsive behaviour. The remained hydroxyl group from aminoalcohol allows benzoxazine to conjugate with desired functional group. The dihydroxyl benzoxazine acts as molecular crosslinker for poly(acrylic acid) by conjugation. The ring-opening reaction brings benzoxazine dimeric unit on the crosslinker which also showed metal ion complexation. The complexation strengthens the cross-linked polymer network. The complex can reversely form by treating with EDTA and $CuCl_2$ solution in cycle. The use of fluorescent phenol in the ring opening also brings fluorescent property. The conjugation of light responsive benzoxazine with rotaxane system followed with ring opening reaction using fluorescent phenol allows us to detect the shuttling of rotaxane. Moreover, the metal ion complexation and cis/trans isomerization were also detected by fluorescent property. The benzoxazine side group polymer can be obtained from conjugation of light responsive benzoxazine with acrylate derivatives. The polymerization with ATRP provides block copolymer. The UV light exposure and metal ion complexation affects morphology of the block copolymer.

บทคัดย่อ

ศรภัทร นิยมสินธุ์ : เบนซอกซาซีนที่ตอบสนองต่อแสงพร้อมทั้งโลหะพันธะไฮโดรเจนฐานโครงสร้างซุปปร้าโมเลกุลของเบนซอกซาซีนไดเมอร์ (Light Responsive with Metallo-, and Hydrogen Bonded Benzoxazine Dimer-based Supramolecular Structure) อ. ที่ปรึกษา : ศาสตราจารย์ ดร. สุวบุญ จิรชาญชัย, 118 หน้า

งานวิจัยนี้มุ่งเน้นศึกษาโมเลกุลที่ตอบสนองต่อสิ่งเร้าโดยพื้นฐานของเคมีซุปปร้าโมเลกุลของเบนซอกซาซีนไดเมอร์ที่เป็นสารเชื่อมขวางซุปปร้าโมเลกุล เบนซอกซาซีนเรืองแสงที่เชื่อมต่อกับโรแทกเซน และพอลิเมอร์ร่วมแบบกลุ่มที่มีเบนซอกซาซีนไดเมอร์เป็นหมู่แทนที่ การใช้อนุพันธ์ของเอโซเบนซีนในการสังเคราะห์เบนซอกซาซีนนำไปสู่โมเลกุลที่มีคุณสมบัติตอบสนองต่อแสงได้ หมู่ไฮดรอกซิลที่เหลือมาจากอะมิโนแอลกอฮอล์ทำให้เบนซอกซาซีนสามารถเชื่อมต่อกับหมู่ฟังก์ชันที่ต้องการได้ เบนซอกซาซีนที่มีหมู่ไฮดรอกซิลเหลือ 2 หมู่ทำหน้าที่เป็นสารเชื่อมขวางของพอลิอะคริลิกแอซิด ปฏิกิริยาเปิดวงของเบนซอกซาซีนทำให้เกิดเบนซอกซาซีนไดเมอร์บนสารเชื่อมขวางซึ่งสามารถเกิดสารประกอบเชิงซ้อนกับไอออนของโลหะได้ สารประกอบเชิงซ้อนนี้ทำให้พอลิเมอร์เชื่อมขวางแข็งแรงขึ้น สารเชิงซ้อนนี้สามารถผันกลับได้โดยใช้สารละลายอีดีทีเอและสารละลายทองแดง การใช้ฟีนอลที่เรืองแสงได้ในการทำปฏิกิริยาเปิดวงของเบนซอกซาซีนทำให้เบนซอกซาซีนสามารถเรืองแสงได้ การเชื่อมต่อเบนซอกซาซีนที่ตอบสนองต่อแสงกับโรแทกเซนตามด้วยปฏิกิริยาเปิดวงของเบนซอกซาซีนด้วยฟีนอลที่เรืองแสงได้ทำให้สามารถตรวจสอบการเคลื่อนที่ของโรแทกเซนได้ นอกจากนี้ การเกิดสารประกอบเชิงซ้อนกับไอออนของโลหะและการเปลี่ยนแปลงคอนฟอร์เมชันของเอโซเบนซีนก็สามารถตรวจสอบได้ด้วยคุณสมบัติการเรืองแสง พอลิเมอร์ที่มีเบนซอกซาซีนเป็นหมู่แทนที่สามารถเตรียมได้จากการเชื่อมต่อเบนซอกซาซีนที่ตอบสนองต่อแสงกับอนุพันธ์ของอะคริเลต ปฏิกิริยาพอลิเมอร์ไรเซชันด้วยเทคนิคเอทีอาร์พีทำให้ได้พอลิเมอร์ร่วมแบบกลุ่ม การฉายแสงยูวีและการเกิดสารประกอบเชิงซ้อนกับไอออนของโลหะส่งผลต่อสัณฐานวิทยาของพอลิเมอร์ร่วมแบบกลุ่ม

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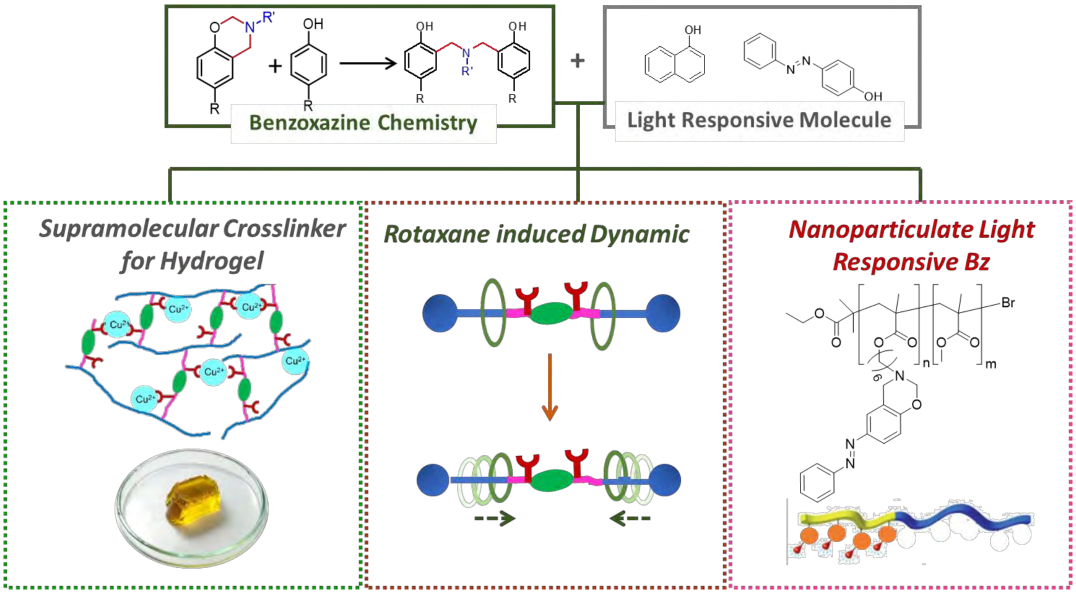
GRAPHICAL ABSTRACT



CHAPTER I
INTRODUCTION

Responsive materials have been attractive for several decades because they can response to external stimuli. They can be inorganic molecules, small organic molecules, macromolecules and polymers. The stimuli can be light, electric field, magnetic field, temperature, chemical etc.

Light responsive materials were widely used in daily life such as photochromic lens, photographic film, street lamp and biosensor. There are several functional groups that can response to light. For example, spiropyran can change the structure between close ring and open ring under UV light. Another one is fluorescent molecule which consists of conjugated bond. The most attractive light responsive functional group is azobenzene. Its conformation can be changed between cis and trans under UV light. The conformational change of azobenzene can control not only the property of molecule such as inclusion phenomena but also bulk material like bending of thin film.

The combination of responsive functional group in one molecule is an attractive way to prepare multi responsive materials. The responsive functional groups tend to consist of aromatic group and/or reactive functional groups which leads the combination more difficult. It will need multi steps modification and conjugation which tend to provide low yield product.

Benzoxazine is generally known as a kind of phenolic resin with good thermal, chemical, electrical, mechanical and physical properties. It can be prepared from phenol, amine and formaldehyde via mannich reaction which is simple and effective approach. Its dimeric unit can form inter- and intramolecular hydrogen bonding and also form metal ion complexation. It might be possible to take its chemistry to combine the responsive functional group together. The responsive benzoxazine can be prepared by simple selecting responsive phenol and amine. To make it useful, further modification of multi responsive benzoxazine for fine tuning is also attractive.

In this work, benzoxazine in combination with rotaxane system was studied. Rotaxane is a mechanically interlock molecular architecture consisting of a “dumbbell shaped molecule” which is threaded through a “macrocycle” (Arico, 2005). It can be applied in various strategies, for example, polymer topology transformation, dynamic crosslinker, and also property-tunable polymer. As macrocycle in rotaxane can be moved and affect the interaction inside and between molecule, it comes to our question whether the rotaxane can fine tune light responsive behavior of benzoxazine, how it is possible.

The modification of benzoxazine as organogel is already reported from linear benzoxazine reacted with dithiol. (Bektas *et. al.*, 2015) To the best of our knowledge, there is no report about multi responsive benzoxazine organogel. It is our goal to prepare supramolecular crosslinker for poly(acrylic acid) by preparing light responsive benzoxazine followed with carrying out ring opening reaction for fluorescent property and metal ion responsive.

Polymerization of benzoxazine as linear polymer via vinyl group and also methacrylate group were already reported. (Jin, Lin *et. al.*, 2011a, Liu, Ying-Xuan *et. al.*, 2016, Ma *et. al.*, 2015) In this case, vinyl monomers containing benzoxazine pendant, which contains azo group as the light responsive monomer were synthesized. The light responsive benzoxazine and its block copolymer was prepared by atom transfer radical polymerization (ATRP). The further carrying out ring opening reaction provides metal ion complexation. UV light and metal ion affected morphology of block copolymer.

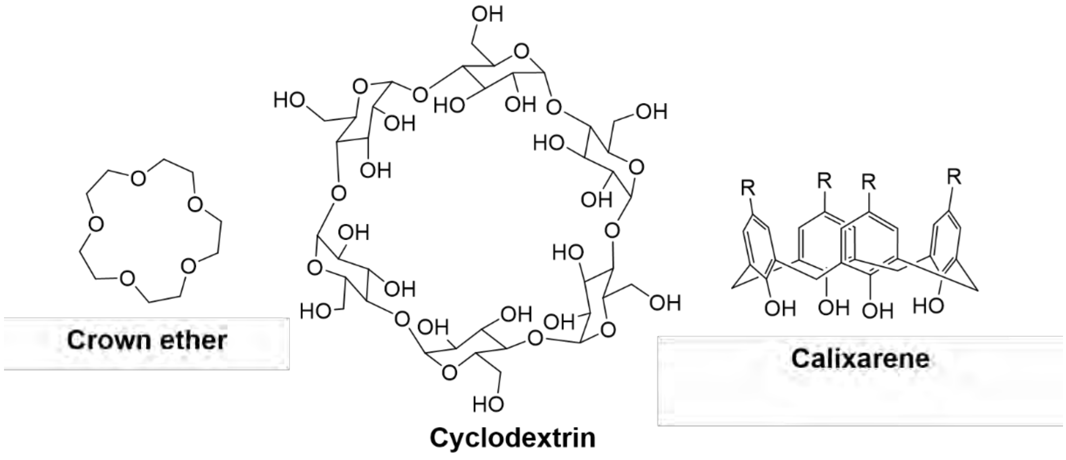
CHAPTER II
LITERATURE REVIEW

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, Jean-Marie, 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.

Supramolecular system consists of host and the guest molecules which specific interact to each other like the lock and key structure under intermolecular forces, including hydrogen bonding (Han *et. al.*, 2014). The examples of well-known host molecules are crown ethers (Pedersen, 1967), cyclodextrins (Khurana *et. al.*, 2014), calixarenes (Guo *et. al.*, 2012), and their various derivatives (Scheme 2.1).

Scheme 2.1 Examples of the well-known host molecules



Crown ether

Cyclodextrin

Calixarene

2.2 Molecular Self-assemblies

Molecular self-assembly is a tool to construct higher order structures under specific noncovalent interaction such as hydrogen bonding(Simanek *et. al.*, 1994), metal coordination (Grancha *et. al.*, 2013), π-π interactions (Vallejos *et. al.*, 2016), and/or electrostatic effects (Lehn, Jean-Marie, 1988). (Figure 2.1) 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 parts and lipophilic parts which separately organized into an ordered structure to minimize interaction energy with two different environments (Azagarsamy *et. al.*, 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.

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

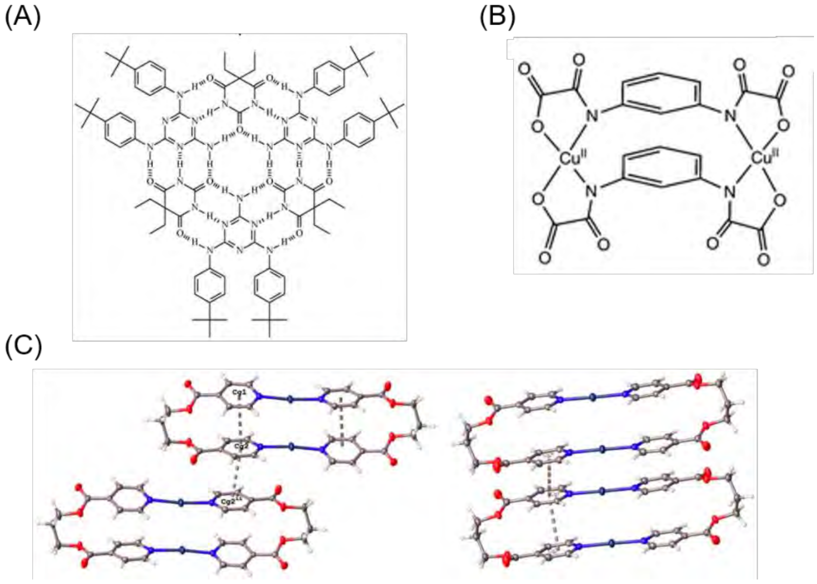


Figure 2.1 Typical examples of supramolecular structure via: (A) hydrogen bonding (B) metal coordination, and (C) π-π interactions. (Bissell *et. al.*, 1994, Corbellini *et. al.*, 2005, Sada *et. al.*, 2001)

2.3 Rotaxane

Rotaxane is mechanically interlocked molecular architecture. The rotaxane can be prepared by various technique (Yang *et. al.*, 2012) (Figure 2.2). Moreover, various kinds of host molecules, such as cyclodexrins, crown-ethers, calixarenes have been reported for the fabrication of pseudorotaxanes and rotaxane (Figure 2.3). Recent developments propose applications for polyrotaxanes and polypseudorotaxanes such as stimuli responsive materials, self-healing polymers, actuators and sensors. The molecular behavior with unique properties is derived from non-covalent interactions in the construction of molecular architectures (Arunachalam *et. al.*, 2014) such as polymer topology transformations, (Aoki *et. al.*, 2014, Aoki *et. al.*, 2015a, Ogawa *et. al.*, 2015b) dynamic crosslinker, (Iijima *et. al.*, 2014, Sawada *et. al.*, 2015) property-tunable polymer (Abe *et. al.*, 2014, Koyama *et. al.*, 2013, Suzuki *et. al.*, 2014, Zhu *et. al.*, 2007b) etc.

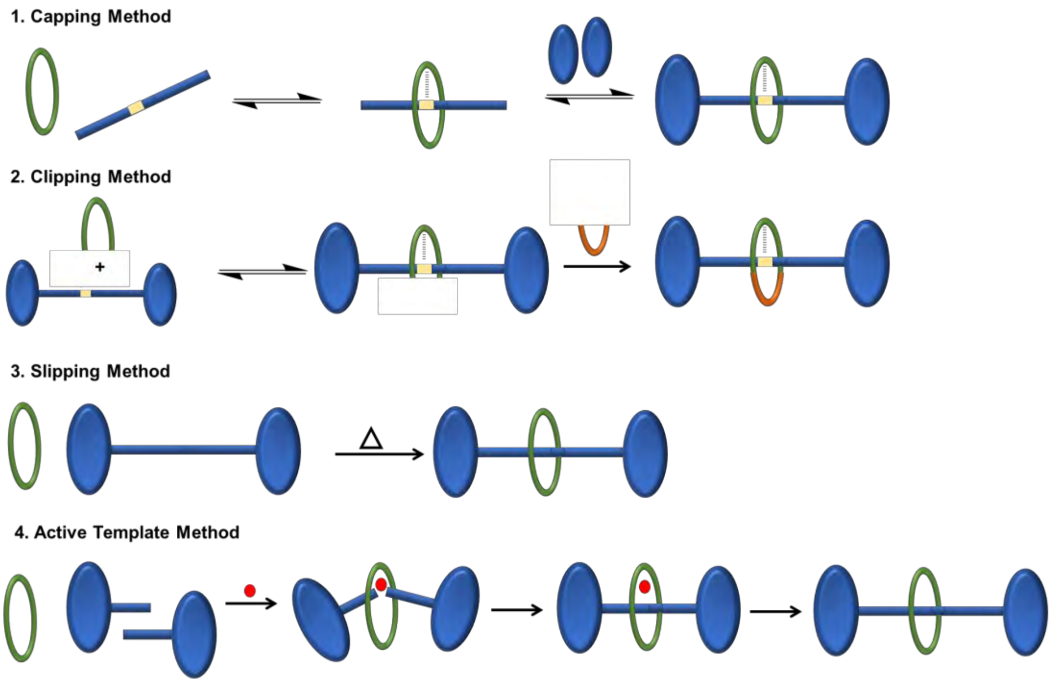
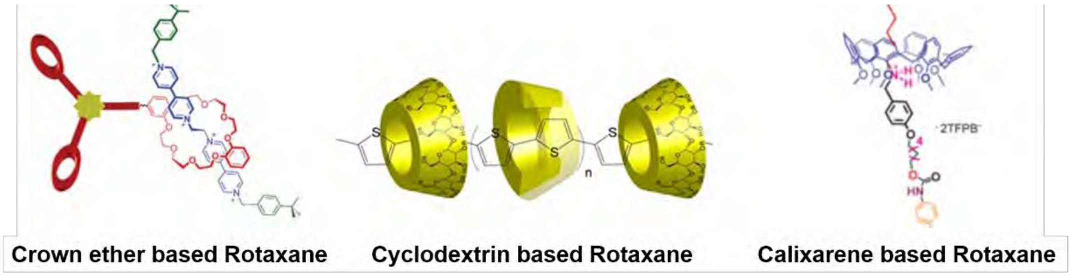


Figure 2.2 Techniques to prepare rotaxane.



Crown ether based Rotaxane　Cyclodextrin based Rotaxane　Calixarene based Rotaxane

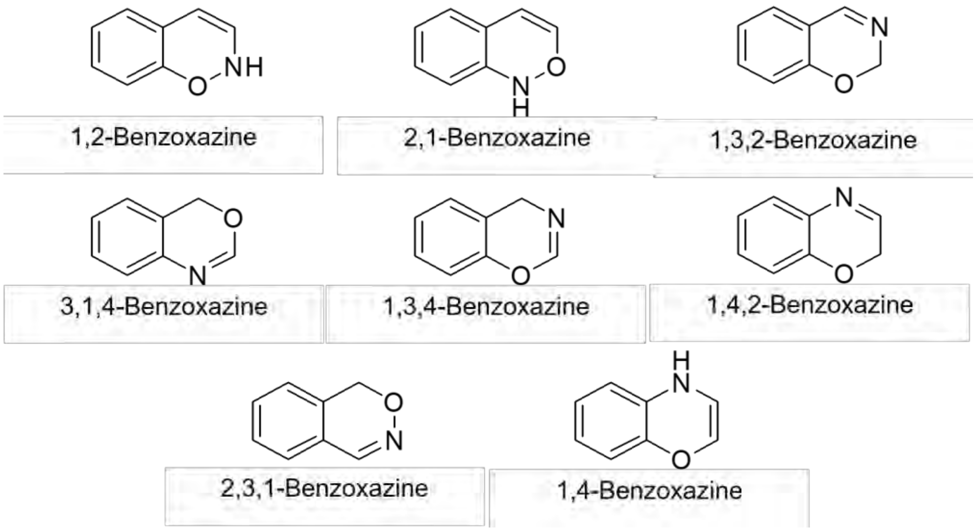
Figure 2.3 Classes of rotaxane. (Loeb *et. al.*, 2005, Takashima *et. al.*, 2006, Talotta *et. al.*, 2012)

2.4 Benzoxazines

2.4.1 Structures and Chemistry of Benzoxazine Derivatives

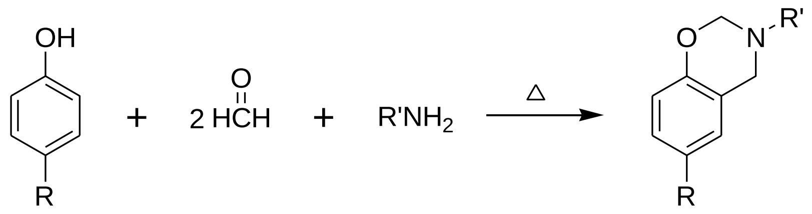
Benzoxazine is a heterocyclic compound, which composes of oxazine ring and benzene ring. There are 8 different methylene position and substituted hydrogen atom position as shown in Scheme 2.2.

Scheme 2.2 Isomers of benzoxazine



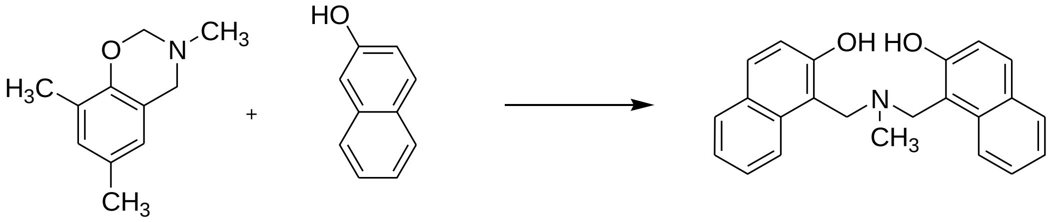
In 1964, the preparation of benzoxazine derivative (3,4-dihydro-1,3-2*H*-benzoxazines) was reported by Burke using Mannich reaction between phenol, formaldehyde and primary amine. (Scheme 2.3)

Scheme 2.3 Preparation of benzoxazine derivative



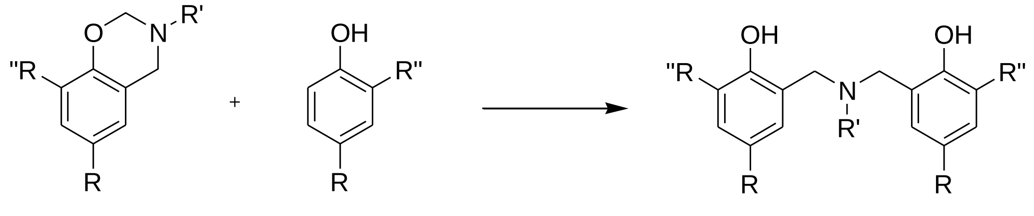
In 1949, Burke reported on the preparation of *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine derivatives, benzoxazine dimer, via a ring opening reaction of benzoxazine. For example, the ring opening reaction of 2,3-dihydro-2-methyl-1H-naphth-(1,2-e)-1,3-oxazine with 2-naphthol provides *N,N*-bis(2-hydroxy-1-naphthylmethyl)methylamine. (Scheme 2.4).

Scheme 2.4 Preparation of *N,N*-bis(2-hydroxy-1-naphthylmethyl)methylamine via ring opening reaction



Chirachanchai and coworkers demonstrated that ring opening reaction of benzoxazine terminates the polymerization at the very first step. This leads to a benzoxazine dimers, *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine derivatives, with high yield. (Scheme 2.5) (Laobuthee *et. al.*, 2001, Laobuthee *et. al.*, 2003, Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2004, Phongtamrug *et. al.*, 2006b) The single crystallography analyses pointed out the unique structure under inter- and intramolecular hydrogen bonds network (Figure 2.4). 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)

Scheme 2.5 Preparation of N,N- bis(2-hydroxyalkylbenzyl)alkylamine derivatives via ring opening reaction



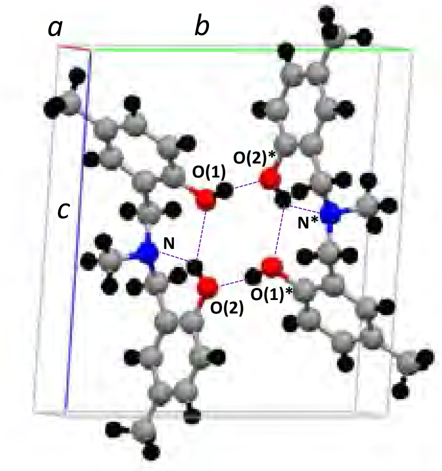


Figure 2.4 Crystal structure of *N,N*-bis(5-methyl-2-hydroxybenzyl) cyclohexylamine. (Phongtamrug *et. al.*, 2006b)

2.4.2 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 molecular performance as a host compound to accept guest species. In the past, Laobuthee *et. al.* reported an inclusion phenomena of *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine derivatives as a host with alkaline picrate salts as a guest. They also demonstrated that the copper ion binding properties of the derivatives is under the double-oxygen-bridged dimeric system insisted by X-ray single crystal analysis (Phongtamrug *et. al.*, 2006a) (Figure 2.5). They also proposed the existence of multi-guest species, i.e., ion and neutral molecules, in a single host-guest framework (Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2004, Phongtamrug *et. al.*, 2006b).

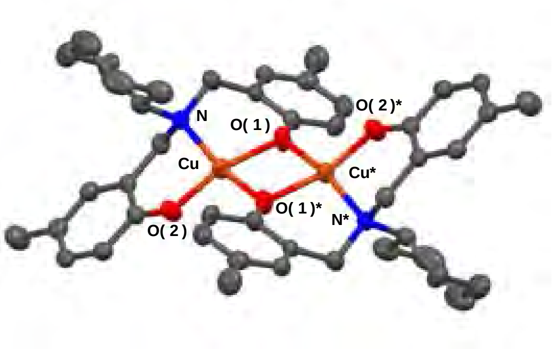


Figure 2.5 Crystal structure of copper ion binding with *N,N*-bis(5-cyclohexyl-2-hydroxybenzyl)cyclohexylamine. (Phongtamrug *et. al.*, 2006b)

2.5 Controlled/Living Radical Polymerization

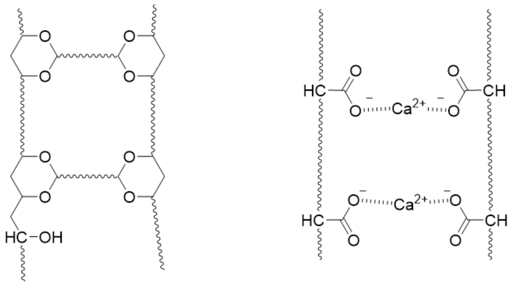
The living polymerization was discovered by Michael Szwarc in terms of living anionic polymerization which widely useful in polymer science.(Szwarc, 1956, Szwarc *et. al.*, 1956) It leads to well-defined polymers with precisely designed molecular structure and morphologies. (Fréchet, 2005, Leibler, 2005, Matyjaszewski, 2005) It has unique behavior among general polymerization, for instance, long life time of growing chain, fast in initiation step, less in proportion of dead chain, slower polymerization rate, and termination rate decrease with time. There were various attempts to develop controlled radical polymerization technique as free radical polymerization could not control polymer molecular weight and molecular weight distribution due to the very short lifetime of the growing chains.(Braunecker *et. al.*, 2007) There are several techniques developed for controlled radical polymerization namely in atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer processes (RAFT), and nitroxide mediated polymerization (NMP)

ATRP is one of the most effective controlled radical polymerization systems. ATRP was developed by Sawamoto and co-workers (Kato *et. al.*, 1995) and Matyjazewski and co-workers (Wang *et. al.*, 1995). It recognized as a powerful tool for the synthesis of a series of complex polymer architectures with controlled molecular weight.(Gao *et. al.*, 2009, Matyjaszewski, 2005) It provides a wide range of macromolecular architecture, including block, star-like, and brush-like copolymers.(Waled *et. al.*, 2014) The system of typical ATRP reaction consists of an initiator, catalyst (transition metal/ligand) and monomer.

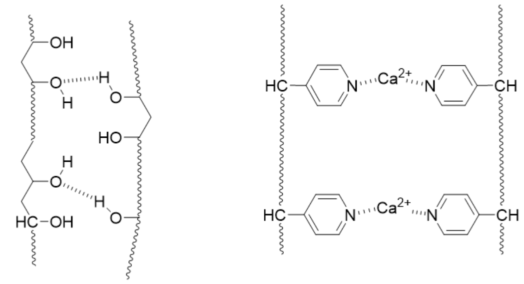
2.6 Polymeric Gels

A polymer gel consists of a cross-linked polymer network with a fluid filling in space of the network. Gels look like solid material but can undergo large deformations. Some of living organisms are made of gels. (Osada *et. al.*, 2004)

Polymeric gel structures can be obtained by either chemical or physical processes. Some gels are cross-linked by covalent bonds (chemical gel), whereas other gels are cross-linked by weak interaction (physical gel), i.e. hydrogen bonds, hydrophobic interaction and ionic interactions. Physical gel is usually reversible so-called sol–gel transitions. Some examples of chemical gel and physical gel are shown in Figure 2.6.



Covalent Bond **Coulombic Bond**



Hydrogen Bond **Coordinate Bond**

Figure 2.6 Examples of chemical and physical gels.

2.7 Light Responsive Polymers

Polymers that can change its shape under light exposure, photodeformable polymers, are mostly based on the photoisomerization such as azobenzenes (Finkelmann *et. al.*, 2001, Yu *et. al.*, 2003a), and photoreactive molecules such as cinnamates (Hideyuki *et. al.*, 2006, Jiang *et. al.*, 2006). The complicated movements like twisting, swimming and rotation have been obtained on photoactive polymer films (Munenori *et. al.*, 2008, Yamada *et. al.*, 2009).

An exposure of light with appropriate wavelength, azobenzenes show reversible trans-cis isomerization which leads to a change in the angle and distance between the two aromatic rings. (Meng *et. al.*, 2010) The change of azobenzene groups linked to macromolecules can induce macroscopic changes in polymeric materials. Azobenzene has been widely reported as light-active liquid-crystal elastomers. (Cviklinski *et. al.*, 2002, Finkelmann *et. al.*, 2001, Ikeda *et. al.*, 2003) A photodeformable polymer film was prepared by polymerization of a liquid-crystal monomer cross-linked with a diacrylate cross-linker. The chemical structures of liquid-crystal monomer and cross-linker used in preparation of the film and the controlled photoinduced bending in precise directions performance are shown in Figure 2.7. (Ikeda *et. al.*, 2003)

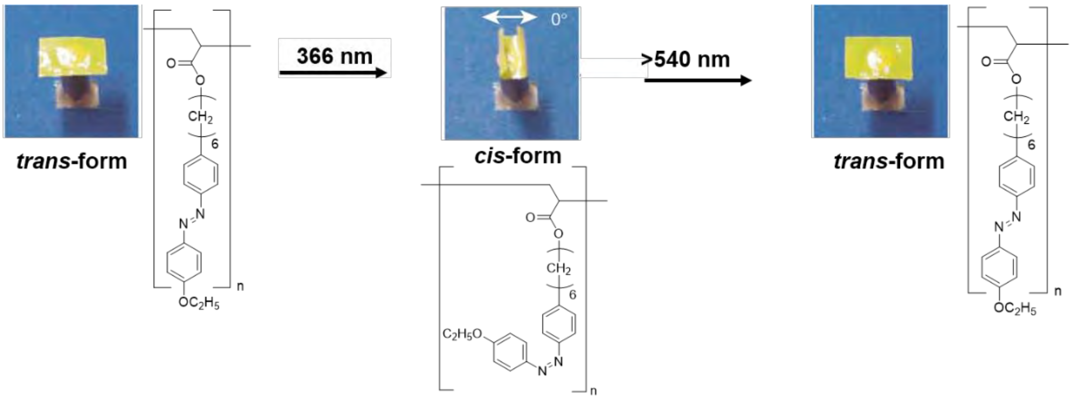


Figure 2.7 Chemical structures of liquid-crystal photodeformable film and its performance. (Ikeda *et. al.*, 2003)

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. Preparation of multi-responsive materials has been widely reported, however, the combination of supramolecular structure with multi-responsive functional group has been rarely reported. Herein, we propose a simple approach to prepare responsive materials which maintain its supramolecular structure. In Chapter III, the polymeric gel with light responsive functional groups are prepared. Moreover, the dimeric unit of benzoxazine also serves as double crosslink unit via metal ion complexation. The fine-tune property of gel via light responsive functional group is expected. In Chapter IV, the combination of light responsive benzoxazine with rotaxane system is prepared. The dynamic of rotaxane unit can tune the responsive behavior of benzoxazine. Moreover, the reversible multi-responsive benzoxazine in combination with rotaxane is expected. In Chapter V, we demonstrate the preparation of light responsive benzoxazine linear polymer and its block copolymer via ATRP. The block copolymer behaviour, metal ion complexation and effect of light responsive unit on the polymer are focused.

CHAPTER III

DUAL-FUNCTION BENZOXAZINES: LIGHT RESPONSIVE AND PHOTOLUMINESCENT PROPERTIES VIA SIMPLE APPROACH

3.1 Abstract

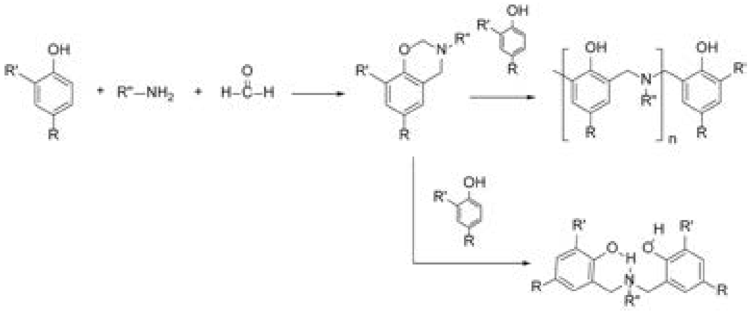
Light responsive benzoxazine monomers were prepared based on benzoxazine chemistry which is simple and high-yield reaction. This is the first time that fluorescent molecule and azobenzene functional group were combined together via oxazine ring. The product still shows properties from both fluorescent and azobenzene molecule.

3.2 Introduction

Optically responsive materials are applied in various kinds of applications, for example, chemosensor, biosensor, photochromic materials, etc. (Liu, Fang *et. al.*, 2010) There are many kinds of functional group which can response to light. A functional group which has been large interested in a decade is azobenzene. Its conformation can be changed between *trans* and *cis* form under UV light. (Kumar *et. al.*, 1989) This change also affects physical property of materials, for example, film bending, hydrophobic-hydrophilic switching. (Russew *et. al.*, 2010, Yu *et. al.*, 2003b) Another light responsive functional group is conjugated bond. It can be rearranged under proper conditions, moreover, some conjugated molecules can emit fluorescent light. (Lee, Sumin *et. al.*, 2012, Such *et. al.*, 2004) It should be noticed that most optically responsive molecules consist of benzene ring in their structure. Although their applications are attractive, it is difficult to promote them to other molecule which needs complicated steps, tends to obtain products in low yields. (Othman *et. al.*, 2007b)

Benzoxazine is an attractive molecule to overcome this problem since it contains benzene ring and can be prepared via simple and effective approach. (Chirachanchai *et. al.*, 2009) It can be synthesized by carrying out mannich reaction of phenol, amine and formaldehyde. Benzoxazine monomer from monophenol can form linear polybenzoxazine but the one from bisphenol forms crosslink polymer network. In addition, its oxazine ring can be opened in the presence of phenol yielding *N,N*-bis(2-hydroxybenzyl)alkylamine, benzoxazine dimer (Scheme 3.1). Moreover, it allows simple modification. So, there are several researches trying to design functional group in benzoxazine, for instance, double-bond-containing benzoxazine monomer which is capable of undergoing photodimerization (Kiskan *et. al.*, 2007) and acetylene-containing benzoxazine which its network can be controlled. (Kiskan *et. al.*, 2008b) Furthermore, our group succeeded in developing supramolecular structure of benzoxazine, for example, benzoxazine dimer forms inter- and intramolecular hydrogen bonding which leads the mannich reaction on benzoxazine dimer yields mono-oxazine instead of di-oxazine. (Laobuthee *et. al.*, 2001) And it can form complex with metal ions. (Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2004, Phongtamrug *et. al.*, 2006b) Moreover, benzoxazine dimer can be used for preparing macroclyclic compound. (Chirachanchai *et. al.*, 2008, Chirachanchai *et. al.*, 2009, Laobuthee *et. al.*, 2003, Rungsimanon *et. al.*, 2008) Because it contains benzene ring in its structute, π-π interaction can be formed which leads benzoxazine monomer can be cured in polymer pocket yielding nanoparticle. (Rungswang *et. al.*, 2011, Rungswang *et. al.*, 2012)

Scheme 3.1 Synthesis of benzoxazine dimer



Benzoxazine might be a good choice for prepare responsive molecule because it is easy to synthesize and there are various properties of benzoxazine as mentioned above which may be useful in responsive applications. Functional benzoxazines can be achieved by using functional amine and phenol as the starting material of benzoxazine. Moreover, the remained functional group can be further modified. There are less researches related to connecting fluorescent molecule with other molecule via oxazine ring. For example, Nath M. and Sharma S. reported about connecting porphyrins derivatives with various kinds of phenol via mannich reaction. (Rodolfo, 2011, Sharma *et. al.*, 2013) It would be more attractive if the different responsive functions were combined together. It will be dual-function molecule which can response with various stimuli in one molecule.

In this work, we purpose the way promote light responsive molecule in benzoxazines by using fluorescent phenol and light responsive or functionalizable amine react with formaldehyde. Meanwhile, the effect of amine and fluorescent phenol on the photoluminescent was also studied. Ring-opening reaction of responsive benzoxazines is in progress.

3.3 Experimental

3.3.1 Materials

4,4′-(9-Fluorenylidene)diphenol (FBP), and 1,5-dihydroxynaphthalene (1,5-DHN) were purchased from Sigma-Aldrich, USA. Paraformaldehyde, 2,4-dimethylphenol and 4-aminoazobenzene were purchased from Merck, Germany. Ethanolamine was purchased from Carlo Erba, Italy. Sodium hydroxide and sodium sulphate anhydrous were purchased from Ajax finechem, Australia. Dioxane, diethyl ether, *N,N'*-dimethylformamide (DMF), chloroform and isopropanol were purchased form RCI Labscan, Ireland. All chemicals were used without further purification.

3.3.2 Synthesis of 6,6'-(9-fluorene-9,9-diyl)bis(3-(4-phenyldiazenyl)phenyl)-3,4-dihydro-2H-1,3-benzoxazine, FA

FA was prepared by using FBP (1.752 g, 5 mmol), paraformaldehyde (0.800 g, 25 mmol), and 4-aminoazobenzene (1.970 g, 10 mmol). First, paraformaldehyde, 4-aminoazobenzene and dioxane were added into three necked flask with stirring at room temperature for 30 min, then, solution of FBP in dioxane was added. The reaction temperature was increased to 110 °C and proceeded at 110 °C for 5 h. After that, dioxane was removed by rotary evaporator. The bulk product was dissolved by diethyl ether and washed with 1 M sodium hydroxide for 3 times and distilled water for 2 times. Finally, the product solution was treated with anhydrous sodium sulphate and dried under vacuum to obtain FA powder. (85 % yields)

FTIR (KBr, cm^{-1}): 824 (s, 1,2,4-tri-substituted benzene), 1232 (s, C-N stretching), 951 (s, C-O-C), 1508 (s, N=N); ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 4.05 (4H, s, Ar-CH_2-O), 5.15 (4H, s, O-CH_2-N), 7.07 (6H, d, J=10 Hz, Ar), 7.49 (12H, m, Ar), 7.89 (14H, m, Ar); MW calcd. = 792.94, ESI-TOF MS: m/z = 793.92 ($M+H^+$).

3.3.3 Synthesis of 2,2'-((9-fluorene-9,9-diyl)bis(2H-1,3-benzoxazine-3,6-diyl)) bis(ethan-1-ol), FE

FE was prepared by the same procedure of FA but change from 4-aminoazobenzene to ethanolamine (0.611 g, 10 mmol). (82 % yields)

FTIR (KBr, cm^{-1}): 3386 (b, O-H stretching), 820 (s, 1,2,4-tri-substituted benzene), 1231 (s, C-N stretching), 931 (s, C-O-C), 1494 (s, N=N); ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 2.66 (4H, t, J = 5 Hz, N-CH_2-C), 3.34 (4H, t, J = 5 Hz, C-

CH_2-OH), 3.80 (4H, s, Ar-CH_2-O), 4.75 (4H, s, O-CH_2-N), 6.63 (2H, m, Ar), 6.88 (2H, m, Ar), 7.48 – 7.31 (6H, m, Ar), 7.90 (2H, m, Ar); MW calcd. = 520.63, ESI-TOF MS: m/z = 543.56 ($M+Na^+$).

3.3.4 Synthesis of 2,2'-(1,7-dihydronaphtho[2,6]bis(1,3-oxazine)-2,8(3,9)-diyl) bis(ethan-1-ol), NE

NE was also prepared by the same procedure of FA but using 1,5-dihydroxynaphthalene (0.801 g, 5 mmol) and ethanolamine (0.611 g, 10 mmol) instead of FBP and 4-aminoazobenzene respectively. (83 % yields)

FTIR (KBr, cm^{-1}): 3400 (b, O-H stretching), 1254 (s, C-N stretching), 960 (s, C-O-C); ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 2.67 (4H, t, J = 5 Hz, N-CH_2-C), 3.74 (4H, t, J = 5 Hz, C-CH_2-OH), 4.44 (4H, s, Ar-CH_2-O), 4.86 (4H, s, O-CH_2-N), 6.84 (2H, dd, Ar), 7.48 (2H, dd, Ar); MW calcd. = 330.16, ESI-TOF MS: m/z = 331.16 ($M+H^+$).

3.3.5 *Cis-trans* isomerization property study

FA, contains azobenzene group, were dissolve in DMF. The solution was left under UV exposure in various period of time. UV-VIS absorbance spectra of solution were measure to observe changing of pattern over time every 15 min.

3.3.6 Study on Ring-opening Reaction of PBzMs

Dimerization of PBzMs were studied according to Laobuthee's report (Laobuthee *et. al.*, 2001). PBzMs were stirred with 2,4-dimethylphenol in dioxane. The reaction was carried out at 80 °C for 3 h. The precipitates was collected and crystallized in chloroform/isopropanol.

3.3.7 Characterizations

Fourier transform infrared (FTIR) spectra were obtained from Bruker ALPHA FT-IR Spectrometer with 32 scans at a resolution of 4 cm^{-1}. Electrospray Ionization Mass Spectra (ESI-MS) were measured by Micro TOF II operated in positive ion mode analyzed by Bruker Compass DataAnalysis 4.0 software. Nuclear magnetic resonance (NMR) spectra were obtained from Bruker Avance 500 MHz NMR spectrometer. Thermal analyses were performed by using a Netzch 200 F3

Maia differential scanning calorimeter. UV-VIS absorption spectra were recorded shimadzu UV-1800 using DMF as a solvent. Fluorescence spectra were recorded on a Agilent Cary Eclipse spectrofluorometer using DMF as a solvent.

3.4 Results and Discussion

3.4.1 Fluorescent emission property of PBzMs

Fluorescent emission properties of PBzMs were characterized. The proper excitation wavelengths of PBzMs for carrying out photoluminescent experiment were determined by UV-VIS absorption spectra as shown in Figure 3.1A. The wavelength at relatively maximum absorption is used for exciting molecule in photoluminescent measurement. The photoluminescent emission spectra of PBzMs are shown in Figure 3.1B.

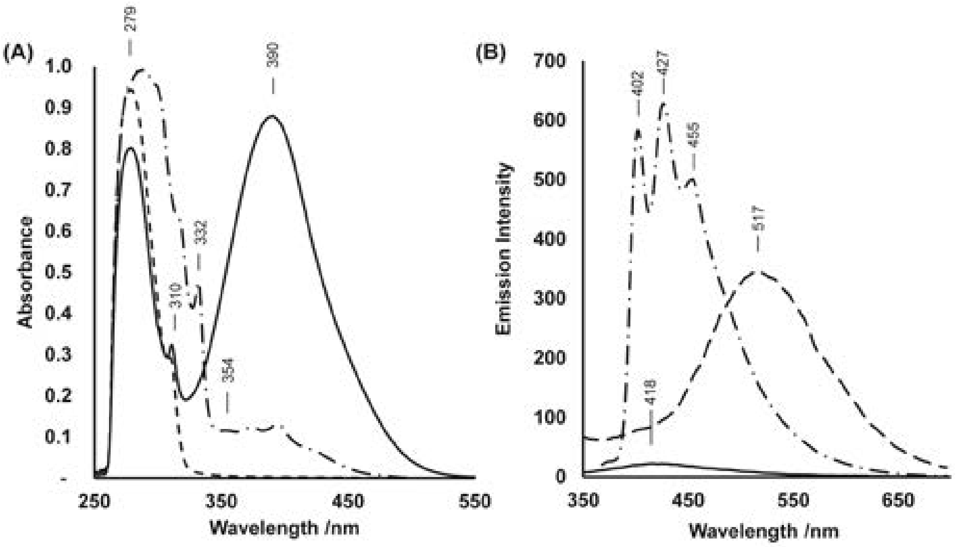


Figure 3.1 (A) UV-VIS absorbance and (B) Photoluminescent emission spectra of FA (——), FE (- - - -) and NE (— · —).

FA absorbs much light at 390, 310 and 279 nm. The optimum exposure for exciting FA is 310 nm. Fluorescent light was emitted at 418 nm. For FE, it absorbs much light at 310 and 279 nm. The optimum exposure for exciting FE is also 310 nm. The highest intensity was emitted at 517 nm. In case of NE, it absorbs light at 394, 354, 332 and 289 nm. The optimum wavelength for exciting NE is 354 nm. This wavelength makes NE emitted light at 402, 427 and 455 nm.

By comparing FA and FE photoluminescent spectra, photoluminescent emission intensity of FE is higher than FA. It should be noticed that the substitution group of amine in FA is azobenzene which is bulky. This may disturb packing of fluorophore which makes FA emits photoluminescent intensity relatively lower than FE.

Moreover, by comparing FE and NE, fluorophore phenol strongly affect photoluminescent spectra both intensity and wavelength. For FE, fluorene fluorophore is steric. It may prevent stacking of fluorophore. Comparing with NE, naphthalene group is planar, relatively less steric hindrance. This makes naphthalene can be packed well which causes high fluorescent intensity.

3.4.2 *Cis-tran*s isomerization property of azobenzene group

Considering azobenzene group in PBzMs, it should be investigated whether this function still remains its property by exposing UV light to FA solution and tracing amount of *cis* and *trans* conformation by measuring UV-vis absorbance spectra. The absorbance at 400 nm represents *cis* conformation and the absorption at 275 nm represents *trans* conformation. We found that *cis-trans* conformation of azobenzene group in FA is still switchable (Figure 3.2). By comparing rate of changing conformation with 4-aminoazobenzene, FA is relatively slower than 4-aminoazobenzene. It could be implied that steric hindrance of oxazine side interrupts changing conformation of azobenzene unit. Anyway, both fluorescent and azobenzene molecule were connected together via oxazine ring yielding dual-function benzoxazine.

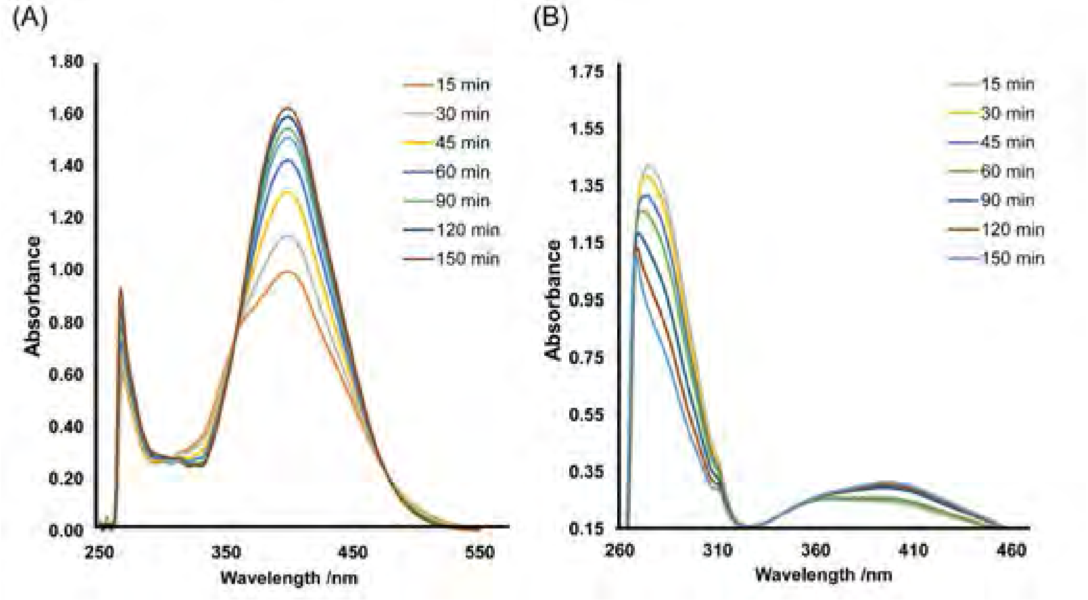


Figure 3.2 UV-vis absorbance spectra over time under UV 365 nm exposure of (A) 4-aminoazobenzene (B) FA.

Moreover, if responsive molecule can form complex with other molecule, i.e. metal ion, the responsiveness will be changed, turned on or quenched. (Dong *et. al.*, 2011, Othman *et. al.*, 2007a, Pramanik *et. al.*, 2008) As mentioned above, benzoxazine dimer can form complex with metal ion. So, ring-opening reaction of PBzMs was studied..

3.4.3 Ring-opening Reaction Study

Ring-opening reaction of FA is not favorable because azobenzene has free ortho position which can be cross-linked with benzoxazine**.** For FE and NE, prepared from aliphatic amine, ring-opening reaction can be occurred confirmed by mass spectra (found $[M+H^+]$ = 765.388128). (Figure 3.3) The complexation ability will be studied further.

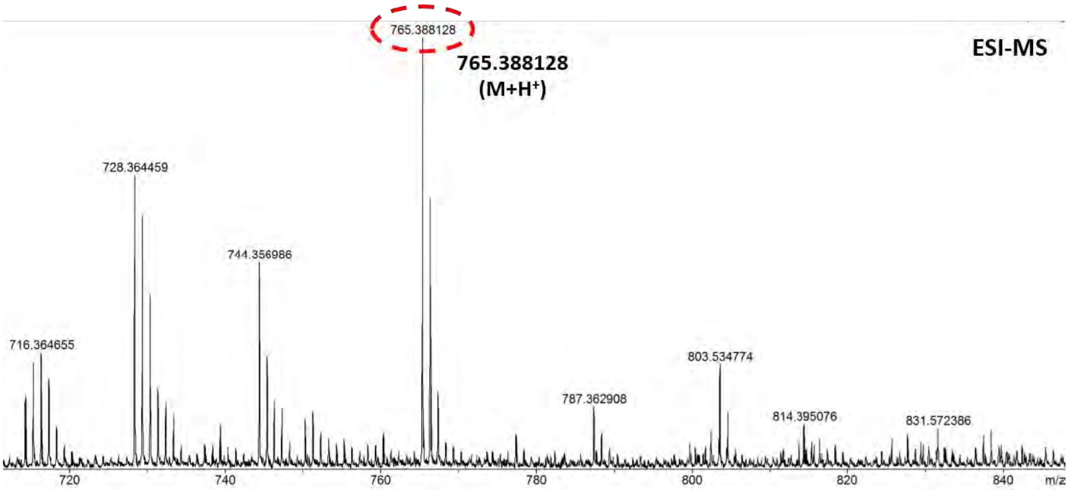


Figure 3.3 Mass spectrum of product from dimerization reaction of FE.

3.5 Conclusions

Dual-function benzoxazines were successfully prepared. It still shows both fluorescent and *cis-trans* isomerization properties. The use of aliphatic amine allows us to further carry out ring-opening reaction which is useful for optical properties. Moreover, the remained hydroxyl group of FE and NE can be further modified to active molecule.

3.6 Acknowledgement

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CHAPTER IV

POLY(ACRYLIC ACID) WITH BENZOXAZINE-BASED SUPRAMOLECULAR CROSSLINKER FOR RESPONSIVE AND REVERSIBLE FUNCTIONAL HYDROGEL

4.1 Abstract

Poly(acrylic acid) (PAA) is known for the hydrogels for decades. The present work demonstrates an approach to develop responsive and reversible PAA hydrogel by applying the supramolecular crosslinker. *N,N'*-Bis(3,5-dimethyl-2-hydroxybenzyl) methylamine derivatives, so-called benzoxazine dimers, are good model crosslinkers. In the first step, azobenzene containing benzoxazine monomer (Bzx) with hydroxyl group (-OH) at the terminals to enable the crosslinking with PAA via ester linkages is designed. In the second step, the ring opening of Bzx by using phenols results in the Bzx dimer which its two dimeric packing structure allows the metal ion to be incorporated as guest species. Based on this concept, PAA crosslinked by azobenzene-based Bzx dimer shows the light responsive functional hydrogel via cis-trans conformational change of azobenzene group under UV light and the tunable gel hardness via metallosupramolecular Bzx dimer. The present work shows the simple way to develop the hydrogel with tunable properties based on the supramolecular crosslinkers.

4.2 Introduction

Advanced polymeric gels have received much attention due to their specific as-desired properties. For example, super tough hydrogels can be obtained under the double network structure as they are under the balance of sacrificial and the sustained matrices. (Gong, 2010, Haque *et. al.*, 2012, Zhang *et. al.*, 2016) The external-stimuli responsive gels can be achieved by combining polymeric chains with responsive functional groups, (Jin, Naixiong *et. al.*, 2011b, Yan *et. al.*, 2012, Yuan *et. al.*, 2012) as seen in the cases of the charge bearable amino and/or carboxylic acid groups to show pH responsiveness (Deng *et. al.*, 2010, Maeda, 2008), the specific functional groups with lower/upper critical transition temperature (UCST or LCST) to initiate thermoresponsiveness (Ahn *et. al.*, 2008, Jin, Naixiong *et. al.*, 2011b, Maji *et. al.*, 2015), the hydrophobic matrices to enable volatile organic compound and oil absorption (Basak *et. al.*, 2012, Roy *et. al.*, 2014), the conformational changeable and/or the host-guest supramolecular structures to function as actuators and sensors, etc. (Chen *et. al.*, 2005, Guang *et. al.*, 2004, Pouliquen *et. al.*, 2007, Shao *et. al.*, 2014, Xiaotao *et. al.*, 2015) In this way, the introduction of the functional groups in the gel is an approach to develop the advanced polymeric gel.

The use of supramolecular polymer to form gel is an alternative way to obtain the gel with dynamic performances and shows responsive behavior with reversibility. (Xiaofan *et. al.*, 2015, Xiaofan *et. al.*, 2017) For example, Shao *et al.* reported poly(N-vinylimidazole-co-methacrylic acid) with triple stimuli-responsive behavior, i.e. temperature, pH, and metal ion, for the use as metal ion sensors. (Shao *et. al.*, 2014) Enke *et al.* proposed metallo-supramolecular polymer networks via the interaction between histidine and zinc ion to exhibit self-healing behavior. (Enke *et. al.*, 2015) Zeng *et al.* demonstrated that triptycene-based bis(crown ether) host and copolymer containing dibenzylammonium guest led to the multi stimuli reversible responsive gel. (Zeng *et. al.*, 2013) The responsive gel obtained from the functional groups in the network was also reported. For example, Wang *et al.* demonstrated poly(acrylic acid) (PAA) and azobenzene cross-linked microcapsules with UV/VIS controlled release system. (Xiaotao *et. al.*, 2015) It is important to note that those high performance gels are mostly based on the functional groups on the matrices rather than the crosslinkers. To our idea, the use of supramolecular crosslinkers is an alternative way to obtain the gel with dynamic behavior, for stimuli-responsiveness.

For the past years, our group has focused on the supramolecular chemistry of mono-phenol based benzoxazine dimers including their versatile molecular designs and their supramolecular structures under hydrogen bond networks and metal complexation. (Yoksan *et. al.*, 2009) As benzoxazine monomer (Bzx) can be prepared via Mannich reaction of phenol, amine and formaldehyde, (Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2004, Phongtamrug *et. al.*, 2006b, Tanphibal *et. al.*, 2016) the stimuli-responsive Bzx can be obtained by simply choosing phenols and/or amine with responsive functions. (Kiskan *et. al.*, 2008a, Kiskan *et. al.*, 2007, Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2004, Phongtamrug *et. al.*, 2006b, Po *et. al.*, 2011, Tanphibal *et. al.*, 2016)

In this work, the use of monophenol-based Bzx as a crosslinker for PAA is designed by modifying Bzx with two hydroxyl groups at its terminal so that the crosslink via ester linkages is possible. In fact, the use of phenol with responsive properties such as azobenzene group containing phenols allows the Bzx crosslinker with light responsive property. Moreover, the ring opening of Bzx by various types of phenols results in Bzx dimer with metallosupramolecular performances. At that time, Bzx dimer, which functions as the crosslinker, is expected to show metal complexation in the gel. Based on the abovementioned points, the present work shows the multiresponsive PAA hydrogel by simply using azobenzene based BZx as the crosslinker.

As the hydrogels with specific properties are expected for several advanced applications, such as sensors, biomedical materials, constructive materials, etc., the simple way to fabricate tunable hydrogels with multi-responsive properties by applying supramolecular crosslinkers can be expected for the hydrogel with responsive properties.

4.3 Experimental

4.3.1 Materials

Poly(acrylic acid) (PAA) (MW 450,000), 3-aminopropanol and copper(II) chloride were purchased from Sigma-Aldrich, Singapore. N-hydroxysuccinimide (NHS), paraformaldehyde, sodium sulphate, 2,4-dimethylphenol and deuterated chloroform were received from Merck Millipore, Germany. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) was purchased from TCI Tokyo Chemical Industry Co., Ltd., Japan. 1-Naphthol (NT) and 4-amimophenol were received from Fluka, Germany. Sodium nitrite was purchased from Univar, Singapore. Sodium hydroxide, hydrochloric acid (HCl), dimethylformamide (DMF), methanol, 1,4-dioxane and chloroform were purchased from RCI Labscan, Thailand. All chemicals were used as received.

4.3.2 Synthesis of 4,4'-dihydroxyazobenzene (Azo-OH)

4-Aminophenol (5 g, 45 mmol) was dissolved in 1 M HCl (100 mL) and kept below 5 ºC. Sodium nitrite (3.15 g, 45 mmol) solution (25 mL) was added dropwise followed by adding a solution of phenol (4.3 g, 45 mmol) in 3 M NaOH (16.25 mL). The cold methanol was added until the brownish solution was clear. The solution was kept in the ice bath for 30 min before allowing to the room temperature. The crude product was recrystallized in water/methanol to obtain Azo-OH. (Yield: 80%)

^{1}H-NMR (500 MHz, CDCl3, 25 °C): $\delta = 7.74$ (d, $J = 8.70$ Hz, 4H, ArH), 6.87 (d, $J = 7.90$ Hz, 2H, ArH). MS (ESI/MicroTOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_{10}N_2O_2$ 213.0659; Found 123.0740.

4.3.3 Synthesis of azobenzene-based benzoxazine (AP-Bzx)

3-Aminopropanol (0.8 g, 10 mmol) and paraformaldehyde (0.8 g, 25 mmol) were mixed in dioxane and toluene (1:1, 30 mL) at 70 ºC for 1 h. Azo-OH (1.09 g, 5 mmol) solution in dioxane (20 mL) was added. The solution temperature was increased to 110 ºC and kept for 6 h. Solvents were removed by evaporation. The crude product was dissolved in chloroform 100 mL and then washed with 0.5 M

NaOH 100 mL for several times and then brine. Organic layer was collected and dried over an excess amount of Na_2SO_4 until the reddish solution was clear. Then, Na_2SO_4 was filtered out and the solvent was evaporated to obtain AP-Bzx. (Yield: 75%)

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 7.77$ (d, $J = 8.60$ Hz, 2H, ArH), 7.66 (s, 2H, ArH), 6.94 (d, $J = 8.57$ Hz, 2H, ArH), 4.36 (s, 4H, OCH_2N), 4.03 (s, 4H, NCH_2Ar), 3.88 (t, 4H, CH_2OH), 2.97 (m, 4H, NCH_2CH_2), 1.78 (m, 4H, $CH_2CH_2CH_2$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 160.4$ (s, *Ar*-O-CH_2), 146.1 (s, *Ar*=N), 124.7 (s, Ar), 122.7(s, Ar), 121.2 (s, Ar), 83.8 (s, NCH_2O), 67.8 (s, HO-CH_2CH_2), 54.9 (s, ArCH_2N), 49.2 (s, NCH_2CH_2), 22.3 (s, $CH_2CH_2CH_2$). Anal. Calcd for $C_{22}H_{28}N_4O_4$: C, 64.06; H, 6.84; N, 13.58 Found: C, 65.50; H, 7.00; N, 10.67. MS (ESI/MicroTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{29}N_4O_4$ 413.2183; Found 413.2252.

4.3.4 Synthesis of PAA-AP-Bzx gel

PAA (5 g, 70 mmol) was dissolved in DMF (100 mL) and kept in ice bath. EDC (0.95 g, 5 mmol) was added to the solution and then NHS (0.57 g, 5 mmol). The solution was stirred for 1 h. AP-Bzx (1 g, 2.5 mmol) solution in DMF (10 mL) was added under vigorous stirring. After the solutions started to be viscous, the stirrer was stopped. The reaction was further kept in ice bath for another 12 h. The gel, PAA-AP-Bzx, was purified by soaking in DMF several times.

4.3.5 Synthesis of PAA-Bzx-DMP gel and PAA-Bzx-NT gel

PAA-Bzx gel (4 g) in DMF (50 ml) was left overnight before adding an excess amount of 2,4-dimethylphenol. The temperature of the solution containing PAA-Bzx gel was increased to 90 ºC for 6 h. Then the gel was purified by washing thoroughly with DMF to obtain PAA-Bzx-DMP gel. In similar, PAA-Bzx-DMP was obtained but using an excess amount of naphthol.

4.3.6 Preparation of PAA-Bzx-DMP-Cu

The PAA-Bzx-DMP (1 g) in water (50 ml) was left overnight before soaking in $CuCl_2$ 40 mM 50 mL for 12 h to obtain the gel, i.e. PAA-Bzx-DMP-Cu.

The amount of incorporated Cu(II) was quantified by the differences in UV-VIS absorption at 795 nm normalized with the dried weight of PAA-Bzx-DMP.

4.3.7 Gel exposure to UV and visible light

The gel obtained were exposed to UV lamp in close chamber under variation of time. The fluorescent spectra and mechanical properties of the gels before and after UV exposure were characterized and plotted with the exposure time. In the case of gel treated by visible light, the gels were simply left under the fluorescent lamp for 1 h. The gels were characterized accordingly.

4.3.8 Instruments and Characterizations

The infrared spectra were recorded with 32 scans at resolution 4 cm^{-1} using a Bruker Alpha FTIR spectrometer in the frequency range of 4000–400 cm^{-1}. ^1H-NMR spectra were recorded by a Bruker Avance Ultrashield Plus NMR spectrometer operated at Larmor frequency of 500.13 MHz. Fluorescence spectra were recorded by a Cary Eclipse spectrofluorometer (Agilent Technologies) equipped with solid sample holder. UV-VIS absorption spectra were recorded by an Agilent cary 300 UV-VIS spectrophotometer. The UV exposure was performed in chamber using UV lamp (RUV 533 BC) covering wavelength from 315 nm to 400 nm. In the case of visible light, the sample were exposed to the room light (fluorescent lamp) with the wavelength from 400 nm to 700 nm. The compressive stress was evaluated with a Lloyd universal testing machine (LRX) at room temperature using a cross head speed of 2 mm/min. XPS spectra were recorded by a Shimadzu Kratos Axis Ultra DLD X-ray photoelectron spectroscope using monochromatic Mg KR radiation (1253.6 eV). The binding energy of C 1s peak was referenced at 284.6 eV, and the high-resolution scans of core level spectra were set to 15 eV pass energy.

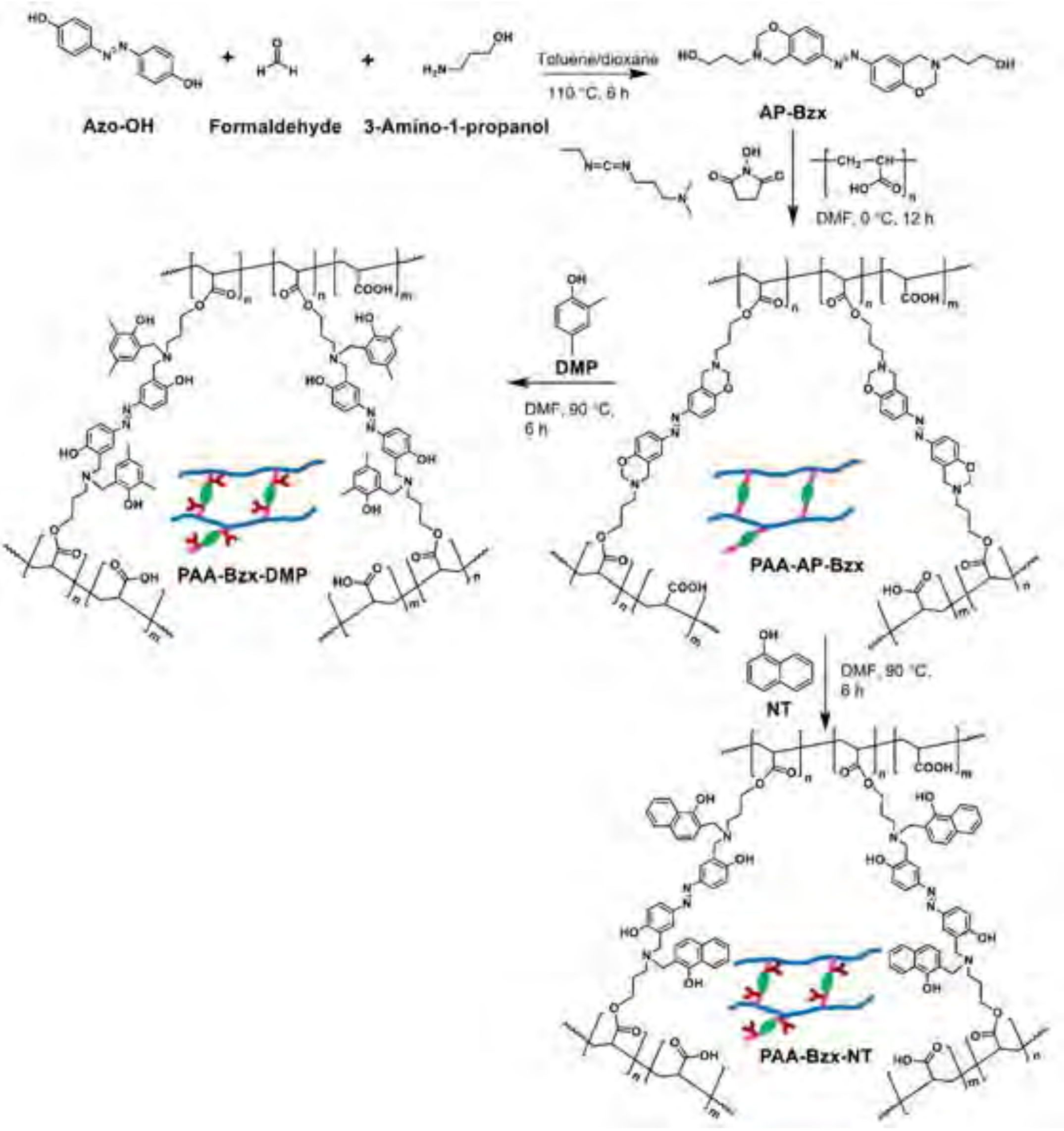
4.4 Results and Discussion

4.4.1 Preparation of PAA-AP-Bzx, PAA-Bzx-DMP, and PAA-Bzx-NT

The PAA-AP-Bzx, PAA-Bzx-DMP, and PAA-Bzx-NT were prepared as scheme 4.1 and in each case, the gel obtained was under Bzx crosslinker. By simply applying light responsive molecules, such as azophenol, Bzx with the specific property can be easily obtained. In addition, in order to apply Bzx unit as the crosslinker, the difunctional azophenol is needed. The important point of molecular design is, therefore, the preparation of Azo-OH which can be prepared by diazotization. Here, Mannich reaction was carried out using Azo-OH and aminoalcohol to give AP-Bzx as confirmed by ^{1}H-NMR (Appendix A). It should be noted that the use of aminoalcohol as primary amine for preparation of Bzx is for the presence of active hydroxyl group. In other words, under this AP-Bzx containing two hydroxyl groups, the conjugation with PAA using EDC and NHS results in PAA-AP-Bzx gel. Although it is difficult to completely remove the unreacted compounds out of the gel, here, the soaking in DMF several times was applied to compensate the purification.

In the past, our group clarified that monophenol Bzx self-terminates after a single ring opening to obtain Bzx dimers. In fact, the Bzx dimers with the aza methylene groups in the combination with phenol units show their metallosupramolecular structure by accepting guest as coordinated species for two units of Bzx dimer. (Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2004) Here, the ring opening of PAA-AP-Bzx in gel state was expected to give dimers. As a consequence, the metal ion responsiveness as additional property can be obtained. In order to achieve the ring opening in gel state, PAA-AP-Bzx was immersed in DMP followed by heating to 90 °C for 6 hours. This step led to PAA-AP-DMP. The use of NT also provided PAA-AP-NT.

Scheme 4.1 Synthesis of PAA-Bzx-DMP and PAA-Bzx-NT



4.4.2 Light responsive behavior of PAA-Bzx-NT

As the formation of Bzx requires phenol, formaldehyde, and amine, the Bzx derivatives can be variously prepared by changing types of phenols. Here, by applying fluorescent phenol in the ring opening reaction to obtain Bzx dimer, the fluorescent gel can be expected. In this work, 1-naphthol (NT) was chosen in the ring opening reaction of PAA-AP-Bzx to yield PAA-Bzx-NT. The fluorescent behavior of the gel was investigated in the swollen state. Excitation wavelength was varied from 200 nm – 400 nm and the emission was from 400 nm – 800 nm. Figure 4.1A shows excitation wavelength at 295 nm gives the highest emission at 480 nm.

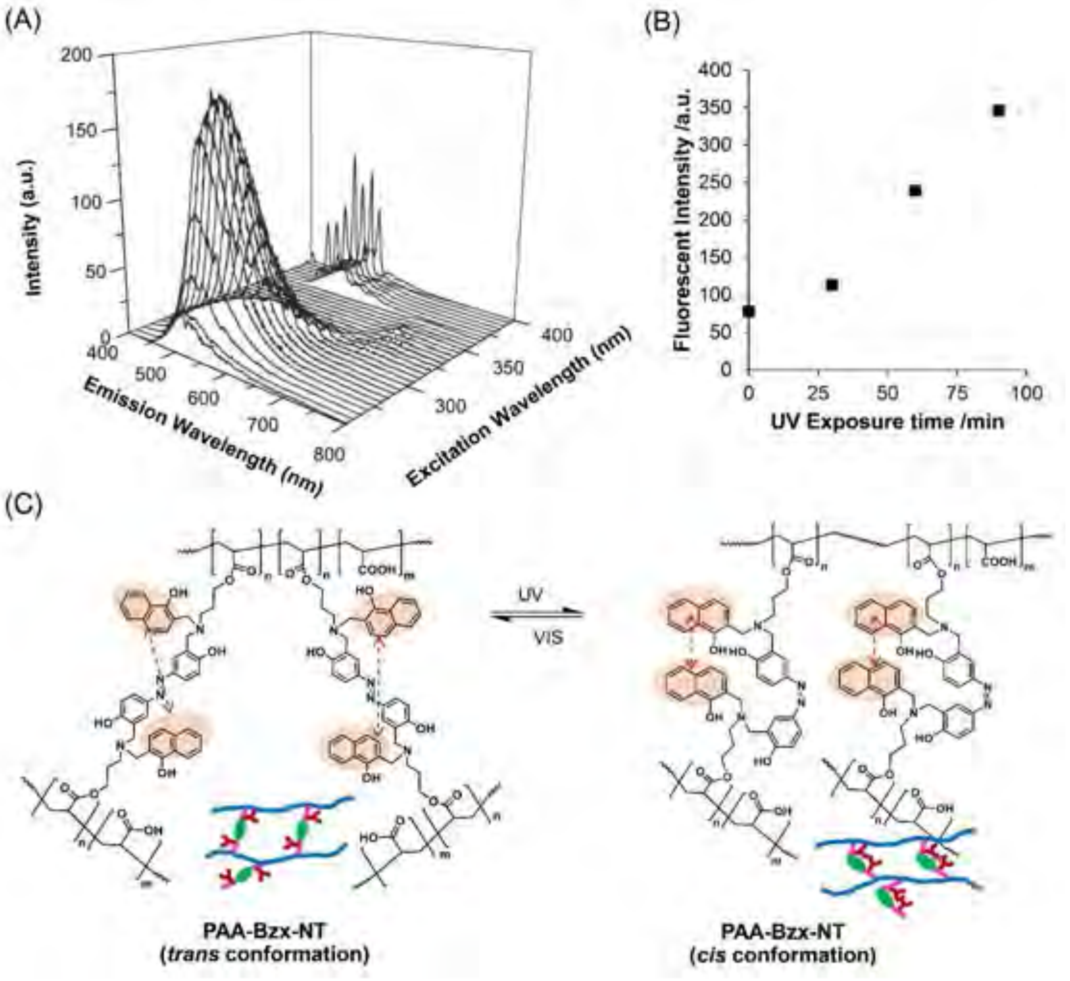


Figure 4.1 (A) 3-D Fluorescent spectra of PAA-Bzx-NT, (B) fluorescent intensity (480 nm) of PAA-Bzx-NT with different UV exposure time (30, 60 and 90 min) and (C) chemical structures and schematic illustrations of cis/trans conformation of azobenzene in PAA-Bzx-NT gel, and the arrows are for comparing the distance of two naphthalene units.

Cis/trans conformational change of azobenzene moiety in PAA-Bzx-NT was studied by exposing UV light to the gel. The fluorescent emission intensity of gel was traced over UV exposure time (Figure 4.1B). The fluorescent emission intensity at 480 nm of PAA-Bzx-NT is increased with an increase of UV exposure time from 30 min to 120 min. This indicates that azobenzene moiety is still active in gel state. The azobenzene conformational change related to fluorescent emission could be simplified by the overlay plots of fluorescent emission spectra and UV absorption spectra (Appendix B). The fluorescent behavior of naphthalene derivatives is known as J-aggregation (aggregation induced emission). (Meher *et. al.*, 2016) The increasing of fluorescent intensity of gel with increasing UV exposure time might be due to the fact that the cis conformation brings naphthol units to be closer to each other (Figure 4.1C) allowing energy transfer effectively.

4.4.3 Metal ion responsive behavior of PAA-Bzx-DMP

In the past, our group reported about metal complexation of Bzx dimers and the x-ray single crystal analysis to insist the metallosupramolecular structure of Bzx dimer. The metal species were coordinated with azamethylene group and phenol. (Phongtamrug *et. al.*, 2006a) In this work, in order to allow metal complexation in the gel, the gel was immersed in $CuCl_2$ solution. The metal ion complexation was traced by using UV-VIS spectroscopy. For example, in the case of PAA-Bzx-DMP, there is a new peak at about 440 nm when the gel was allowed immersing in the $CuCl_2$ (40 mM) solution for 12 hours, PAA-Bzx-DMP with $CuCl_2$ (Figure 4.2A). However, for $ZnCl_2$ system, PAA-Bzx-DMP with $ZnCl_2$, the new peak was not observed (Figure 4.2A). Figures 4.2B and 4.2C illustrate the PAA-Bzx-DMP with Cu(II) complexation.

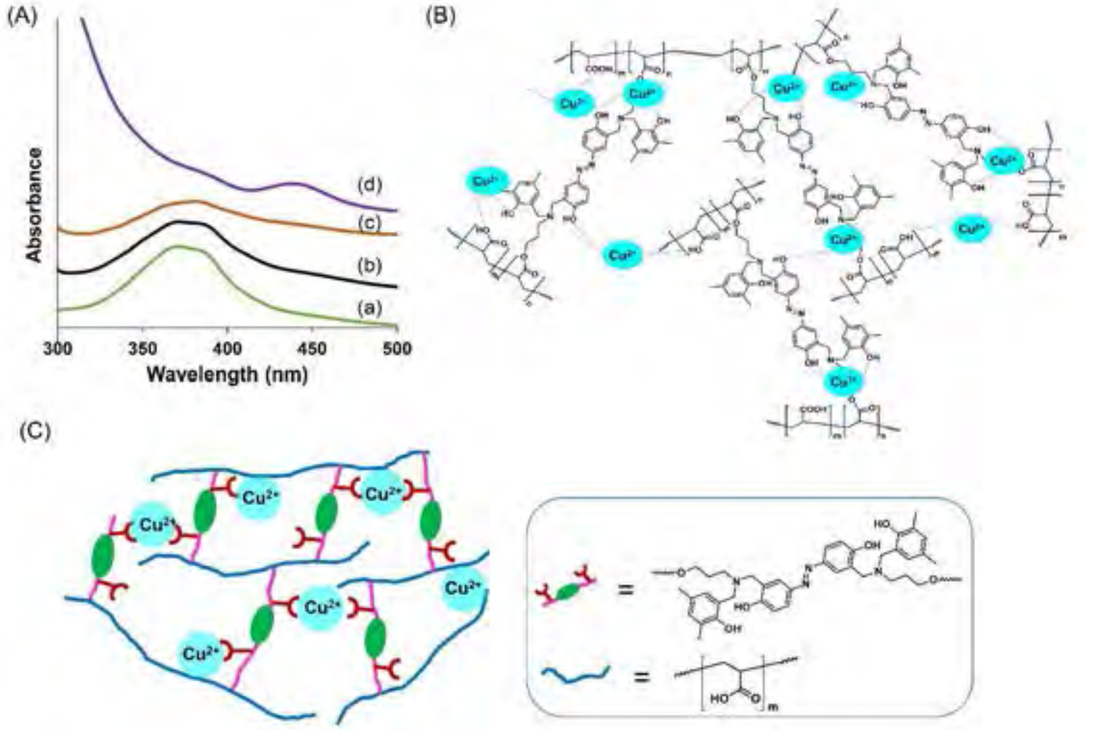


Figure 4.2 (A) UV-VIS absorption spectra of (a) PAA-AP-Bzx, (b) PAA-Bzx-DMP, (c) PAA-Bzx-DMP with $ZnCl_2$ and (d) PAA-Bzx-DMP with $CuCl_2$, (B) structure of PAA-Bzx-DMP with Cu(II) complexation, and (C) schematic illustration of PAA-Bzx-DMP with Cu(II) complexation.

It is important to mention that after Cu(II) was incorporated in the gel, the gel became greenish and harder. The swelling ratio was drastically decreased from 600% to about 14%. The compressive stress at 50% strain of PAA-Bzx-DMP before and after Cu(II) complexations were evaluated. The results show that compressive stress of PAA-Bzx-DMP with Cu(II) was as high as 249 kPa which is much higher than that of PAA-Bzx-DMP (9.05 kPa). It comes to the question whether the Cu(II) content controls the gel strength. The concentrations of $CuCl_2$ solution were varied from 2 mM to 40 mM. The amount of Cu(II) incorporated in PAA-Bzx-DMP was quantified by the differences in UV-VIS absorption at 795 nm. The plots between the amount of Cu(II) incorporated in the gel and the compressive stress clearly identified that how the gel strength could be controlled by the ionic interaction. For example, when the Cu(II) was as high as 41.2 mg, the compressive stress at 50% strain of the PAA-Bzx-DMP increases from 22 kPa to ~250 kPa

(Figure 4.3A). This implies the metal ions play the role as the crosslinker in PAA-Bzx-DMP gel whereas the gel strength can be simply controlled by the content of Cu(II). This confirms that the PAA-Bzx-DMP gel consists of 2 networks, i.e., the covalent bond (ester bond) between PAA and AP, and the coordination between Cu(II) and Bzx-DMP units. In other word, the Bzx-DMP plays the role as crosslinker with two functions, i.e. the covalent crosslink as well as the ionic crosslink.

The network stability, as a consequence of Cu(II) complexation, was further studied by soaking the PAA-Bzx-DMP-Cu in DI water. It was found that swelling ratio of the gel remained and there is no Cu(II) leaked form the network (Appendix C).

It comes to the question whether Cu(II) can be removed and how the gel is changed. By simply immersing PAA-Bzx-DMP-Cu in EDTA solution for 24 h, the gel recovered the swelling of PAA-Bzx-DMP. The removal of Cu(II) initiates the swelling ratio from 14% to 150%. Although the swelling ratio of the PAA-Bzx-DMP gel after Cu(II) removal by EDTA solution is much lower than that of original PAA-Bzx-DMP, the Bzx-DMP crosslinker allows controllable gel strength as well as reversible gel swelling. The incomplete swelling reflects the strong Cu(II) complexation with Bzx-DMP until a certain amount remained in the networks. The swelling was plotted with the EDTA treatment to confirm how the swelling could be reversible by the Cu(II) incorporation and EDTA treatment. When the PAA-Bzx-DMP-Cu gel was treated in cycle with EDTA followed by re-immersing in $CuCl_2$, the swelling ratio in each step and each cycle shows the zig-zag patterns insisting the reversible swelling (Figure 4.3B).

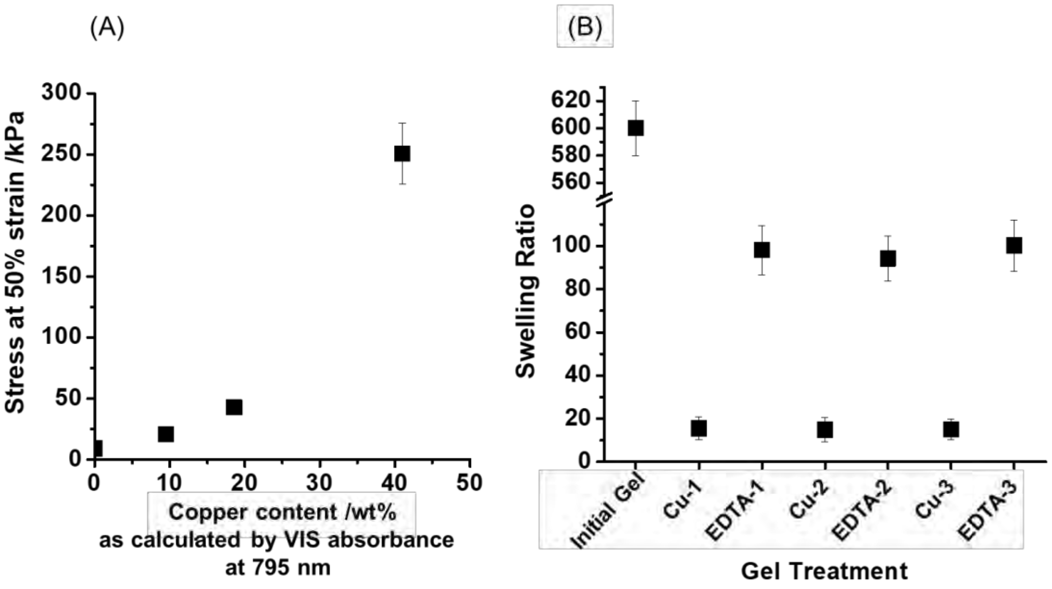


Figure 4.3 (A) Stress at 50% strain of PAA-Bzx-DMP with different incorporated content of $CuCl_2$, and (B) swelling ratio after the cycles of treating with $CuCl_2$ and EDTA in cycles.

The interaction between copper and PAA-Bzx-DMP was also confirmed by X-ray photoelectron spectroscopy (XPS) analysis. Figure 4.4A shows the peaks of binding energy O 1s of PAA-Bzx-DMP at 529.5 and 530.4 eV which refer to C-O and C=O bond, respectively. In contrast, PAA-Bzx-DMP-Cu shows new bands of O 1s at 534.4 and 531.2 eV which are shifted to the higher binding energy. The formation of copper complex with carboxylate and hydroxyl groups (Figure 4.4C) imply the coordination of Cu(II) with N and O in Bzx-DMP as illustrated in Figures 4.2B and 4.2C. As expected, the new peak of Cu 2p at 932.7 eV for PAA-Bzx-DMP-Cu (Figure 4.4D) as compared to PAA-Bzx-DMP (Figure 4.4B) confirms the formation of complexation of Cu(II) with oxygen atom of Bzx-DMP unit.

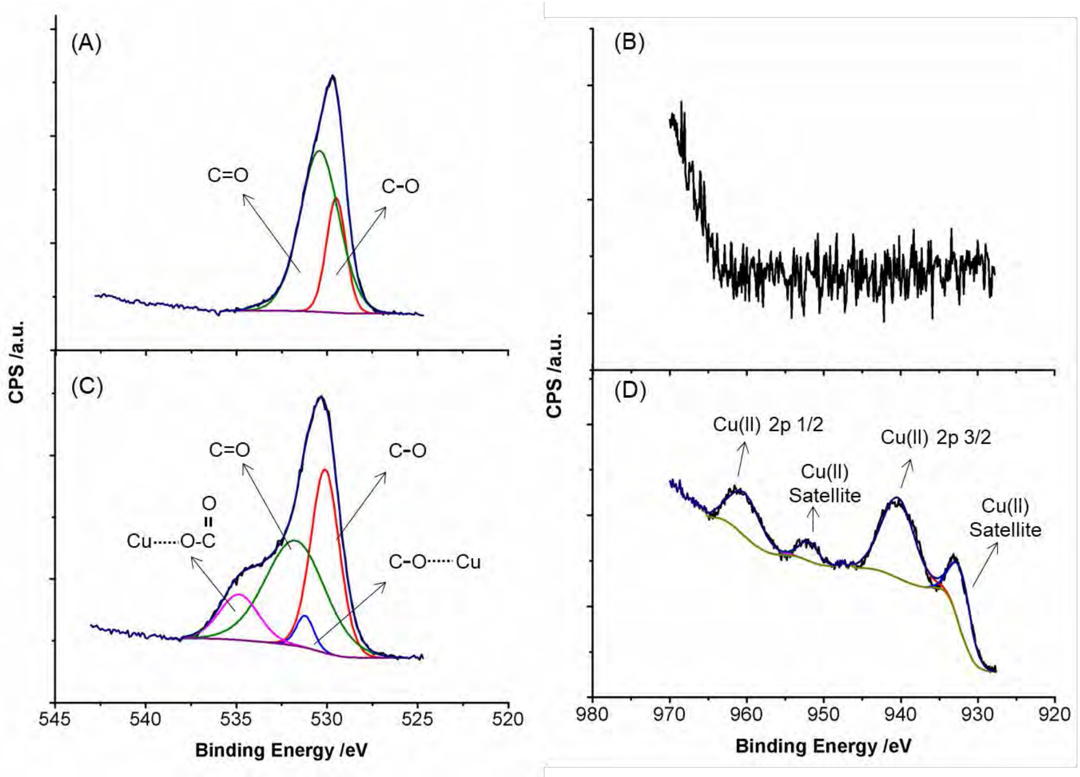


Figure 4.4 High resolution XPS spectra of (A) O 1s region for PAA-Bzx-DMP, (B) Cu 2p region for PAA-Bzx-DMP, (C) O 1s region for PAA-Bzx-DMP-Cu, and (D) Cu 2p region for PAA-Bzx-DMP-Cu.

4.4.4 UV light responsive behavior of PAA-Bzx-DMP

As azobenzene in the PAA-Bzx-DMP gel might initiate the UV responsive due to the cis/trans conformation, it is possible that the change in conformation induces the change in metal complexation. Here, the comparative studies of copper incorporation between PAA-Bzx-DMP with and without UV exposure was investigated. After exposure to UV light for 1 h, the PAA-Bzx-DMP-UV-1h obtained was soaking in 40 mM $CuCl_2$ solution. The amount of incorporated Cu(II) was evaluated by UV-VIS spectra. It was found that the increases of Cu(II) in PAA-Bzx-DMP was relatively more significant than that of PAA-Bzx-DMP-UV-1h. The decrease in Cu(II) incorporation might be due to the increase of cis conformation of azobenzene as a consequence of UV exposure time. When the UV exposure time to PAA-Bzx-DMP was increased to 2 h, followed by soaking in copper solution, the PAA-Bzx-DMP-UV-2h obtained showed further decreases in Cu(II) incorporation ability (Figure 4.5A). This confirmed that cis conformation of azobenzene obstructs the adsorption of copper(II) ion on the gel.

The Cu(II) release after treating with EDTA solution under UV exposure was also investigated. Here, PAA-Bzx-DMP-Cu was treated with EDTA solution under UV light. The Cu(II) removal was evaluated by measuring the absorbance at 736 nm belonging to Cu(II) in EDTA solution. It was found that in the case of PAA-Bzx-DMP-Cu under UV exposure, the Cu(II) can be removed from the gel and the removal rate was higher than that of the PAA-Bzx-DMP-Cu without UV exposure (Figure 4.5B). In other words, the UV exposure accelerates the copper extraction from the gel. The result supports how the cis conformation of azobenzene obstructs the Cu(II) complexation.

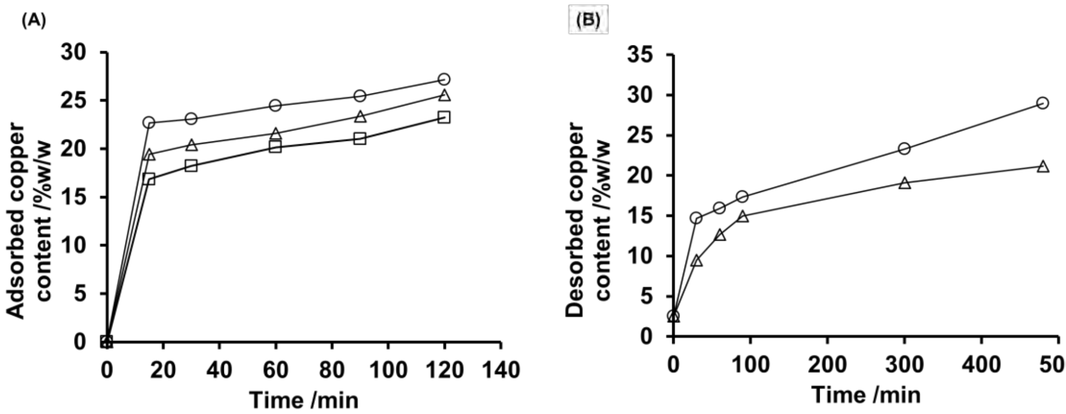


Figure 4.5 (A) Incorporated Cu(II) content of; (○) PAA-Bzx-DMP, (△) PAA-Bzx-DMP-UV-1h, and (□) PAA-Bzx-DMP-UV-2h. (B) Copper content remained in PAA-Bzx-DMP-Cu after various treating time with EDTA solution (○) under UV exposure, and (△) without UV exposure.

It comes to the question whether the cis/trans conformation leads to any significant changes in gel strength. Here, the compressive strength of the PAA-Bzx-DMP gel before and after UV exposure were evaluated. For the PAA-Bzx-DMP, after UV exposure for 2 h (PAA-Bzx-DMP-UV-2h), stress at 50% strain of gel was 23.2 kPa. The value was not significantly different as compared to the that of PAA-Bzx-DMP (22.3 kPa). For PAA-Bzx-DMP incorporated with Cu(II), PAA-Bzx-DMP-Cu, the compressive stress was 250.2 kPa which is similar to the one after UV exposure, PAA-Bzx-DMP-Cu-UV-2h, (258.3 kPa) (Figure 4.6). This indicates the conformational change of azobenzene rarely show the effect on the compressive stress of gel.

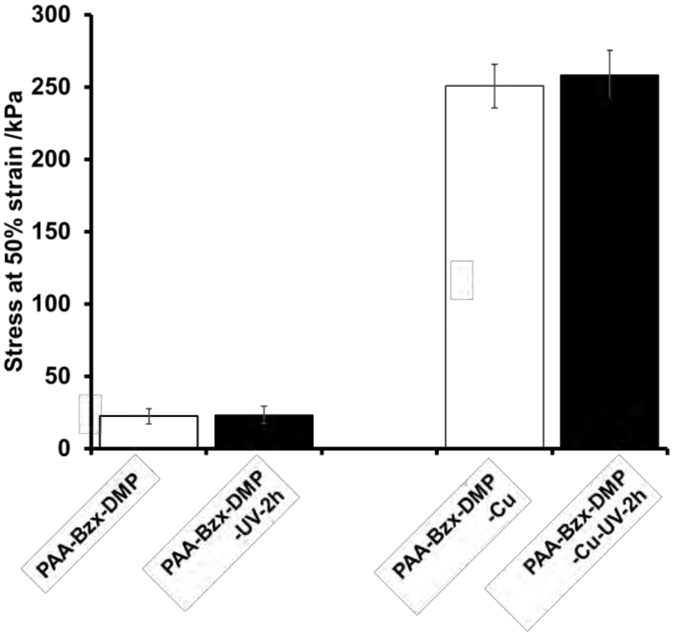


Figure 4.6 Stress at 50% strain of PAA-Bzx-DMP, PAA-Bzx-DMP-UV-2h, PAA-Bzx-DMP-Cu and PAA-Bzx-DMP-Cu-UV-2h.

4.5 Conclusions

The present work demonstrated the multi-responsive gel via the functions of crosslinker. Bzx is a good model of crosslinker as its structure can be verified by selecting the type of phenols for light responsive, type of amine for the crosslink functional group. In addition, the ring opening Bzx monomer to be Bzx dimer leads to the complexation ability with specific metals. In this work, the use of aminopropanol in combination with dihydroxyazobenzene (Azo-OH) was the key of success to prepare AP-Bzx crosslinker. By simply applying PAA crosslink with AP-Bzx, the light responsive gel was obtained. At that time, the gel showed the Cu(II) responsive with tunable hardness property. In AP-Bzx ring opening step, the use of mono-phenols led to the UV controllable Cu(II) complexation. When mono-phenols was naphthol, the gel developed the fluorescence responsive function. The present work clarified a simple approach for multi-responsive hydrogel by using the multi-responsive crosslinker as seen from the benzoxazines and their dimers.

4.6 Acknowledgements

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CHAPTER V

MULTI-RESPONSIVE ROTAXANE WITH TUNABLE FLUORESCENCE UNDER AZOBENZENE-BASED BENZOXAZINE STRUCTURE

5.1 Abstract

Rotaxane is known for the mechanically interlocked molecule for a decade. The present work demonstrates a method to prepare multi-responsive rotaxane by conjugating with multi-responsive supramolecule. Benzoxazine dimers, *N, N'*-Bis(3,5-dimethyl-2-hydroxybenzyl) methylamine derivatives, are good model because its simple chemistry. The azobenzene containing benzoxazine with remaining hydroxyl group for further conjugation with rotaxane is designed. The ring opening of rotaxane using fluorescent phenol provides benzoxazine dimer with metal ion responsive and fluorescent properties. Based on this concept, light responsive benzoxazine conjugated with rotaxane system shows light, metal ion and rotaxane shuttling responsiveness which can be followed by fluorescent signal. The present work shows the simple way to develop rotaxane with multi-responsive functions using supramolecular chemistry of benzoxazine dimer prepared from light responsive phenol.

5.2 Introduction

For the past decade, responsive materials have received much attention due to their unique properties, for example, controllable conformation, adjustable solubility and reversible molecular assembly. The most common studies with external stimuli are temperature, light, pH, and mechanical force, which can be applicable in chemosensor, biosensor, photochromic materials, etc. A light responsive functional group which has received much attention for decades is azobenzene. Its conformation can be changed between *trans* and *cis* forms under UV light. (Kumar *et. al.*, 1989) This reversibility effectively controls the physical property of materials, for example, film bending, hydrophobic-hydrophilic switching. (Russew *et. al.*, 2010, Yu *et. al.*, 2003b) The conjugated bond is also recognized for light responsiveness. Under the proper conditions, the conjugated molecules such as naphthalene, fluorene and etc. are known to emit the fluorescent. (Lee, Sumin *et. al.*, 2012, Such *et. al.*, 2004) It should be noted that most optically responsive molecules consist of benzene ring in their structure. Although their responsiveness is attractive, it is difficult to incorporate them to other molecules dus to the complicated modification steps resulting in low yields. (Othman *et. al.*, 2007b)

On this viewpoint, the present work proposes azobenzene derivative under benzoxazine molecular structure. Since benzoxazine is flexible in molecular design by simply changing simple phenol to azobenzene phenol, the azobenzene derivative under benzoxazine molecular structure can be obtained. In addition, when benzoxazine develops ring-opening (ROP) to be benzoxazine dimer, the dimer also forms metal ion complexation. Moreover, our research group succeeded in developing supramolecular structure of benzoxazine, for example, benzoxazine dimer which shows inter- and intramolecular hydrogen bonding and also metal ions complexation. (Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2004, Phongtamrug *et. al.*, 2006b)

Rotaxanes are mechanically interlocked molecule consisting of linear molecular as guests encircled by macrocyclic molecule as host. In general, the linear molecules are stabilized in the macrocycles by end capping the terminals with some bulky groups. Various classes of host molecules, such as crown-ethers, cyclodextrins, calixarenes were reported for the rotaxane fabrication. Polyrotaxanes are potential advanced materials such as self-healing polymers, stimuli responsive materials, molecular machines, actuators and sensors. The incorporated non-covalent interactions in the molecule impacts on the molecular behaviors (Arunachalam *et. al.*, 2014) such as polymer topology transformations, (Aoki *et. al.*, 2014, Aoki *et. al.*, 2015b, Ogawa *et. al.*, 2015a, Ogawa *et. al.*, 2015b) dynamic crosslinking, (Iijima *et. al.*, 2014, Sawada *et. al.*, 2015) tunable light responsiveness (Abe *et. al.*, 2014, Koyama *et. al.*, 2013, Sandanayaka *et. al.*, 2010, Suzuki *et. al.*, 2014, Zhu *et. al.*, 2007a) and etc.

It comes to our question whether azobenzene-based benzoxazine and aromatic-based crown ether performs any specific performances under rotaxane structure or not. In fact, the unique properties of those rotaxane are induced by the change of the interaction between the macrocycle and the linear molecule. On this viewpoint, the use of azobenzene-based benzoxazines are subjected to initiate not only the molecular interaction either π-π or charge-charge but also development of fluorescence as a consequence of molecular shuttling. It can be expected that the rotaxane obtained shows the effect on fluorescence emission. This comes to our study on light and metal ion responsive benzoxazine dimer in rotaxane system. The present work, for the first time, demonstrates how benzoxazine initiates the multi-responsiveness to rotaxane with the role of benzoxazine dimer containing azobenzene.

5.3 Experimental

5.3.1 Materials

Phenol, 2-naphthol, copper(II) chloride and 3-amino-1-propanol was purchased from Sigma-Aldrich Corporation. 4-aminophenol, 3,5-dimethylbenzaldehyde, 4-aminomethylbenzoic acid, tributylphosphine (Bu_3P), dibenzo-24-crown-8 (DB24C8), N,N'-dicyclohexylcarbodiimide (DCC), sodium triacetoxyborohydride ($NaBH(OAc)_3$), and sodium borohydride ($NaBH_4$) were purchased from Tokyo Chemical Industry Co., Ltd., Japan. Potassium hydroxide, sodium hydroxide, ammonium hexafluorophosphate (NH_4PF_6), toluene and 1,4-

dioxane were purchased from Wako Pure Chemical Industries Ltd., Japan. Paraformaldehyde, sodium nitrite, methanol, N-methyl-2-pyrrolidone (NMP), chloroform and dichloromethane were purchased from Nacalai Chemicals, Ltd., Japan. All chemicals and solvents were used as received.

5.3.2 Characterizations

^{1}H- (500 MHz) and ^{13}C- (125 MHz) nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 500 spectrometer using $CDCl_3$ and DMSO-d_6 as the solvent. The spectra were referenced to tetramethylsilane as the internal standard. IR spectra were recorded on a Bruker Alpha spectrometer. Matrix-assisted laser desorption/ionization–time of flight–mass spectrometry (MALDI–TOF–MS) were recorded on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser and with pulsed ion extraction. The operation was performed at an accelerating potential of 20kV using the linear-positive ion mode. The sample polymer solution (1 mg ml^{-1}) was prepared in THF or $CHCl_3$, and the matrix (dithranol) and cationizing agent (sodium trifluoroacetate) were dissolved in THF (10mg and 1mg ml^{-1}, respectively). The polymer solution and the matrix solution were mixed and deposited onto a sample target plate and allowed to dry in air at room temperature. Mass values were calibrated by the two-point method with insulin b plus Hþ at 3497.96 and R-cyanohydroxy cinnamic acid dimer plus H^+ at 379.35. Preparative GPC was performed using a HPLC LC-918 instrument from the Japan Analytical Industry equipped with a Megapak-Gel 201C. UV-VIS absorption spectra were recorded by an Agilent cary 300 UV-VIS spectrophotometer. Fluorescence spectra were recorded by a Cary Eclipse spectrofluorometer (Agilent Technologies). The UV exposure was performed in chamber using UV lamp (RUV 533 BC) covering wavelength from 315 nm to 400 nm.

5.3.3 Synthesis of **5**

5.3.3.1 Synthesis of azobenzene-based benzoxazine (AP-Bzx)

3-Aminopropanol (0.8 g, 10 mmol) and paraformaldehyde (0.8 g, 25 mmol) were mixed in dioxane and toluene (1:1, 30 mL) at 70 ºC for 1 h. Azo-OH (1.09 g, 5 mmol) solution in dioxane (20 mL) was added. The solution temperature was increased to 110 ºC and kept for 6 h. After removing the solvents, the crude product obtained was dissolved in chloroform 100 mL and then washed with 0.5 M NaOH 100 mL several times and then brine. The organic layer was collected and dried over an excess amount of Na_2SO_4 until the reddish solution was clear. Then, Na_2SO_4 was filtered out and the solvent was removed to obtain AP-Bzx. (Scheme 5.1A) (Yield: 75%)

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 7.77$ (d, $J = 8.60$ Hz, 2H, ArH), 7.66 (s, 2H, ArH), 6.94 (d, $J = 8.57$ Hz, 2H, ArH), 4.36 (s, 4H, OCH_2N), 4.03 (s, 4H, NCH_2Ar), 3.88 (t, 4H, CH_2OH), 2.97 (m, 4H, N$CH_2$$CH_2$), 1.78 (m, 4H, $CH_2$$CH_2$$CH_2$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 160.4$ (s, *Ar*-O-CH_2), 146.1 (s, *Ar*=N), 124.7 (s, Ar), 122.7(s, Ar), 121.2 (s, Ar), 83.8 (s, NCH_2O), 67.8 (s, HO-$CH_2$$CH_2$), 54.9 (s, Ar$CH_2$N), 49.2 (s, N$CH_2$$CH_2$), 22.3 (s, $CH_2$$CH_2$$CH_2$). Anal. Calcd for $C_{22}H_{28}N_4O_4$: C, 64.06; H, 6.84; N, 13.58 Found: C, 65.50; H, 7.00; N, 10.67. MS (ESI/MicroTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{29}N_4O_4$ 413.2183; Found 413.2252.

5.3.3.2 Synthesis of ***1***

3,5-dimethylbenzaldehyde (2.7 g, 20 mmol) and 4-aminomethylbenzoic acid (3.2 g, 20 mmol) were mixed in methanol 50 ml and triethylamine 10 ml. The reaction was carried out under reflux for 6 h. The solution was filtered followed by removing the solvent to obtain **1**. (Scheme 5.1B) (Yield: 85%)

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.33$ (s, 1H, CC*H*N), 8.05 (d, $J = 7.90$ Hz, 2H, Ar*H*), 7.40 (s, 2H, Ar*H*), 7.34 (d, $J = 7.08$ Hz, 2H, Ar*H*), 7.08 (s, 2H, Ar*H*), 4.85 (s, 2H, NCH_2Ar), 2.35 (s, 6H, CH_3Ar)

5.3.3.3 Synthesis of ***2*** *and* ***3***

A solution of **1** (2.70 g, 10 mmol) in methanol (20 ml) was added to the $NaBH_4$ solution (1.9 g, 50 ml). The reaction was allowed at room temperature for 12 h before removing the solvent. The product was dissolved in chloroform and dried under vacuum for 2 h to obtain **2**. The compound **2** (2.30 g, 9 mmol) was dissolved in a small amount of methanol (2 ml) followed by adding 12 M HCl (2 ml). The solution obtained was poured in diethyl ether and the precipitates were collected.

The product obtained was further dissolved in a small amount of methanol (2 ml) before adding the concentrated solution of NH_4PF_6. The product was precipitated in water. (Yield: 75%)

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.99 (d, *J* = 8.24 Hz, 2H, Ar*H*), 7.59 (d, *J* = 8.15 Hz, 2H, Ar*H*), 7.07 (s, 2H, Ar*H*), 7.05 (s, 1H, Ar*H*), 4.23 (s, 2H, ArC*H*$_2$N), 4.08 (s, 2H, ArC*H*$_2$N), 2.28 (s, 6H, ArC*H*$_3$)

5.3.3.4 Synthesis of **5**

The compound **3** (0.50 g, 1.20 mmol) was mixed with DB24C8 (0.64 g, 1.44 mmol) in dried dichloromethane for 15 min. DCC (0.74 g, 3.60 mmol), AP-Bzx (0.12 g, 0.3 mmol) and Bu_3P (2 mg, 0.01 mmol) was added to the solution. The reaction was carried out at room temperature for 48 h. The product was purified by preparative GPC. (Yield: 50%)

5.3.4 Ring opening reaction of **5**, **6**

Compound **5** (0.25 g, 0.12 mmol) was dissolved in dioxane (15 ml). Excess amount of 2-naphthol was added to the solution. The solution was heated to 100 °C and kept for 12 h to obtain **6** crude product. The product was purified by column chromatography using mixture of chloroform and methanol (3:1 v/v) as mobile phase.

5.3.5 Shuttling of **6** by methylation, **7**

6 (0.1 g, 37.3 μmol) were mixed with paraformaldehyde (44.8 mg, 1.5 mmol), $NaBH(OAc)_3$ (79.5 mg, 0.375 mmol) and triethylamine (0.15 g, 1.5 mmol) in NMP solvent (5 ml). The reaction was carried out at 70 °C for 24 h. The product was purified by preparative GPC.

5.3.6 Metal ion complexation, (**7**/Cu^{2+})

Compound **7** (20 mg, 0.01 mmol) was dissolved in chloroform (2 ml). An excess amount of $CuCl_2$ (15 mg, 0.11 mmol) was added to the solution and left stirring for 2 h. The solution was collected followed by removing the solvent to obtain **7**/Cu^{2+}.

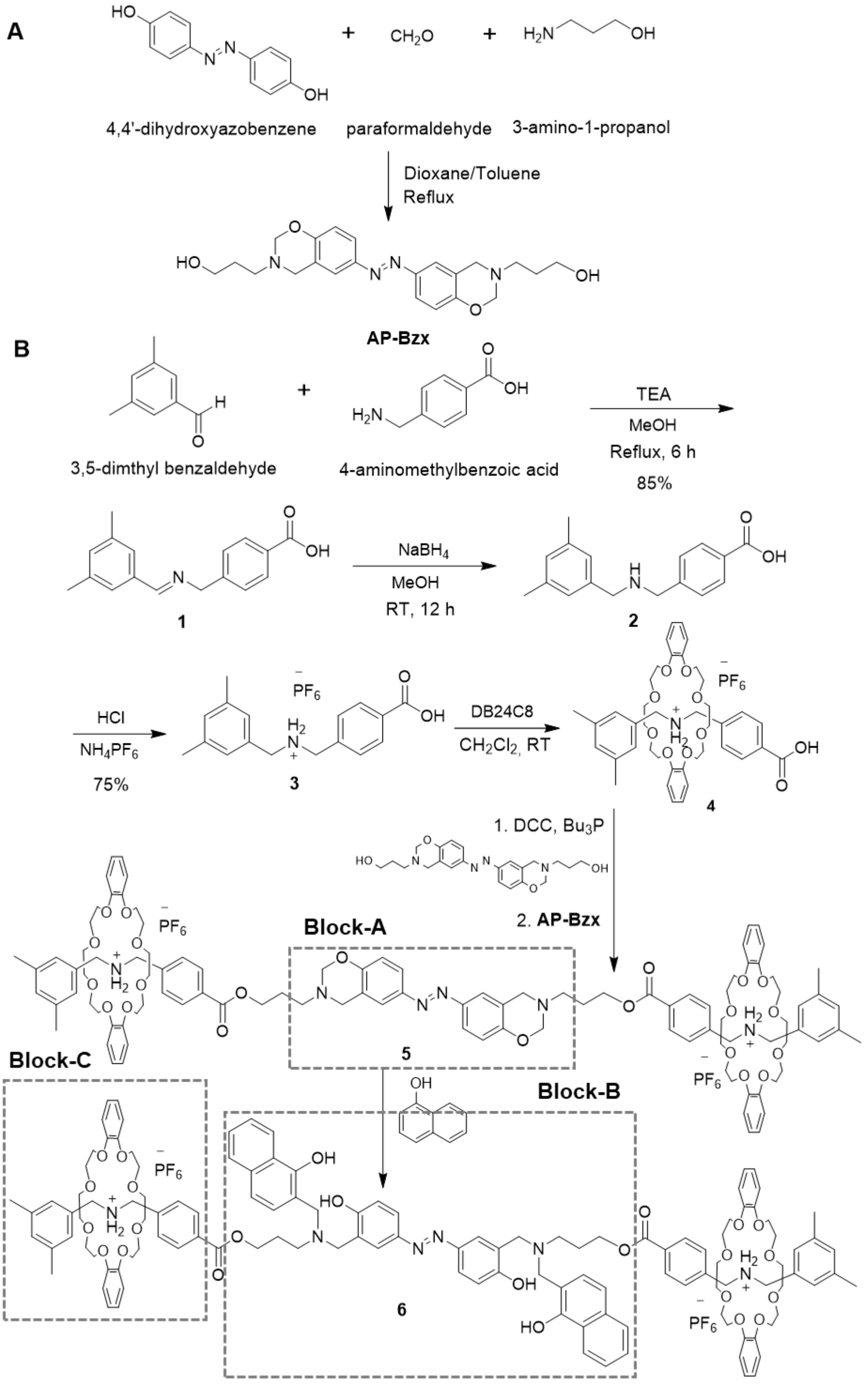
5.4 Results and Discussions

5.4.1 Preparation and characterization of 5

Compound **5** was prepared as shown in Scheme 5.1. The AP-Bzx as an axel component was combined with simple rotaxane. The preparation of AP-Bzx was accomplished by using light responsive phenol, i.e. azophenol, in combination with aminoalcohol. Mannich reaction was carried out using 4,4-dihydroxyazobenzene (Scheme 5.1A). The aminoalcohol was used as the amine derivative to obtain AP-Bzx. In this way, the benzoxazine obtained contains -OH group at terminal for further conjugation with the charges containing molecule (e.g. **3**) to obtain the axel component which perform the interaction with macrocycle. The AP-Bzx was characterized by ^{1}H-NMR (Figure 5.1A).

The terminal end of axel component of **5** was designed by using tertiary ammonium ion end capped with 3,5-dimethylbenzyl group. The reaction between 3,5-dimethylbenzaldehyde and 4-aminomethylbenzoic acid in the presence of triethylamine in methanol resulted in **1**. (Clifford *et. al.*, 2002) The product was characterized by ^{1}H-NMR as shown in Figure 5.1B. The presence of significant methine proton signal at 8.33 ppm and the integral ratios of other signals support the formation of **1**. Compound **1** was further reduced by $NaBH_4$ followed by protonation using HCl and anionic exchange using NH_4PF_6. The absence of methine proton in ^{1}H-NMR spectrum indicates the successful reduction of **1** and the formation of **3** (Figure 5.1C). Then, the interlocking of crown ether with the terminal group of **5** by mixing **3** as axel with DB24C8 as macrocycle in dry dichloromethane. It should be noted that the neat **3** was insoluble in dichloromethane, however, when 3 formed interaction with crown ether, the compound obtained, **4**, become soluble. In the next step, AP-Bzx was conjugated with **4** using DCC and Bu_3P as conjugating agent. The product obtained was purified by preparative GPC and characterized by ^{1}H-NMR and MALDI-TOF-MS. The ^{1}H-NMR signal of crown ether shifts from 4.15 ppm, 3.90 ppm and 3.80 ppm to 4.64 ppm, 4.41 ppm and 4.10 ppm indicate the formation of rotaxane (Figure 5.1D and Figure 5.1E). Moreover, MALDI-TOF-MS also supports molecular weight of 5 at 1,956.20 Da which refers to M-PF_6 (Cal. M-PF_6 = 1957 Da) (Figure 5.2).

Scheme 5.1 Synthesis of **5**



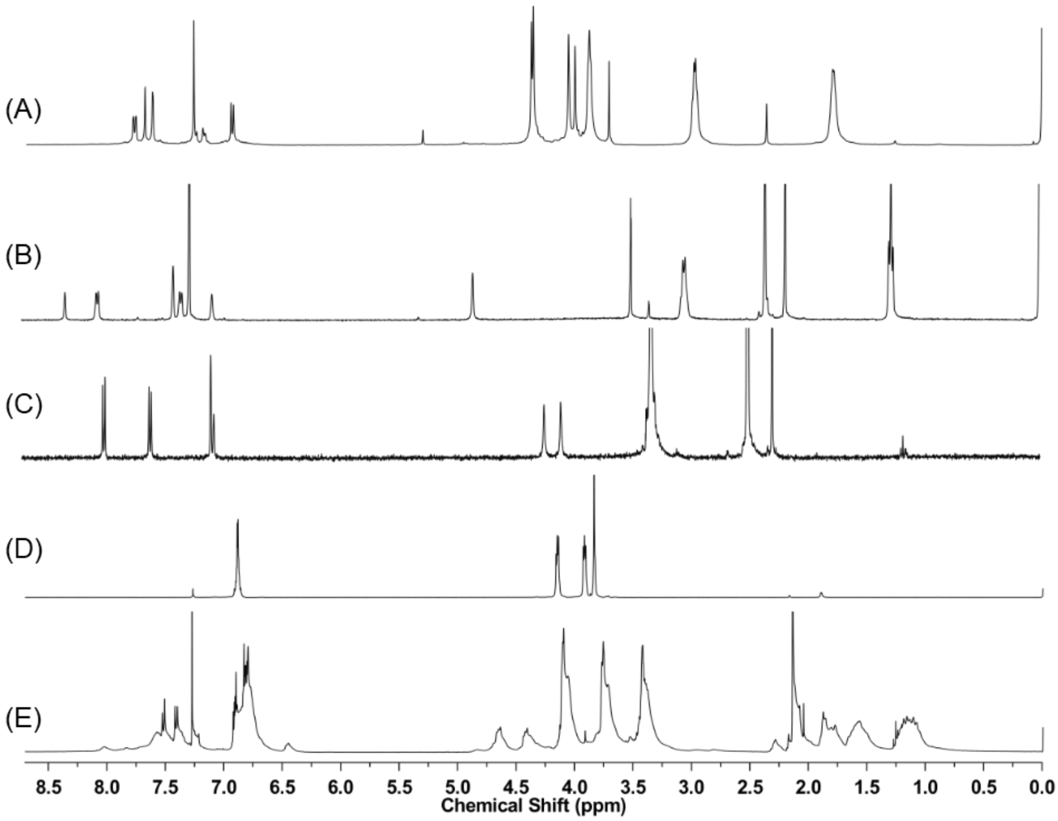


Figure 5.1 ^{1}H-NMR Spectra of (A) AP-Bzx, (B) **1**, (C) **3**, (D) DB24C8, and (E) **5**.

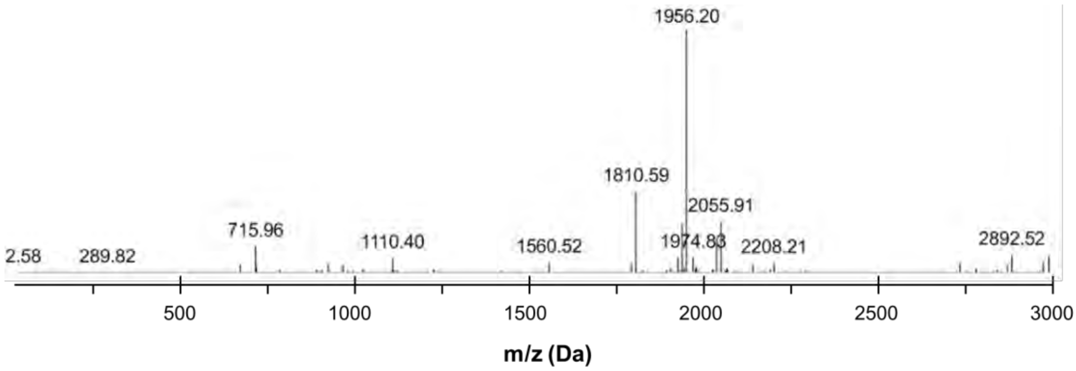


Figure 5.2 MALDI-TOF-MS Spectrum of **5**.

5.4.2 Ring opening reaction of **5** and characterization

In fact, regarding benzoxazine to benzoxazine dimer, (Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2004, Phongtamrug *et. al.*, 2006b) at this step, **5** also performs additional property, i.e. metal ion complexation (see 5.4.5) the ROP of Block-A in **5** can be achieved by adding phenol to result Block-B in **6**.

5.4.3 Shuttling of **6** to be **7**

The rotaxane shuttling provides dynamic interaction. The methylation was carried out to induce the rotaxane shuttling by mixing **6** with paraformaldehyde, triethylamine, NaBH(OAc)$_3$ in NMP at 70 °C. The product was purified by preparative GPC based on the retention time, compound **7** was collected manually. The shifting proton signal referring to DB24C8 of **6** indicates the successful synthesis of **7**. Moreover, the shuttling was further investigated by 2D NOESY NMR. The spectrum shows the correlation of proton signal at 4.0 and 6.75 referring to the -CH$_2$- proton of DB24C8 and the protons on aromatic ring (Figure 5.3). This indicates that the methylated **6** at Block-C moiety leading to the shuttling of DB24C8 to the adjacent aromatic ring.

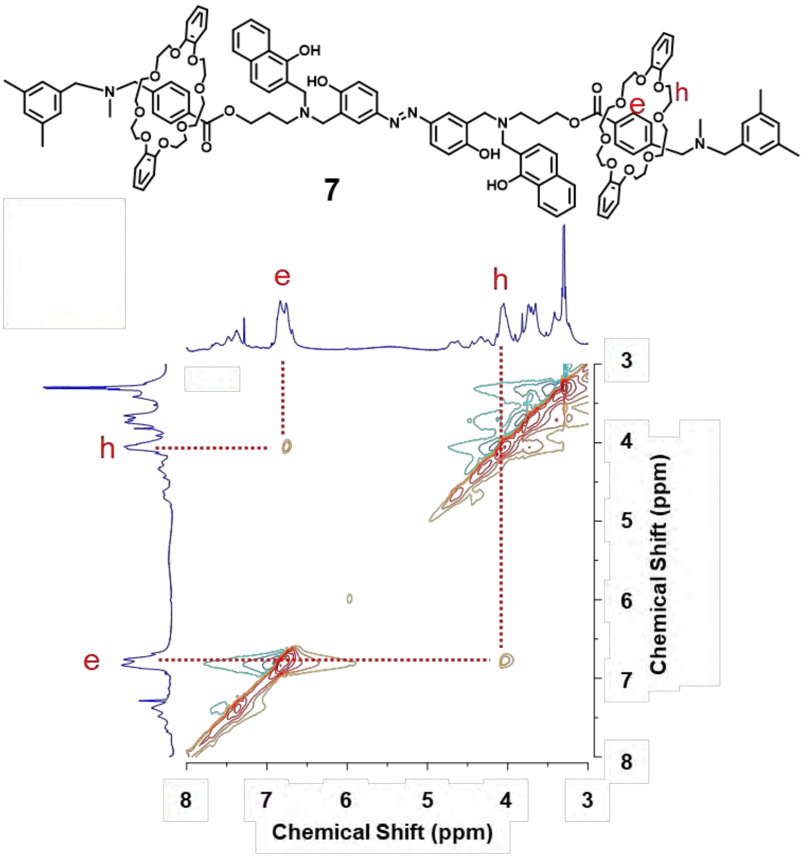


Figure 5.3 2D NOESY NMR of **7**.

5.4.4 Light responsive behavior and fluorescent property

It should be noted that the fluorescent moiety in the Block-B (Scheme 5.1) also performs the change depending on the shuttling of DB24C8. The fluorescent behavior of **6** and **7** were investigated. It was found that the fluorescent excitation and emission wavelengths of **6** are 485 and 560 nm, respectively (Figure 4.4A). In contrast, for **7**, they are 320 and 455 nm, respectively (Figure 5.4B). The fluorescent behavior of these two molecules is different. This implied the difference in charge transfer mechanism between naphthalene unit and DB24C8. For **7**, the excitation and emission peaks of **7** are relatively higher energy than those of **6**. This means the charge transfer is more effective indicating the lowering in distance between two moieties as illustrated in Figures 5.4C and 5.4D.

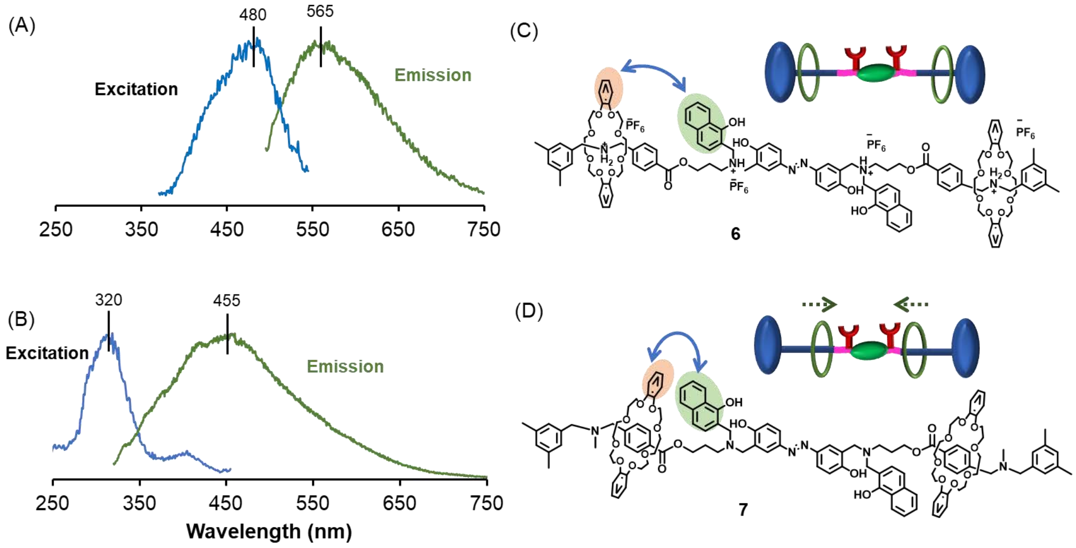


Figure 5.4 Excitation and emission fluorescent spectra of (A) **6** and (B) **7**, and schematic illustration of (C) **6** and (D) **7**.

As Block-B contains azobenzene unit which is light responsive functional group, the cis/trans conformational change of azobenzene in **7** was studied by exposing **7** solution to UV light. The fluorescent intensity of **7** was traced over UV exposure time. Fluorescent behavior of naphthalene derivatives is known as J-aggregation (aggregation induced emission). (Meher *et. al.*, 2016) The increase in fluorescent intensity of solution after UV exposure for 1 h might be due to the stacking of aromatic. Considering the cis-trans conformation of azobenzene group, it was expected that the increase in peak intensity suggests the energy transfer between naphthol units become more effective (Figure 5.5).

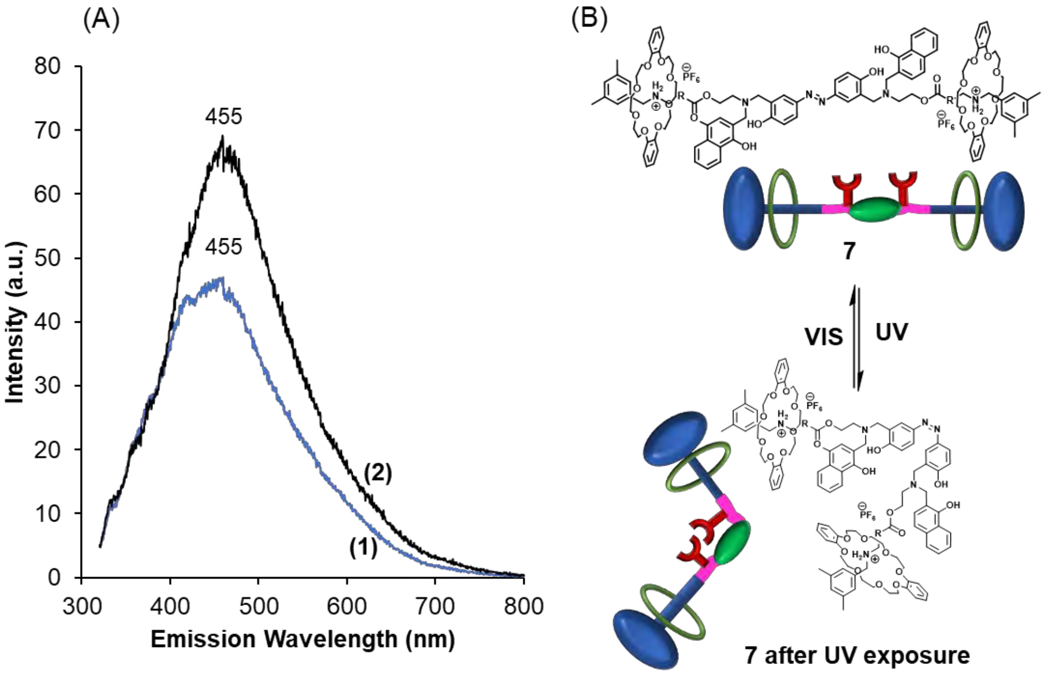


Figure 5.5 (A) Emission fluorescent spectra of **7** (1) before and (2) after UV exposure and (B) schematic illustration of **7** after UV/VIS exposure.

5.4.5 Metal ion complexation

In the past, our group studied about benzoxazine dimeric unit and metal ion complexation insisted by X-ray single crystal analysis indicating the metallosupramolecular structure of benzoxazine dimer. (Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2006b) In this work, in order to access the metal ion complexation in **7**, $CuCl_2$ was added to the **7** solution in chloroform. The formation of metal ion complexation was traced by fluorescent behavior. The **7** that form complexation with copper(II) ion, **7**/Cu^{2+}, clearly shows different fluorescent emission pattern compared with **7** (Figure 5.6A). It might be due to the formation of copper complexation with benzoxazine dimer affects in energy transfer mechanism as there are 3 different peaks in the fluorescent emission pattern (Figure 5.6A(1)).

Effect of UV light on fluorescent behavior of **7**/Cu^{2+} was also studied. After exposing **7**/Cu^{2+} solution to UV light, the fluorescent emission spectrum is as same as **7**/Cu^{2+} but increase in intensity (Figure 5.6A(2)). It is also because cis conformation brings the responsive unit to be closer to each other as illustrated in (Figure 5.6B).

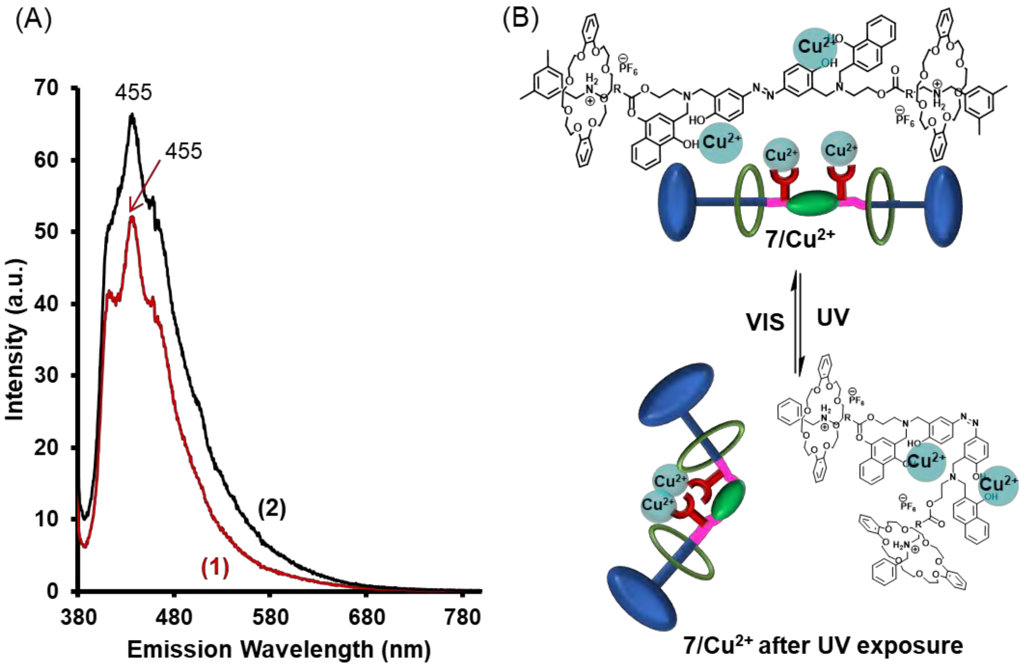


Figure 5.6 (A) Emission fluorescent spectra of (1) **7**/Cu^{2+} and (2) **7**/Cu^{2+} after UV and (B) schematic illustration of **7**/Cu^{2+} and **7**/Cu^{2+} after UV exposure.

5.5 Conclusions

The present work demonstrated benzoxazine containing rotaxane system with light and metal ion responsive. Benzoxazine with multi-responsive functions can be achieved by simply choosing light responsive phenol and functional amine for further conjugation with rotaxane system. The ring opening of benzoxazine allows us to access metal ion complexation. In this work, the conjugation of light responsive benzoxazine with rotaxane system followed with ring opening reaction using fluorescent phenol is a key to achieve multi-responsive benzoxazine containing rotaxane system. The product showed light responsive behavior with an increase in fluorescent intensity. Moreover, the copper(II) responsive with changing in fluorescent emission spectra pattern. The rotaxane shuttling also affects the fluorescent behavior of the molecule. The present work clarifies an approach for multi-responsive rotaxane using fluorescent labeling benzoxazine dimer.

5.6 Acknowledgements

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CHAPTER VI

INCORPORATION OF BENZOXAZINE PENDANTS IN POLYMER CHAIN: A SIMPLE APPROACH TO ADD-UP MULTI-RESPONSIVE FUNCTIONS

6.1 Abstract

External stimuli responsive polymers can be derived from the functional side group in copolymers. Benzoxazine dimer is a good candidate for expressing multi-responsive properties based on the type of phenol in combination with its metal complexation. The present work proposes vinyl monomer containing benzoxazine pendant, which contains azo group as the functional monomer. The copolymerization with methylmethacrylate (MMA) via atom transfer radical polymerization (ATRP) leads to a blockcopolymer, specifically, PA-Azo-C3-b-PMMA, which forms uniform nanoparticles. The ring opening of benzoxazine monomer results in dimer pendants. The copolymer obtained, PA-Azo-C3-b-PMMA, shows multi-responsive functions in terms of metal ion complexation, and UV responsiveness through the dimer pendants and azobenzene groups. The UV exposure results in loss of uniformity of the nanoparticles as well as a decrease in size. This work demonstrates the role of benzoxazine pendants in developing PMMA copolymer showing external stimuli responsive functions.

6.2 Introduction

Recently, polymers with responsive functions have received much attention due to their unique properties and potential applications such as chemosensor, biosensor, photochromic materials, and drug delivery, (Liu, Fang *et. al.*, 2010) including other smart materials. Several polymers with various responsive functions have been reported; for example, (i) reversible solid-liquid transition polymer under controllable conformations of azobenzene (Zhou *et. al.*, 2016), (ii) photoresponsive polymer with tunable morphologies under supramolecular interaction between azobenzene and cyclodextrin in the polymer chains (Zhao, Qiang *et. al.*, 2016), (iii) thermoresponsive poly(*N*-alkylacrylamide), poly(*N*-vinyl caprolactam), poly(*N*-ethyl oxazoline), etc. with adjustable solubility under shifts of inter- and intramolecular hydrogen bonding (Gandhi *et. al.*, 2015), and (iv) light- and temperature-triggered poly(*N*-isopropylacrylamide) in combination with azobenzene group (Boissiere *et. al.*, 2011), etc.

Bisphenol-based benzoxazine (Bzx) is well known as a thermosetting polymer with properties superior to phenolic resins. (Ning *et. al.*, 1994) The Bzx monomer can be prepared via Mannich reaction of phenol, amine and formaldehyde before ring opening polymerization during the process of curing with phenols. (Chirachanchai *et. al.*, 2009) In the case of monophenol-based Bzx, polymerization to deliver linear polymers has not yet been reported. Instead, a self-termination after a single ring opening occurs, and this leads to Bzx dimer in which phenols are linked with an aza-methylene unit. (Chirachanchai *et. al.*, 2011) In the past, our group focused on supramolecular structure of Bzx dimer and clarified the reason behind the self-termination, which is related to the strong inter- and intramolecular hydrogen bond of the two Bzx dimers. (Laobuthee *et. al.*, 2001) In fact, Bzx forms complexes with metal ions (Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2004, Phongtamrug *et. al.*, 2006b) and continues the macrocyclization with ditosyl or diester compounds (Chirachanchai *et. al.*, 2009, Rungsimanon *et. al.*, 2008). Currently, our group is also working with monophenol-based Bzx with specific functions; for example, Bzx monomer containing a double-bond for photodimerization (Kiskan *et. al.*, 2007) and Bzx with acetylene side groups for thermochromic effect. (Kiskan *et. al.*, 2008b)

Thus, the question arises whether Bzx can be developed as a polymer with responsive functions or not. On this question, it is known that the most responsive behaviors are mainly due to the polymer pendant groups. The various interactions between the pendant groups lead to the performance of polymer, as seen in the well-known cases of thermoresponsive poly (*N*-isopropylacrylamide) (PNIPAM) and pH responsive poly(2-dimethylaminoethyl methacrylate) (PDMAEMA). In fact, the precise-structures control of the responsive polymers are also the key factors.(Kiskan *et. al.*, 2008a) Many studies have demonstrated the function of multi-responsive polymers based on the block copolymers. (Fan *et. al.*, 2014, Schmalz *et. al.*, 2010, Suchao-in *et. al.*, 2009, Zhao, Yue, 2012, Zhao, Yi *et. al.*, 2010) Polymers with precise structures, especially for vinyl and acrylate polymers, can be obtained from the controlled living radical polymerization.

Based on the abovementioned supramolecular chemistry of Bzx, a question arises regarding how we can design precise structure of polymers with pendant Bzx. In fact, vinyl polymers with Bzx were reported previously (Jin, Lin *et. al.*, 2011a, Koz *et. al.*, 2010, Liu, Ying-Xuan *et. al.*, 2016, Matyjaszewski *et. al.*, 2014) but mainly focused on the preparation of homopolymer and random copolymer. The present work, in contrast, aims to show a molecular design of vinyl polymers containing multi-responsive Bzx pendants. Here, it is expected that Bzx dimer side groups obtained from ring opening reaction express their specific properties, i.e. the inter- and intramolecular hydrogen bond networks, and metal responsive functions. In addition, by simply applying phenols with light responsive properties to prepare Bzx, the multi-responsive Bzx vinyl monomer can be obtained. In order to obtain the precisely controlled Bzx polymer, the polymerization is based on atom transfer radical polymerization (ATRP).

6.3 Experimental

6.3.1 Materials

3-Amino-1-propanol, 4-phenylazophenol, ethyl α-bromoisobutyrate (EBiB), tris[2-(dimethylamino) ethyl] amine (Me_6TREN), copper(I) bromide (CuBr) and copper(II) chloride ($CuCl_2$) were purchased from Sigma-Aldrich Corporation, Singapore. 6-Amino-1-hexanol, acryloylchloride, methacryloylchloride, 4,4' -dinonylbipyridine (Dnbpy) and N, N, N', N'', N''-pentamethyldiethylenetriamine (PMDETA) were purchased from Tokyo Chemical Industry Co., Ltd., Japan. Dichloromethane, chloroform, hexane, ethyl acetate, toluene, dioxane, anisole, triethylamine, methylmethacrylate (MMA), and magnesium sulphate ($MgSO_4$) were purchased from Wako Pure Chemical Industries Ltd., Japan. Paraformaldehyde, sodium hydroxide (NaOH), and deuterated chloroform ($CDCl_3$) were purchased from Merck Millipore, Germany. The MMA was passed through an alumina short column to remove inhibitor before use. Other chemicals and solvents were used as received.

6.3.2 Synthesis of azobenzene-based Bzx monomer with C3 and C6 alkyl chain (Azo-C3, Azo-C6)

3-Amino-1-propanol (3.03 g, 40 mmol) and paraformaldehyde (3.03 g, 100 mmol) were dissolved in toluene/dioxane (1:1))100 ml at 70 °C for 2 h. A solution of 4-phenylazophenol (8 g, 40 mmol) in dioxane 20 mL was added with stirring, and the temperature was increased to 110 °C and kept constant for 6 h before evaporating the solvent. The crude product was dissolved in chloroform (150 mL) and then washed by 0.5 M NaOH (100 mL) 3 times before brine. The organic layer was collected and dried over an excess amount of $MgSO_4$ until the reddish solution was clear. The solution was filtered, and the solvent was removed to obtain Azo-C3. Similarly, Azo-C6 was prepared using 6-amino-1-hexanol (4.73 g, 40 mmol). (Appendix D)

6.3.3 Synthesis of Azobenzene-Bzx acrylates with C3 and C6 alkyl chain (Acry-Azo-C3, Acry-Azo-C6) and Azobenzene-Bzx methacrylates with C3 and C6 alkyl chain (Meth-Azo-C3, Meth-Azo-C6)

Azo-C3 (5.33 g, 18 mmol) and triethylamine (3.62 g, 36 mmol) were dissolved in dichloromethane (100 mL) while the mixture was stirred in an ice bath for 30 min. Acryloyl chloride (2 g, 22 mmol) in dichloromethane (10 mL) was added dropwise to the solution. The reaction was further carried out at room temperature for 12 h. The excess reagents and solvent were removed by evaporation. The crude was dissolved in chloroform (150 mL) and washed with 0.5 M NaOH (100 mL) several times before brine. The organic layer was collected and dried over excess $MgSO_4$ until a clear solution was obtained. The solvent was removed to obtain Acry-Azo-C3. The product was further purified by column chromatography using neutralized silica and hexane/ethyl acetate 5:1 as eluent. Similarly, Acry-Azo-C6 was obtained using Azo-C6 (7 g, 18 mmol). In the cases of Meth-Azo-C3 and Meth-Azo-C6, similar procedures were carried out using methacryloylchloride (2.34 g, 22 mmol) in combination with Azo-C3 (5.33 g, 18 mmol) and Azo-C6 (7 g, 18 mmol), respectively.

Acry-Azo-C3 (Yield: 78 %) ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.05 (d, J = 2.4 Hz, 1H, ArH), 7.94 – 7.84 (m, 3H, ArH), 7.56 – 7.44 (m, 3H, ArH), 7.24 (d, J = 8.6 Hz, 1H, ArH), 6.61 (m, 1H, CH_2CH), 6.36 (m, 1H, CHCH$_2$), 6.24 – 6.13 (m, 1H, CH_2CH), 6.07 (m, 2H, CH_2CH), 4.33 (s, 2H, OCH_2N), 3.87 (s, 1H, ArCH_2N), 3.85 (t, J = 5.3 Hz, 2H, OCH_2CH$_2$), 2.88 (t, J = 5.6 Hz, 2H, NCH_2CH$_2$), 1.86 – 1.60 (m, 2H, CH$_2$CH_2CH$_2$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): δ = 167.5 (s, O–C=O), 157.2 (Ar-OCH$_2$), 152.8 (s, Ar-N=N), 146.6 (s, Ar-N=N), 136.5 (s, Ar), 130.3 (s, CH_2=CH), 129.1 (s, CH$_2$=CH), 125.2 (s, Ar), 123.7 (s, Ar), 122.5 (s, Ar), 121.8 (s, Ar), 116.9 (s, Ar), 83.2 (s, OCH_2N), 64.6 (s, OCH_2CH$_2$), 51.3 (s, ArCH_2N), 50.2 (s, NCH_2CH$_2$), 29.7 (S, CH$_2$$CH_2CH_2$). IR (ATR): ν = 2935, 2858, 1716, 1637, 1596, 1494, 1323, 1299, 1237, 1167, 1104, 1017, 945, 920, 825 cm^{-1}. MS (ESI/MicroTOF) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{21}N_3O_3$ 352.1656; Found 352.1684.

Acry-Azo-C6 (Yield: 83 %) ^{1}H-NMR (500 MHz, CDCl$_3$, 25 °C): *δ* = 7.95 – 7.75 (m, 3H, Ar*H*), 7.63 (s, 1H, Ar*H*), 7.55 – 7.40 (m, 3H, Ar*H*), 6.92 (d, *J* = 8.9 Hz, 1H, Ar*H*), 6.42 (m, 1H, C*H*$_2$CH), 6.14 (m, 1H, CH$_2$C*H*), 5.84 (m, 1H, C*H*$_2$CH), 4.97 (s, 2H, OC*H*$_2$N), 4.18 (t, *J* = 6.4 Hz, 2H, OC*H*$_2$CH$_2$), 4.11 (s, 1H, ArC*H*$_2$N), 2.78 (t, *J* = 7.49 Hz, 2H, NC*H*$_2$CH$_2$), 1.80 – 1.30 (m, 8H, CH$_2$C*H*$_2$CH$_2$). ^{13}C-NMR (125 MHz, CDCl$_3$, 25 °C): *δ* = 167.5 (s, O–*C*=O), 157.2 (*Ar*-OCH$_2$), 152.8 (s, *Ar*-N=N), 146.6 (s, *Ar*-N=N), 136.5 (s, *Ar*), 130.3 (s, *CH*$_2$=CH), 129.0 (s, CH$_2$=*CH*), 125.1 (s, Ar), 123.7 (s, *Ar*), 122.5 (s, *Ar*), 121.9 (s, *Ar*), 116.9 (s, *Ar*), 83.2 (s, O*CH*$_2$N), 64.6 (s, O*CH*$_2$CH$_2$), 51.3 (s, Ar*CH*$_2$N), 50.2 (s, N*CH*$_2$CH$_2$), 28.6 – 25.5 (m, CH$_2$*CH*$_2$CH$_2$). IR (ATR): ν = 2935, 2858, 1716, 1637, 1605, 1576, 1494, 1323, 1299, 1237, 1167, 1104, 1017, 920, 825 cm^{-1}. MS (ESI/MicroTOF) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{27}N_3O_3$ 394.2125; Found 394.2107.

Meth-Azo-C3 (Yield: 81 %) ^{1}H-NMR (500 MHz, CDCl$_3$, 25 °C): *δ* = 8.10 – 7.80 (m, 4H, Ar*H*), 7.60 – 7.44 (m, 3H, Ar*H*), 7.09 (s, 1H, Ar*H*), 6.41 (s, 1H, C*H*$_2$CCH$_3$), 5.82 (s, 1H, C*H*$_2$CCH$_3$), 4.34 (s, 2H, OC*H*$_2$N), 3.89 (s, 1H, ArC*H*$_2$N), 3.87 (t, *J* = 5.1 Hz, 2H, OC*H*$_2$CH$_2$), 2.89 (t, *J* = 5.9 Hz, 2H, NC*H*$_2$CH$_2$), 2.12 (s, 1H, C*H*$_3$CH), 1.86 – 1.60 (m, 2H, CH$_2$C*H*$_2$CH$_2$). ^{13}C-NMR (125 MHz, CDCl$_3$, 25 °C): *δ* = 167.5 (s, O–*C*=O), 157.2 (*Ar*-OCH$_2$), 152.8 (s, *Ar*-N=N), 146.6 (s, *Ar*-N=N), 136.4 (s, CH$_3$*C*=CH$_2$), 130.3 (s, *Ar*), 129.1 (s, *Ar*), 125.5 (s, CH$_3$C=*CH*$_2$), 122.4 (s, *Ar*), 121.9 (s, *Ar*), 116.6 (s, *Ar*), 83.1 (s, O*CH*$_2$N), 64.6 (s, O*CH*$_2$CH$_2$), 51.3 (s, Ar*CH*$_2$N), 50.2 (s, N*CH*$_2$CH$_2$), 29.7 (s, CH$_2$*CH*$_2$CH$_2$), 18.3 (s, *CH*$_3$C=CH$_2$). IR (ATR): ν = 2935, 2858, 1716, 1637, 1596, 1446, 1316, 1267, 1233, 1178, 1054, 1025, 927, 920, 768 cm^{-1}. MS (ESI/MicroTOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{23}N_3O_3$ 366.1812; Found 366.1827.

Meth-Azo-C6 (Yield: 84 %) ^{1}H-NMR (500 MHz, CDCl$_3$, 25 °C): *δ* = 7.92 – 7.75 (m, 3H, Ar*H*), 7.65 – 7.40 (m, 4H, Ar*H*), 6.92 (m, 1H, Ar*H*), 6.12 (s, 1H, C*H*$_2$CCH$_3$), 5.57 (s, 1H, C*H*$_2$CCH$_3$), 4.97 (s, 2H, OC*H*$_2$N), 4.16 (t, *J* = 6.54 Hz, 2H, OC*H*$_2$CH$_2$), 4.11 (s, 1H, ArC*H*$_2$N), 2.79 (t, *J* = 5.4 Hz, 2H, NC*H*$_2$CH$_2$), 1.96 (s, 1H, C*H*$_3$CH), 1.80 – 1.20 (m, 8H, CH$_2$C*H*$_2$CH$_2$). ^{13}C-NMR (125 MHz, CDCl$_3$, 25 °C): *δ* = 167.5 (s, O–*C*=O), 157.2 (*Ar*-OCH$_2$), 152.8 (s, *Ar*-N=N), 146.6 (s, *Ar*-N=N), 136.4

(s, $CH_3\mathit{C}{=}CH_2$), 130.3 (s, *Ar*), 129.1 (s, *Ar*), 125.5 (s, $CH_3C{=}\mathit{CH_2}$), 122.4 (s, *Ar*), 121.9 (s, *Ar*), 116.6 (s, *Ar*), 83.1 (s, $O\mathit{CH_2}N$), 64.6 (s, $O\mathit{CH_2}CH_2$), 51.3 (s, $Ar\mathit{CH_2}N$), 50.2 (s, $N\mathit{CH_2}CH_2$), 30.5 – 26.5 (m, $CH_2\mathit{CH_2}CH_2$), 18.3 (s, $\mathit{CH_3}C{=}CH_2$). IR (ATR): ν = 2935, 2858, 1716, 1637, 1605, 1576, 1494, 1323, 1299, 1237, 1167, 1104, 1017, 920, 825 cm^{-1}. MS (ESI/MicroTOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{29}N_3O_3$ 408.2282; Found 408.2245.

6.3.4 Polymerization of Acry-Azo-C3, Acry-Azo-C6, Meth-Azo-C3 and Meth-Azo-C6 (PA-Azo-C3, PA-Azo-C6, PM-Azo-C3 and PM-Azo-C6)

Ligand (Dnbpy, PMDETA, or Me_6TREN) (0.6 mmol or 255.5, 108.3, 144 mg, respectively) was dissolved in anisole (0.3 ml) in a glass tube with a magnetic bar and stopcock. After degassing and purging with Ar gas, CuBr (0.06 mmol, 8.97 mg) was added to the solution. Acry-Azo-C3 (500 mg, 1.37 mmol) was mixed with an EBiB initiator (4.06 mg, 0.006 mmol) in anisole (0.3 ml) and purged with Ar in a different tube. The CuBr/ligand solution was transferred to a solution of EBiB and Acry-Azo-C3. The mixture was also treated with Ar for 15 min before sealing. The solution temperature was increased to 70 °C and kept for 12 h. The reaction was quenched by opening the glass vessel to the air. The crude product was dissolved by chloroform (10 ml) and passed through a short alumina column. Then, the polymer was purified by precipitation in hexane (3 iterations) to obtain PA-Azo-C3. PA-Azo-C6, PM-Azo-C3 and PM-Azo-C6 were synthesized similarly using Ary-Azo-C6, Meth-Azo-C3 and Meth-Azo-C6 (500 mg), respectively.

6.3.5 Polymerization of Acry-Azo-C3-*block*-MMA (PA-Azo-C3-b-PMMA)

Me_6TREN (144 mg, 0.6 mmol) was dissolved in anisole (0.3 ml) in a glass tube with a magnetic bar and stopcock. CuBr (0.06 mmol, 8.97 mg) was added to the solution after degassing and purging with Ar. MMA (500 mg, 5 mmol) was mixed with PA-Azo-C3 (50 mg, 0.032 mmol) in anisole (0.3 ml) in another tube. After MMA/PA-Azo-C3 was degassed and purged with Ar, the CuBr/Me_6TREN solution was transferred to a solution of MMA/PA-Azo-C3. The mixture was also treated with Ar for 15 min before sealing. The solution temperature was increased to 70 °C and kept for 12 h. The reaction was quenched by opening the glass vessel to the air. The crude product was dissolved by chloroform (10 ml) and passed through a short alumina column. Then, the polymer was purified by successive precipitation in methanol/hexane mixture 3 times to obtain PA-Azo-C3-b-PMMA.

6.3.6 Polymerization of Acry-Azo-C3-*random*-MMA (PA-Azo-C3-ran-PMMA)

The PA-Azo-C3-ran-PMMA was synthesized in the same way as PA-Azo-C3, but using mixed Acry-Azo-C3 and MMA (0.25 g, 0.68 mmol and 0.25 g, 2.5 mmol, respectively) in anisole (0.3 ml) and Me_6TREN (144 mg, 0.6 mmol) as a ligand in anisole (0.3 ml). The polymerization was carried out at 70 °C for 24 hr.

6.3.7 Ring-opening reaction of PAA-Azo-C3-b-PMMA (PA-Azo-C3-DIMER-b-PMMA)

PA-Azo-C3-b-PMMA (50 mg, 0.14 mmol) was dissolved in 1 ml of anisole. An excess amount of 2,4-dimethylphenol (100 mg, 0.8 mmol) was added. The reaction temperature was increased to 100 °C for 6 h. The crude product was purified by precipitation in hexane (3 iterations) to obtain PA-Azo-C3-DIMER-b-PMMA.

6.3.8 Complexation formation of PA-Azo-C3-DIMER-b-PMMA and $CuCl_2$ (PA-Azo-C3-DIMER-b-PMMA with Cu(II))

PA-Azo-C3-DIMER-b-PMMA (20 mg, 0.04 mmol) was dissolved in 2 ml of chloroform. An excess amount of $CuCl_2$ (15 mg, 0.11 mmol) was added to the solution with stirring for 2 h. The precipitates were filtered out. The solvent was removed by evaporation to obtain PA-Azo-C3-DIMER-b-PMMA with Cu(II).

6.3.9 Characterizations and Instruments

^1H- (500 MHz) and ^{13}C- (125 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 500. The spectra were referenced to tetramethylsilane as the internal standard. ESI MS experiments were conducted with an ESI-quadrupole time-of-flight (qToF) mass spectrometer (micrOTOF-Q II, Bruker, Germany). The following settings were applied. Flow rate of the sample solution by syringe pump infusion 180 μL h^{-1}, nebulizer nitrogen pressure 0.2 bar, nitrogen dry gas temperature 180 C, dry gas flow rate 2.0 L/min. Nitrogen (N_2) served as the collision gas. UV-VIS spectra were recorded by Agilent Cary 300 UV-Visible spectrophotometer. The number-average molecular weight (M_n) and molecular weight distribution of the polymer were determined using a Shimadzu LC-20AD gel permeation chromatography (GPC) unit equipped with four Shodex GPC K-802.5, 803, 804, and 805 columns connected in series, and a Shimadzu RID-10A refractive index detector. Chloroform was used as an eluent at a flow rate of 1.0 mL/min. Particle size and zeta potential were measured by a Malvern Zetasizer Nano ZS at 25 °C. Morphological studies were done using a Hitachi transmission electron microscope H-7650 at an operating voltage of 100 kV. X-ray photoelectron spectra were recorded by a Shimadzu Kratos Axis Ultra DLD XPS using monochromatic Mg KR radiation (1253.6 eV). The binding energy of C 1s peak was referenced at 284.6 eV, and the high-resolution scans of core level spectra were set to 15 eV pass energy. The UV exposure was performed in a chamber using a UV lamp (RUV 533 BC) covering wavelengths from 315 nm to 400 nm. In the case of visible light, the samples were exposed to the room light (fluorescent lamp) with wavelengths from 400 nm to 700 nm. The polarity of polymer was calculated via GAMESS Interface based on the Hartree–Fock method with 6-311G basic set. Molecules were first optimized using the MM2 method.

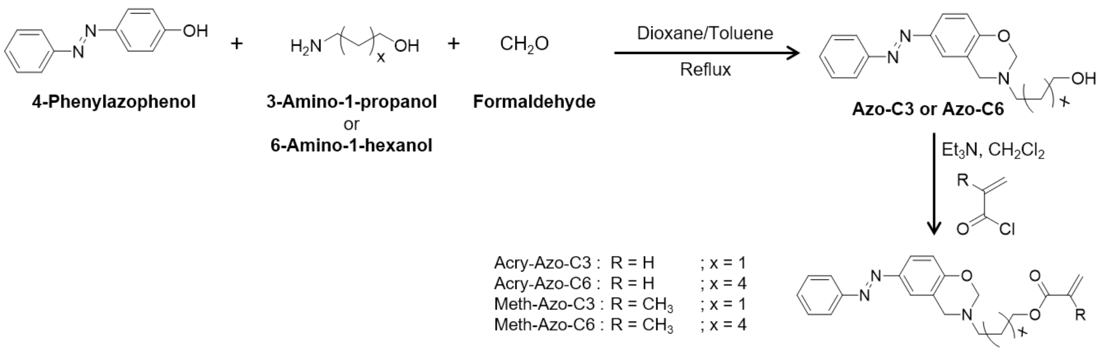
6.4 Results and Discussions

6.4.1 Synthesis of Acry-Azo Bzx/Meth-Azo Bzx

The acrylate and methacrylate monomers containing Bzx pendant i.e. Acry-Azo, and Meth-Azo, were prepared as shown in Scheme 6.1. By simply applying azobenzene derivatives as phenol in the preparation of Bzx, Bzx-Azo with light responsive function can be obtained. In order to obtain a vinyl monomer containing Bzx pendant, alkyl aminoalcohol was selected. In the first step, a Mannich reaction was carried out using 4-phenylazophenol and 3-amino-1-propanol and 6-

amino-1-hexanol to give Azo-C3 and Azo-C6 (Appendix D). Acryloyl chloride and methacryloyl chloride were chosen as they are highly reactive to form ester bond with Azo-C3 and Azo-C6 by nucleophilic acyl substitution in dichloromethane using triethylamine both as catalyst, and for removing HCl by-products. Column chromatography was also carried out to obtain high purity of Acry-Azo-Bzx and Meth-Azo-Bzx for ATRP. Their structures were characterized by FTIR and ^{1}H-NMR.

Scheme 6.1 Preparation of Acry/Meth-Azo-C3 and Acry/Meth-Azo-C6



The FTIR spectra of Acry-Azo-Bzx and Meth-Azo-Bzx are shown in Figure 6.1A. The peaks at 920 and 1235 cm^{-1} confirm the oxazine ring. The carbonyl of acryloyl chloride at 1762 cm^{-1} shifted to 1716 cm^{-1} indicates the successful conjugation to form an ester bond. Figure 6.1B shows the chemical shifts in the range of 6.5 – 7.0 ppm for aromatics, and those in the range of 6.63 – 5.57 ppm for acrylate and methacrylate moieties. The singlets at 4.33, 3.87 and 4.97, 4.11 ppm are for the methylene protons belonging to Bzx-C3 and Bzx-C6, respectively. The remaining signals refer to the alkyl chain.

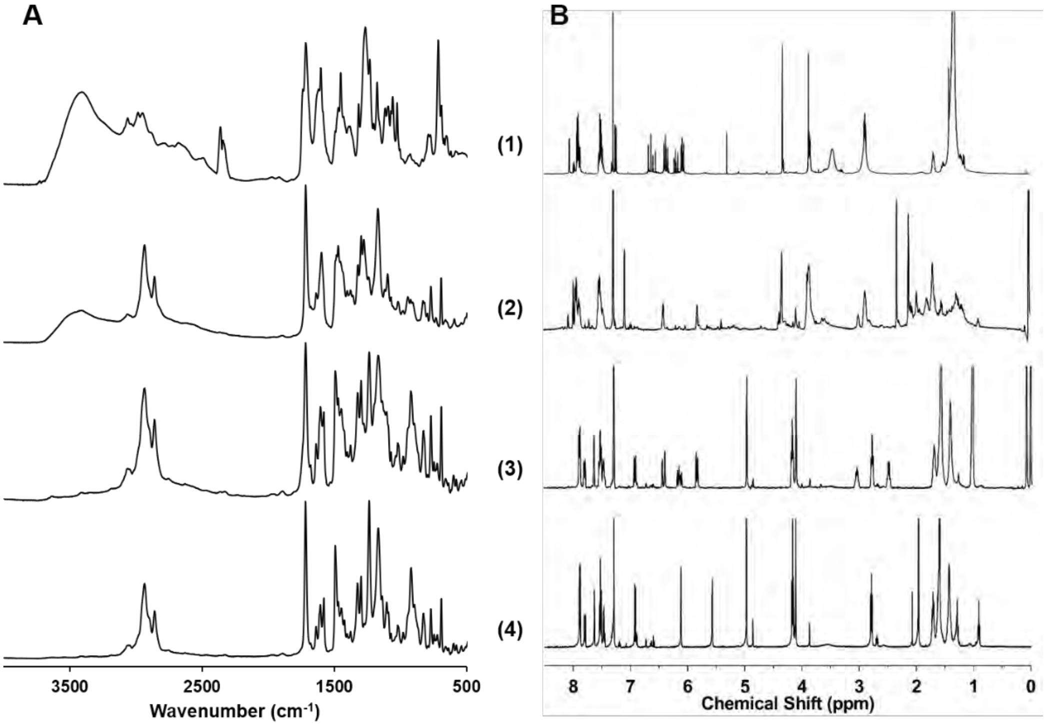


Figure 6.1 (A) FT-IR spectra and (B) ^{1}H-NMR spectra of (1) Acry-Azo-C3, (2) Meth-Azo-Co, (3) Acry-Azo-C6, and (4) Meth-Azo-C6.

6.4.2 Polymerization of the Acry-Azo-Bzx and Meth-Azo-Bzx

For most controlled radical polymerizations, atom transfer radical polymerization (ATRP) is known as a practical technique; however, the ligand has to be carefully considered. (Boyer *et. al.*, 2016, Ma *et. al.*, 2015, Matyjaszewski *et. al.*, 2001, Tang *et. al.*, 2008) Preliminary study on polymerizations of Acry-Azo-Bzx and Meth-azo-Bzx indicate a limitation of molecular weight, which might be due to the complexation of Cu(I) with Bzx. The interaction of monomer with Cu(I) was also confirmed by UV-VIS (Appendix E). UV-VIS spectrum of Acry-Azo-C3 shows an absorption peak at 356 nm regarding the trans conformation of azobenzene. For mixture of Acry-Azo-C3 and Cu(I), the spectrum shows new peak at below 300 nm. However, the peak cannot be detected due to the solvent cut-off wavelength. The new peak indicates the interaction between Acry-Azo-C3 and Cu(I). (Hrishikesan *et. al.*, 2013) To clarify the condition of polymerization in detail, a series of polymerization condition tests were carried out as shown in Scheme 6.2 and Table 6.1.

Scheme 6.2 Polymerization of Acry-Azo-C3, Acry-Azo-C6, Meth-Azo-C3 and Meth-Azo-C6

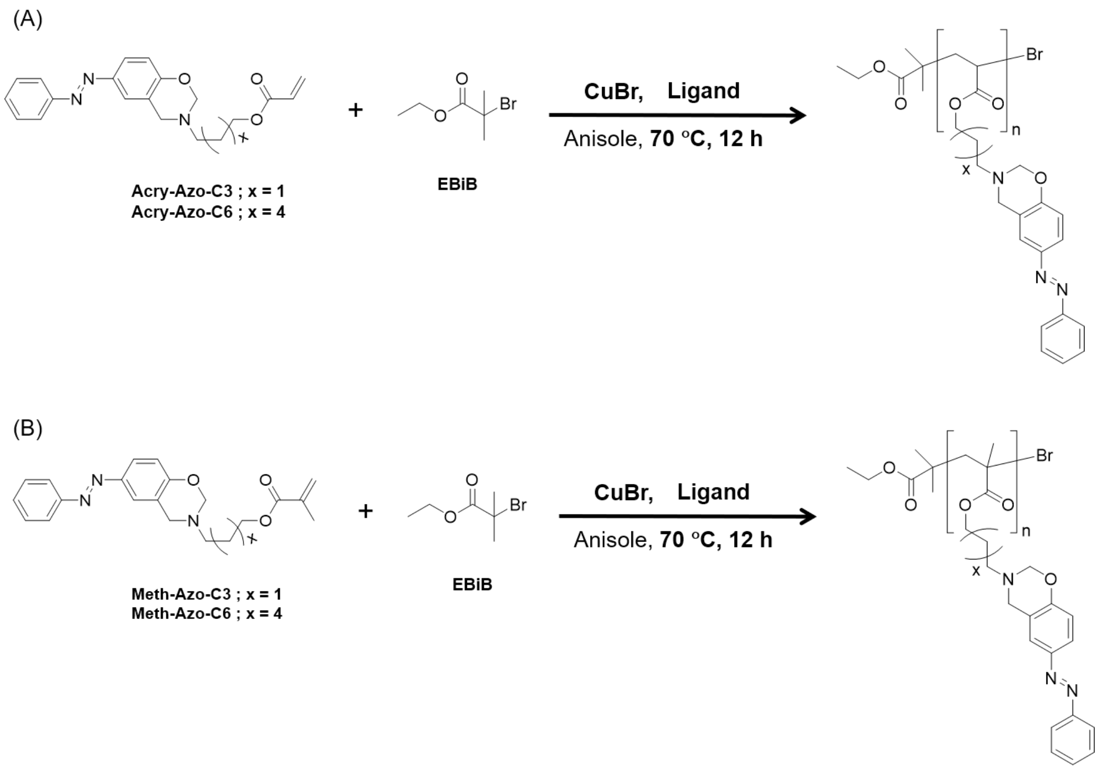
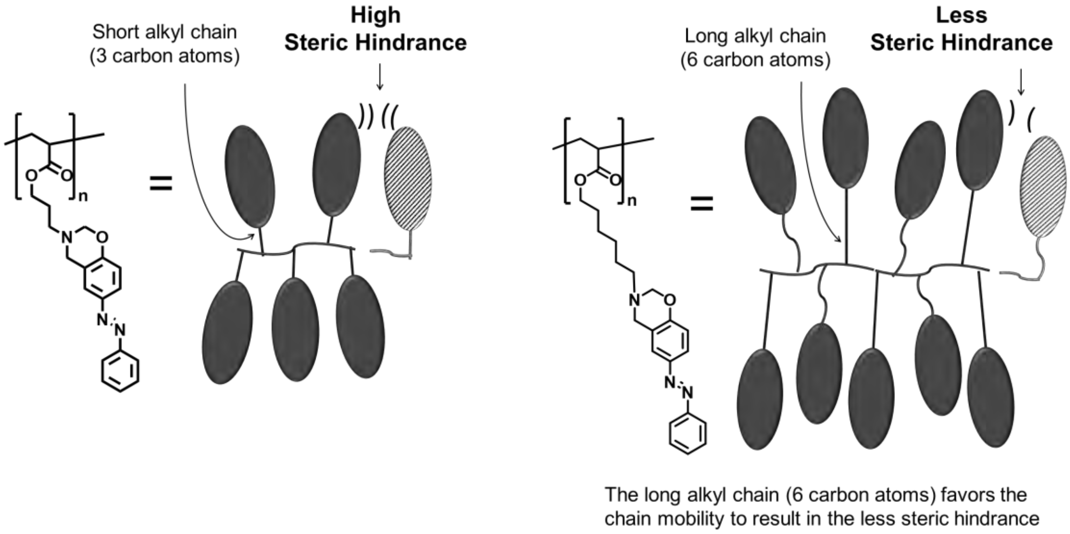


Table 6.1 ATRP conditions and the information of polymers obtained

Entry	Monomer	Ligand	Mn (Theoretical)	Mn (GPC)	PDI	% conversion
1	Acry-Azo-C3	Dnbpy	10,000	900	1.15	10
2	Acry-Azo-C3	PMDETA	10,000	1,000	1.26	12
3	Acry-Azo-C3	Me_6TREN	10,000	1,600	1.32	15
4	Acry-Azo-C6	Me_6TREN	10,000	2,600	1.51	25
5	Meth-Azo-C3	Me_6TREN	10,000	3,600	1.32	38
6	Meth-Azo-C6	Me_6TREN	10,000	9,000	2.52	90

A series of investigations of Acry-Azo-C3 polymerization (Entries 1-3) was performed to clarify the appropriate ligand for ATRP of Bzx containing acrylate derivatives. Since Cu(I) complexation with Acry-Azo-C3 may terminate the polymerization, three ligands with different K_{ATRP} values were chosen, i.e. Me_6TREN > PMDETA >Dnbpy. (Ma *et. al.*, 2015) An increase of K_{ATRP} indicates an increase in the stability of Cu(I)-ligand, which results in an increase of the polymerization rate. It was found that the ligand with higher K_{ATRP} leads to a polymer with higher molecular weight (entry 3). This might be due to the ligand with higher K_{ATRP} stabilizing Cu(I). On the other hand, the ligand with lower K_{ATRP} tends to lose its activity and Cu(I) appears to mainly form a complex with Bzx, leading to termination. However, the molecular weights obtained are still far from expectation and calculated values. This reflects the fact that the ATRP was obstructed by steric hindrance of the Bzx monomer. Scheme 6.3 shows how alkyl chain length influenced the ATRP. For the longer alkyl chain length (6 carbon atom), the chain mobility favors the less steric hindrance and as a result another monomer unit could be connected leading to the higher molecular weight (~ 9000 Dalton).

Scheme 6.3 Illustration indicating steric hindrance of PA-Azo-C3 and PA-Azo-C6. Black part refers to polymer chain and grey-patterned part refers to new monomer unit



When the alkyl chain length was changed from C3 to C6 (Entry 4), it was found that molecular weight of the polymer obtained had increased. This implied more effective polymerization for the monomer with less steric hindrance. However, the molecular weight of the polymer obtained is still relatively low. The problem might be due to the reactivity and stability of the acrylate radicals. It is known that the acrylate group is quite reactive in combination with Me_6TREN. (Nanda *et. al.*, 2003)

In the cases of methacrylate monomer, (Entries 5, and 6), it was found that PM-Azo-C6 shows high molecular weight and that it is almost the same as the calculation, based on the feed ratio. However, the polymer obtained was difficult to dissolve in most organic solvents except the hot DMF, DMAc and NMP.

6.4.3 Polymerization of the PA-Azo-C3-b-PMMA

PMMA is considered to be a good block, and it resembles PA-Azo-C3. Therefore, in order to obtain the block copolymer, PA-Azo-C3 was applied as a macroinitiator for co-polymerization with MMA (Scheme 6.4). The polymer obtained shows a molecular weight close to the theoretical value (Mn = 40 000) (Table 6.2, Entry 1). This confirmed that the preparation of PA-Azo-C3-b-PMMA was successful. It is important to note that, although the high molecular weight polymers were not achieved, the termination seemed to be based on the bulkiness of Bzx monomer itself.

Scheme 6.4 Polymerization of PA-Azo-C3-b-PMMA

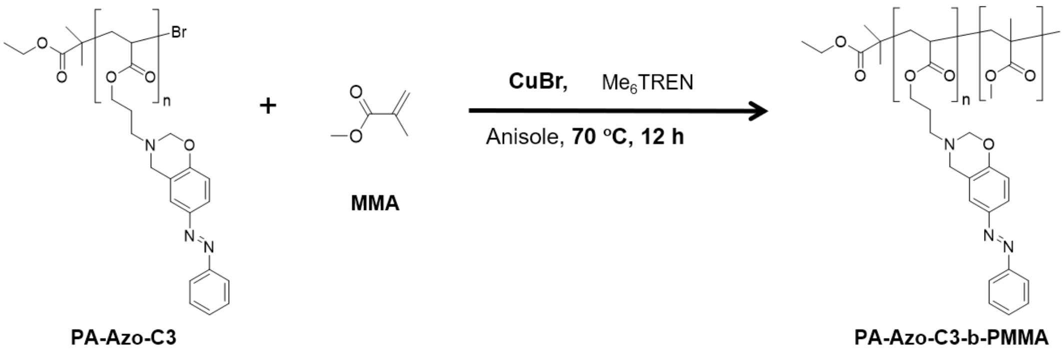


Table 6.2 Conditions and results of polymerization of block copolymer and random copolymer

Entry	Monomer	Initiator	Mn (Expected)	Mn (GPC)	PDI	% conversion
1	MMA	PA-Azo-C3 (entry 4, table 5.1)	40,000	39,000	1.43	95
2	Acry-Azo-C3 + MMA	EBiB	40,000	35,000	1.34	95

6.4.4 Polymerization of Acry-Azo-C3-*random*-MMA, PA-Azo-C3-ran-PMMA

A random copolymer was also prepared in order to study the effect of the polymer architecture. Similar procedures as PA-Azo-C3 were applied but using the mixed monomer between Acry-Azo-C3 and MMA. The result shows the molecular weight of random polymer to be about 35,000 Dalton, and close to calculated value (Mn_{cal} = 40,000) (Table 6.2**,** Entry 2). This also confirmed that the high molecular weight of PA-Azo-C3 was obstructed due to its steric hindrance. In other words, the comonomer MMA with less steric hindrance in the system allows the random copolymerization of Acry-Azo-C3 monomer.

6.4.5 Nanoparticle formation and UV responsive and reversible performance

A solution of PA-Azo-C3-b-PMMA in $CHCl_3$ was prepared (0.01 mg/ml). The solution was dropped on a carbon coated TEM grid and allowed to dry naturally. PA-Azo-C3-b-PMMA forms the nanoparticles as observed by TEM (Figure 6.2 (A)). The nanoparticles show core-shell morphology as defined by its brightness contrast. In order to figure out which block is the core, the solubility parameters, δ, of the chloroform, PA-Azo-C3, and PMMA were calculated (Percec *et. al.*, 2006) and found to be 9.3 (Fedors, 1974), 9.17, and 8.16 $cal^{1/2}cm^{-3/2}$, respectively (see Appendix F). The estimation of polarity of polymer by determining dipole moment (D) of molecule based on Hartree–Fock method (Arnold *et. al.*, 2000) was also carried out. The results showed that the dipole moments of PMMA and PA-Azo-C3 were 6.29 Debye and 2.80 Debye, respectively. It is clear that either calculation gives similar trends. This suggests that the PMMA and PA-Azo-C3 might be the core and shell, respectively as illustrated in Figure 6.3. The fact that δ of PA-Azo-C3 is close to that of $CHCl_3$ indicating PA-Azo-C3 was in the shell part of the nanoparticle. The nanoparticles were further exposed to UV light to initiate light response based on azobenzene group. Figure 6.2 (B) shows the images of PA-Azo-C3-b-PMMA in $CHCl_3$ after UV exposure with swelling and no clear phase separation. In the case of PA-Azo-C3-b-PMMA, the result suggests how the block copolymers with different hydrophobicity and hydrophilicity tend to nanoparticles. (Binder *et. al.*, 2005, Ruoff *et. al.*, 1993) When it comes to the case of a random copolymer, i.e. PA-Azo-C6-ran-PMMA, the non-uniform particles in various morphologies and without phase contrast are observed (Figure 6.2 (F)). For PA-Azo-C3-b-PMMA in methanol, the nanoparticles obtained also show the core shell morphology (Figure 6.2 (D)). PA-Azo-C3-b-PMMA in methanol, after UV exposure, also shows the same nanoparticle morphology, but with decreases in size (Figure 6.2 (E)). When the sample in Figure 6.2 (B) (PA-Azo-C3-b-PMMA in $CHCl_3$ with UV exposure) was treated with visible light, the nanoparticle formation was recovered, as shown in Figure 6.2 (C). The results imply the reversible UV responsiveness of PA-Azo-C3-b-PMMA. ^{1}H-NMR also confirmed the nanoparticle morphological change by broadening of aromatic signal upon UV exposure indicating PA-Azo-C3 block was rarely dissolved in $CDCl_3$ (Appendix G). On the other hand, PA-Azo-C3 moiety became the core of the nanoparticle instead of the shell as a consequence of UV exposure.

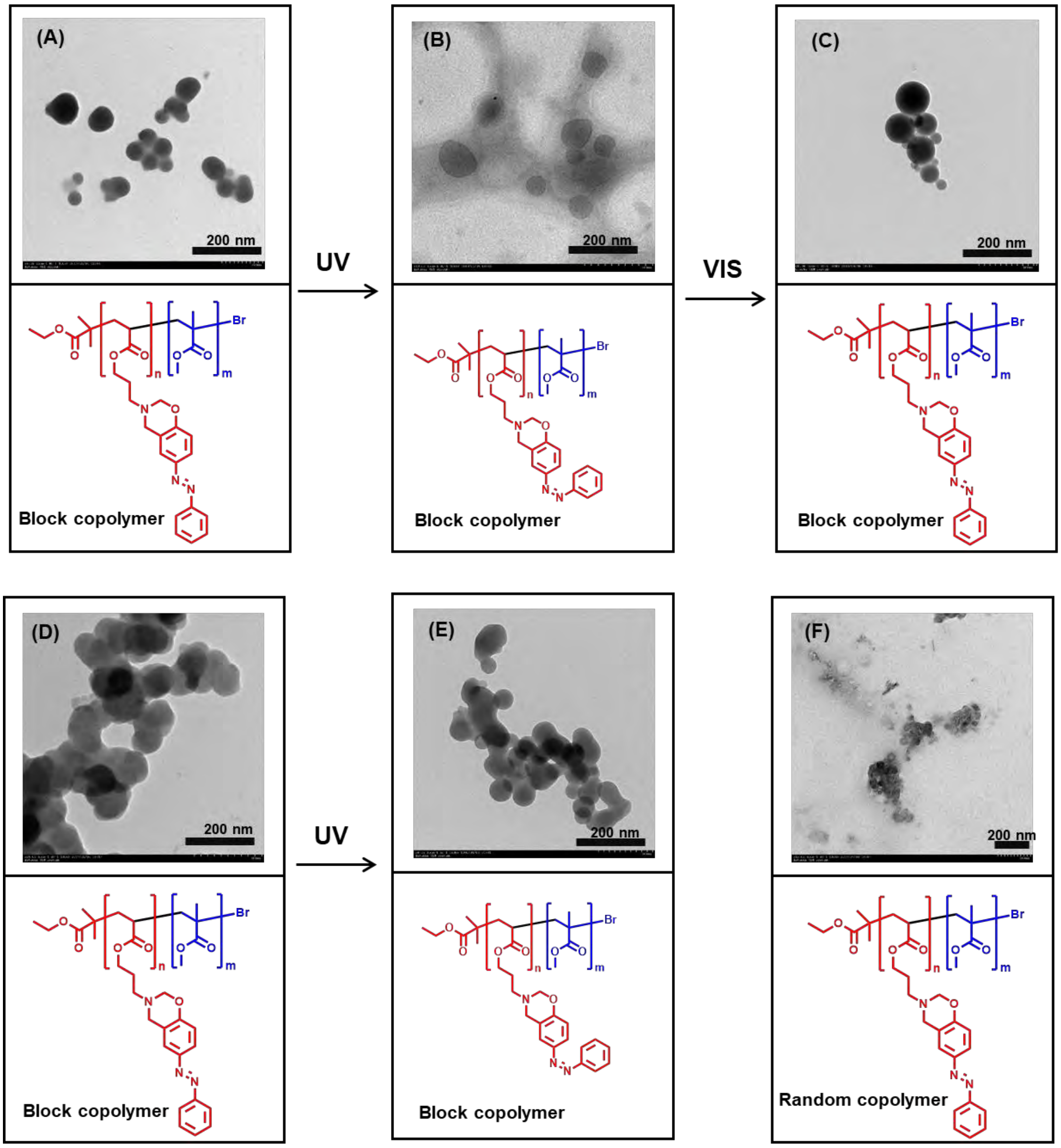


Figure 6.2 Nanoparticle formation of (A) PA-Azo-C3-b-PMMA in $CHCl_3$, (B) PA-Azo-C3-b-PMMA in $CHCl_3$ with UV exposure, (C) PA-Azo-C3-b-PMMA in $CHCl_3$ with UV exposure followed by Vis exposure, (D) PA-Azo-C3-b-PMMA in methanol, (E) PA-Azo-C3-b-PMMA in methanol with UV exposure, and (F) PA-Azo-C6-ran-PMMA in $CHCl_3$.

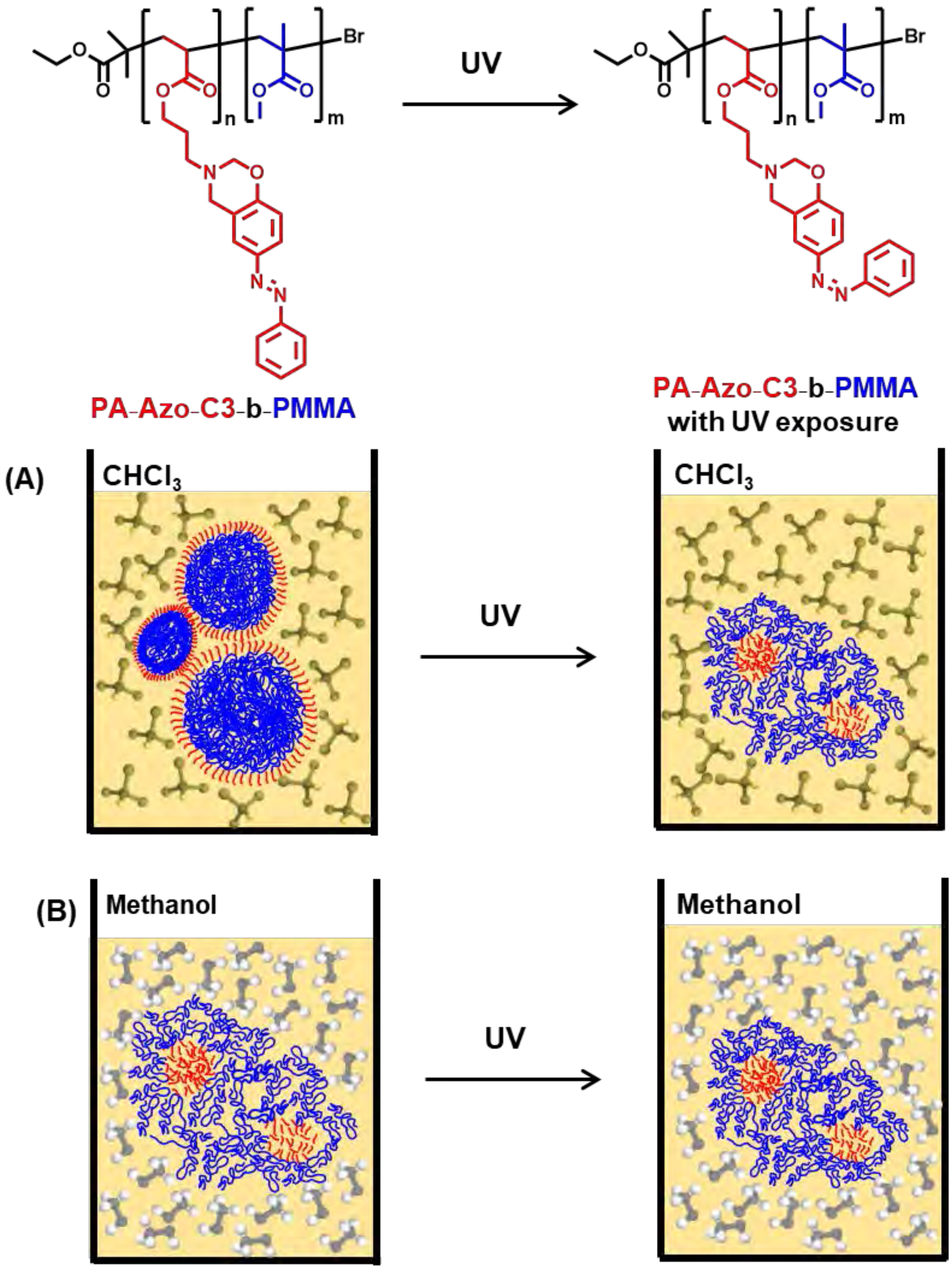


Figure 6.3 Schematic of nanoparticle formation of PA-Azo-C3-b-PMMA in (A) $CHCl_3$ and (B) Methanol.

The sizes of nanoparticles in the solution were observed using dynamic light scattering (DLS) in order to evaluate the effect of the organic phase on nanoparticle formation (Figure 6.4). As the δ of PA-Azo-C3-b-PMMA is close to that of methanol (14.28 $cal^{1/2}cm^{-3/2}$) rather than that of chloroform, it is natural to see more swelling; in other words, larger nanoparticle size of PA-Azo-C3-b-PMMA in methanol. Figure 6.4 also clarifies the UV responsiveness of PA-Azo-C3-b-PMMA as seen from the decreases in size. The significant decrease in size when the nanoparticles were in methanol suggests more efficient conformational changes of the azobenzene unit in PA-Azo-C3-b-PMMA particles when they are in relatively good solvent.

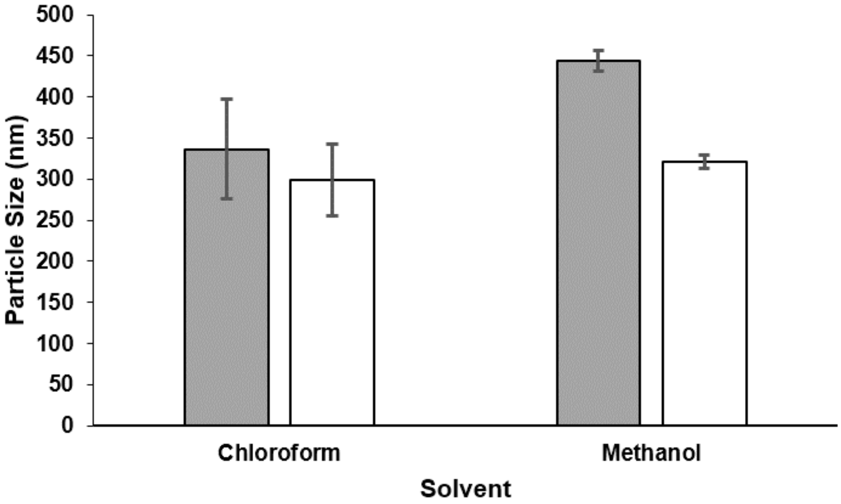


Figure 6.4 Particle size of PA-Azo-C3-b-PMMA dispersed in chloroform and methanol before (■), and after (□) UV exposure.

It comes to the point whether the core-shell structure can be further confirmed by XPS technique. The XPS spectrum of the block copolymers before and after UV exposure were compared. The PA-Azo-C3-b-PMMA was dissolved in chloroform and dropped on a glass surface. The solvent was dried naturally in the dark. For PA-Azo-C3-b-PMMA in $CHCl_3$ (Figure 6.5 (A)), C1s spectrum was curve-fitted with three-components at (I) 284.74 eV, (II) 285.85 eV and (III) 287.23 eV which are associated with C–*C*–C, C–*C*–O/C–*C*–N, and O–*C*–N, respectively. The O1s spectrum was also curve-fitted at (I) 530.13 eV, (II) 530.96 eV and (III) 533.82 eV which are for C=O, Ar–O–N, and C–O–C, respectively. After the PA-Azo-C3-b-PMMA solution was exposed to UV light, but before dropping and drying on glass surface, the changes of C 1s and O 1s spectra were observed. In other words, the content of C 1s peak at position (II) increased from 43 % to 54%, whereas the content of O 1s peak at position (II) decreased from 61% to 10% (Figure 6.5 (B)). The results confirm that changes in trans-cis conformation lead to a decrease in the interaction with $CHCl_3$, and, as a consequence, the PA-Azo-C3 blocks did not mainly exist on the surface. In other words, the azobenzene moieties prefer to be the core when they are in cis conformation. To clarify this, the PA-Azo-C3-b-PMMA in methanol was also investigated. Figure 6.5 (C) shows C 1s spectrum of PA-Azo-C3-b-PMMA composed of the three-components at (I) 284.87 eV, (II) 285.86 eV and (III) 287.10 eV. In the case of O 1s, the spectrum shows three components at (I) 530.27 eV, (II) 530.79 eV and (III) 532.80 eV. Comparing to the spectrum in $CHCl_3$, the peak area, which represents the quantity of each component, is different. For example, the percentages of C 1s peak at position (II) of PA-Azo-C3-b-PMMA obtained from chloroform and from methanol are 43.27 and 23.7, respectively. This suggests that Bzx blocks are more likely to stay at core when the copolymer is in methanol. The result is relevant to the magnitude of δ as mentioned above. After the PA-Azo-C3-b-PMMA in methanol was exposed to UV, the C 1s peak at position (II) increased, whereas O 1s peak at position (II) decreased (Figure 6.5 (D)). This reflects the fact that the Bzx block in cis conformation self-assemble as the core.

6.4.6 PA-Azo-C3-DIMER-b-PMMA and its complexation with Cu(II)

As Bzx dimers contain N and O atoms to coordinate with metal ions, as reported in the past (Chirachanchai *et. al.*, 2011, Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2004), it is expected that the PA-Azo-C3-b-PMMA shows another multi-responsive function, i.e. metal responsiveness. Here, the ring opening of the Bzx block by 2,4-dimethylphenol was carried out (Scheme 6.5) to obtain the Bzx dimer block in PA-Azo-C3-DIMER-b-PMMA. Although the ROP of aromatic with phenol including Bzx are commonly accompanied by the side reaction, in our case, the fact that the aromatic of 2,4-dimethylphenol is already substituted with the methyl group at both ortho and para position, no side reaction was occurred. This leads the ring-opening reaction occurred with high yield (>90%). The chemical structure was confirmed by ^{1}H-NMR. (see Appendix H) In order to identify the metal responsiveness, an excess mole of $CuCl_2$ (as compared to Bzx dimer block) was added to the chloroform solution of PA-Azo-C3-DIMER-b-PMMA.

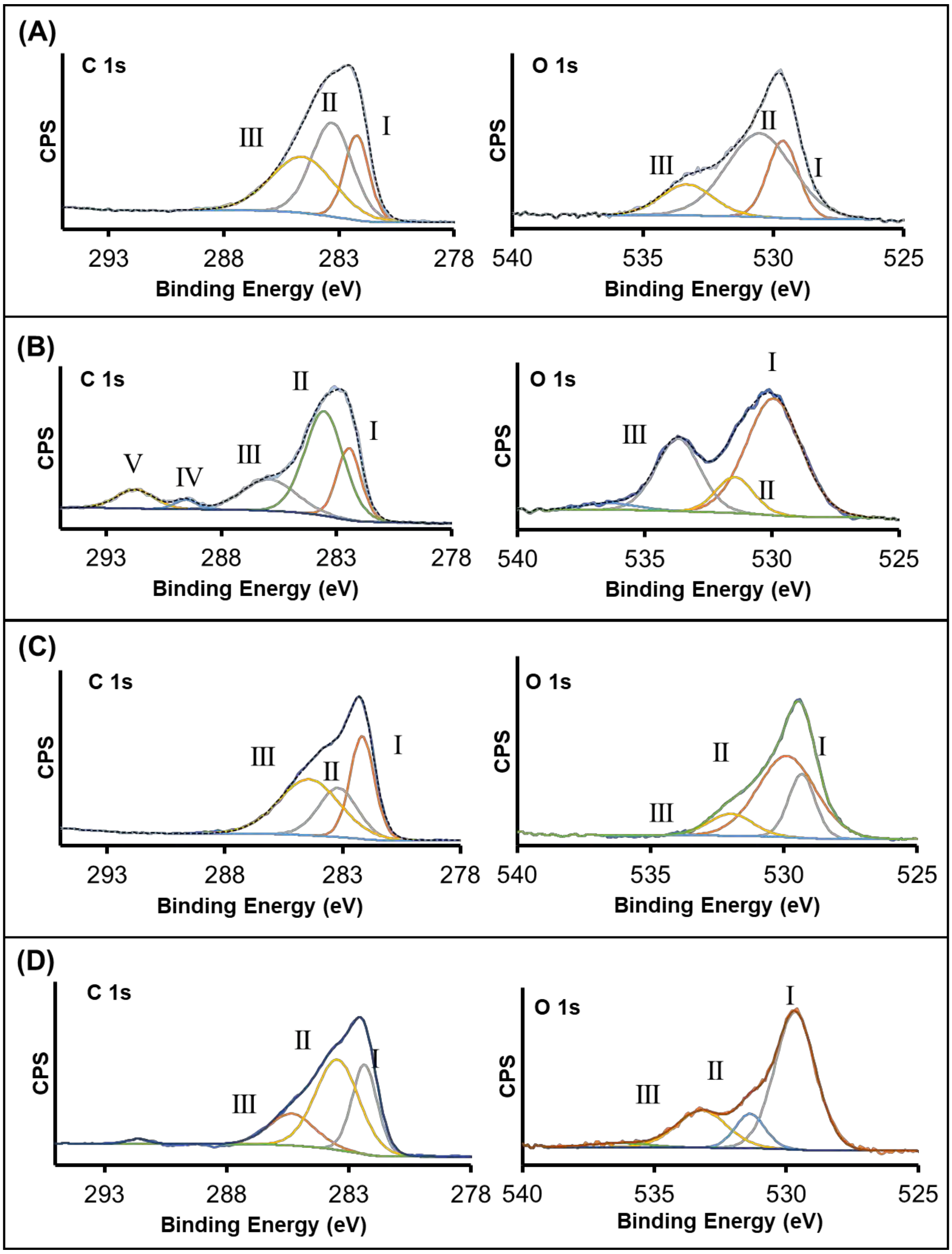
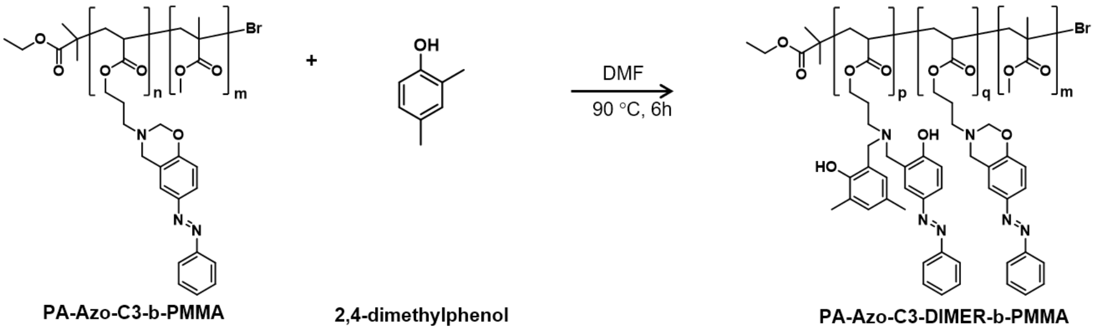


Figure 6.5 Narrow scan XPS spectra of (A) PA-Azo-C3-b-PMMA prepared from $CHCl_3$ solution, (B) PA-Azo-C3-b-PMMA in $CHCl_3$ after UV exposure, (C) PA-Azo-C3-b-PMMA in methanol, and (D) PA-Azo-C3-b-PMMA in methanol after UV exposure.

Scheme 6.5 Ring opening reaction of PA-Azo-C3-b-PMMA to obtain PA-Azo-C3-DIMER-b-PMMA



The metal complexation was traced by UV-VIS spectroscopy. Figure 6.6 (A) shows the UV-VIS spectrum of PA-Azo-C3-DIMER-b-PMMA with an absorption peak at 356 nm. After Cu(II) complexation, the product showed hypsochromic shift to 340 nm. This implies changes in the electronic system as a consequence of the Cu(II) complexation between the oxygen atoms of the hydroxyl group.(Dearden, 1963, Lee, Seoung Ho *et. al.*, 2004) Moreover, XPS was also carried out to investigate the complexation formation of block copolymer and Cu(II) ion (Figure 6.6 (B)). For PA-Azo-C3-DIMER-b-PMMA, C1s and O1s spectra were curve fitted to find that the positions are almost the same position as that of PA-Azo-C3-b-PMMA. The spectrum of PA-Azo-C3-DIMER-b-PMMA after being treated with $CuCl_2$ shows quite different patterns from that of PA-Azo-C3-DIMER-b-PMMA. There are two new peaks of C1s (at 290.1 and 292.6 eV) and two other new peaks of O1s (at 537.4 and 534.7) eV, which can be attributed to the carboxylate and alkoxide complexation. The results confirm the complexation of PA-Azo-C3-DIMER-b-PMMA with Cu(II).

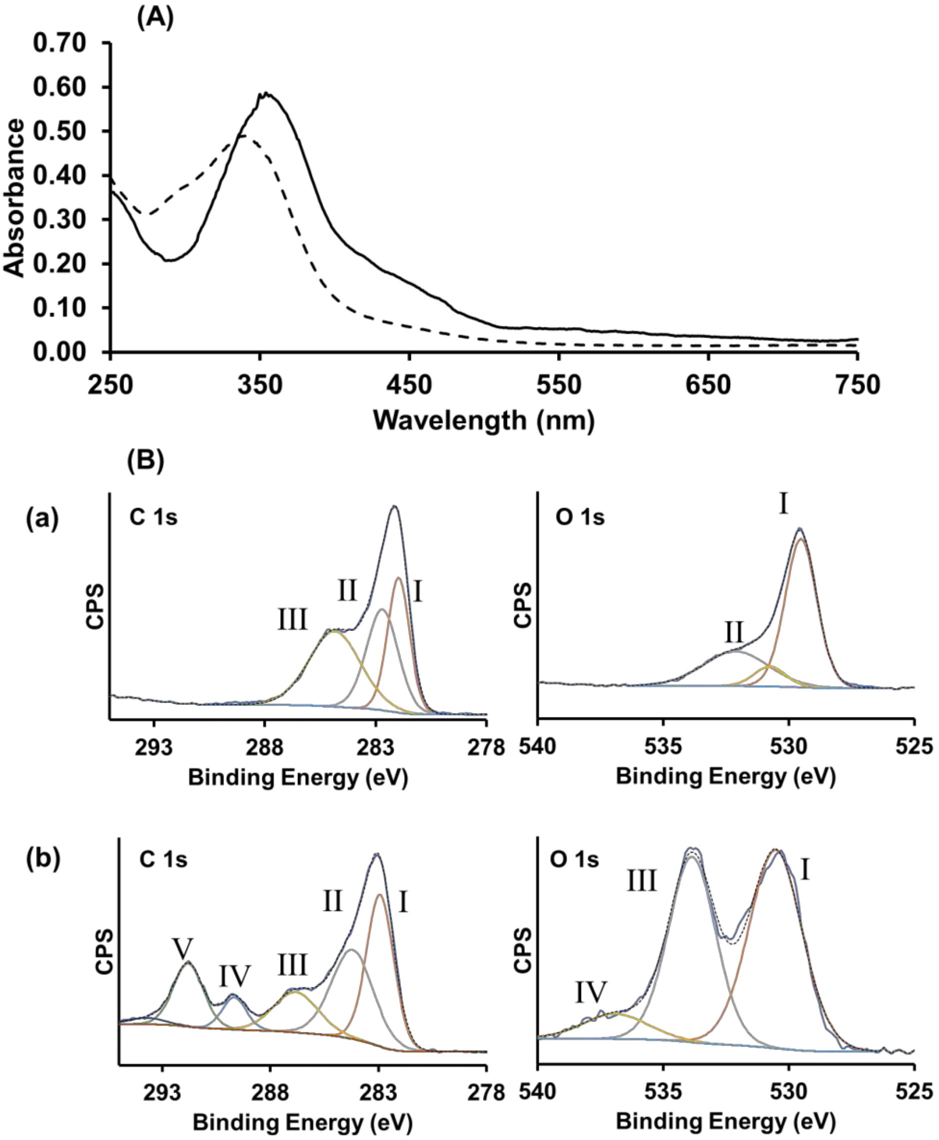


Figure 6.6 (A) UV-VIS spectra of (_____) PA-Azo-C3-DIMER-b-PMMA in $CHCl_3$, (------) PA-Azo-C3-DIMER-b-PMMA in $CHCl_3$ with $CuCl_2$, (B) Narrow scan XPS spectra based on C 1s and O 1s of (a) PA-Azo-C3-DIMER-b-PMMA in $CHCl_3$ and (b) PA-Azo-C3-DIMER-b-PMMA in $CHCl_3$ with $CuCl_2$.

Figure 6.7 (A) shows TEM micrographs of PA-Azo-C3-DIMER-b-PMMA prepared from $CHCl_3$ solution, in which the nanoparticles tend to aggregate. This suggests an inter- and intra-molecular H-bond network as reported previously. At this stage, the average aggregation size is about 100 nm. After exposing the solution of (A), i.e. PA-Azo-C3-DIMER-b-PMMA in $CHCl_3$ to UV light (Figure 6.7

(B)), the morphology of the nanoparticles and the size did not change. After treating (A) with Cu(II), i.e. PA-Azo-C3-DIMER-b-PMMA with $CuCl_2$ (Figure 6.7 (C)), the contrast of the nanoparticles is different from that of (A). In other words, PA-Azo-C3-DIMER-b-PMMA with Cu(II) shows dark spots, implying dense aggregation. The dark spots reflect the high electron density of the incorporated Cu(II). In fact, similar aggregation size, as large as 100 nm, was also clarified. Previously, our group reported on the X-ray structure analysis of Bzx dimers, which transforms their hydrogen bond network to metal coordination with the same packing structure. (Phongtamrug *et. al.*, 2006a, Phongtamrug *et. al.*, 2004) Based on our previous report, it is reasonable to see that the aggregation of (A) is maintained to result in (C). After exposing (C) solution to UV light, the morphology still shows dark spots in the matrices, implying Cu(II) incorporation (Figure 6.7 (D)). It should be noted that, at this stage, the polymer may lose its packing structure, as seen from the bright images of matrices. An attempt to remove Cu(II) from (C) was made by treating it with EDTA to find that the morphologies change to (E) (Figure 6.7 (E)). It is significant that the morphology of (E) is similar to that of (A). This indicates that Cu(II) complexation can be resolved by EDTA solution. Similarly, when (E) was further exposed to UV light, the morphology of the nanoparticles did not change, as illustrated in Figure 6.7 (F). After (E) was added with $CuCl_2$ in $CHCl_3$, the nanoparticles with Cu(II) were identified, as seen in Figure 6.7 (G). Here, it is important that the morphology of (G) is similar to that of (C). The similarity between (E) and (A), and between (C) and (G), suggests reversible Cu(II) complexation via EDTA and $CuCl_2$ treatment.

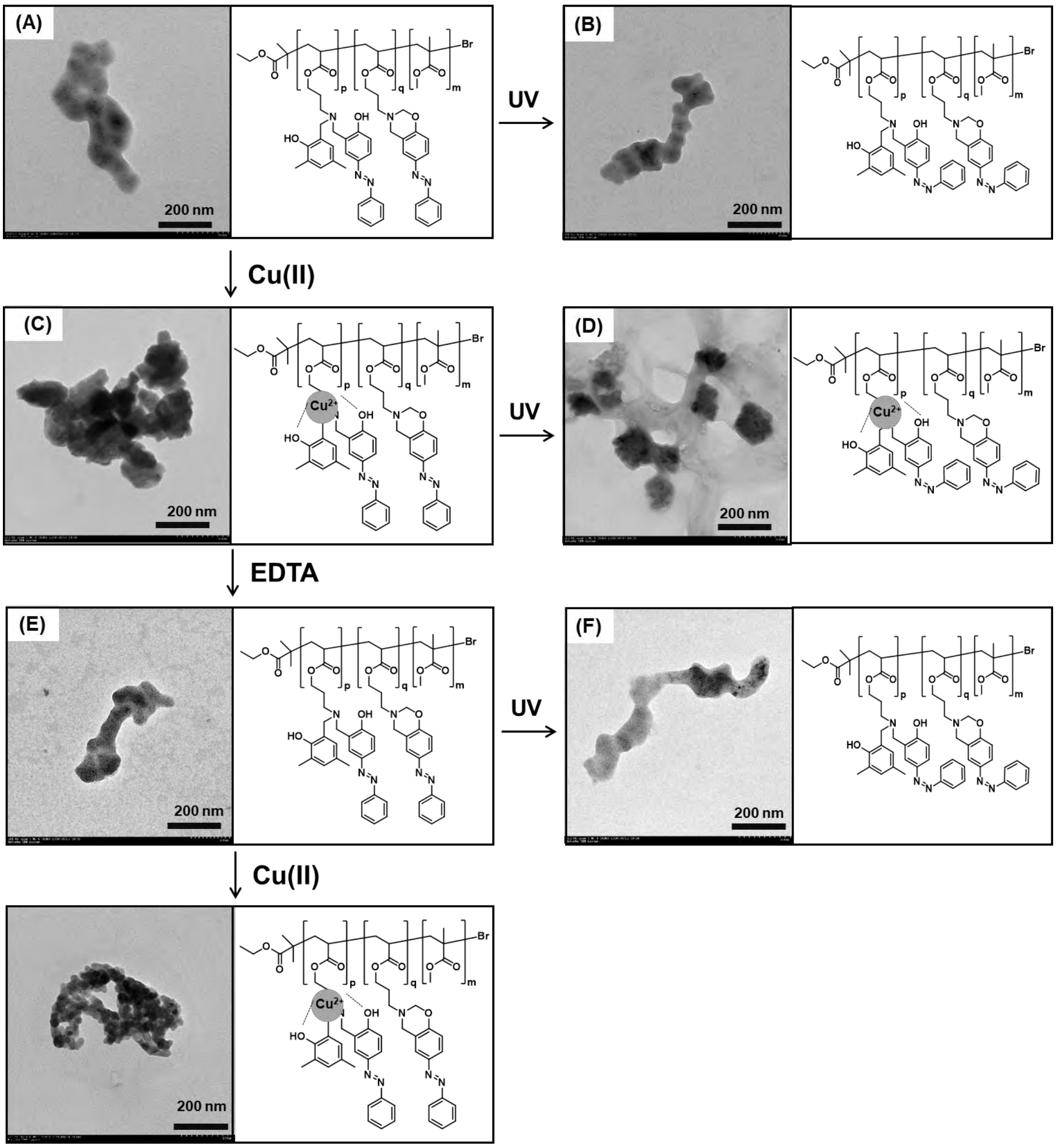


Figure 6.7 TEM micrographs of (A) PA-Azo-C3-DIMER-b-PMMA in CHCl$_3$, (B) PA-Azo-C3-DIMER-b-PMMA in CHCl$_3$ with UV exposure, (C) PA-Azo-C3-DIMER-b-PMMA in CHCl$_3$ with CuCl$_2$, (D) PA-Azo-C3-DIMER-b-PMMA in CHCl$_3$ with CuCl$_2$ and UV exposure, (E) PA-Azo-C3-DIMER-b-PMMA in CHCl$_3$ after treating with EDTA, (F) PA-Azo-C3-DIMER-b-PMMA in CHCl$_3$ after Cu(II) removal with UV exposure, and (G) PA-Azo-C3-DIMER-b-PMMA in CHCl$_3$ after treating with EDTA followed by treating with CuCl$_2$.

6.5 Conclusions

The present work demonstrats the use of Bzx under azophenol pendant to develop multi-responsive polymer. Acrylic acid modified with Bzx was prepared followed by copolymerizing with MMA via ATRP techniques. As the bulkiness of Bzx obstructed the polymerization of Bzx block, the molecular weight was limited at a certain level, even though the optimal ligand was used. In the case of PA-Azo-C3-b-PMMA, the polymer obtained showed PMMA core- PA-Azo-C3 shell nanoparticles. UV exposure led to reversed morphology, with PA-Azo-C3 core as a consequence of a cis-trans conformational change of the azobenzene group. The ring opening of Bzx led to the Cu(II) complexation, which resulted in nanoparticle aggregation. The sequential treatment with $CuCl_2$ and EDTA allowed the reversible morphology, indicating Cu(II) incorporation and release in PA-Azo-C3-DIMER-b-PMMA matrices.

6.6 Acknowledgements

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CHAPTER VII
CONCLUSIONS

Based on supramolecular chemistry of benzoxazine dimeric unit in combination light responsive moiety, our study is concerning (i) a supramolecular crosslinker for poly(acrylic acid) with light responsive behavior, (ii) the combination of fluorescent labelling light responsive benzoxazine with rotaxane system and (iii) the benzoxazine dimer side group as copolymer with multi responsive functions. In case of supramolecular crosslinker, the use of dihydroxyl azobenzene with amino in benzoxazine synthesis provides benzoxazine bearing dihydroxyl group which is able to conjugate with polymer chain. The further carrying out ring opening reaction using fluorescent phenol provides fluorescent property to the gel. Moreover, the use of phenols allows the metal ion complexation which also enhance strength of the gel with decrease in swelling ratio. The complexation was reversible by treating with EDTA and $CuCl_2$ solution in cycle. The combination of light responsive benzoxazine with rotaxane system was also achieved by using benzoxazine bearing dihydroxyl group. The hydroxyl groups were conjugated with rotaxane part. The further ring opening reaction of benzoxazine using fluorescent phenol brings fluorescent property to benzoxazine with rotaxane system. The shuttling of rotaxane can be detected by the fluorescent behavior. Moreover, the metal ion complexation was also detected and reversible. UV light induces the change in conformation of azobenzene which increased fluorescent intensity. The copolymer with benzoxazine dimer side group was achieved by conjugating benzoxazine bearing hydroxyl group with acrylate derivatives. Polymerization of the monomer using controlled radical polymerization allows preparing block copolymer. The benzoxazine blocks also response to UV light by changing morphology and hydrodynamic diameter. The metal ion complexation was also formed after ring opening reaction. The unique properties of benzoxazine dimer can be applied in cross-linked polymer network, block copolymer and supramolecules.

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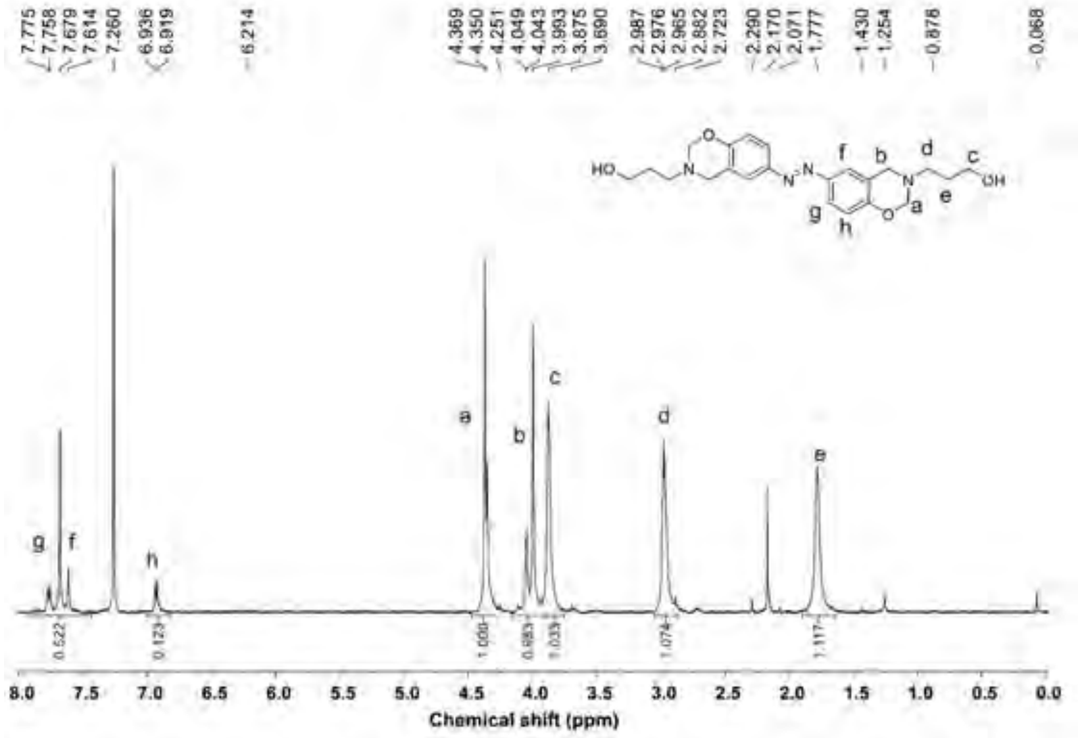
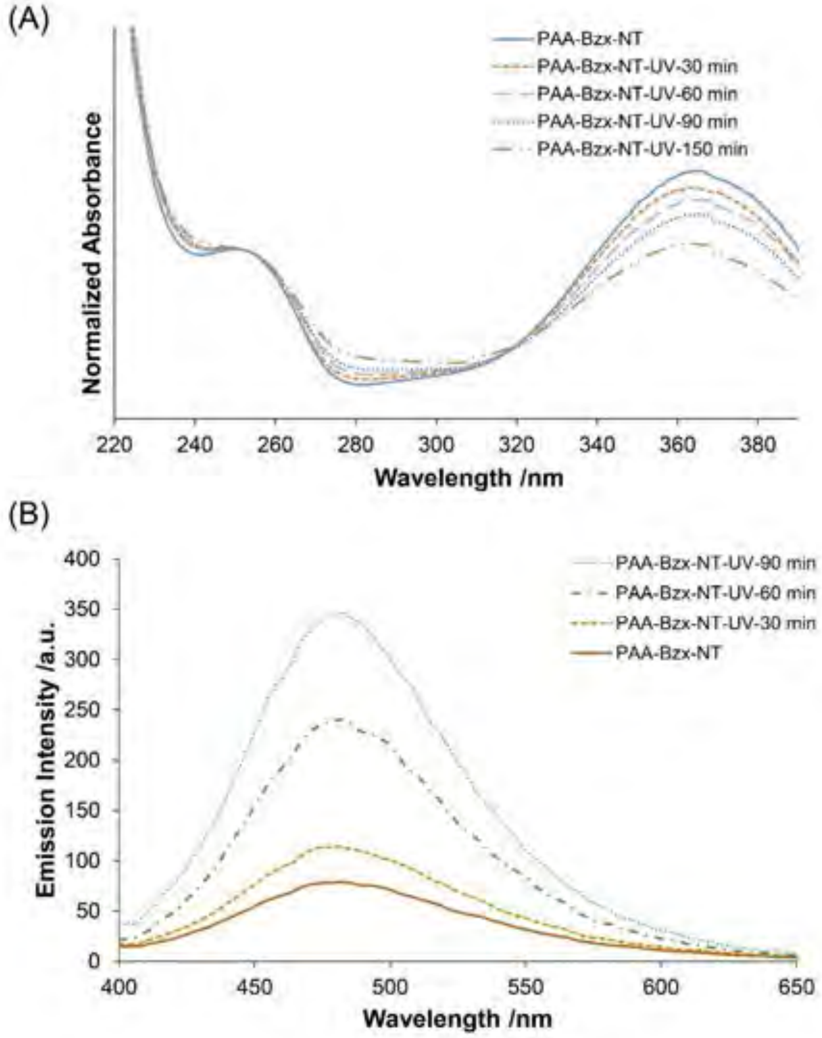
APPENDICES

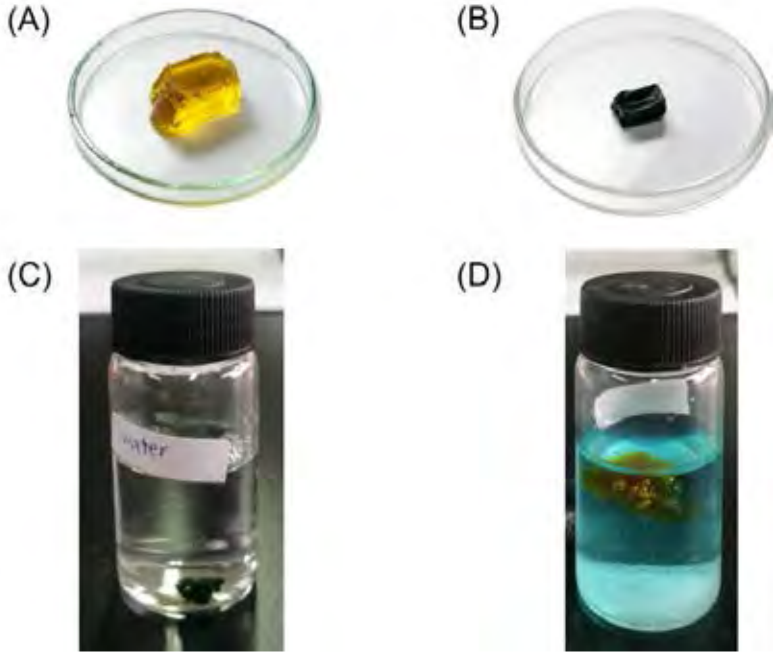
Appendix A : ^{1}H-NMR Spectrum of AP-Bzx.



Appendix B : (A) UV-Vis absorption spectra and (B) Fluorescent emission spectra excited at 295 nm of PAA-Bzx-NT over UV exposure time.



Appendix C : Photographs of (A) PAA-Bzx-DMP gel, (B) PAA-Bzx-DMP-Cu gel, (C) PAA-Bzx-DMP-Cu in DI water, and (D) PAA-Bzx-DMP-Cu in EDTA solution for 24 h.



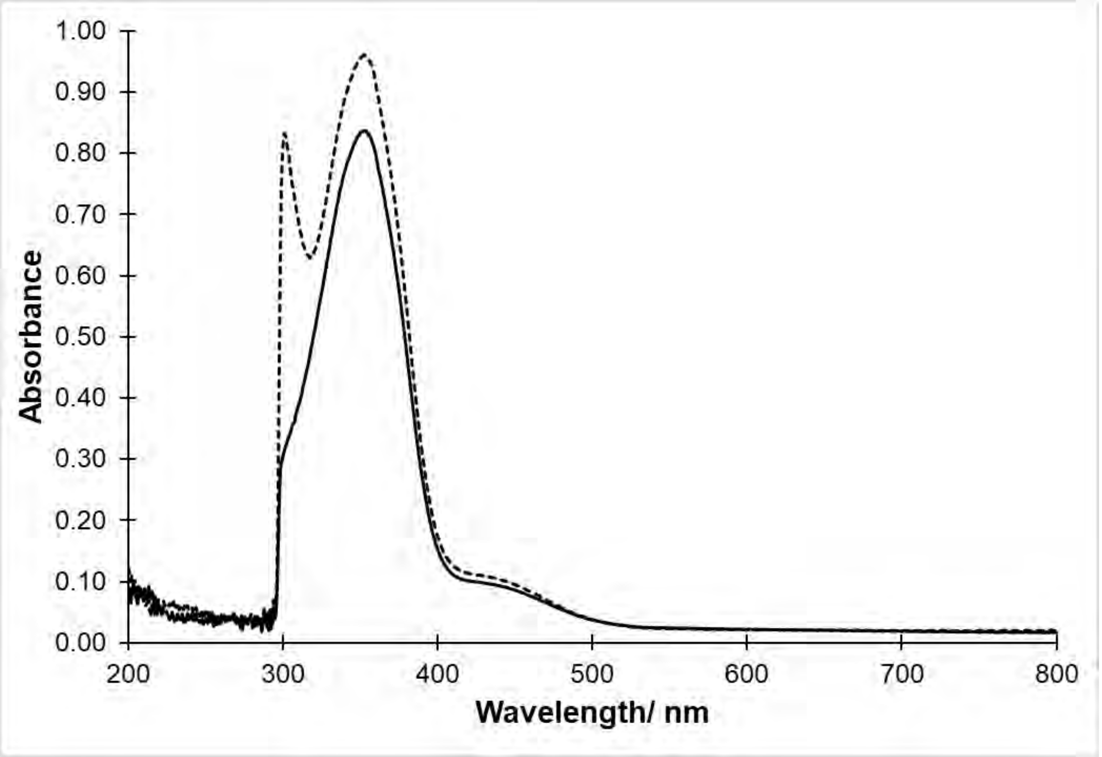
Appendix D : Structural Characterization of Azobenzene-based Bzx monomer (Azo-C3, Azo-C6)

The azo azobenzene-based benzoxazine monomers were successfully prepared as confirmed by ^{1}H-NMR as follows. The product obtained shows significant signal at 4.39 and 4.10 ppm for Azo-C3 and 4.98 and 4.13 ppm for Azo-C6 referred to oxazine ring formation.

Azo-C3 (Yield: 80 %) ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.95 – 7.84 (m, 3H, ArH), 7.56 – 7.40 (m, 4H, ArH), 6.98 (d, J = 8.8 Hz, 1H, ArH), 4.39 (s, 2H, OCH_2N), 4.10 (s, 1H, $ArCH_2N$), 3.90 (t, J = 5.3 Hz, 2H, $HOCH_2CH_2$), 3.00 (t, J = 5.6 Hz, 2H, NCH_2CH_2), 1.82 (m, 2H, $CH_2CH_2CH_2$).

Azo-C6 (Yield: 85 %) ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.95 – 7.75 (m, 3H, ArH), 7.55 – 7.40 (m, 4H, ArH), 6.91 (d, J = 8.02 Hz, 1H, ArH), 4.98 (s, 2H, OCH_2N), 4.13 (t, J = 5.3 Hz, 2H, $HOCH_2CH_2$), 4.11 (s, 1H, $ArCH_2N$), 2.78 (t, J = 5.6 Hz, 2H, NCH_2CH_2), 1.70 – 0.8 (m, 8H, $CH_2CH_2CH_2$).

Appendix E : Investigation the interaction between benzoxazine and Cu(I)

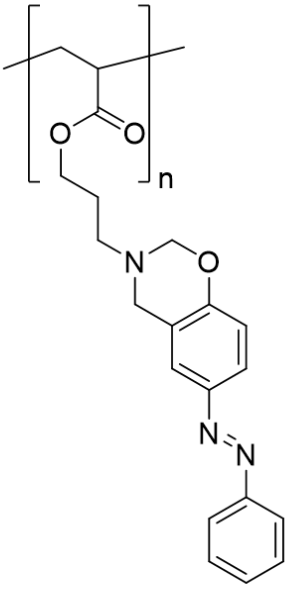


UV-VIS spectra of (―――) Acry-Azo-C3 and (------) mixture of Acry-Azo-C3 and Cu(I) in anisole

UV-VIS spectrum of Acry-Azo-C3 shows an absorption peak at 356 nm. For mixture of Acry-Azo-C3 and Cu(I), the spectrum shows new peak at below 300 nm. However, the peak cannot be detected due to the solvent cut-off wavelength. The new peak indicates the interaction between Acry-Azo-C3 and Cu(I).

Appendix F : Polymer solubility parameter calculation

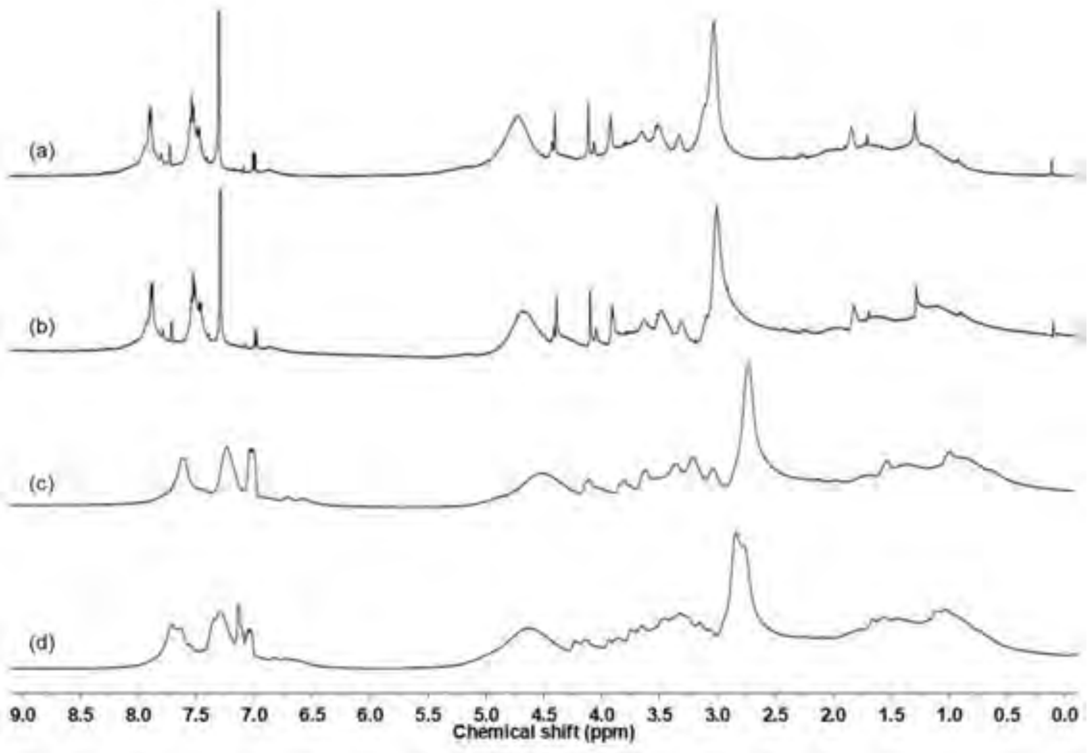
The polymer solubility was estimated according to the literature “Robert, F. (1974). A method for estimating both the solubility parameters and molar volumes of liquids. Polymer Engineering & Science, 14(2), 147-154”.

<table>
<tr><td rowspan="12"> </td><td colspan="3">**Molecular weight** = 351.41 g/mol</td></tr>
<tr><th>Group</th><th>Molar Group Constant</th><th>Amount</th></tr>
<tr><td>Methylene</td><td>133</td><td>6</td></tr>
<tr><td>Methine</td><td>28</td><td>1</td></tr>
<tr><td>Ester</td><td>310</td><td>1</td></tr>
<tr><td>Phenyl</td><td>735</td><td>1</td></tr>
<tr><td>Tri-substituted benzene</td><td>558</td><td>1</td></tr>
<tr><td>Azo</td><td>-11.4</td><td>1</td></tr>
<tr><td>Tertiary amine</td><td>61</td><td>1</td></tr>
<tr><td>Ether</td><td>70</td><td>1</td></tr>
<tr><td>Conjugate</td><td>30</td><td>1</td></tr>
<tr><td>**Total**</td><td colspan="2">2578.6</td></tr>
</table>

$$\delta = \frac{\rho \sum G}{M}$$

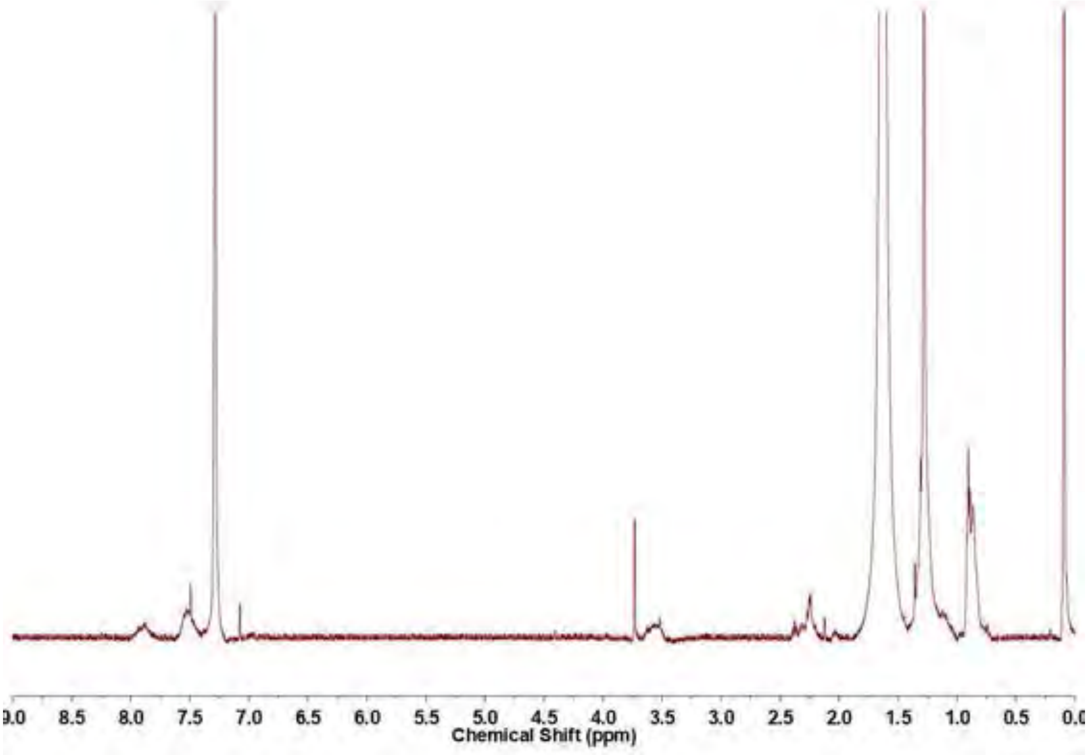
$$= \frac{1.10 \times 2578.6}{351.41} = 8.16$$

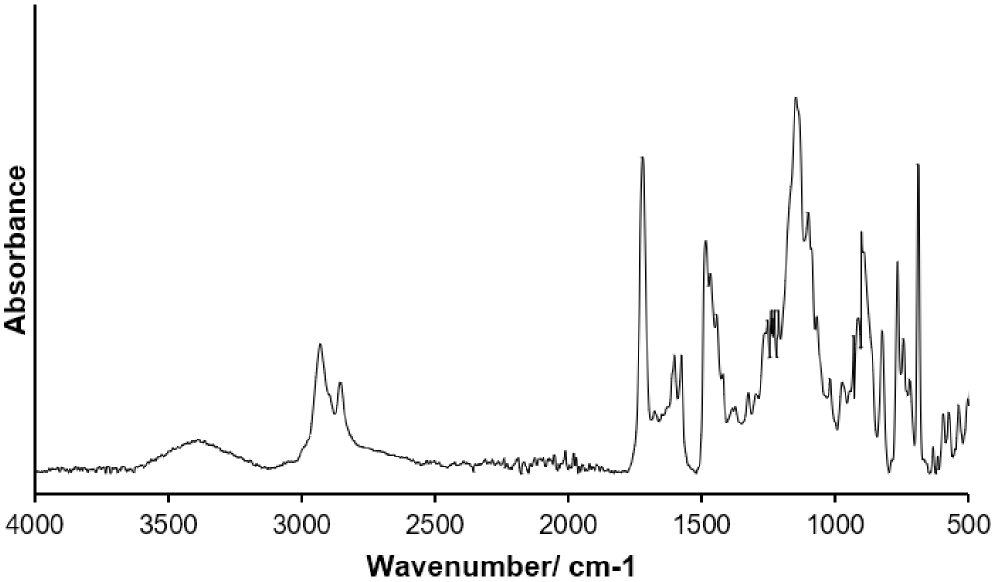
Appendix G : ^{1}H-NMR spectra of PA-Azo-C3-b-PMMA during UV exposure



^{1}H-NMR spectra of PA-Azo-C3-b-PMMA (a) before and after UV exposure for (b) 30 min, (c) 60 min, and (d) 90 min.

Appendix H : ^{1}H-NMR and FT-IR spectra of PA-Azo-C3-DIMER-b-PMMA





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2. Niyomsin, S., Hirai, T., Takahara, A., Chirachanchai, S. (2018). Incorporation of Benzoxazine Pendants in Polymer Chain: A Simple Approach to add-up Multi-responsive Functions, Macromolecular Chemistry and Physics, Volume XX, XX December 2018, Pages XXX-XXX. (accepted)
3. Niyomsin, S., Takata, T., Chirachanchai, S. (2019). Multi-responsive Rotaxane with Tunable Fluorescence under Azobenzene-based Benzoxazine Structure, Macromolecular Chemistry and Physics, Volume XX, XX December 2018, Pages XXX-XXX. (submitted)
4. Niyomsin, S., Chirachanchai, S. (2019). Dual-function Benzoxazines: Light Responsive and Photoluminescent properties via Simple Approach, Organic Letters, Volume XX, XX December 2018, Pages XXX-XXX. (to be submitted)

Presentations:

Poster Presentation

1. Niyomsin, S., Chirachanchai, S.*, “Benzoxazine-based Light and Metal Ion Responsiveness under Gel Network”, The 5th Polymer Conference of Thailand, Pathumwan Princess Hotel, Bangkok, 18th – 19th June 2015.
2. Niyomsin, S., Kotaki, M., Chirachanchai, S.*, “As-spun Fiber of Benzoxazine/SEBS for Optically Responsive Applications”, The 4th Polymer Conference of Thailand, Pathumwan Princess Hotel, Bangkok, 20th – 21st March 2014.
3. Niyomsin, S., Chirachanchai S.*, “Changing Benzoxazines to Optically Responsive Materials”, The 3rd Polymer Conference of Thailand, Pathumwan Princess Hotel, Bangkok, Thailand, March 28th – 29th, 2013.

Oral Presentation

1. Niyomsin, S., Hirai, T., Takahara, A., Chirachanchai, S.*, “Multi-responsive Copolymer through the Functions of Benzoxazine Dimer Pendants”, International Conference on Advanced and Applied Petroleum, Petrochemicals, and Polymers 2018 (ICAPPP 2018), Chulalongkorn Main Auditorium and Maha Chulalongkorn Building, Bangkok, 18th – 20th December 2018.
2. Niyomsin, S., Chirachanchai, S.*, “Multi-responsive Molecule Based on Benzoxazine Dimers having Rotaxane System”, The 6th Polymer Conference of Thailand, Pathumwan Princess Hotel, Bangkok, 30th June – 1st July 2016.
3. Niyomsin, S., Kotaki, M., Chirachanchai, S. “Optically Responsive Benzoxazine/SEBS Electrospun Fiber”. IUPAC World Polymer Congress (Macro 2014), Chiangmai, Thailand, July 6th -11th, 2014.
4. Niyomsin, S., Chirachanchai, S., “Optically Responsive Benzoxazine”. 246th ACS National Meeting & Exposition, Indiana, USA, September 8th –12th September 2013.