Synthesis and Application of PPE-Based Fluorescence Chemosensor

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Summary

The design of chemosensors has attracted many interests in the past few years because of their highly specific for the detection of biologically relevant cations, such as Na^+, K^+, Mg^{2+}, and Ca^{2+}. However, how to enhance the selectivity toward the specific cation in the present of other ions is still a challenge part for the metal ion detector. For example, with the presence of Na^+, K^+, and Mg^{2+} ions, Ca^{2+} ions is hardly separated. It is well-known that, when disturbing with alkaline or alkaline-earth metal ions, the combination of crown-ether and organic chromophores shows distinctive signals variation at its optical properties. This phenomenon makes the crown-ether as a good sensor precursor toward series of metal ions. Even though a variety of crown-ether and related macrocycle-based chemosensors are well developed, the corresponding acyclic- polyether-(podand)-based sensors are rarely studied. In most of the acyclic- polyether-(podand)-based sensors systems, the binding of the sensor with a metal ion can show an amplified signal through a charge-transfer either an electron-transfer or an energy-transfer process. In this thesis we demonstrate a novel design of highly specific Ca^{2+} ion sensor. This new foldamer structure, which is in the conformation of a rigid-flexible-rigid bichromophore, is explored by introducing metal-ion into the sensor. And the prominent differences of optical properties also can be identified by signals shifting or quenching in fluorescence.

In this thesis, the novel fluorescence chemosensors consisting of alternating oligo(*p*-phenyleneethynylene) chromophores and flexible oligo(ethylene oxide) segments were obtained. Their solvent-induced and cation-induced aggregation behavior was established by optical and ^1H NMR spectroscopic studies. Selective fluorescence quenching by Ca^{2+} was achieved in a solution of a polymer with a backbone of tetra(*p*-phenyleneethynylene) and penta(ethylene-oxide) in alternation. In addition, the conformational preference of a representative polymer in solid state was investigated by atomic force microscopy (AFM) images.

Synthesis and Application Studies of Fluorescence Chemosensor Based on PPE

Chapter 1 Introduction

Recently in the field of supramolecular host-guest chemistry and molecular recognition, fluorescence chemosensor with properties of molecular device has been rapidly developed at the new frontier of science.[1-4] Its emergence closely relates to development of supramolecular science, such as molecular assemble, host-guest chemistry, non covalent bond interaction, as well as structural and luminescent properties of intramolecular conjugated electron-transfer compounds. On the other hand, its development also closely relates to many practical problems, coming from many scientific and technical fields, e.g. chemistry, biology, medicine and environmental science. As such many significant and extensive applications, we should notice that research in fluorescence chemosensor is a rising field with many undiscovered properties..

1.1. Fluorescence Chemosensor

As chemosensors exhibit various signal transduction systems (optical, electrochemical, etc.), fluorescence has became one of the most useful response systems for optical readout. Among the different chemical sensors, fluorescence-based sensors present many advantages. For example, their fluorescence measurements are usually very sensitive, low cost, easily performed and versatile.[6]

1.1.1. Configuration & Principal Mechanism of Fluorescence Chemosensor

Chemosensor is usually composed of two basic parts: a receptor unit or an ionophore and a signaling unit.[7] The function of receptor unit captures specific species, while signaling unit releases a signal to indicate that the alien species have been captured. The design of fluorescence chemical sensors is based on the mechanism of host-guest interaction. Its characteristic is that host units with structure of cavum as receptor unit for alien species are able to interact with guest unites to form host-guest complex by specificity interaction. Thereby it presents good selectivity towards guest molecule. The recognize system of chemosensor connects certain chemical parameter (usually concentration) of analytes with signaling unit together. After received signal from receptor unit, signal unit transfer the signals to electronic system in the form of voltage, electricity or light. Through electrode, fiber or mass-sensitive device to amplify or switch output, ultimately, the response signal from recognize system is convert to available analytical signal and the quantity of analyte in sample is determined.

In photochemistry sensor research field, the equilibrium constant for a complex formation between sensitive carrier and recognized molecule decides the sensitivity and reversibility of sensor. When sensitive carriers respond to target molecule and produce response signal, the response sensitivity is related to the following chemical equilibrium:

$$K_{eq} = \frac{[\text{Host-guest Complex}]}{[\text{Dissociative Host}][\text{Dissociative Guest}]}$$

In this equation, K_{eq} is the equilibrium constant for a complex formation. With the constant concentration of analyzed target (dissociate guest) in solution, the sensitivity of sensor system highly depends on the concentration of host-guest complex. Usually K_{eq} is increased to enhance sensitivity of sensor through choosing diverse chemical recognize carrier or change effective condition in system. However, it may cause the low speed of reversible response, sometimes even unreversible response.[8, 9] Therefore, how to effectively enhance the sensitivity of sensor and barely affect on reversibility become a big challenge to the traditional sensory mode.

In the 1990's, professor Timothy M. Swager (head of chemistry department, Massachusetts Institute of Technology, USA) proposed a novel principle of responding and amplifying signal, called "molecular wires". His group connected single sensitive carrier to a compositive and interactive molecular wires by chemical conjugated bond, which can amplify chemosensory signals by many orders of magnitude without increment of equilibrium constant for a complex formation.[11, 12] Their sensor principles are now extensively practiced by many research groups around the world and become the basis of a number of emerging sensor technologies. None the less there are still many basic scientific principles to be determined.

1.1.2. The Response Amplify System of Conjugated Polymer

In our knowledge, plastic is a good insulator. Otherwise, we should not use it as insulation in electric wires. But now the time has come when we have to change our views. Plastic can indeed be made to behave very like a metal under certain circumstances. In the past two decades, many interests were attracted on conductive properties of conjugated polymers. A great effort has been devoted to the design and synthesis of diverse conjugated polymer with the structure of π-electron delocalization, which possess excellent performance in electrics, magnetics and optics. The Royal Swedish Academy of Science has announced the 2000 Noble Prize in chemistry, was awarded jointly to Professor (Emeritus) Hideki Shirakawa (Institute of Materials Science, University of Tsukuba, Japan), Professor Alan J. Heeger (University of California at Santa Barbara, USA) and Professor Alan G. MacDiarmid (University of Pennsylvania, USA) for their revolutionary discovery and development of conductive polymers.

1.1.2.1. Structure and Bandgap of Conjugated Polymers

Conjugated polymers are the fundamental materials of molecular wires which can act as a conduit to transfer electrons between sites in a truly molecular electronic device. The essential structural characteristic of all conjugated polymers is their quasi-infinite π-system extending over a large number of recurring monomer units (see table 1.1). Although the chemical structures of these materials are represented by alternating single and double bonds, in reality, the electrons that constitute the π-bonds are delocalized over the entire molecule, hence also known as delocalized electron polymers or conjugated polymer.

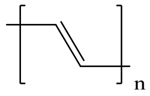
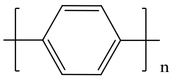
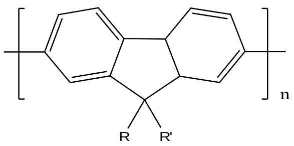
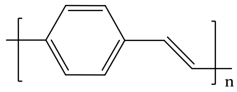
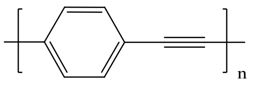
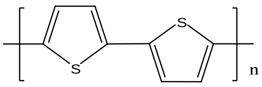
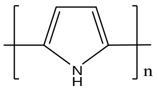
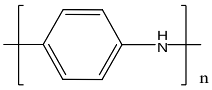
Polymer	**Chemical Name**	**Formula**	**Bandgap （eV）**	**Absorb wavelength （nm）**
PA	Trans-polyacetylene		1.5	825
PPP	Poly(p-phenylene)		3.3	410
PF	Polyfluorene		3.2	390
PPV	Poly(p-phenylenevinylene)		2.5	495
PPE	Poly(p-phenyleneethylene)		2.8	400
PT	Polythiophene		2.0	620
PPy	Polypyrrole		3.1	400
PANi	Polyaniline		3.2	390

Table 1.1 Some common conjugated polymers[13]

Polyacetylene (PA) is one of the simplest conjugated polymers and has served as the prototypical conjugated polymer. Poly(*p*-phenylene) (PPP), as well as its derivatives, are important materials due to their electrical conductivity after doping, whereas pure PPP is a good insulator. On the other hand, PPP is well blue light-emitting organic electroluminescent materials for their good thermal stability and excellent quantum efficiency in blue light wave band.[14] Polythiophene (PT), Polypyrrole(PPy) and its derivatives have also been attracted much interest in the field of polyconjugated organic polymers. In these molecules, the *p* orbit offered by atom N and S connect individual conjugated section together which makes continuity of overlap orbit. Compared with PA, PT and PPy are more stable in the ambience and possess diversity of structure. Polyfluorene (PF) has also been studied extensively as a new blue light electroluminescent material in recent years. PF polymerized by biphenyl joint in site 9 has good thermal stability and high fluorescence efficiency.

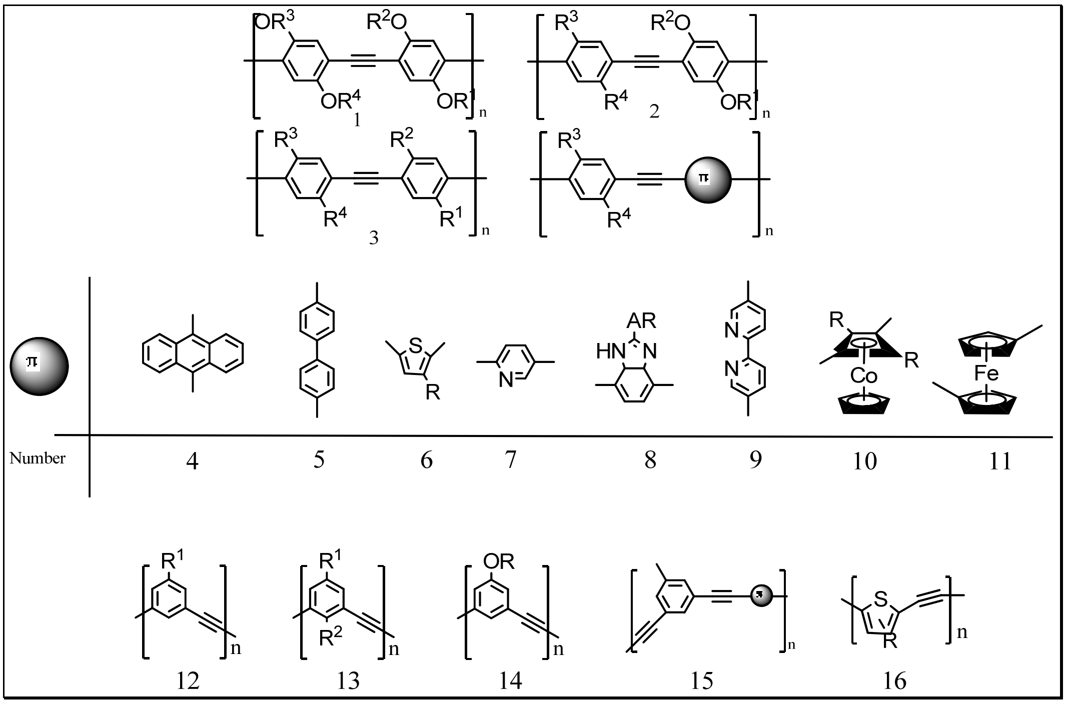


Figure 1.1 Some common compounds with PPE structure

Among the conjugated polymers, poly(*p*-phenylenevinylene) (PPV) has been studied and applied initially as electroluminescent materials. It has high photoluminescent efficiency in both solid and liquid states due to its linear and rigid backbone structure.[2,10,15] However, poly(phenylene-ethynylene) (PPE; see Figure 1.1), which shows similar structure to PPV, has attracted much less attention in the polymer community in spite of their fascinating properties. Recently the groups of Swager,[16] Müllen[17] and Weder[18,19] demonstrated that PPE with their unique property profile are fantastic materials in many different areas as explosive detection, molecular wires and chemosensors. Figure 1.1 shows the common types of poly(aryleneethynylene)s (PAEs).

1.1.2.2. The Signal Amplification Principle of Conjugated Polymers

The main feature of the above conjugated polymer is existence of long-range conjugated π-bond. The cloudy π-electron has mobility along the whole conjugated chain. The long-range conjugated π-electron not only reduces the bandgap between bonding orbital and antibonding orbital, but also makes two bands broader. Meanwhile, it increases more inner band orbitals. Consequently, the bandgaps among the inner band orbitals are also reduced. The bandgap between bonding and antibonding in π-conjugated system is quite small, usually 1.5-3eV, which is close to the bandgap between conduction band and valence band in inorganic semiconductor system (bonding band and antibonding band are also called the conduction band and valence band respectively). Therefore, most of conjugated polymers exhibit properties of semiconductor. And their conductivity is around 10^{-12}—10^{-4}S/cm.

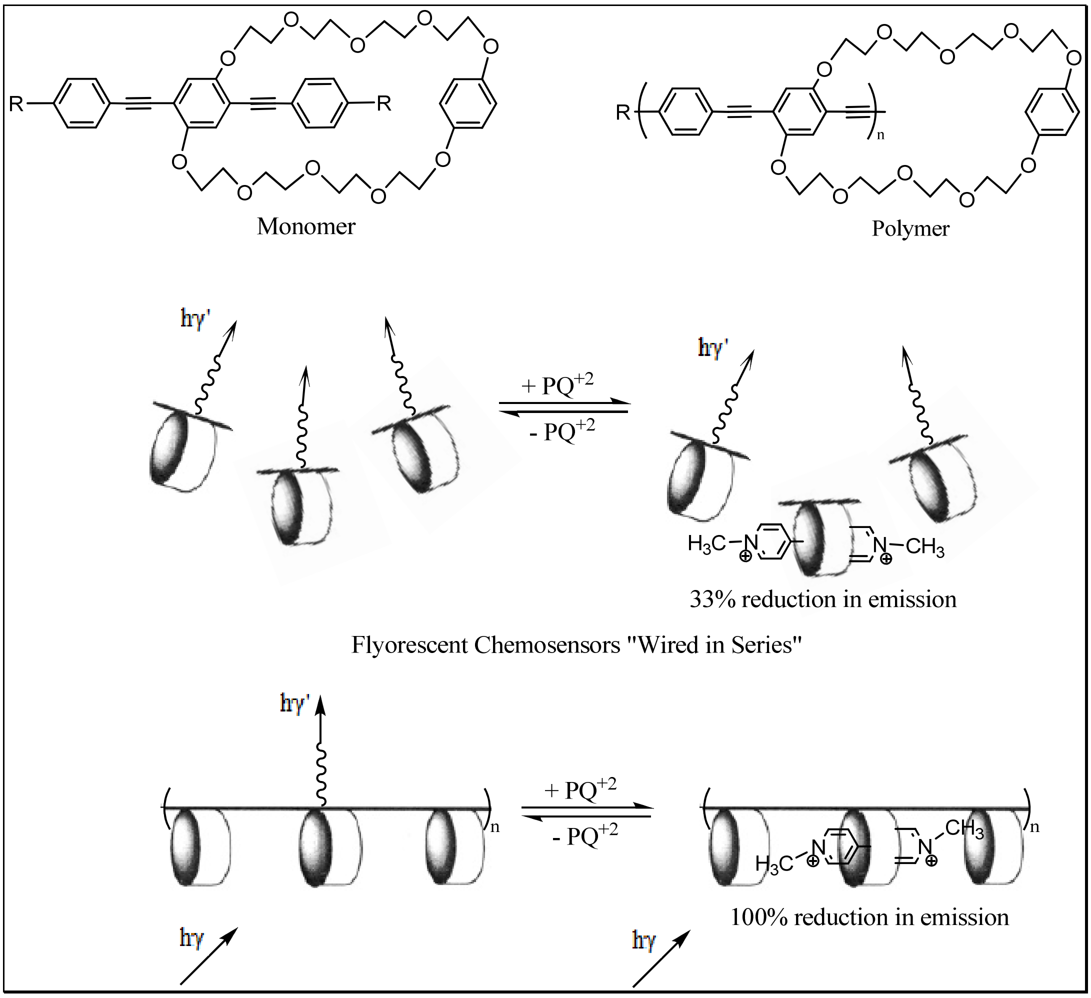


Figure 1.2 The signal amplification of conjugated polymers

Through absorption of photon or chemical doping, electron can easily transfer from bonding band to antibonding band. The doping can increases the conductivity of polymers by many orders of magnitude, which could be very close to the conductivity of metal. Due to their unique structures, conjugated polymers exhibit many excellent photoelectric properties. Thereby, conjugated polymers can be applied extensively in conductive materials,[26,27] lighting emitting devices (LEDS),[28] chemosensor,[29] photoelectric chemistry, secondary battery[30] and other photoelectric devices.

Muti-fluorophore with same special selectivity can be connected together through

π-electron system, which indicates it forms conjugated polymer with special structure (see Figure 1.2).[31] Each neighboring fluorophore becomes an interactive integrity through conjugated π-electron. When one of fluorophore has interaction with analyte, the whole joint system will show homologous response. The receptor behavior of single fluorophore influences on the photoelectric properties of multiple joint fluorophores. Compared with separated fluorophore, the conjugated polymers with joint fluorophores structures present amplificatory signals. Taking the fluorescence quenching in Figure 1.2 for example, three monomers produce fluorescence in excited states. When any one of them bond with quencher, only one third of fluorescence will be quenched effectively in whole system. However, when the monomers are linked together to form molecular wire polymers by conjugated bond, the polymer chains absorb photons (hv) from excited wave to generate exciton or equal carrier which of them can transfer along whole conjugated system. In the absence of quencher, exciton has a radiative combination and emits photo to generate fluorescence (hv'). However, according to the signal amplification chemosensor theory based on new molecular wire carrier and its application research, when exciton (or carrier) encounters quencher binding with any fluorophore in transportation, the electron excited to conductive band and begin to transfer. Electron transfers from polymer to quencher, and then opposite electron migrates to polymer. The result shows that transportation of exciton or carrier along conjugated chain is blocked and molecular in excited states are effectively deactive, finally, which terminates the emitting of photo in the entire polymer chain. It presents the fluorescence from all fluorophores are effectively quenched and achieves amplification of responding signal. Conjugated polymers, which show collective respond property, create a new prospect for research and design of high sensitive and reversible sensor.

1.1.2.3. The Common Synthetic Methods of Poly(*p*-phenyleneethylene) (PPE)

The synthesis of cycles and linear polymers with PAE structure refers to forming C-C single bond between phenyl and alkyne as well as alkyne and alkyne. The coupling reaction between phenyl and alkyne usually occur in Pd/Cu-catalyzed Sonogashira coupling reaction,[25] Mortreux-Mori alkyne bond exchange reaction[26] and Pd/Cu-catalyzed Stephens-Castro coupling reaction.[27] Next, the generally accepted mechanism and application of Sonogashirac coupling reaction will be discussed.

The Pd-catalyzed coupling of terminal alkynes to aromatic bromides or iodides in amine solvents has been known since 1975. It is called Heck-Cassar-Sonogashira-Hagihara coupling reaction[25] which is probably one of the most frequently used C-C bonds forming process in organic chemistry. This kind of coupling reaction forms C-C single bonds between sp- and sp2-hybridized carbon centers. The generally accepted mechanism of this reaction is depicted in Figure 1.3.

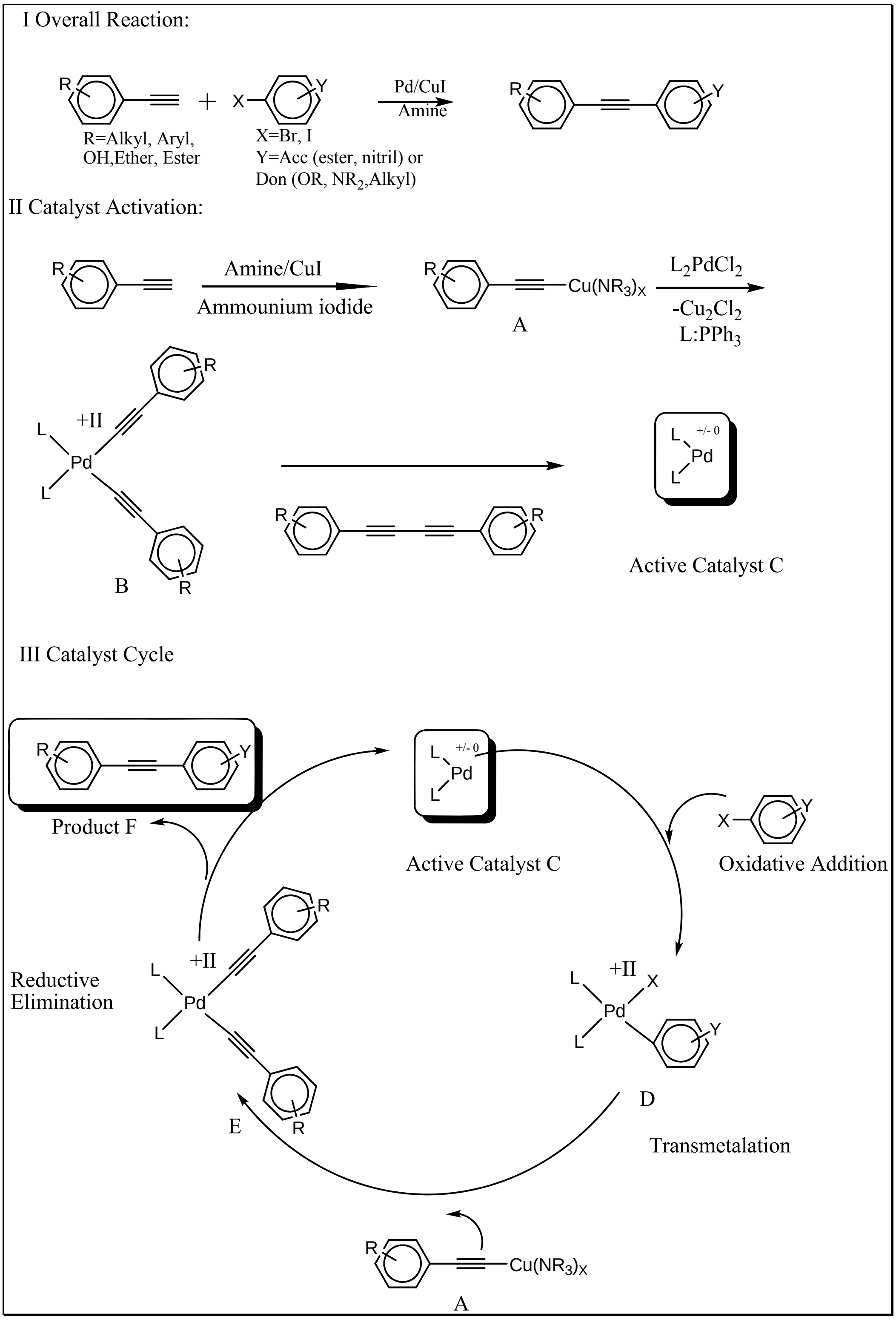


Figure 1.3[24] The mechanism of Sonogashira coupling reaction

In most cases, the commercially available $(Ph_3P)_2PdCl_2$ is the catalytic source of

Pd. This catalyst in its oxidized form is inactive. In the first step (scheme I) two molecular of a cuprated alkyne, A, transmetalate the Pd catalyst precursor and form B. B is not stable under the reaction condition but reductively eliminates a symmetrical butadiyne and creates the active catalyst C. In an oxidative addition the aromatic bromide or iodine forms the intermediate D, which after transmetalation with A leads to the diorgano-Pd species E. This species undergoes reductive elimination to the product and re-forms the active catalyst C.

1.1.2.4. Characterization of Fluorescence

Among the different chemosensors, fluorescence-based ones present many advantages: high sensitivity on fluorescence measurements (even single molecule detection is possible, although only under special conditions), low cost, easy implementation, versatile, offering subnanometer spatial resolution with submicron visualisation and submillisecond temporal resolution. The versatility of fluorescence-based sensors originates from the wide number of parameters that can be tuned in order to optimize the convenient signal. In most cases, the change of luminescence intensity represents the most directly detectable response to target recognition. However, other properties such as excited state lifetime and fluorescence anisotropy have also been preferred as diagnostic parameters, since they are less affected by the environmental and experimental conditions.[6]

1.1.2.5. Application of Conjugated Polymer in Fluorescence Chemosensor

The utility of conjugated polymers for fluorescence-based sensing was first demonstrated by Zhou and Swager.[11,12] They found that the act of “wiring receptors in series” creates superior sensitivity over a small molecule indicator. An obvious amplification singal could be observed, because the delocalized electronic structure of conjugated polymer (i.e., energy bands) facilitated efficient energy migration over large distances. Many studies have been done to demonstrate this principle. For example, the monomer and polymer were chosen as receptor to bind with paraquat and related compounds. Both of them displayed effectively fluorescence quenching. Compared with monomer, however, polymer exhibited a greatly enhanced sensitivity in the binding of the paraquat by the cyclophane to form a rotaxane complex.

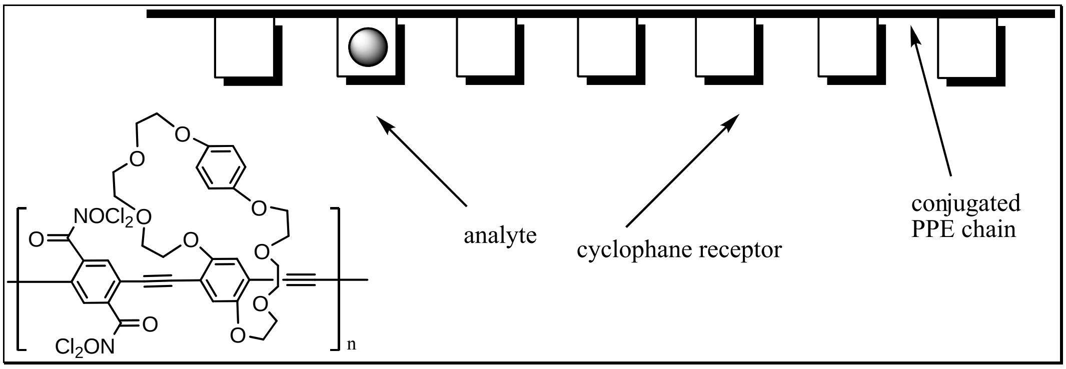


Figure 1.4 Application of PPE as sensor

The original proposal of this effect is facile energy migration along the polymer backbone to the occupied receptor sites (Figure 1.4). In this figure, the signal is amplified due to the fact that the polymer need only have a small fraction of receptor sites occupied to affect complete quenching.

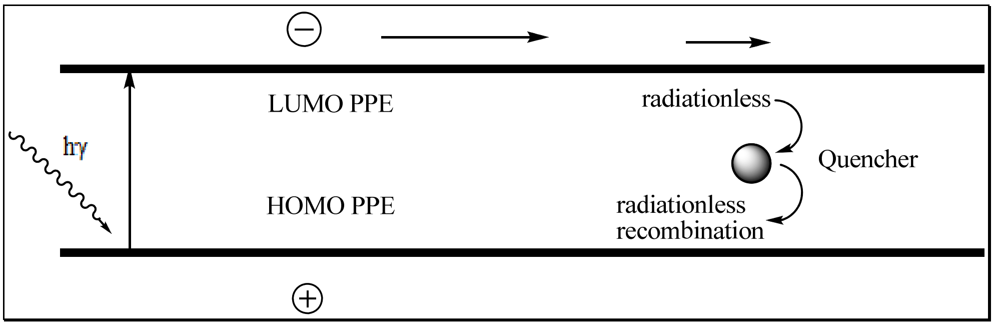


Figure 1.5 Electric bandgap structure of PPE

The exciton produced by radiation can be delocalized extensively along the whole polymer chain. When binding analytes happened, these excitons transfer from HUMO (Highest Occupied Molecular Orbital) of polymer to LUMO (Lowest Unoccupied Molecular Orbital) of paraquat, while simultaneity the opposite electrons transfer to polymer. As a result, the polymer's fluorescence is quenching effectively (Figure 1.5).In contrast with a monomeric indicator, every receptor must be occupied for complete quenching. Swager[12] demonstrated that the effect was molecular weight dependent and at low to intermediate degrees of polymerization, the signal amplification increased with molecular weight. Once the molecular weight exceeded the average diffusion length of the excitation (ca. Mn =100 000), the effect was independent of molecular weight.

Subsequent studies,[34] on thin films of PPE with cyclophane structure prepared by Langmuir-Blodgett deposition, revealed a very high rate of energy transport between polymer layers ($k=10^{11}$ s^{-1}) and an average exciton diffusion length that is greater than 100 Å.

The signal amplification resulting from energy migration in conjugated polymers was applied in 1998 by Yang and Swager for the detection of explosives, specifically 2, 4, 6-trinitrotoluene (TNT) and 2, 4-dinitrotoluene (DNT)[16, 35]. The impetus for developing such a system is the fact that there are roughly 120 million unexploded land mines worldwide and current methods of detection are limited. The challenge is to detect minute amounts of explosives leached from the land mines. These studies extended the methods reported by Zhou and Swager[11] on isolated molecules in solution to thin film structures. The energy migration-based amplification is much greater in thin films, which display two- or three-dimensional structures, as compared with what is found in one-dimensional systems (i.e., isolated polymers in solution). This effect is due to that in one dimension a random walk of excitations necessarily revisits the same receptor sites multiple times. The amplification is increased by the excitation sampling the greatest number of potential analyte binding sites. Hence, a three-dimensional topology, wherein it is improbable that an exciton will visit the same site multiple times, is superior.

To facilitate binding of TNT and DNT, as well as create a stable emissive thin film of a poly- (phenyleneethynylene), Yang and Swager[16, 35] developed a series of porous polymers utilizing a rigid shapepersistent iptycene scaffold (Figure 1.6). The porous structure served to prevent direct interactions between the polymer backbones (chromophores), which generally lead to quenching, and to create a structure that behaves as a “sponge” for electron-poor π-electron accepting analytes.

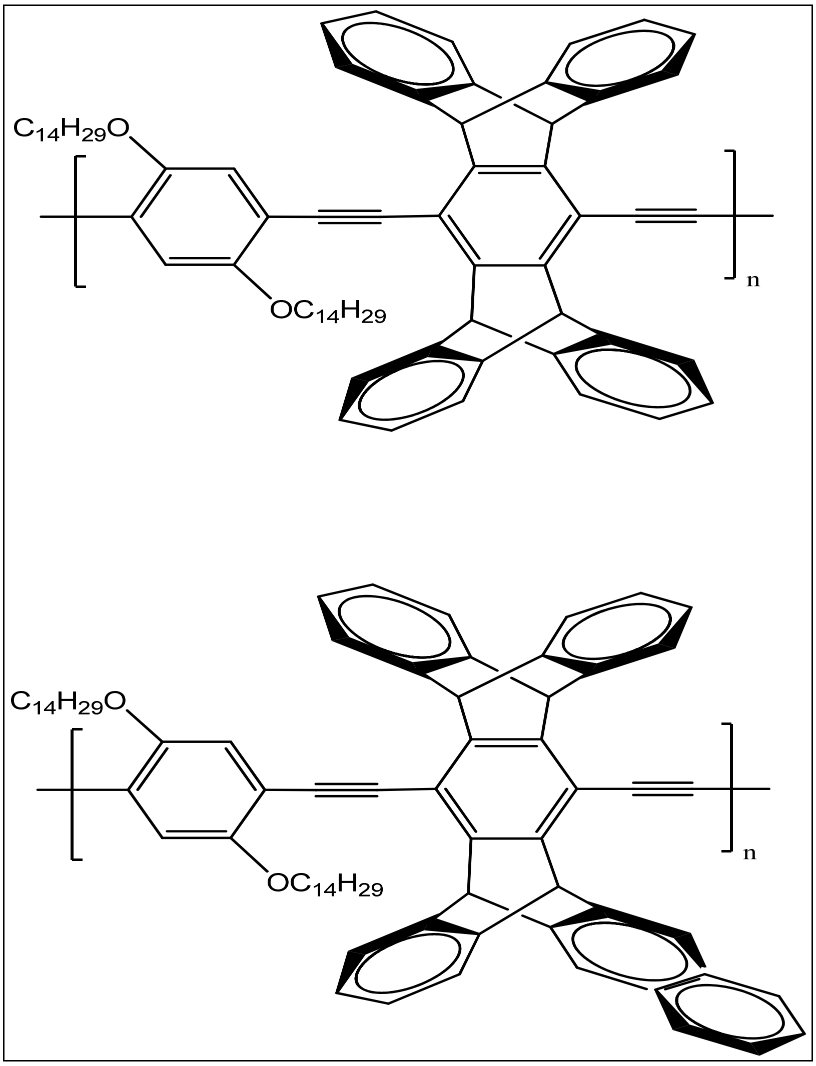


Figure 1.6 Porous conjugated polymers

1.1.3. The Signal Recognition System of Fluorescence Chemosensor

Based on host-guest interaction, the preparation of signal recognition system of sensor is quite important in research on chemosensor. The characterization of these fluorescence chemsonsor is that host molecular with cavum as receptor recognizes alien species. It is the specific binding of a guest molecule to a complementary host molecule. The molecules are able to identify each other using noncovalent interactions, such as hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π-π interactions, and/or electrostatic effects. One of the key applications of this field is the construction of molecular sensors.

In 1967, C.J.Pederson described the methods of synthesizing crown ethers (cyclic polyethers).[36] The donut-shaped molecules were the first in a series of extraordinary compounds that form stable structures with alkali metal ions. Cram expanded upon Charles Pedersen's ground-breaking synthesis of crown ethers, basically two-dimensional organic compounds that are able to recognize and selectively combine with the ions of certain metal elements. Cram synthesized molecules that took this chemistry into three dimensions, creating an array of differently shaped molecules that could interact selectively with other chemicals because of their complementary three-dimensional structures.[37] His work represented a large step toward the synthesis of functional laboratory-made mimics of enzymes and other natural molecules whose special chemical behavior is due to their characteristic structure. Later Jean-Marie Lehn achieved the synthesis of cage-like molecules, comprising a cavity inside which another molecule could be lodged. Organic chemistry enabled him to engineer cages with the desired shape, thus only allowing a certain type of molecule to lodge itself in the cage. This was the premise for an entire new field in chemistry, sensors. Such mechanisms also play a great role in molecular biology.

The importance of supramolecular chemistry was recognized by the 1987 Nobel Prize for Chemistry which was awarded to Donald J. Cram, Jean-Marie Lehn, Charles

J. Pedersen in recognition of their work in this area. The development of selective "host-guest" complexes in particular, in which a host molecule recognizes and selectively binds a certain guest, was cited as an important contribution.

In host-guest chemistry, typical of the host compounds are crown ether, cyclodextrin and calixarene. These compounds have macrocycle structure. The different compound has different space in the host lattice. Hence, design of chemosensor could base on that these molecules with different hosts which exhibit different selectivity towards other guest molecules. It is important role of choosing proper host molecule and fluorophore according to structure character of determining matter to design fluorescence chemosensor with excellent performance.

Since 1967 Pedersen[36] first reported unique selectivity ability of crown ethers for alkaline metal and alkaline earth metal ion, macrocycles crown ethers have been made distinctive progress in its theory, synthesis and application. Their research area involves chemistry, biology, atomic energy, agriculture and other related disciplines. However, crown ethers may be bioavailable and can cause adverse effects in living organisms. Furthermore, the synthesis of classical crown ethers involves many steps, therefore these compounds are often quite expensive. All of these reasons limit its research and application. In the 1970s, after developed on amide and ether based pseudocrown ether sequent, Simon and Vogelt[54, 55] innovated a new research filed in organic chemistry, pseudocrown ether. Past over thirty yeas the great progress have been made in this field and more than increasing one hundred of pseudocrown ethers have been synthesized

Pseudocrown ethers are cheap because the starting materials are common, inexpensive. And the synthesis is relatively simple, requiring only a few steps. Pseudocrown ethers are nontoxic because these systems are polymeric and therefore nonbioavailable.[53] Thus, pseudocrown ethers are promising sensors instead of traditional crown ethers. Pseudocrown ethers are chain compound with repeat units, poly (ethylene oxide) (-CH_2CH_2O-). The binding characteristics of classical and pseudocrown ethers to metal ions are similar because the basic structure of the crown is nearly the same. End-group concept proposed by Vogetle[56] is significant in guidance of molecular design. Owing to they are flexible ligand, pseudocrown ethers can effectively change their coordinate reactivity and coordinate selectivity through altering their end-group's structures and species, so called "end-group effect". Pseudocrown ethers possess well coordinate selectivity for metal ion, because their self present different extent of flexibility responding to different metal ions. Their flexible extent not only depends on the structures and species of end group, but also depends on amount of repeat units ethylene oxide and the combinative mode between end group and poly (ethylene oxide) chain.

In recent years, either various function groups have been subtly induced to configuration of pseudocrown ethers through different chemical reaction or the location of poly (ethylene oxide) has been changed, by which a lot of novel psedudocrown ethers have been synthesized (Figure 1.7). In term of combinative mode between end group and poly (ethylene oxide) chain, pseudocrown ethers are divided into the several following types, amide type(1), ether type(2), ester type(3), ether ketone type(4), dihydroxy-benzene type(5), biphenol type (6), quinine ether type(7), schiff base type(8), squaric acid type(9), pheno-ether type(10) and tetrathiafulvalene type(11).

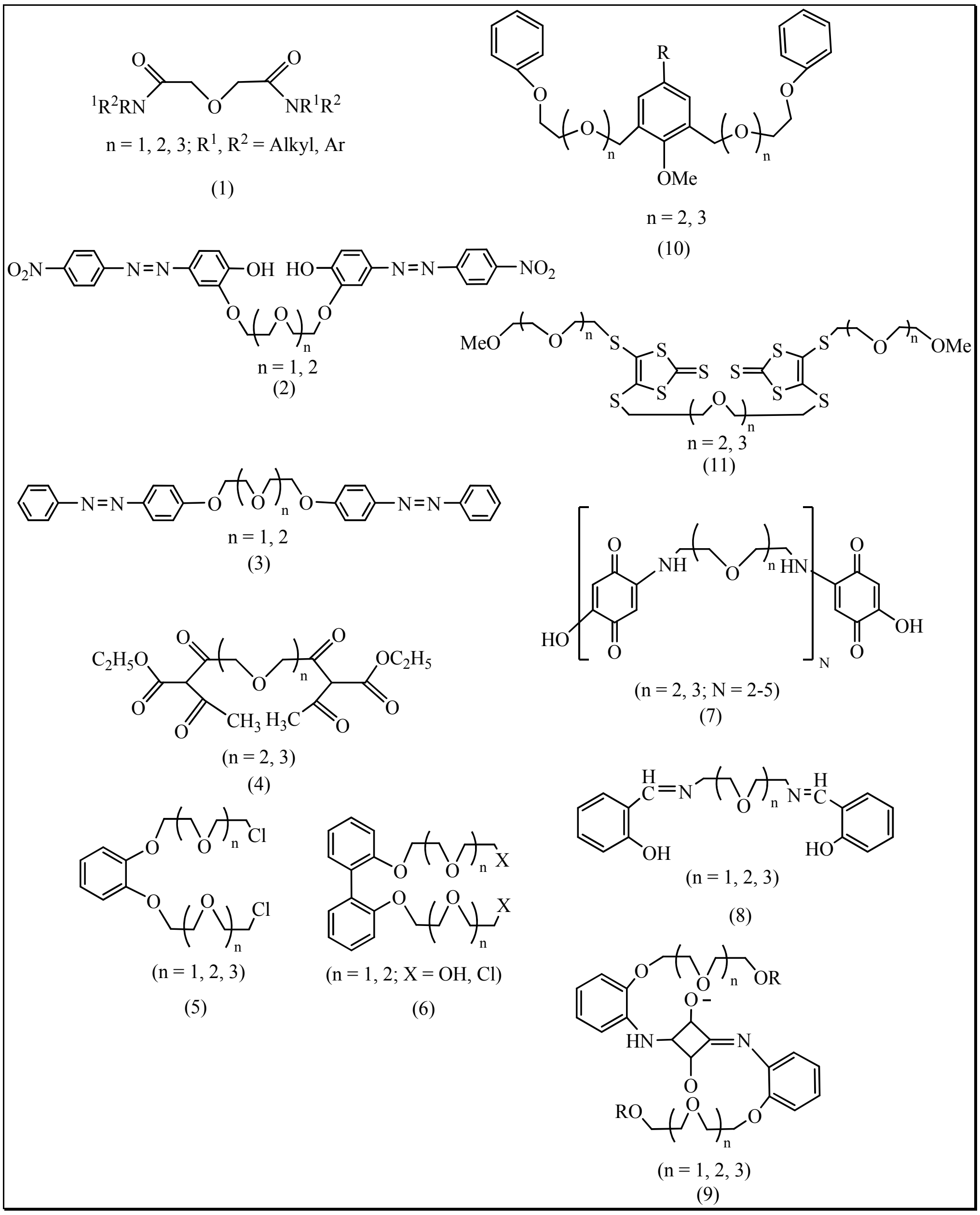


Figure 1.7 Various kinds of pseudocrown ethers

Compared with crown ethers, pseudocrown ethers not only retain excellent coordinate selectivity abilty for metal ion, and also have simple synthesis, high yield, low cost, low toxic or nontoxic and other advantages. Pseudocrown ethers present the promising prospect of application, because they display outstanding performance in metal enrichment, extraction separation, chemosensor, organic chemistry, analytical chemistry, biochemistry and agriculture.

1.2. Study on Self-assembly Behavior of Well Organized π-Conjugated Polymer

As organic functional materials, the π-conjugated polymer can apply in organic electrooptical devices, such as solar cells,[57] light emitting diodes (LEDs),[58] field effect transistors (FETs)[59,60] and chemosensors.[61] The research on their nanoscopic and mesoscopic also show a growing interest because the micro-structure of well organized π-conjugated polymer is important in above fields. Their precise chemical structure and conjugation length make that their self-assembly behavior can be easily controlled, consequently, they presents special functional properties.[62]

1.2.1. Current Status and Prospects of Studies

Block copolymers reveal a wide variety of phases. Therefore, they appear to be ideal candidates for the development of new functional materials. Recently block copolymers consisting of flexible and rodlike blocks have attracted much attention. Rod chain and soft chain in the same system show distinctive properties and typical self unique self-assembly behavior. First, the property of rod parts tending to regular arrangement makes their phase separation behavior complex. Second, the rigid parts formed by aggregation of rod chain are also in favor of their self-assembly behavior. Third, compared with soft-soft block polymers, rod-soft block polymers give rise to Flory-Huggins χ-parameters larger. Hence, rod-soft oligomers with low molecular weight also show certain phase separation property to accomplish self-assembly.

Molecular self-assembly is a key concept in supramolecular chemistry since assembly of the molecules is directed through noncovalent interactions, such as hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π-π interactions, and/or electrostatic effects.[63] Using polymer chain to construct self-assembly nanostructured materials has become current one of the utmost importance topic. The novel functional nanomaterials by self-assembly has developed in many fields.[64] In self-assembly polymer, it is focused on their behavior in dilute solution.

The polymer's conformation has great influence on their luminescence properties, especially for concentration quenching and aggregation. The primary measure to solve these problems is the impactful control of their microstructure. One of solutions is adding flexible chain to form rod-coil block polymer. Organized one, two or three-dimensional conformation by self-assembly can effectively adjust conjugated polymer's luminescence properties. Many groups have reported extraordinary work in self-assembly of rod-coil block polymers.

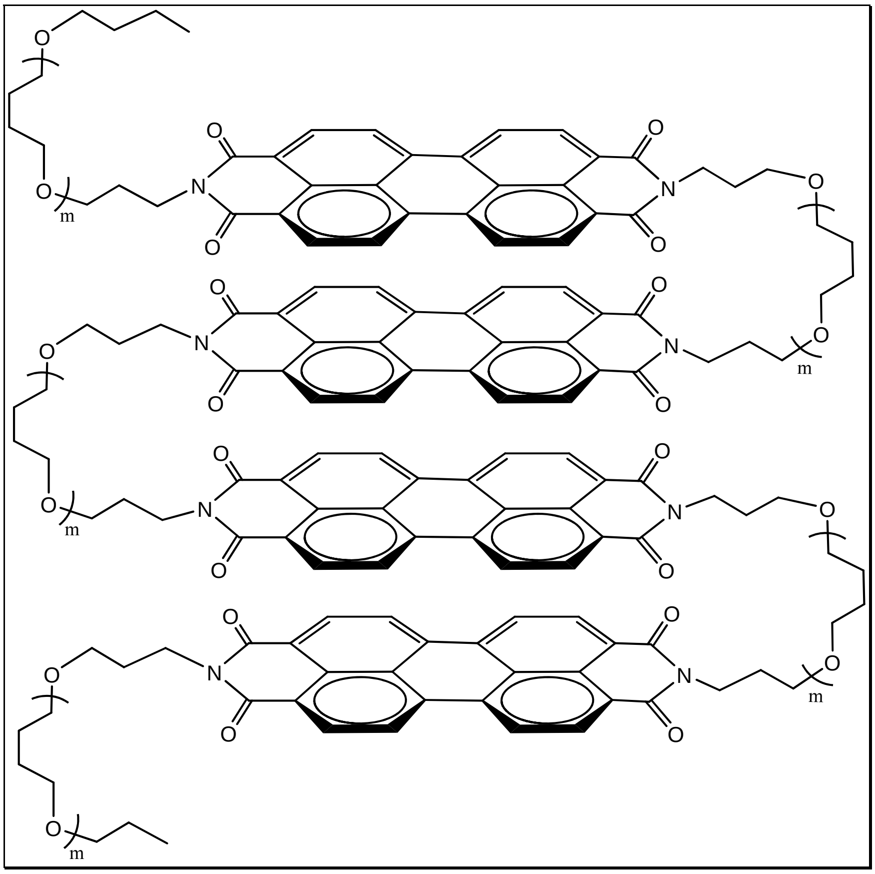


Figure 1.8 The structure of alternating Perylene Bisimide–PolyTHF

Edda[65] investigated the absorption and fluorescent properties of three alternating copolymers, which is consisting of polyTHF segments of different length (3, 14, 33 repeat units respectively) and perylene bisimides. In o-dichlorobenzene, the chromophores self organize to form H-like aggregates (see Figure 1.8). These polymers self organize in solution via π-π stacking of the chromophores. UV-vis absorption and fluorescence studies revealed that the extent of π-π stacking in o-dichlorobenzene (ODCB) decreased with increasing temperature and increasing length of the polyTHF segment. Originated mainly from nonaggregated monomeric perylene bisimides, the fluorescence quantum yield of the self-organized phase was also strongly decreased quenched

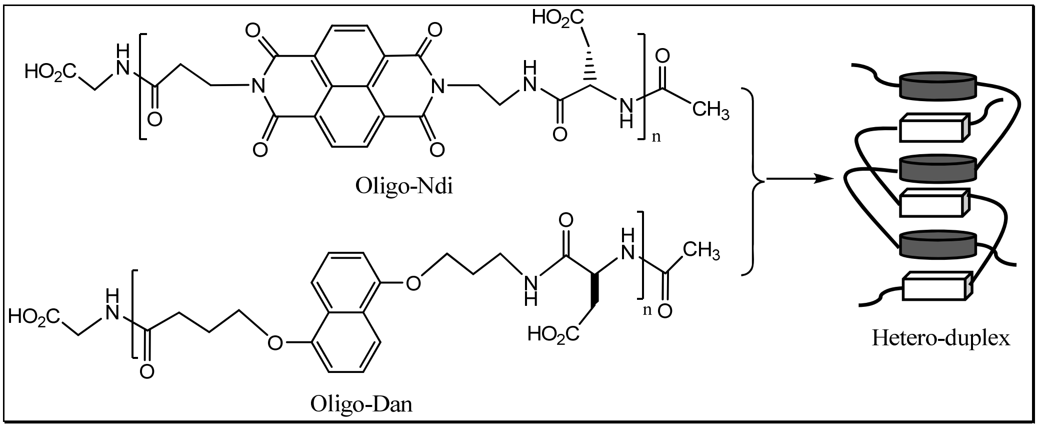


Figure 1.9 Hetero-duplex structures

Iverson group[66] explored this aromatic-aromatic interaction in an intermolecular format to create a first-generation hetero-duplex system that self-assembles in water. Oligomers of alternating electron-rich 1,5-dialkoxy-naphthalene (Dan) and electron-deficient 1,4,5,8-naphthalene-tetracarboxylic diimide (Ndi) units (see Figure 1.9), termed aedamers, were among the first foldamers to demonstrate folding in aqueous solution. For stacking of aromatic units in aqueous solution, desolvation of stacked structures (i.e., the hydrophobic effect) is important. Electrostatic interactions make significant contributions as well. For this system, desolvation of the aromatic surfaces provides the dominant driving force for complexation. However, the strength of the interaction seems to be modulated by the geometry of the stacked structure which, in turn, is dictated by electrostatic complementarity. Simply put, the complex between the relatively electron-deficient Ndi and relatively electron-rich Dan units exhibits stacking in an electrostatically preferred face-centered geometry allowing for maximum desolvation of the aromatic surfaces in water.

Suhrit Ghosh[67] reported synthesized polymers containing alternating electron-rich and electron-deficient aromatic units above mentioned in single polymer chain. He demonstrated that by proper design, flexible synthetic macromolecules can be made to fold under the influence of relatively weak intrachain intersegment interactions, such as charge-transfer complex formation, assistance in tandem by solvophobic effects and metal-ion complexation. The formation of intrachain charge-transfer complex between the adjacent donor and acceptor units not only provides the driving force for the formation of the anticipated folded structure but also serves as a spectroscopic probe to examine the formation of such a structure.

1.2.2. The Research Significance of Self-assembly Behavior

Until recently research in this field has been focused mainly on methodologies for the synthesis and characterization of π-conjugated oligomers with long axis dimensions up to 10 nm.[68-70] Another major issue, which attracts increasing attention, is the control of the spatial orientation and packing of oligomers through the design of molecular and supramolecular architectures. The control of molecular assembly to give well-defined structures on the nanoscale can be carried out via different complementary approaches: (i) Self-assembly can take place in solution; the details of the aggregation behavior are governed by parameters such as the substitution on the conjugated backbone, the nature of the solvent, or the temperature. (ii) Because conjugated oligomers can be sublimed, it is also possible to follow their assembly as they form thin deposits on surfaces from individual molecules in the vapor phase; in that case, interactions with a solvent are absent and the driving forces controlling the aggregation are the intermolecular interactions between the conjugated species and the substrate surface. (iii) Another possibility is to generate thin deposits from conjugated compounds molecularly dispersed in a solution; aggregation takes place during the deposition and then depends on the interplay among the conjugated molecules, the solvent, and the substrate surface.

Studies of the organization in solution of chirally β-substituted polythiophenes provided profound insights into the solid-state organization of solution cast films[71]. The formation of supramolecular interactions via hydrogen-bonding arrays in combination with $\pi-\pi$ stacking has also been used to self-assemble oligothiophenes into one-dimensional arrays on surfaces, generating a material with remarkable high charge carrier mobility.[72] In other examples, the Langmuir-Blodgett or the layer-by-layer technique have been used for the self-assembly of monolayers of oligo- or polythiophenes.[73]

1.3. Project Objective

In conclusion, based on conjugated polymers, fluorescence chemosensors are one of the most widely investigated frontiers. Herein, it is necessary to complement and develop its related theory further. According to literatures and applications in conjugated polymer and pseudocrown ether, we will design and synthesize a series of conjugated polymer with pseudocrown ether to improve existing sensor's deficiency in low selectivity and single recognition mode. We focus on three aspects which are shown below.

- Design and synthesis of conjugated luminescence chemosensors with the pseudocrown ethers structure. A series of alternating PPE-ethylene oxide copolymers will be synthesized by using Sonogashira coupling reaction and characterized by optical and NMR spectroscopy.
- Research on selectivity and sensitivity of fluorescence chemosensors. It has been studied that alkaline metal and alkaline earth metal ion can quench the fluorescence of PPE derivates in organic solvent. We also propose the principle of selective recognition. Induced by coordination between metal ion and ethylene oxide chain, the aggregation of polymer would cause quenching of fluorescence intensity to complete amplification sensor function. We will try to confirm this principle by UV-vis, fluorescence and NMR spectroscopy.
- Research on self-assembly behavior of well organized π-conjugated polymer. Polymers will be controlled in solid and solution status to form specific structures by imposing solvophobic property of flexible chain, coordinate effect of metal ion and aggregation of conjugated polymer to exploit more widely application prospect in the future.

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Chapter 2 Synthesis and Characterization of PPE-Based Fluorescence Chemosensor

2.1. Introduction

Well-defined π-conjugated alternating copolymers play an important role in the field of fluorescent chemical sensors due to their tailor-made conjugated structures designed to give high sensitivities to analytes.[1-9] Many of these examples possess distinctive functional moieties such as crown ether in **1**[10] and sugars in **2**[9] attached to the polymer backbone. On the other hand, control of spatial orientation and packing of copolymers through molecular assembly and aggregation of the polymer chains has also been reported to enhance their electrochemical and/or optical properties. Such examples include alternating segments of oligothiophenes and oligoethylene oxide moieties,[11] perylene bisimide chromophores and polytetrahydrofuran,[12,13] diamine (which contains the appropriate naphthalene and oligoethylene oxide moieties) and pyromellitic dianhydride,[14] and 1,5-dialkoxynaphthalene and 1,4,5,8-naphthalenetetra carboxylic diimide.[15]

Poly(para-phenyleneethynylene)s (PPEs) are known to exhibit good thermal, oxidative stability and superior photophysical properties in solution. PPEs also show collective optical and conducting properties that are sensitive to minor external structural perturbations or to electron density changes within the polymer backbone in the presence of analytes.[16] Polymer **3**[9] and related systems[17,18] with externally attached oligo-(ethylene oxide) moieties were reported to show effective metal-responsive properties. Relatively smaller molecules of the type **4** were also studied for selective metal ion sensing.[19,20]

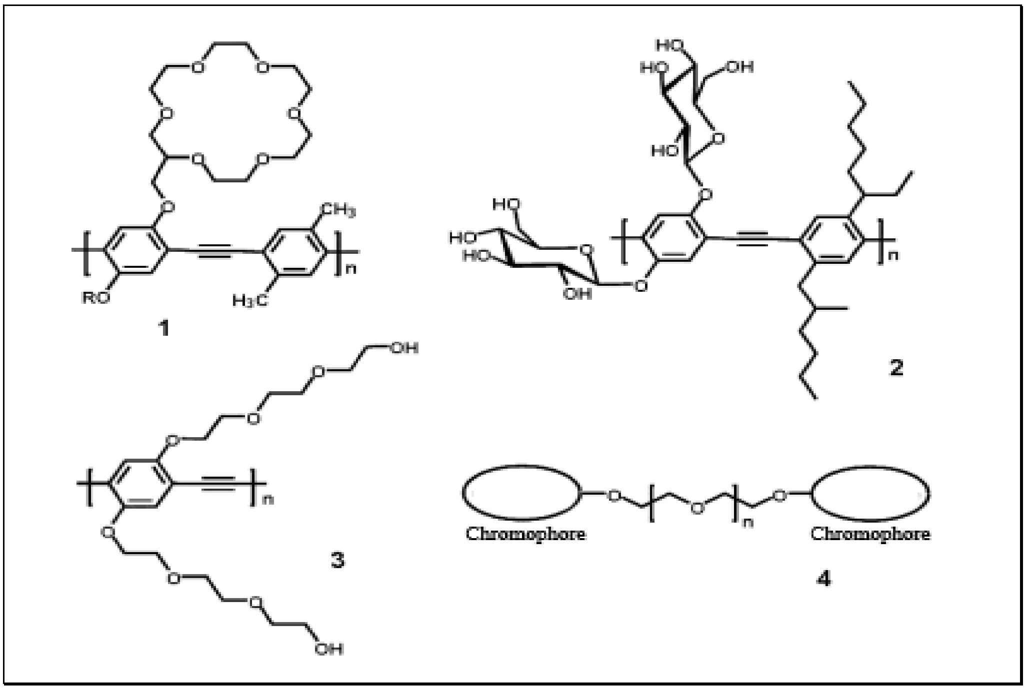
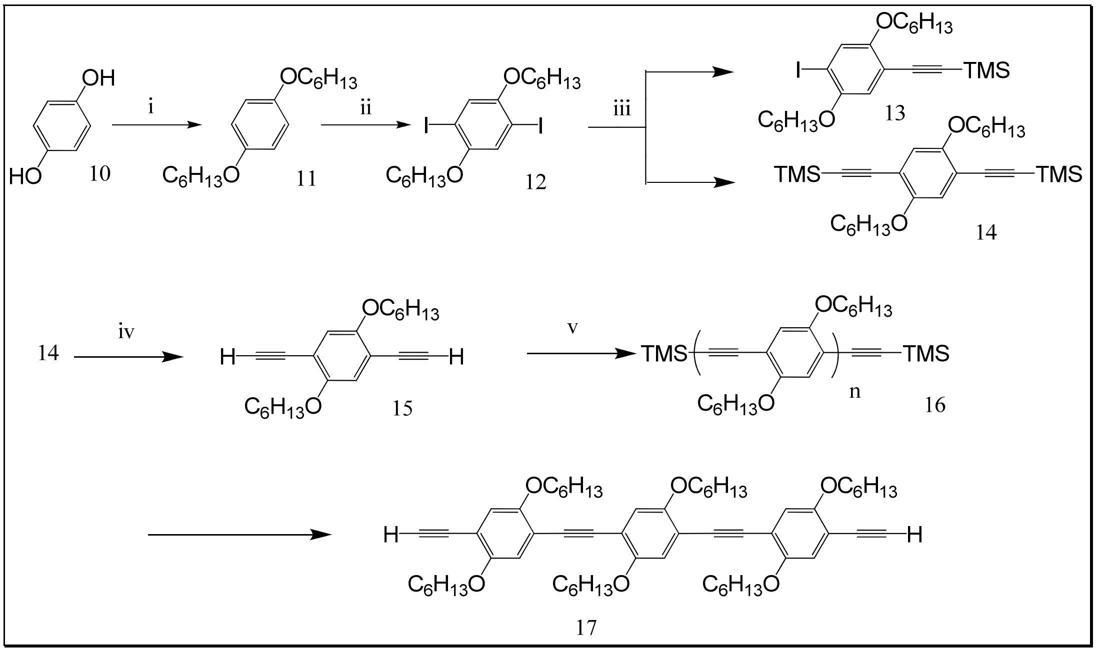


Figure 2.1 Some typical fluorescence chemosensors

In this thesis, we will explore directed folding in the polymer backbone itself in polymers with alternating segments of oligo(para-phenyleneethynylene) and oligo(ethylene oxide). The rod-coil structure of these polymers is expected to induce folding in tandem under appropriate conditions. The π-conjugated oligo-PPEs could form an excimer while the soft segments of oligo(ethylene oxide) could impart solvophobic effect and metal ion complexation ability. These driving forces are expected to induce aggregation formation in solution albeit dependent on the conformational mobility of the polymers.

2.2. Experimental details

2.2.1. Synthesis and Characterization of Oligo(*p*-phenyleneethynylene) (OPE)



Reagents and conditions: (i) Bromohexane, KOH/EtOH, reflux, 24 h; (ii) KIO_3, I_2, $AcOH/H_2SO_4/H_2O$, 80 °C, 24 h; (iii)$Pd(PPh_3)_2Cl_2$ (5 mol %), CuI (5 mol %), ^{i}Pr_2NH, trimethylsilylacetylene, reflux, 1h; (iv) MeOH/THF, 5 N NaOH, rt, 2 h; (v)1a, $Pd(PPh_3)_2Cl_2$ (5mol %), CuI (5 mol %), ^{i}Pr_2NH/THF, rt, 15 h.

Scheme 2.1 synthetic rout to conjugated OPE

1,4-dihexyloxybenzene (11)

A suspension of powdered KOH (50.0 g, 0.9 mol) and anhydrous ethanol (400 mL) stirred and degassed at room temperature for 30 minutes. Hydroquinone (38.5 g, 0.35 mol) in anhydrous ethanol (150 mL) was added dropwise. To the stirred mixture, bromohexane (148.0 g, 0.9 mol) in anhydrous ethanol (50 mL) was added. After stirring for 24 h with heating at reflux, the ethanol was evaporated at reduced pressure. The brownish residue was poured into water (500 mL) and extracted with ethyl acetate twice. The combined ethyl acetate layer was washed with water, brine, and dried over anhydrous magnesium sulfate. The white product (74.0 g, 76%) was obtained by recrystallization from ethanol after ethyl acetate was removed under reduced pressure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (s, 4H), 3.90 (t, 4H), 1.80-1.70 (m, 4H), 1.46-1.30 (m, 12H), 0.90 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ153.2, 115.4, 68.7, 31.6, 29.4, 25.8, 22.6, 14.0.

1,4-dihexyloxy-2,5diiodobenzene (12)

To a solution of 1,4- dihexyloxybenzene (11.1 g, 0.04 mol), 90 mL of acetic acid, 7 mL of water, and 3 mL of concentrated H_2SO_4 were added KIO_3 (10.3 g, 0.048 mol) and I2 (13.1 g, 0.048 mol). The reaction mixture was stirred at 80 °C for 24 h and then cooled to room temperature. After most of the acetic acid was evaporated under reduced pressure, aqueous Na_2SO_3 (20%) was added until the brown color of iodine had disappeared. The mixture was poured into ice water with Na_2CO_3 (500 mL) and extracted with hexane (3×200 mL). The combined organic layer was washed with water and brine and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give a yellow solid. The white crystals (12.7 g, 60%) were obtained by recrystallization from ethanol. ^{1}H NMR (400 MHz, CDCl3): δ 7.17 (s, 2H), 3.92 (t, 4H), 1.84-1.75 (m, 4H), 1.55-1.34 (m, 12H), 0.91 (t, 6H). ^{13}C NMR (100 MHz, CDCl3): δ 152.9, 122.8, 86.3, 70.3, 31.4, 29.1, 25.7, 22.6, 14.0.

2,5-Dihexyloxy-4-[(trimethylsilyl)ethynyl]iodobenzene (13)

To a solution of 1,4-dihexyloxy-2, 5-diiodobenzene (7.95 g, 0.015 mol), CuI (0.14 g, 0.75 mmol), and $Pd(PPh_3)_2Cl_2$ (0.53 g, 0.75 mmol) in 100 mL of diisopropylamine was added (trimethylsilyl) acetylene (1.47 g, 0.015 mol). The mixture was stirred at room temperature for 15 h. After removal of the solvent under reduced pressure, light yellow oil (1a; 3.30 g, 44%) was purified using silica gel with hexane/CH_2Cl_2 (20:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (s, 1H), 6.81 (s, 1H), 3.96-3.91 (m, 4H), 1.84-1.72 (m, 4H), 1.56-1.33 (m, 12H), 0.88 (t, 6H), 0.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ154.9, 151.7, 123.9, 116.3, 113.4, 100.8, 99.4, 87.9, 70.1, 69.8, 31.6, 29.3, 25.7, 22.6, 14.0.

1,4-Bis[(trimethylsilyl)ethynyl]- 2,5-bis(hexyloxy)benzene (14)

To a solution of 1,4-dihexyloxy-2, 5-diiodobenzene (7.95 g, 0.015 mol), CuI (0.14 g, 0.75 mmol), and $Pd(PPh_3)_2Cl_2$ (0.53 g, 0.75 mmol) in 100 mL of diisopropylamine was added (trimethylsilyl)acetylene (2.94 g, 0.03 mol). The mixture was stirred at reflux for 1 h. After cooling, dichloromethane (100 mL) was added, and the white ammonium iodide precipitate was filtered off. The solution was passed through a short silica gel column using toluene as eluent. After the solvent was evaporated under reduced pressure, the white crystals 1b (6.3 g, 89%) were obtained by recrystallization from ethanol. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (s, 2H), 3.93 (t, 4H), 1.81-1.76 (m, 4H), 1.53- 1.33 (m, 12H), 0.88 (t, 6H), 0.25 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ154.5, 117.8, 114.5, 101.5, 100.4, 69.9, 32.0, 29.7, 26.1, 23.0, 14.3.

General Procedure for the Preparation of 15, 17: Methanol and NaOH (5 N) were added at room temperature to a stirred THF solution of 1b and 3b, the reaction mixture was stirred for 2 h. After removal of the solvent under reduced pressure, 15, and 17 were separated by column chromatography, respectively.

1,4-Bis(ethynyl)-2,5-bis(hexyloxy)benzene (15)

The above general procedure was applied on methanol (30 mL) and NaOH (2 mL, 5 N) in a stirred solution of 1b (2.82 g, 0.006 mol) in THF (20 mL). The solvent was evaporated, and the residue was poured into 100 mL of water and extracted with hexane twice. The combined hexane layer was washed with water and brine and dried over anhydrous $MgSO_4$. The pale yellow solid 1c (1.82 g, 93%) was obtained after the solvent was removed. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (s, 2H), 3.97 (t, 4H), 3.33 (s, 2H), 1.84-1.75 (m, 4H), 1.50-1.26 (m, 12H), 0.90 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ154.4, 118.3, 113.8, 82.8, 80.2, 70.1, 31.9, 29.5, 26.0, 23.0, 14.4.

TMS-Terminated Trimer (16)

A mixture of 1,4-Bis(ethynyl)-2,5-bis(hexyloxy) benzene 1c (1.63 g, 5mmol), 2,5-dihexyloxy-4-[(trimethylsilyl)ethynyl]iodobenzene (1a) (6.25 g, 12.5 mmol), CuI (0.095 g, 0.5 mmol), and $Pd(PPh_3)_2Cl_2$ (0.351 g, 0.5 mmol) in 60 mL of diisopropylamine and 30 mL of THF. The bright yellow solid 3b (4.82 g, 90%) was obtained after chromatography using silica gel with hexane/ CH_2Cl_2 (4:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (s, 2H), 6.98 (s, 2H), 6.96 (s, 2H), 4.05-3.97 (m, 12H), 1.87-1.84 (m, 12H), 1.59 - 1.53 (m, 12H), 1.36-1.28 (m, 24H), 0.93-0.88 (m, 18H), 0.28 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 153.9, 153.8, 117.9, 117.7, 117.5, 115.0, 114.7, 114.2, 101.6, 100.5, 91.9, 91.8, 70.1, 69.9, 32.0, 29.7, 26.1, 23.0, 14.4, 0.4.

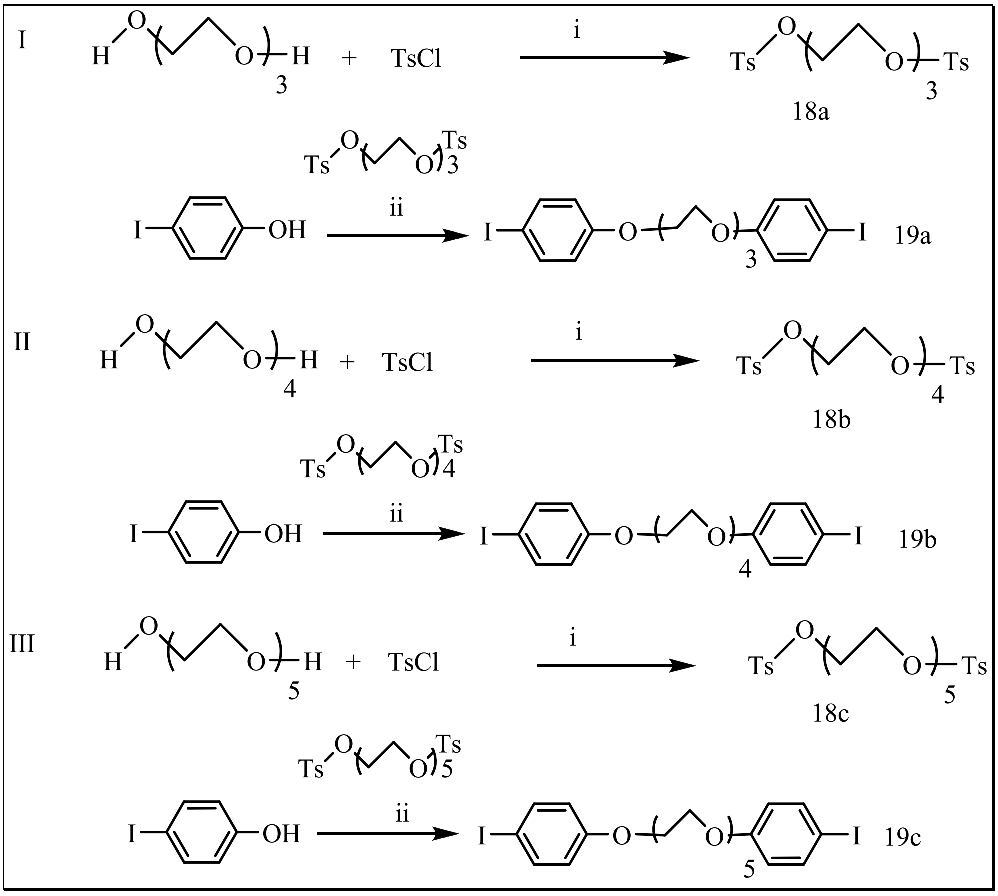
Deprotected Trimer (17)

The above general procedure was applied on methanol (45 mL) and NaOH (2 mL, 5 N) in a stirred solution of 3b (2.64 g, 2.47mmol) in THF (100 mL). The bright yellow solid 17 (2.02 g, 87%) was obtained after chromatography using gel with hexane/ CH_2Cl_2 (4:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (s, 2H), 6.98 (s, 2H), 6.97 (s, 2H), 4.09-4.02 (m, 12H), 3.34 (s, 2H), 1.94-1.84 (m, 12H), 1.54-1.28 (m, 36H), 0.97- 0.89 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ154.6, 154.0, 153.8, 118.5, 117.8, 117.6, 115.5, 114.8, 113.1, 92.0, 91.6, 82.6, 80.5, 70.2, 70.2,70.1, 32.3, 32.0,30.1, 29.7, 29.7,26.1, 23.0, 14.4.

2.2.2. Synthesis and Characterization of Flexible Oligo(ethylene oxide)

Tri(ethylene oxide)-di(p-toluenesulfonate) (18a)

A 42 g (0.22mol) of toluenesulfonyl chloride was added dropwise to a THF solution of 15.0 g (0.1 mol) of tri(ethylene glycol) monoethyl ether and 20.2 g (0.2 mol) of triethylamine at 0℃. After stirring for 12 h, the reaction mixture was filtered and the filtrate was evaporated. The residue was then extracted with CH_2Cl_2/10%HCl and the organic layer was concentrated under reduced pressure. The crude extract was purified by silica gel column chromatography using hexane/ethyl acetate (1:1) as eluent to give the desired product as a viscous oil (43 g, yield 94%). ^{1}H NMR (400 MHz, CDCl3): δ7.80 (d, 4H), 7.35 (d, 4H), 4.15 (t, 4H), 3.67(t, 4H), 3.53(t, 4H), 2.42(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ144.8, 132.9, 129.8, 127.9, 70.6, 69.2, 68.6, 21.6.



TsCl=toluenesulfonyl chloride
Reagents and conditions: (i) THF/Triethylamine, 0℃, 12h; (ii) K_2CO_3, Acetone/DMF, reflux, 3days.

Scheme 2.2 Synthetic rout to flexible oligo-(ethylene oxide)

Tri(ethylene oxide)-di(4-iodobenzene)-ether (19a)

A 13.8 g (0.030 mol) sample of compound 3d was added to a solution (60 ml of acetone/2 ml of DMF) of 13.2 g of 4-iodophenol (0.06 mol) and 6.2 g of potassium carbonate (0.045 mol), and the mixture was allowed to reflux for 3 days. The reaction mixture was filtered and the filtrate was evaporated and then the residue was extracted with CH_2Cl_2/H_2O and the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude extract was purified by silica gel column chromatography using hexane/ethyl acetate(1:2) as eluent to give the desired product as white crystals(15.8 g, yield 95%).^{1}H NMR (400 MHz, $CDCl_3$):δ 7.53 (d, 4H), 6.68 (d, 4H), 4.07 (t, 4H), 3.84(t, 4H), 3.73(S, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ158.7, 138.2, 117.1, 83.0, 70.9, 69.7, 67.6.

Tetra(ethylene oxide)- di(p-toluenesulfonate) (18b)

A 42 g (0.22 mol) of toluenesulfonyl chloride was added dropwise to a THF solution of 19.4 g (0.1 mol) of Tetra (ethylene glycol) monoethyl ether and 20.2 g (0.2 mol) of triethylamine at 0℃. After stirring for 12 h, the reaction mixture was filtered and the filtrate was evaporated. The residue was then extracted with CH_2Cl_2/10%HCl and the organic layer was concentrated under reduced pressure. The crude extract was purified by silica gel column chromatography using hexane/ethyl acetate (1:1) as eluent to give the desired product as a viscous oil (47.2 g, yield 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ7.80 (d, 4H), 7.35 (d, 4H), 4.15 (t, 4H), 3.67(t, 4H), 3.53(m, 8H), 2.42(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ144.8, 132.9, 129.8, 127.9, 70.6, 70.5, 69.2, 68.6, 21.6.

Tetra(ethylene oxide)- di (4-iodobenzene) –ether (19b)

A 18.0 g (0.030 mol) sample of compound 4d was added to a solution (60 ml of acetone/2 ml of DMF) of 13.2 g of 4-iodophenol (0.06 mol) and 6.2 g of potassium carbonate (0.045 mol), and the mixture was allowed to reflux for 3 days. The reaction mixture was filtered and the filtrate was evaporated and then the residue was extracted with CH_2Cl_2/H_2O and the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude extract was purified by silica gel column chromatogramphy using hexane/ethyl acetate(1:2) as eluent to give the desired product as white crystals (17.0 g, yield 95%).^{1}H NMR (400 MHz, $CDCl_3$): δ7.54 (d, 4H), 6.70 (d, 4H), 4.07 (t, 4H), 3.84(t, 4H), 3.73(m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ158.7, 138.2, 117.1, 83.0, 70.8, 70.7, 69.6, 67.5.

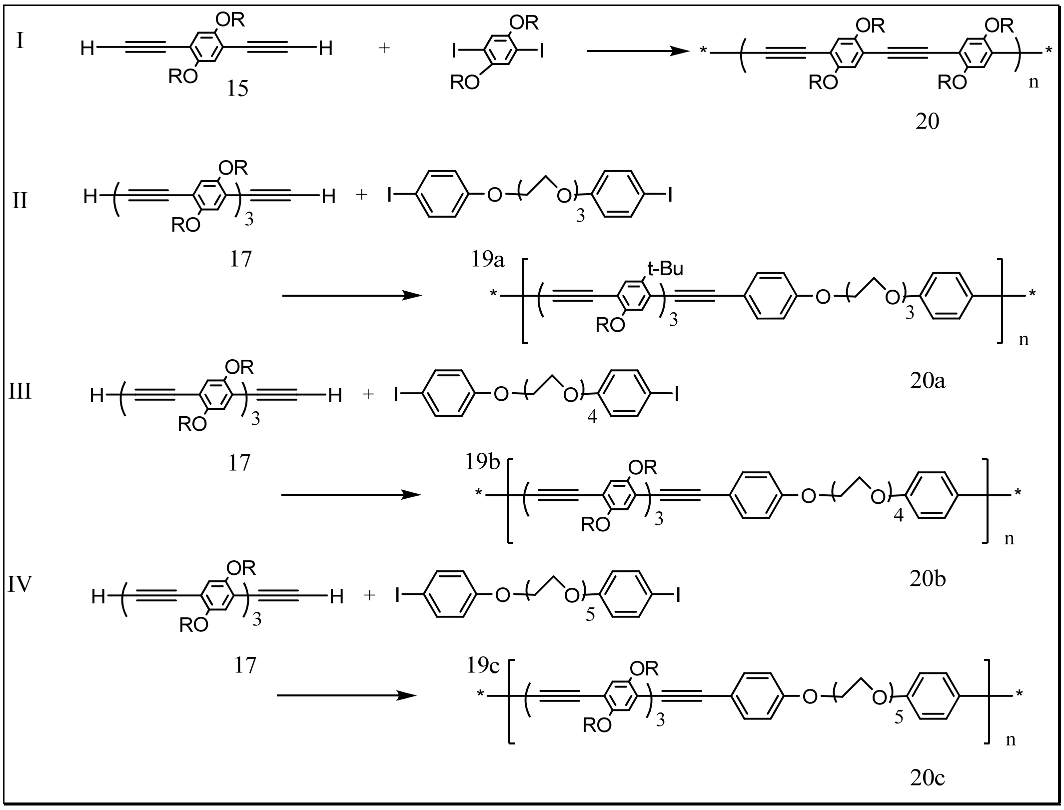
Penta(ethylene oxide)-di(p-ditoluenesulfonate) (18c)

A 42g (0.22mol) of toluenesulfonyl chloride was added dropwise to a THF solution of 23.8 g (0.1 mol) of Penta (ethylene glycol) monoethyl ether and 20.2 g (0.2 mol) of triethylamine at 0℃. After stirring for 12 h, the reaction mixture was filtered and the filtrate was evaporated. The residue was then extracted with CH_2Cl_2/10%HCl and the organic layer was concentrated under reduced pressure. The crude extract was purified by silica gel column chromatography using hexane/ethyl acetate (1:1) as eluent to give the desired product as a viscous oil (51.2g, yield 94%). ^{1}H NMR (400 MHz, CDCl3): δ7.80 (d, 4H), 7.35 (d, 4H), 4.15 (t, 4H), 3.67(t, 4H), 3.53(m, 12H), 2.42(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ144.8, 133.0, 129.8, 127.9, 70.7, 70.5, 69.2, 68.6, 21.6.

Penta(ethylene oxide)- di (4-iodobenzene) –ether (19c)

A 19.3 g (0.030mol) sample of compound 3d was added to a solution (60 ml of acetone/2 ml of DMF) of 13.2 g of 4-iodophenol (0.06 mol) and 6.2 g of potassium carbonate (0.045 mol), and the mixture was allowed to reflux for 3 days. The reaction mixture was filtered and the filtrate was evaporated and then the residue was extracted with CH_2Cl_2/H_2O and the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude extract was purified by silica gel column chromatography using hexane/ethyl acetate(1:2) as eluent to give the desired product as white crystals (18.3g,yield 95%).^{1}H NMR (400 MHz, CDCl3): δ7.54 (d, 4H), 6.70 (d, 4H), 4.07 (t, 4H), 3.82(t, 4H), 3.67(m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ158.7, 138.2, 117.1, 83.0, 70.8, 70.6, 69.6, 67.5.

2.2.3. Synthesis of Polymers



Reagents and conditions: (i) $Pd(PPh_3)_4$ (5 mol %), CuI (5 mol %), *i*-Pr_2NH/toluene (1:2), 60 °C, 1day.

Scheme 2.3 Preparation of (*p*-phenyleneethylene)(ethylene oxide) polymer 20 and 20a-c (R=n-C_6H_{13})

General Procedure for the Preparation of 20 and 20a-c: A mixture of 1.1 mole ratio of diethynyl compound (15 and 17), 1.0 mole ratio of diiodo compound (19a-c) were polymerized for polymer by using the Sonogashira coupling reaction in the presence of 5% $(PPh_3)_4Pd$, 5% CuI in toluene and diisopropylamine at 60 °C for 1 day. The iodobenzene (0.3 equiv) was added to the mixture, which reacted for another 3 h. The polymer was precipitated in ethanol, filtered, washed and dried under vacuum at room temperature:

Poly(phenyleneethynylene) (20)

1,4-Bis(ethynyl)-2,5-bis(hexyloxy)benzene (0.200g, 0.22mmol), 1,4-dihexyloxy-2,5diiodobenzene (0.106g, 0.20mmol), and iodobenzene as polymer end groups (0.1 equiv) were polymerized for polymer **20** by using the Sonogashira crosscoupling reaction in the presence of 5% $(PPh_3)_4Pd$ and 5% CuI in 24ml solution of diisopropylamine/toluene(1:2) at 60 °C for 1day. The iodobenzene (0.3 equiv) was added to the mixture, which reacted for another 3 h. The polymer was precipitated in methanol twice, filtered, and dried under vacuum at room temperature: ^{1}H NMR (400 MHz, $CDCl_3$): 7.01 (s, 2H), 6.99 (s, 2H), 6.96 (s, 2H), 4.06-3.96 (m, 12H), 1.85-1.82 (m, 12H), 1.51-1.34 (m, 36H), 0.91- 0.87 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): 154.6, 154.0, 153.8, 118.5, 114.8, 113.1, 92.0, 91.6, 82.6, 80.5, 70.2, 70.2, 70.1, 32.3, 32.0, 30.1, 29.7, 29.7, 26.1, 23.0, 14.4. Calcd. For $(C20H28O2)_n$: C, 79.96%; H, 9.39%. Found: C, 77.48%; H, 8.13%. Gel permeation chromatography analysis (mobile phase: THF, polystyrene standards) indicates that Mw of the polymer is 24

560, and its polydispersity is 2.31.

Polymer (20a)

1,4-Bis(ethynyl)-2,5-bis(hexyloxy)benzene (0.200g, 0.22mmol), monomer 3d(0.110g, 0.20mmol), and iodobenzene as polymer end groups (0.1 equiv) were polymerized for polymer **20a** by using the Sonogashira coupling reaction in the presence of 5% $(PPh_3)_4Pd$ and 5% CuI in 24ml solution of diisopropylamine/toluene(1:2) at 60 °C for 1day. The iodobenzene (0.3 equiv) was added to the mixture, which reacted for another 3 h. The polymer was precipitated in methanol twice, filtered, and dried under vacuum at room temperature: ^{1}H NMR (400 MHz, $CDCl_3$): 7.46 (d, 4H), 7.00 (s, 6H), 6.88 (d, 4H) , 4.17 (t, 4H), 4.03-3.93 (m, 12H), 3.89 (t, 4H), 3.77 (S, 4H), 1.85-1.82 (m, 12H), 1.54-1.28 (m, 36H), 0.97- 0.89 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): 153.8, 138.4, 133.2, 131.8, 128.5, 118.3, 114.8, 71.1, 70.9, 69.9, 67.7, 31.9, 29.5, 25.9, 22.9, 14.3. Calcd. For $(C80H104O6)_n$: C, 78.39%; H, 8.55%. Found: C, 75.56%; H, 8.73%. Gel permeation chromatography analysis (mobile phase: THF, polystyrene standards) indicates that Mw of the polymer is 102 052, and its polydispersity is 1.17.

Polymer (20b)

1,4-Bis(ethynyl)-2,5-bis(hexyloxy)benzene (0.200g, 0.22mmol), monomer 4d(0.110g, 0.20mmol), and iodobenzene as polymer end groups (0.1 equiv) were polymerized for polymer **20b** by using the Sonogashira coupling reaction in the presence of 5% $(PPh_3)_4Pd$ and 5% CuI in 24ml solution of diisopropylamine/toluene(1:2) at 60 °C for 1day. The iodobenzene (0.3 equiv) was added to the mixture, which reacted for another 3 h. The polymer was precipitated in methanol twice, filtered, and dried under vacuum at room temperature: ^{1}H NMR (400 MHz, $CDCl_3$): 7.46 (d, 4H), 7.00 (s, 6H), 6.88 (d, 4H) , 4.17 (t, 4H), 4.03-3.93 (m, 12H), 3.89(t, 4H), 3.77(S, 8H), 1.85-1.82 (m, 12H), 1.54-1.28 (m, 36H), 0.97- 0.89 (m, 18H). ^{13}C NMR (100 MHz, CDCl3): 153.8, 138.4, 133.2, 131.8, 128.5, 118.3, 114.8, 71.1, 70.9, 69.9, 67.7, 31.9, 29.5, 25.9, 22.9, 14.3. Calcd. For $(C82H108O11)_n$: C, 77.57%; H, 8.57%. Found: C, 76.12%; H, 9.25%. Gel permeation chromatography analysis (mobile phase: THF, polystyrene standards) indicates that Mw of the polymer is 136 655, and its polydispersity is 1.27.

Polymer (20c)

1,4-Bis(ethynyl)-2,5-bis(hexyloxy)benzene (0.200g, 0.22mmol), monomer 5d(0.110g, 0.20mmol), and iodobenzene as polymer end groups (0.1 equiv) were polymerized for polymer 20c by using the Sonogashira coupling reaction in the presence of 5% $(PPh_3)_4Pd$ and 5% CuI in 24ml solution of diisopropylamine/toluene(1:2) at 60 °C for 1day. The iodobenzene (0.3 equiv) was added to the mixture, which reacted for another 3 h. The polymer was precipitated in methanol twice, filtered, and dried under vacuum at room temperature: ^{1}H NMR (400 MHz, $CDCl_3$): 7.46 (d, 4H), 7.00 (s, 6H), 6.88 (d, 4H) , 4.17 (t, 4H), 4.03-3.93 (m, 12H), 3.89(t, 4H), 3.77(S, 4H), 1.85-1.82 (m, 12H), 1.54-1.28 (m, 36H), 0.97- 0.89 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): 153.8, 138.4, 133.2, 131.8, 128.5, 118.3, 114.8, 71.1, 70.9, 69.9, 67.7, 31.9, 29.5, 25.9, 22.9, 14.3. Calcd. For $(C84H112O12)_n$:

C, 76.79%; H, 8.59%. Found: C, 73.96%; H, 8.51%. Gel permeation chromatography analysis (mobile phase: THF, polystyrene standards) indicates that Mw of the polymer is 133 027, and its polydispersity is 1.67.

2.3. Results and Discussion

2.3.1. Synthesis and Characterization of Polymers

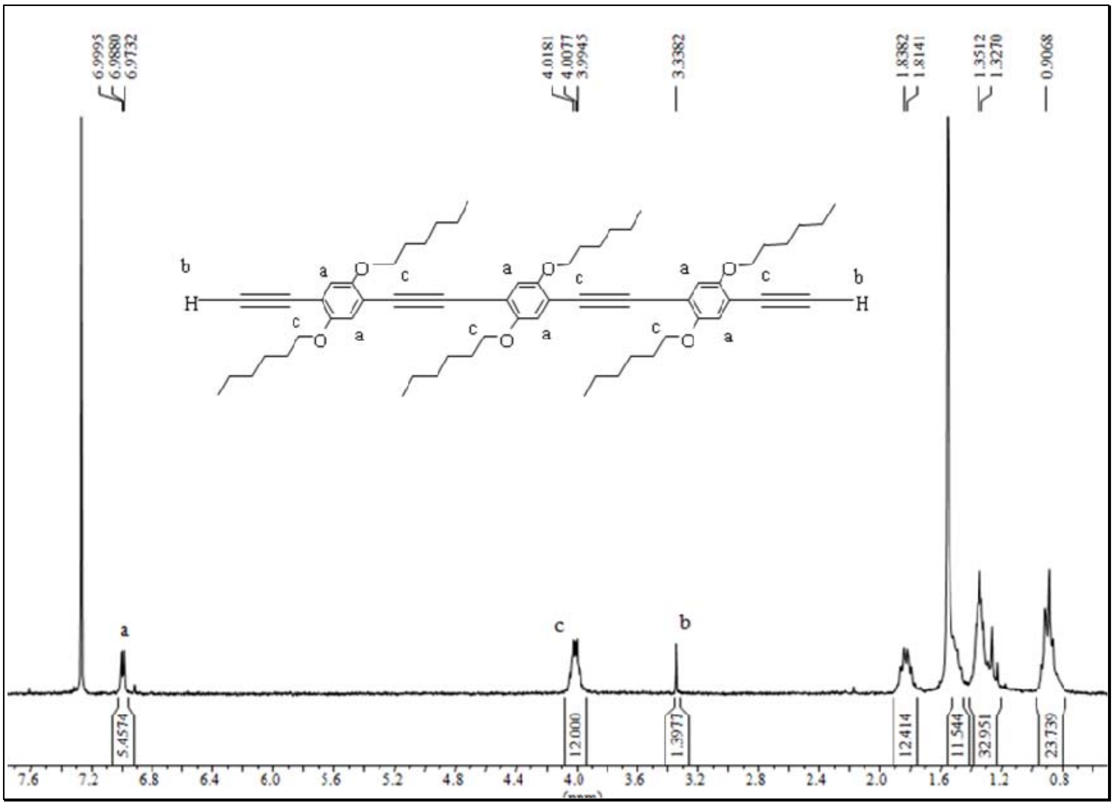


Figure 2.2 The ^{1}H NMR spectra of deprotected trimer (17) ($CDCl_3$)

In our synthetic rout to polymer, there were separate synthesis of conjugated rod chain for signal amplification and flexible chain for metal ion detecting. After that, both parts were connected together by polymerization.

For the synthesis of conjugated chain, first alkyl chains were introduced to the side chain of backbone to increase solvability of conjugated molecule. The oligomers, 1,4-bis[(trimethylsilyl)ethynyl]-2,5-bis(hexyloxy)benzene (**14**) and TMS ((trimethylsilyl)acetylene)-terminated trimer (**16**), were synthesized by Sonogashira coupling reaction. Removal of the protection group TMS of **14** and **16** generated the desilylated 2,5-dihexyloxy-1,4-bis (ethynyl) benzene (**15**) and deprotected trimer (**17**) (detail in scheme 2.1). As the Figure 2.2 shown, the aromatic protons peaks (6H) appeared at near δ7.00 and the alkyne protons peaks (2H) appeared at near δ3.34. In additon, the peaks (12H) at δ4.00 and the peaks (multiple H) at below δ2.00 belonged to alkyl chain linked with aromatic ring.

The monomers, tri(ethylene oxide)-di(4-iodobenzene)-ether (**19a**), tetra(ethylene oxide) -di (4-iodobenzene) –ether (**19b**) and penta(ethylene oxide) - di(4-iodobenzene) –ether (**19c**) were synthesized referring to literature procedures[22] (detail in scheme 2.2). The aromatic protons peaks (8H) appeared at near δ7.51 and δ6.67 (Figure 2.3 & Figure 2.4). In addition, the peaks (multiple H) at δ4.00 belonged to ethylene oxide chain. The only difference of their NMR spectra was different integral area at δ3.76 (Figure 2.4). The longer ethylene oxide chain showed a larger integral area.

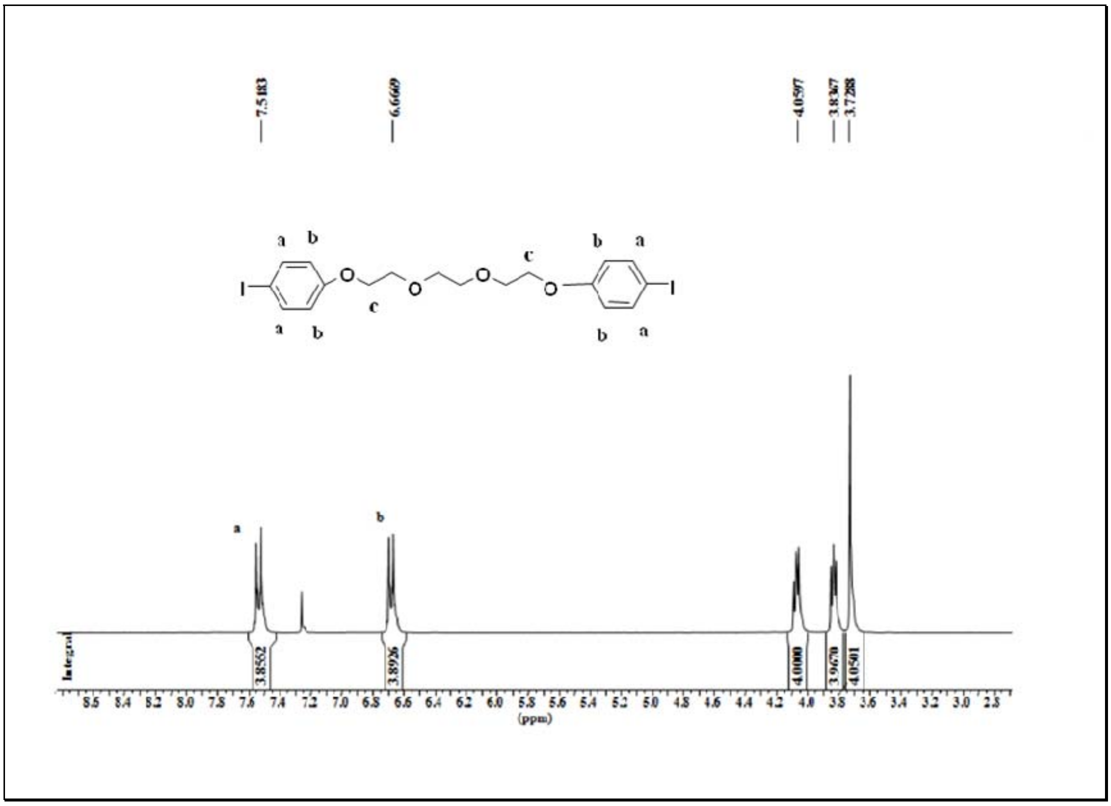


Figure 2.3 The ^{1}H NMR spectrum of tri(ethylene oxide)-di(4-iodobenzene)– ether (19a) (CDCl$_3$)

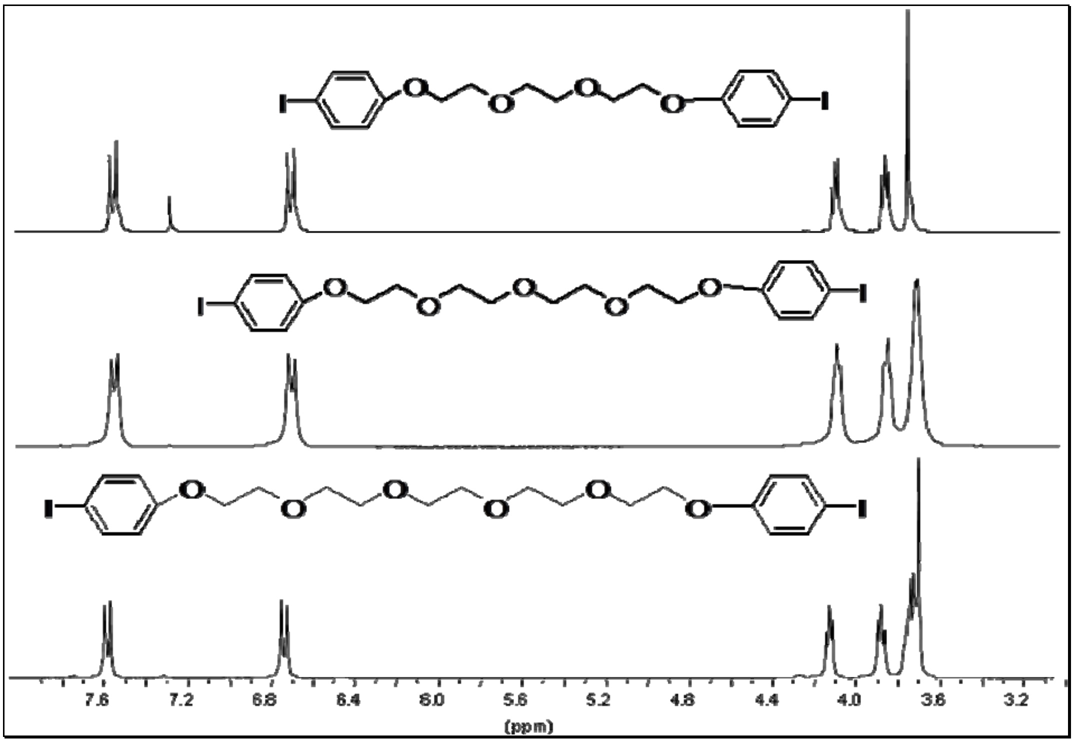


Figure 2.4 The comparison of ^{1}H NMR spectra of ethylene oxide (CDCl$_3$)

Pd(0)-catalyzed Sonogashira coupling reaction was employed to synthesize the polymers **20** and **20a-c** (see scheme 2.3). It has been established that the reaction has a tendency to produce insoluble cross-linked polymers in the stepwise polymerization process.[21] Reaction conditions for the polymerization process in our work such as temperature, time, concentration, solvent and catalyst were carefully considered and optimized. The Sonogashira coupling reaction was favorably carried out in a dilute solution and relatively low temperature to reduce the possibility of cross-linking between branches; thus, the poor solubility of the polymer could be avoided.

The trimer (**17**) reacted respectively with ethylene oxide chains **19a, 19b** and **19c** which have different lengths of soft segment and also iodine as terminated functional group, in molar ratios 1.1:1. The polymers were obtained in solvent (diisopropylamine/toluene, 1:2) with $Pd(PPh_3)_4$ (5 mol %) and CuI (5 mol %) as catalyst. After 24 hours polymerization, iodobenzene was added to the system and reacted for another 3 hours to cap the polymer. Slightly yellow amorphous materials were obtained through precipitation from methanol. The low concentration of solution and lower temperature were found to be key factors in determining the solubility of the products. The solubility of polymers was good in common organic solvents such as toluene, THF, chloroform, and methylene chloride. The molecular structures of the polymers were characterized by ^1H NMR and ^{13}C NMR spectroscopy. Characteristic signals of the phenyleneethynylene units and ethylene oxide units were observed in ^1H-NMR.

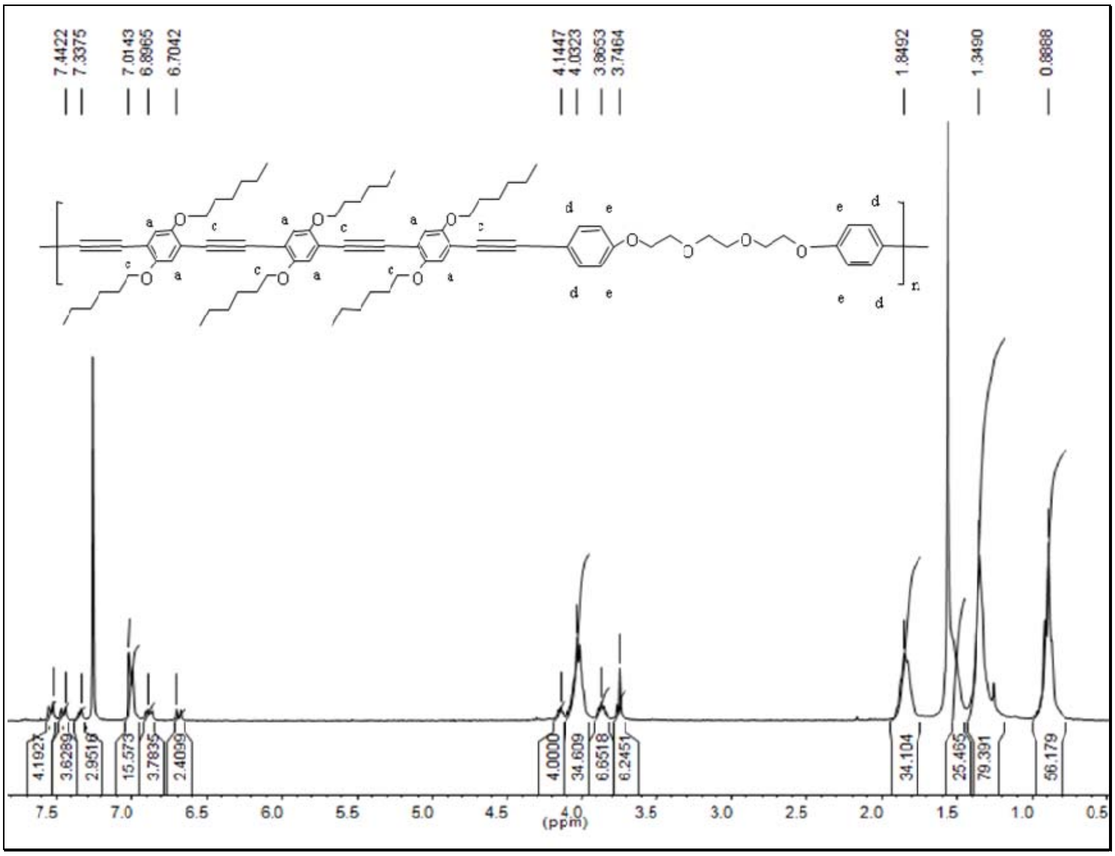


Figure 2.5 The ^1H NMR spectrum of 20a ($CDCl_3$)

The aromatic rings show different chemical shifts in OPE chain (δ7.01) and ethylene oxide chain (δ6.70 toδ7.52) (Figure 2.5). The ratio of the phenylene ethynylene units to ethylene oxide units can be calculated by the integral areas of the phenyl proton peaks in their ^1H NMR spectra. Compared with the phenyl signal of these two units, the calculated ratio was 6:9, which consisted with theoretic value of 6:8. In addition, the alkyl protons peaks in OPE appeared at δ4.03 and below δ2.00, while the other peaks from δ4.14 to δ3.75 indicated the alkyle of ethylene oxide chain. The chemical shift of polymer **20a** approximated to the corresponding monomers' chemical shift. The difference of these three polymers was different lengths of flexible chain. The different integral areas at δ3.76 (Figure 2.6) can be observed on their ^1H

NMR spectra. The one with longer ethylene oxide chain displayed the larger integral area.

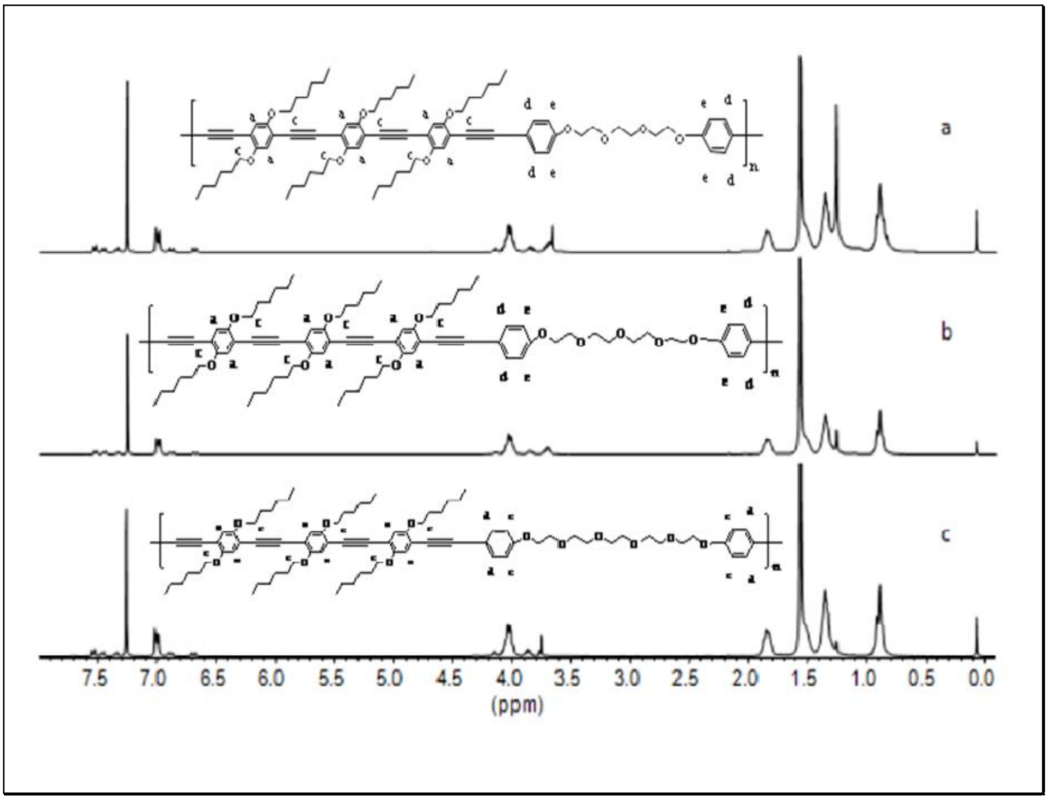


Figure 2.6 The ^{1}H NMR spectra of polymers ($CDCl_3$)

2.3.2. Molecular Weight Distribution and Optical Properties of Polymers

The average molecular weight for the polymers **20** and **20a-c** and their polydispersity index (PDI) were determined by gel permeation chromatography (GPC) against polystyrene standard (Table 2.1). In general the polymers **20a-c** have significantly higher molecular weights and more desirable polydispersity than **20**. As the length of the ethylene oxide chain increasing, the polydispersity of the polymer became less satisfactory in going from **20a** to **20b** to **20c**.

Polymer	Molecular Weight Distribution		Optical Properties	
	M_w	Polydispersity	λ_{max}(UV nm)	λ_{max}(PL nm)
20	24,560	2.31	414	466
20a	102,052	1.17	428	474
20b	136,655	1.27	428	474
20c	133,027	1.67	428	474

Table 2.1 Molecular weight distribution and optical properties of copolymers 20 and 20a-c

The absorption and emission maxima of PPE **20** were 414 nm and 466 nm, respectively (Table 2.1; Figure 2.7&2.8). These polymers **20a-c** were essentially identical (Figure 2.10) at 428 nm and 474 nm, respectively, independent of the number of ethylene oxide repeating units. The observed red-shift going from **20** to **20a-c** was somewhat unexpected as the conjugation in repeating phenyleneethynylene units were disrupted by the oligo(ethylene oxide) segments in going from **20** to **20a-c**. This however could be a positive indication that with greater flexibility in the polymer backbone, polymers **20a-c** would be able to coil and the red-shift was a result of transannular π-π interaction between intramolecular oligo(phenyleneethynylene) segments.

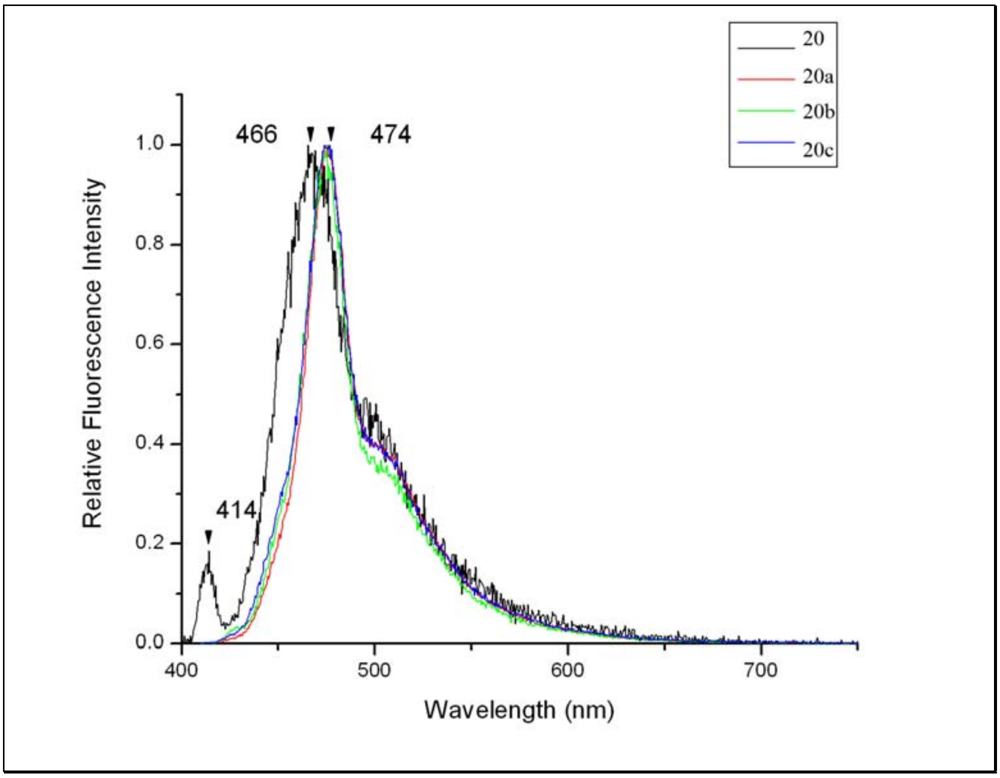


Figure 2.7 Absorption spectrum of polymers 20, 20a-c ($CHCl_3$)

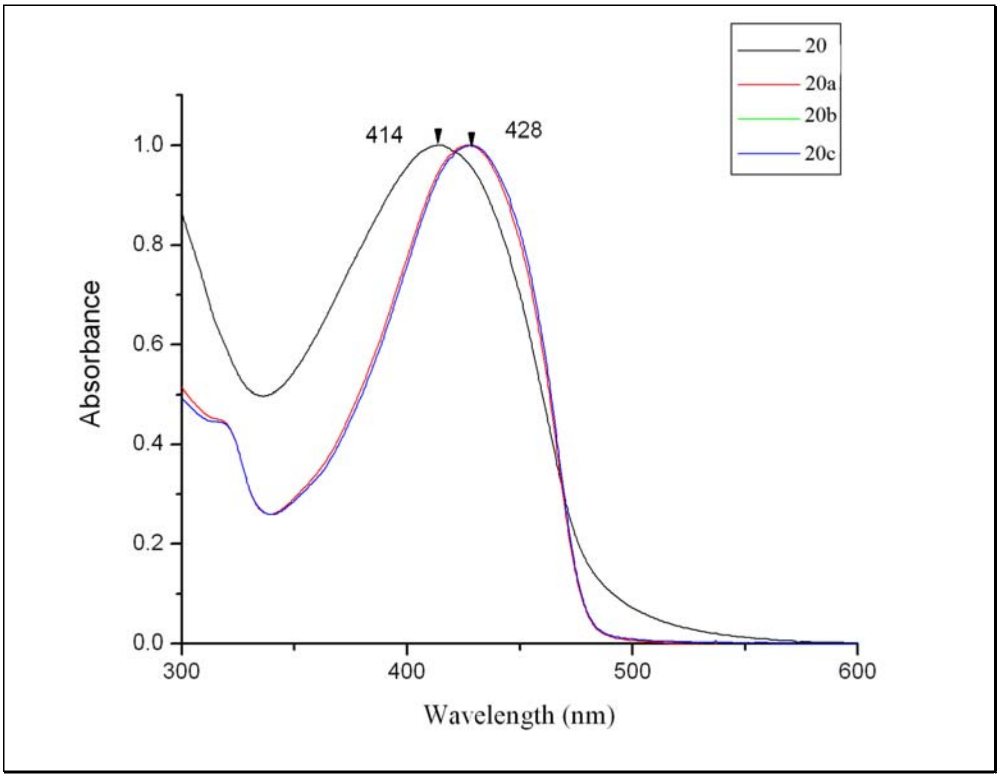


Figure 2.8 Emission spectrum of polymers 20, 20a-c ($CHCl_3$)

2.4. Conclusion

In conclusion, the polymers **20a-c** with alternating segments of oligo (para-phenyleneethynylene) and oligo(ethylene oxide) as well as the model compound **20** have been synthesized by Sonogashira coupling reaction. The introduction of flexible chain, ethylene oxide, in the polymer backbone significantly changed the conformation of polymers as well as their optical properties, as compared with their corresponding analogous **20** which was lack of flexible chain. The transannular π-π interaction between intramolecular oligo(phenyleneethynylene) segments envisioned a potential application of polymers **20a-c** in the fluorescence chemosensor. The intermediate products and final products were characterized by ^{1}H NMR, ^{13}C NMR, GPC, UV-vis and FL spectroscopy, and their structures were also identified.

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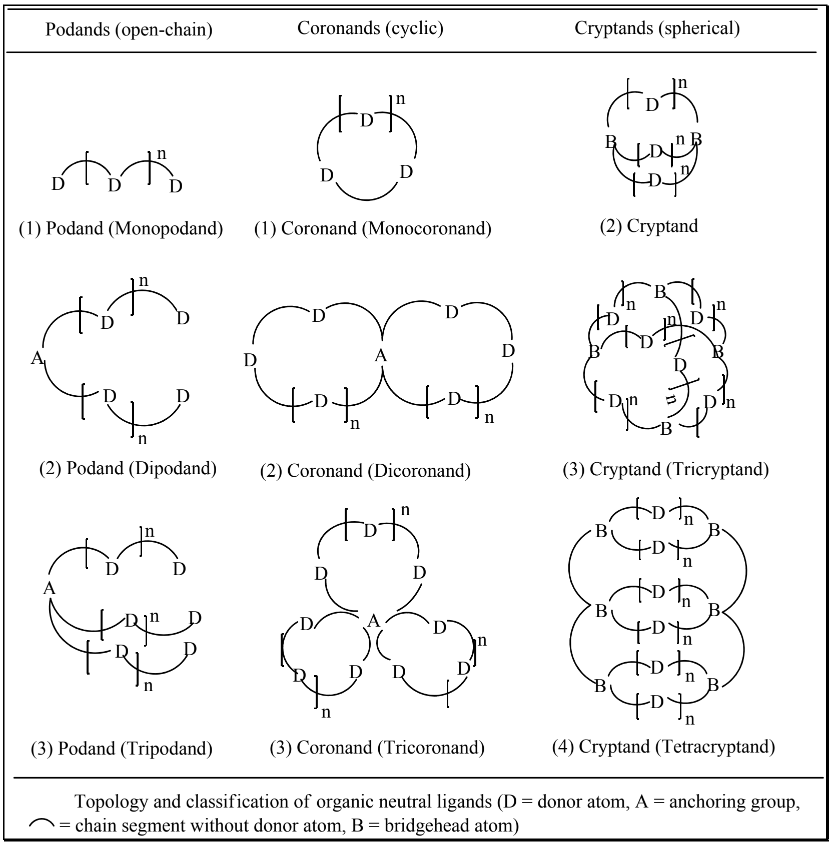
Chapter 3 The Application of Fluorescence Chemosensors in Ion Detection

3.1. Introduction

As these noncyclic crown ethers and their derivatives show strong complexation ability, the conformation of these compounds changes drastically from a linear structure to a pseudocyclic one upon the complex formation with metal ions. From the topology point of view, these neutral coordination compounds of organic ether are divided into three types (see Figure 3.1):[1] acyclic compounds as podand; mono-Cyclic compounds as coronand; poly-cyclic compounds as cryptand. They are called podate, coronate and cryptate respectively upon formation of coordination compounds with metal ion.

The C-C bonds in podand and coronand both can distort and rotate freely. This specific property makes them more elastic on coordination with metal ions. Furthermore, they would have different coordination ability when different donor atom were introduced. For example, 18-crown-6 with donor atom O has strong affinity to alkaline earth metal and alkaline metal, while S or N as donor atom it has strong affinity to transition metal.[2] For their extensive solvency and coordination ability with metal cation, organic ethers have been applied in photochemical responsive, thermally responsive, selective ion transport, chemosensor and phase-transfer catalysis.[3-7]



Topology and classification of organic neutral ligands (D = donor atom, A = anchoring group, ⌒ = chain segment without donor atom, B = bridgehead atom)

Figure 3.1 Types of the neutral coordination compounds of organic ether[1]

Vögtle et al studied artificial noncyclic crown ether derivatives decades before.[8,9] It demonstrated that oligo-oxyethylene compounds, appending quinoline units at their terminals, can bind K^+ strongly via electrostatic interaction between the ion and oxygen atoms with the aid of π-π interaction between end-capped quinolines. Nakahama et al.[10-13] demonstrated that a series of synthetic carboxylic ionophores exhibit high selectivity for K^+ over Na^+ in the ion transport experiment across the dichloromethane liquid membrane. This excellent selectivity for K^+ could be explained by the high lipophilicity of helical K^+ complex.

When the conformational change of noncyclic crown ether is converted into physical signals, such as UV absorption and fluorescence, etc, the metal ion sensors could be more sensitive than crown ethers. On the basis of this idea, Nakamur's group[14,15] synthesized novel fluorescent reagents that have two fluorescent chromophores (anthracene, pyrene, fluorene, etc.) symmetrically or asymmetrically placed at both terminals of 1,3-diamino-4,7,10-trioxatridecane. Furthermore, their complexations with alkali and alkaline earth cations were examined. The complexation brought a shift of the emission maximum from 400 to 490 nm. This indicated that the two anthracenes adopted in stack conformation upon ion complexation. A fluorescent regent containing two asymmetric fluorescent chromophores (one side was anthracene (electron donor) and the other was anthraquinone (electron acceptor)) gave emission quenching of the anthracene monomer upon the addition of alkaline earth cations. When anthracene approaches anthraquinone upon complexation, a rapid electron-transfer quench of the anthracene excited state occurs. The large fluorescence maximum shift and the quenching of anthracene fluorescence indicate a clear binding event. Moreover, it is expected that if the chain length at the oxyethylene moiety becomes longer, a conformational change would be significantly increased upon the formation of a complex. This large conformational change is favorable for making ion and molecular sensing systems.[16-20]

In chapter 2, a series of novel polymers consisting of alternating oligo-(p-phenylene ethynylene)s chromophores and flexible oligo-(ethylene oxide) segments of different lengths have been synthesized. In this chapter, we will investigate the polymers' recognition ability for alkaline earth metal and alkaline metal by UV-vis, FL and ^{1}H NMR spectra; study the influence of lengths of ethylene oxide on the recognition selectivity to metal; and also explore the influence of change of conjugated polymer's conformation on their physical and optical properties.

3.2. Experimental Detail

3.2.1. UV-vis and FL Measurements

UV-Vis spectra were recorded in a Shimadzu UV-3150 spectrometer. Dilute polymer solution in spectra-grade acetonitrile (10^{-5}-10^{-6} mol/ml, based on monomer molecular weight) were used for analysis. FL spectra were recorded in a Shimadzu RF-5300PC spectrometer. The sample condition was the same as UV-Vis's.

Metal perchlorate solutions were prepared in acetonitrile (spectroscopic grade). Solution of a polymer was prepared by dissolving the polymer in acetonitrile, aided by sonication and slight warming in a water bath if necessary. Metal ion titrations were carried out by adding small volumes of the metal solutions in a quartz cuvette. After the addition of metal salt solution to the 4-ml cuvette, the solution was shaken well and kept for 5 min before recording the absorption and emission spectra.

3.2.2. ^{1}H NMR Measurement

The ^{1}H NMR spectra were determined using $CDCl_3$ (unless other stated) as solvent at room temperature on a Varian Mercury Plus400 (400 MHz) Fourier transform nuclear magnetic resonance spectrometer. The concentration of samples was 2mg/ml. Scan times of small molecule were 32. All chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) as an internal standard. The volume of all samples was about 0.8ml.

Polymers were prepared in $CDCl_3$ (2 mg/ml) according to repeat units. The sample volume was about 0.8 ml in NMR tube. Metal perchlorate solutions were prepared in spectroscopic grade acetonitrile (1.0×10^{-2}M). Add 0.1 ml metal solution to NMR tube per time. The solution was shaken well and kept for 5 min before recording the ^{1}H NMR data.

3.3. Results and Discussion

3.3.1. Emission Spectrum Study on Metal Ion Detection

To find out whether metal ions could be detected by the synthesized polymers, a series of experiments were conducted in the presence of different metal salts under various conditions. Unexpectedly, the polymers **20a** and **20b** showed no appreciable response in their emission spectra in the presence of the series of alkaline and alkaline earth metal ions Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+}. The partial loop in the oligo(ethylene oxide) segment does not resemble closely the corresponding crown ethers and thus the optimum binding ability to the metal ions would differ. It is clear that both the size of folded partial loop in the polymer chain and the charge density of the metal ions do not match well for coordination in polymers **20a** and **20b** and the metal ions studied.

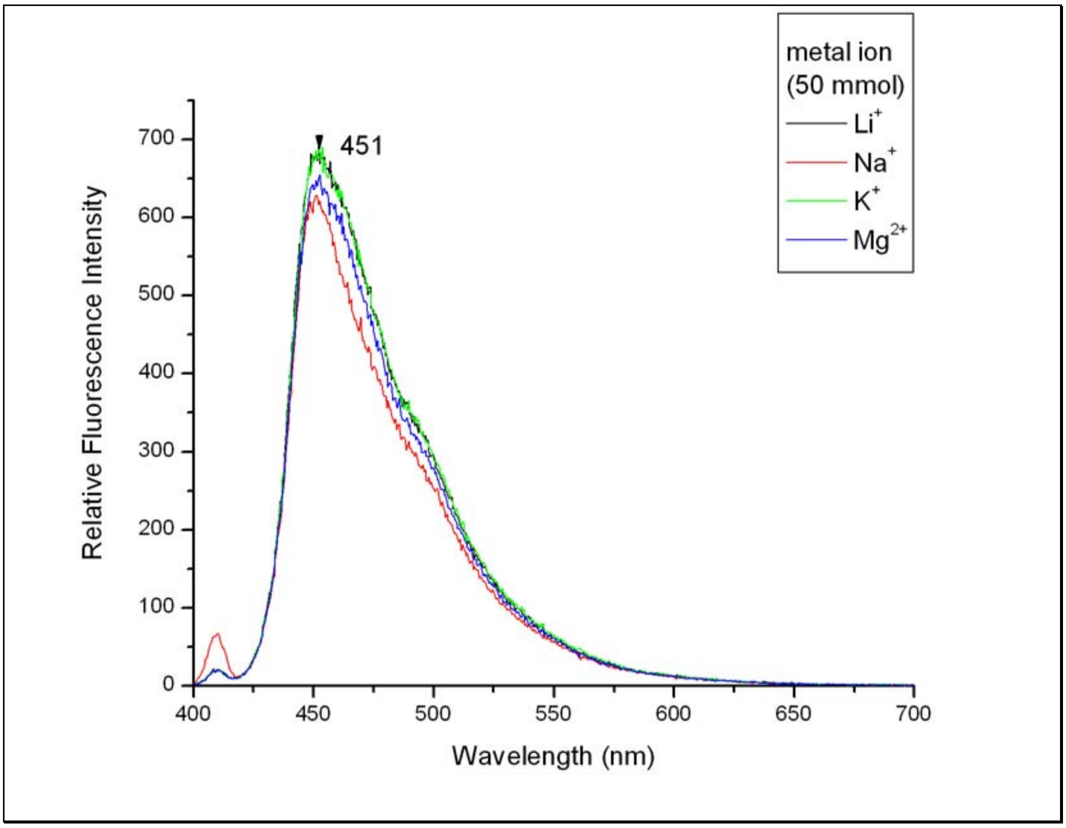


Figure 3.2 Emission spectra of 20c (1 μM) in acetonitrile with separate addition of Li^+, Na^+, K^+ and Mg^{2+} (50 mmol).

Addition of salts (50 mmol) of Li^+, Na^+, K^+, and Mg^{2+} to a solution of polymer **20c** (1 μM) showed slight changes in its emission spectra (Figure 3.2). Spectrum with Na^+ indicated a relatively more obvious decrease in emission at about 451 nm and a small increase in a new emission at about 410 nm. However, this phenomenon was observed with significant changes in the emission spectra of **20c** with the addition of $Ca(ClO_4)_2$ as shown in Figure 3.3. Upon gradual addition of $Ca(ClO_4)_2$, the intensity of fluorescence emission maximum of **20c** at 451 nm decreased with a concomitant increase in intensity of the peak at 410nm. The polymer **20c** was completely quenched with addition of a large amount of quantum of Ca^{2+}. The observed changes in the emission behavior of **20c** in the presence of Ca^{2+} ions can be rationalized on the basis of significant metal ion-induced folding of the oligo(ethylene oxide) segment to form a stacked foldamer with two or more face-to-face oligo(phenyleneethynylene) segments (see Figure 3.4). The fluorescence intensity of **20c** became weaker gradually with the addition of $Ca(ClO_4)_2$. It may be caused by the internal conversion from upper excited state into a lower one occurs immediately, and the emission from a lower excited state is theoretically forbidden.[21]

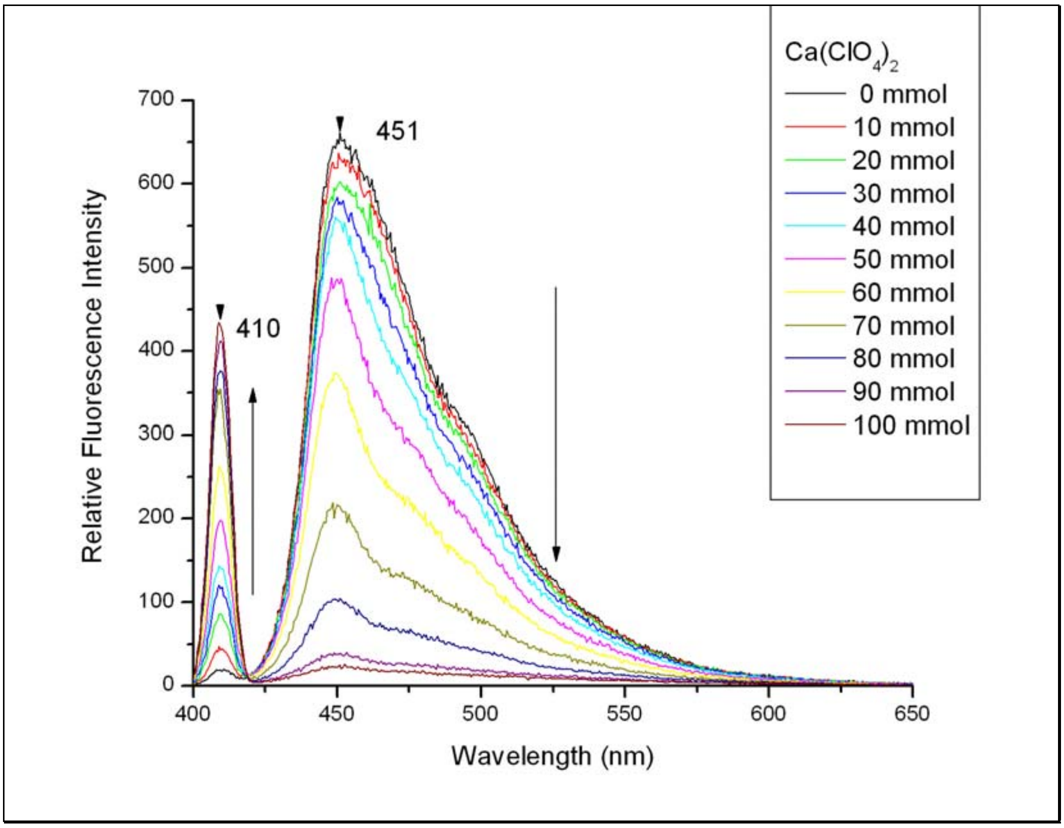


Figure 3.3 Emission spectrum of 20c (1 μM) in acetonitrile with progressive addition of $Ca(ClO_4)_2$ (0 to 100 mmol at 10 mmol increment).

The response sensitivity for Ca^{2+} in our study of **20c** was much lower than values reported for oligomers such as **4**.[22] Quenching of the intense fluorescence emission of

20c was however specific toward Ca^{2+} under the same conditions, whereas addition of Li^{+}, Na^{+}, K^{+}, or Mg^{2+} did not show any appreciable changes. This illustrates a unique ability of **20c** to selectively bind Ca^{2+} in the presence of other alkali and alkali earth metal ions. The difference in the binding ability of **20a-c** with various cations under investigation can be attributed to several factors. The number of coordinating oxygen atoms, the size of the pseudo crown cavity, the charge density and the coordination behavior of the cation all play a significant role in the binding interactions.[23] In addition, the flexibility of the polymer backbone which allows the oligo(ethylene oxide)segment to fold should also be an important factor in such polymer's binding properties. Additionally, **20c** with five oxygen atoms is found to selectively bind to Ca^{2+}, which is similar to such polyether chains in reported oligomeric examples.[24,25]

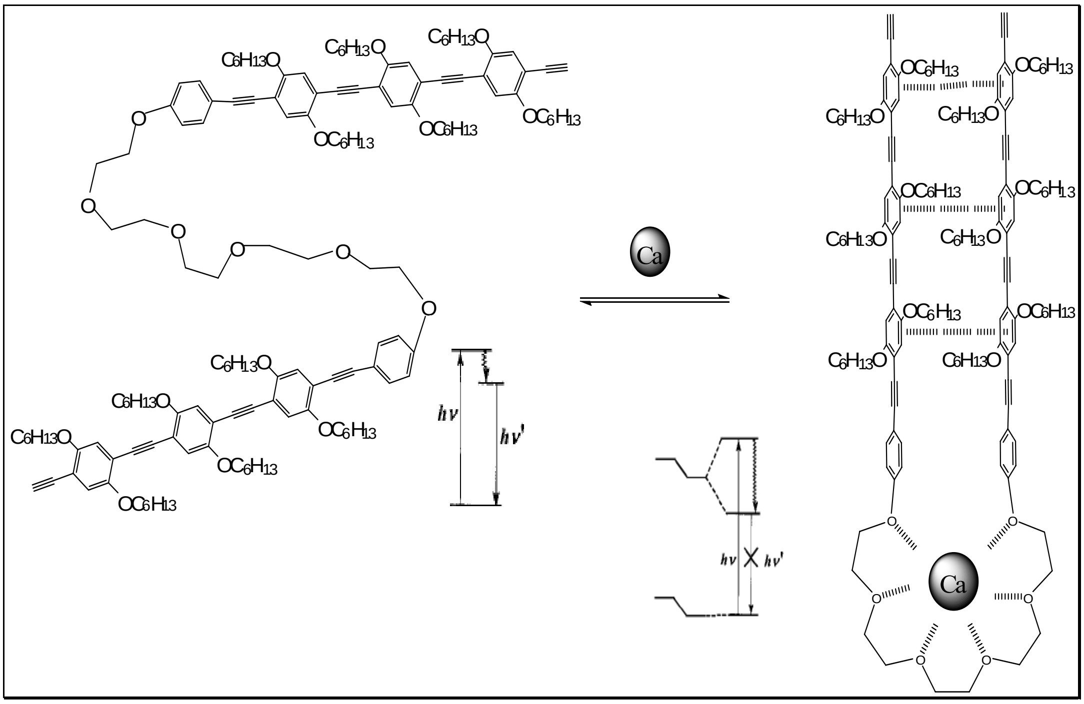


Figure 3.4 The Ca^{2+} induced foldamer of H-type and the corresponding allowed transition and forbidden transition in their two conformations.

However, the polymer **20c** only showed significant changes towards Ca^{2+} upon the addition of excessive Ca^{2+}. The small molecular pseudocrown ether can form coordination compounds with metal ions in the ratio of one to one, however, the polymeric pesudocrown ether based chemosensor had quite lower sensitivity in detecting metal ions. One of the reasons was that the molecular chain of polymer was too long to change their conformation easily, even though there was strong coordination effect between metal ion and polymer. Compared with small molecule, the longer polymer chain especially needed much more drive force to form that folding structure, which finally resulted in low sensitivity.

3.3.2. Binding Studies by ^1H NMR

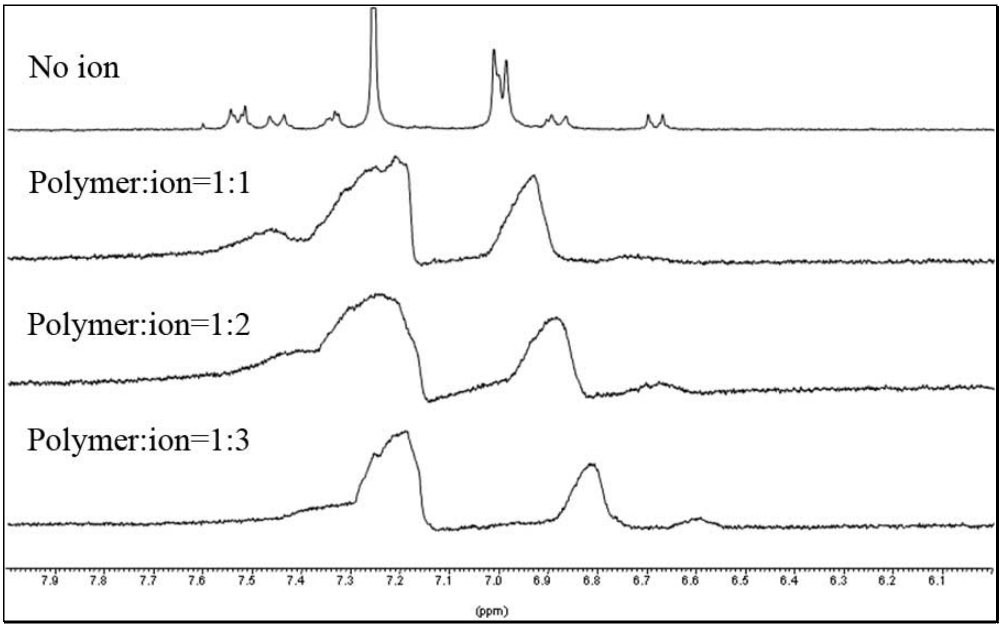


Figure 3.5 Aromatic region of ^1H NMR spectra of 20c in increasing Ca^{2+}: polymer ratios (see Experimental).

UV and FL spectra clearly indicate structural changes of polymer **20c** upon complex formation. To further coordination of metal ion to the oligo(ethylene oxide) segment of **20c,** ^{1}H NMR spectra of **20c** were monitored before and after the addition of Ca^{2+} ions in different polymer:**Ca^{2+}** ratios (Figure 3.5), which further support the proposed formation of coordination compound.

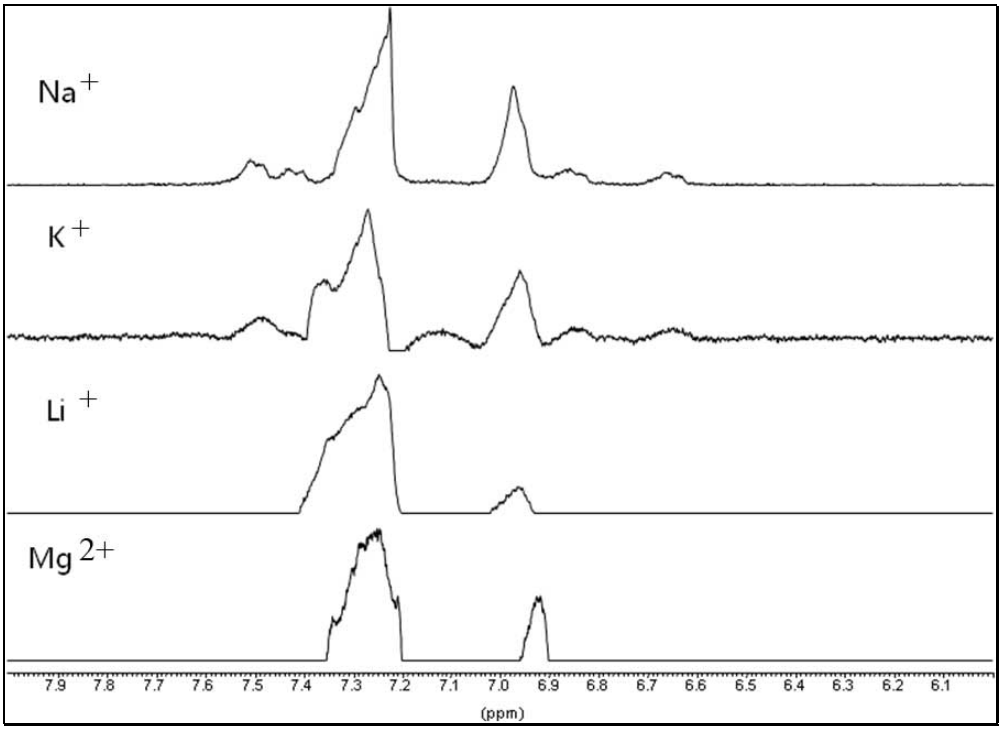


Figure 3.6 Aromatic region of ^{1}H NMR spectra of 20c in the presence of Na^+, K^+, Li^+, Mg^{2+}.

The ^{1}H NMR study was carried out in the absence and presence of metal cations in $CDCl_3/CH_3CN$ (1:1 v/v) at 30℃. The changes in chemical shift of the ^{1}H NMR spectra of **20c** with increment of Ca^{2+} are shown in Figure 3.5. With addition and progressive increments of Ca^{2+}, aromatic signals of phenyleneethynylene broadened and showed continual upfield shifts from δ 7.01 to δ 6.82 (⊿δ=0.19). Moreover, in Figure 3.6 the addition of Li^+, Na^+, K^+, and Mg^{2+} ions did not cause any significant change in the ^{1}H NMR spectrum of **20c**, which further supported selectivity of **20c** toward Ca^{2+}. In spite of that, there was still interactive coordination effect between metal ion and flexible chain of polymer. As the size of the metal ion didn't match with the size of the pseudo crown cavity, however, they just incompletely matched each other. So their chemical shift didn't change, whereas the induced metal ion had effect on chemical environment of polymer, which finally made peak broad (see Figure 3.6). This result consists with the conclusion drawn from UV-vis and FL spectra.

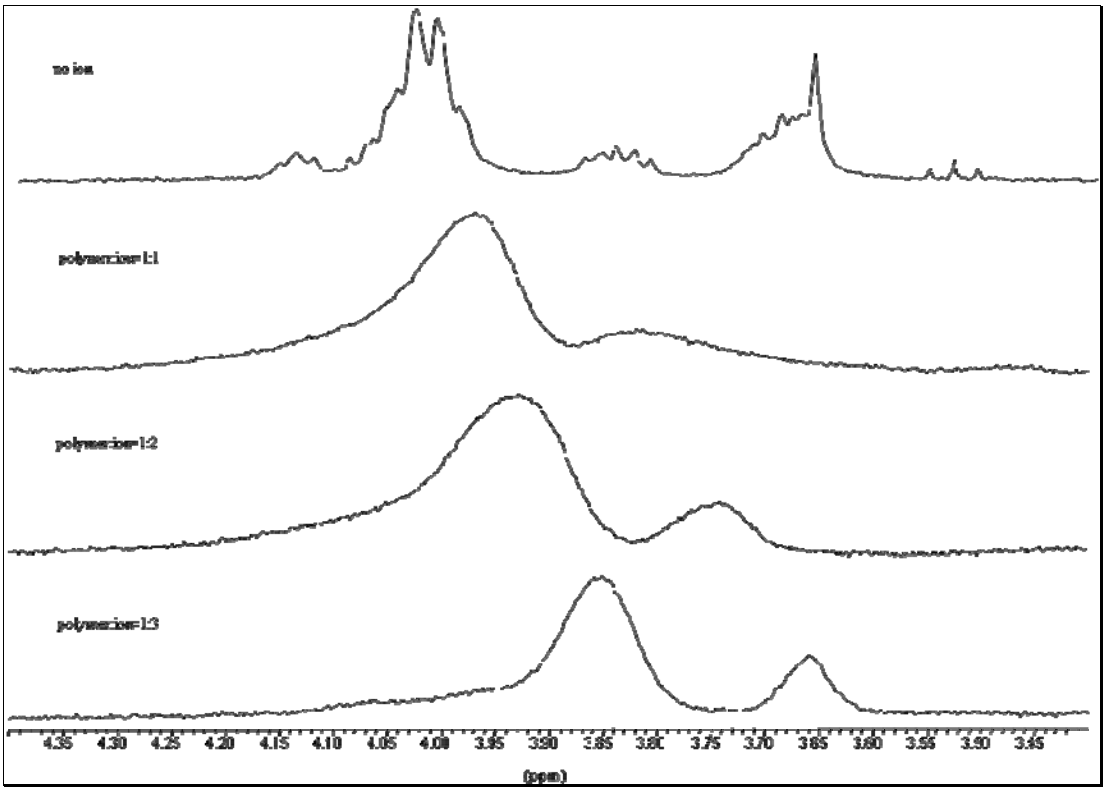


Figure 3.7 Oxyethylene region of ^{1}H NMR spectra of 20c in increasing Ca^{2+}: polymer ratios (see Experimental).

Furthermore, methylene signals of phenyleneethynylene also changed (see Figure 3.7), which shifted to high magnetic field from δ 4.03 to δ 3.85 ($\varDelta\delta = 0.18$) and became broad as well. This result could be explained by deshielding effect due to conjugated π-π stacking of the benzene. Methylene signals of ethylene oxide also changed (see Figure 3.7), which shifted to high magnetic field from δ3.84 to δ 3.65 ($\Delta\delta$＝0.19) and became weak and broad as well. These significant shifts observed for the methylene protons are consistent with deshielding effect resulting from metal ion coordination to the oligo(ethylene oxide) segment. With the foldamer formed due to the coordination process, appreciable transannular deshielding of aromatic protons would be observed from π-π stacking of the conjugated oligo(phenyleneethynylene) segment.

From the above NMR results, it was because that the coordination effect made polymer and metal ions form coordination compounds which caused changes in the chemical shift of polymer. This result is consistent with the conclusion drawn from UV-vis and FL spectra. In addition, the addition of these metal ions did not cause any significant change in the ^{1}H NMR spectrum of polymer **20a** and **20b**.

3.4. Conclusion

In this chapter, our work focused on utilization of coordination effect between polymer and metal ion, assisted with flexible chain solvophobic effect and conjugated polymer's tendency to π－π aggregation to achieve aim of recognition and detecting metal ion. Changes in absorbance and emission spectra were used to recognize the signal of metal ion, and changes in NMR were used to further identify the formed coordination compounds. With the addition of $Ca(ClO_4)_2$ in acetonitrile, polymer **20c** formed the H-type complex with Ca^{2+}, consequently, which caused fluorescence quenching. While it didn't cause any changes in the emission and absorption spectra of polymer **20a** and **20b**, because it didn't form that folding structure with the addition of the other metal ions in acetonitrile. The binding properties in such cases mainly depended on the number of oxygen atoms, the size of the pseudo crown cavity, the charge density, and the coordination number of the cation. These factors were the reasons for the specific binding of Ca^{2+} ions with **20c**. In the end, we investigated the changes in ^{1}H NMR of polymer after addition of metal ion to further confirm the combination of polymer and metal ion.

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Chapter 4 Study on Self-Assembly Behavior of Organized π-Conjugated Polymer

4.1. Introduction

Despite conjugated polymers exhibit excellent conductivity, there still remains many important questions about the nature of the electronic states in conjugated polymers. In particular, the influence of interactions among chains on the electronic properties in the solid state is a matter of major current interest.[1-5] Interchain interactions can have a major impact on the operation of devices, since they not only determine the charge transport properties, but also determine the efficiency of emission in LEDs, or the charge separation process in photodiodes. More generally, energy and charge transport in a molecular solid are critically dependent on the intermolecular interactions, which in turn are dependent on the molecular packing. Therefore, it is of utmost importance to investigate and control the effects of ordering and structure in conjugated polymers, from the nanometer scale through the mesoscale (100–1000 nm) to the optical scale (>1000 nm). In the nanometer regime, the aim is to synthesize stable materials with high luminescence efficiencies by control of the intra- and intermolecular structures.[4, 6] In the mesoscale regime, the goal is to use polymer mixtures (polymer blends) or block copolymers to explore phase separation processes and generate well defined structures (in terms of properties and dimensions). Block copolymers, which are the main research subject in materials science, could be incorporated into a large range of devices, such as photodiodes, where charge separation occurs at the interface between the phases.[7]

In the past few years, intensive research has been dedicated to the control of the solid-state organization of conjugated polymers and oligomers.[8, 9] The goal is to control the π-aggregation of the conjugated polymers, which can lead to aggregate (even in solution) or excimer formation that can impact the LED operation.[10] Approaches to avoid undesired aggregation of rigid polymer chains, include the use of bulky side chains,[11] endgroups,[12] or cross-linkable groups.[13,14] The aggregation can also be controlled via hydrogen bonding between side groups attached to the conjugated backbone.[15-18]

Block copolymers, in general, can generate a variety of morphologies[16,17] due to the selective solvation in solution and the microscopic phase separation in the solid state. Therefore, they provide a novel, nonlithographic, alternative route to nanostructures. Among the different types of block copolymer architectures, coil–coil diblock copolymers have been studied most intensively, and their phase diagram is now reasonably well understood.[18] Replacing one blocks of a coil–coil block copolymer by rigid crystallizable segment has a number of consequences. In the field of conjugated polymers, controlling their morphology via the synthesis of block copolymers including at least one conjugated sequence and one non-conjugated sequence is also attracting much interest. The self-assembly of macromolecules, including a π-conjugated sequence, constitutes a promising strategy for the construction of well-defined and stable nanometer-sized structures with chemical functionalities and physical properties, which could be exploited in optoelectronic devices.

4.2. Experimental Detail

4.2.1. Solvent-induced Aggregation

Precise concentration (10^{-6} – 10^{-7} M) of the polymer was prepared in $CHCl_3$ (spectroscopic grade). A sample of the polymer solution (0.4 mL) was transferred to a 4 mL cuvette. Additional volume of $CHCl_3$ and CH_3OH in a specific ratio was then added. The solution was mixed well and kept for 5 min before recording the absorption and emission spectra of the sample.

4.2.2. AFM Studies

Polymers were prepared in CH_3CN (0.1 mg/ml) according to repeat unites. After dropped to surface of mica, the sample was kept slowly evaporation for 48h. Atom force microscopy images were recorded on a SPM-9500 J3 of Shimadzu. And operation of AFM was in tapping mode.

4.3. Result and Discussion

4.3.1. Solvent-Induced Aggregation Behavior of 20a-c

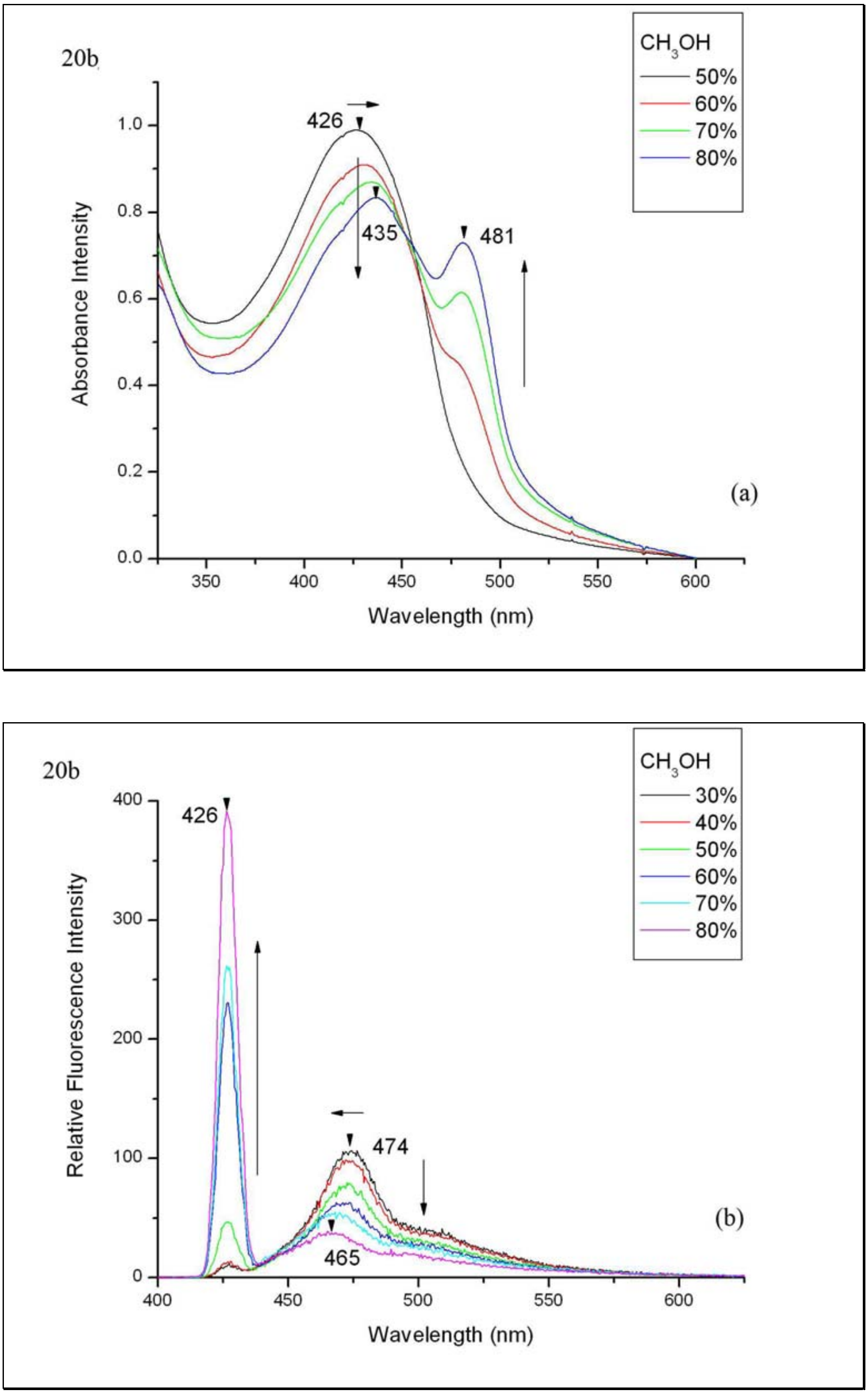
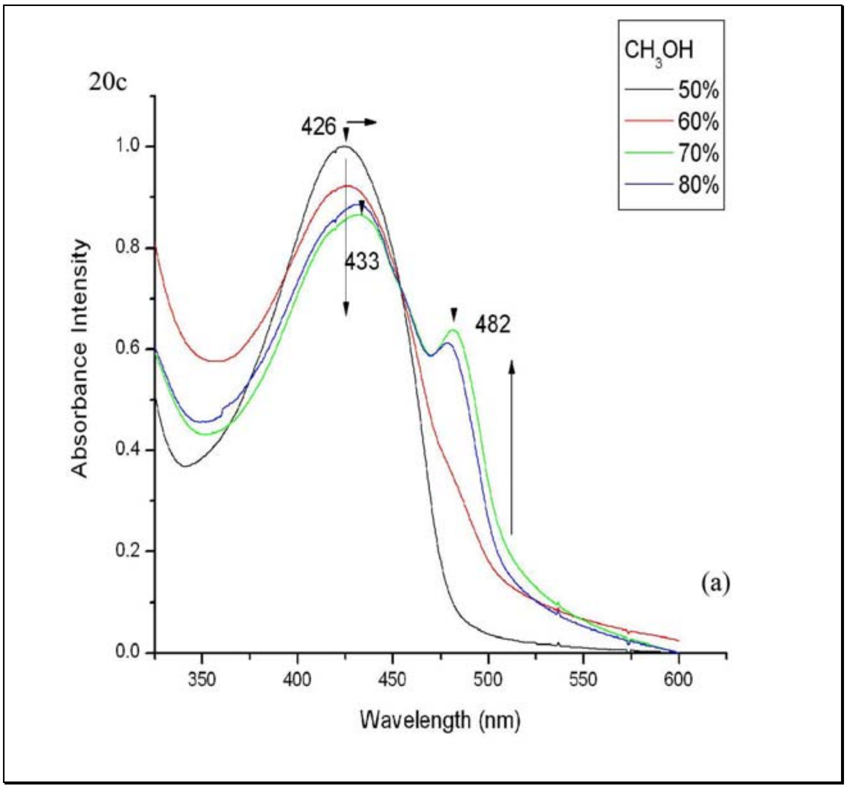


Figure 4.1 Variation in (a) UV/Vis and (b) FL spectra of polymer 20b in $CHCl_3$ with increasing percentage (%) of methanol

To examine whether the solvophobic effect in the oligo(ethylene oxide) segment can be utilized to induce folding structure, a solvent titration experiment was carried out in chloroform/methanol. Appreciable and similar changes in the absorption band intensity with increasing methanol composition were evident in the polymer **20b** as illustrated in Figure 4.1a. In this case, a progressive albeit small red-shift was observed for absorption at about 426 nm with increasing the percentage of methanol. In addition, the intensity of the 426 nm peak decreased with a concomitant increase in the intensity of a shoulder peak at 482 nm. The above phenomena were attributed to aggregation between oligo(ethylene oxide) segment and polar methanol molecules, resulting in folding of the oligo(ethylene oxide) unit and stacking of the oligo(phenyleneethynylene) segments at the two ends. The through-space π–π interactions will be reflected in the appreciable red-shift observed. When the concentration of methanol was lower than 50%, there was no obvious change in the absorption band indicating that the polymer chain could still be fully stretched in the solution. Once the concentration of methanol was higher than 50%, the polymer chain began to wrap gradually to form a partial loop. Not only an appreciable red-shift was observed for absorption at about 426 nm but a new shoulder peak at 482 nm due to the aggregation and change in molecular framework was clearly detectable. The aggregation phenomenon was apparently saturated at methanol concentrations of higher than 80% as reflected by no further change in the absorption spectra (Figure 4.1a).

The above aggregation phenomenon not only affected the absorption, but also the emission spectra. As the percentage of methanol in chloroform increased, polymer **20b** showed a significant decrease in the intensity of emission peak at about 474 nm accompanied by an even more significant increase in the intensity of a new peak at 426 nm as shown in Figure 4.1b. The observed changes in the emission spectroscopy with increased methanol composition could also be rationalized on the basis of the solvent-induced folding of the chromophores to form face-to-face stacked foldamers as discussed earlier. When the intensity of emission peak decreases, fluorescence of folded polymers is expected to be weaker compared with unfolded polymers because the internal conversion from an upper excited state into a lower one occurs immediately, and the emission from a lower excited state is theoretically forbidden.[21]



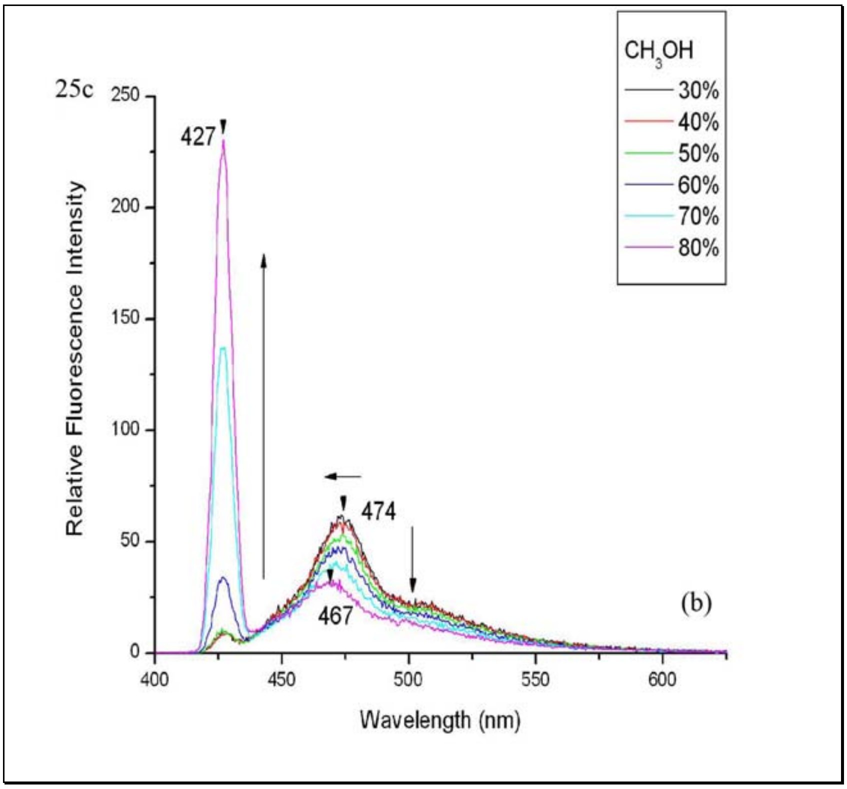
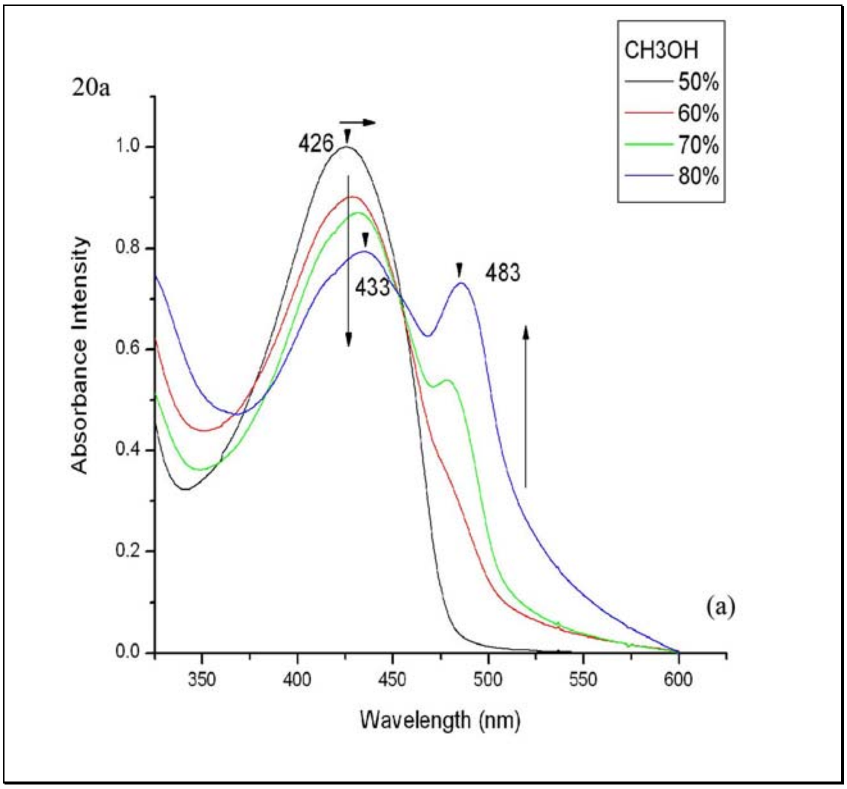


Figure 4.2 Variation in (a) UV/Vis and (b) FL spectra of polymer 20c in $CHCl_3$ with increasing percentage (%) of methanol



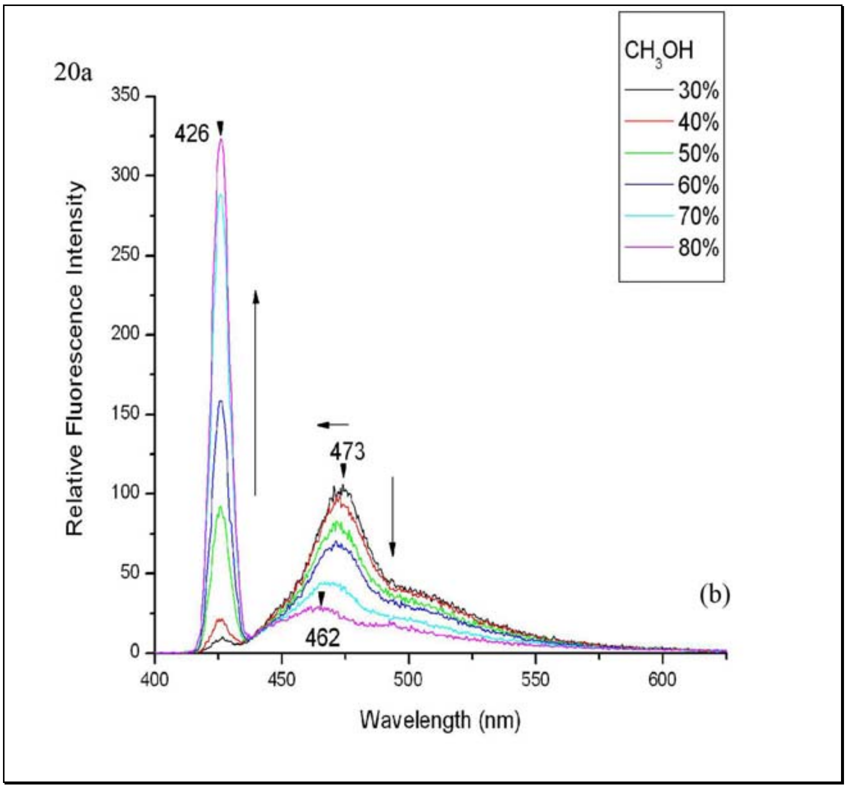
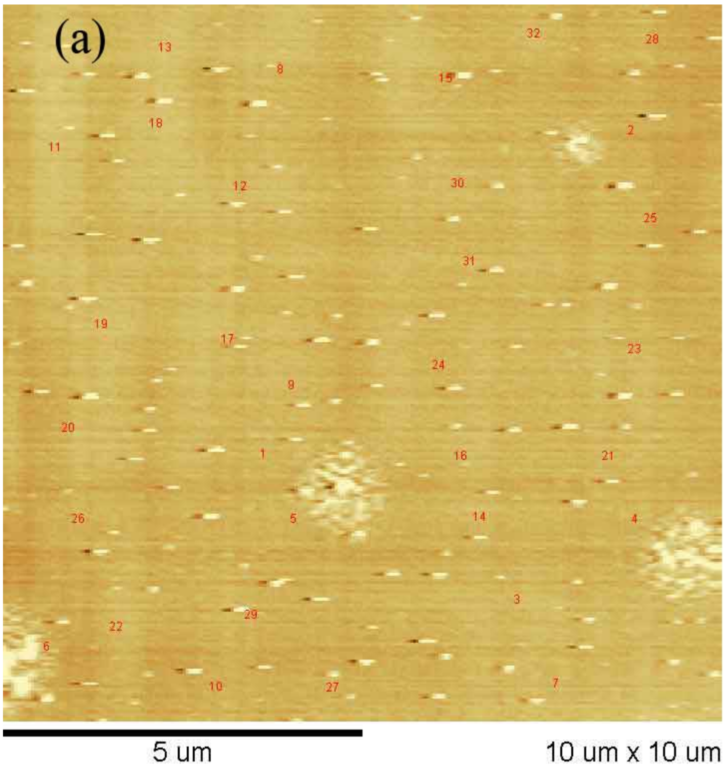


Figure 4.3 Variation in (a) UV/Vis and (b) FL spectra of polymer 20a in $CHCl_3$ with increasing percentage (%) of methanol

In addition, appreciable and similar changes in the absorption and emission band intensity with increasing methanol composition were evident in other two polymers **20a** and **20b** as illustrated in Figure 4.2 and Figure4.3. These two polymers can form π—π folding structure by solvent-induced aggregation as well as **20c**. Although they couldn't strongly change their conformation in solution by metal ion-induced coordination effect, which further confirmed that the number of oxygen atoms and the size of the pseudo crown cavity were extremely important for the binding ability of chemosensor.

4.3.2. Morphology Studies by AFM

It is evident that polymers **20a-c** showed aggregation behavior in polar solvents such as methanol and acetonitrile. The shape and size of these aggregates could be further investigated by AFM measurements on deposits prepared from their solutions. Polymer **20b** was used as a representative model in this study. From a thermodynamic stand point, assembly in solution is governed by a balance between interactions of conjugated molecules and solvent molecules while the morphology of deposits depends on molecular-surface interactions. Solid-state deposits of monolayer thickness were generated from a very dilute solution (0.1 mg/ml) of **20b** dispersed in acetonitrile. Upon slow evaporation, all three types of interactions (molecule-molecule, molecule-solvent and molecule-surface) played an important role, which provided additional tenability for the controlled formation of conjugated nanostructures.



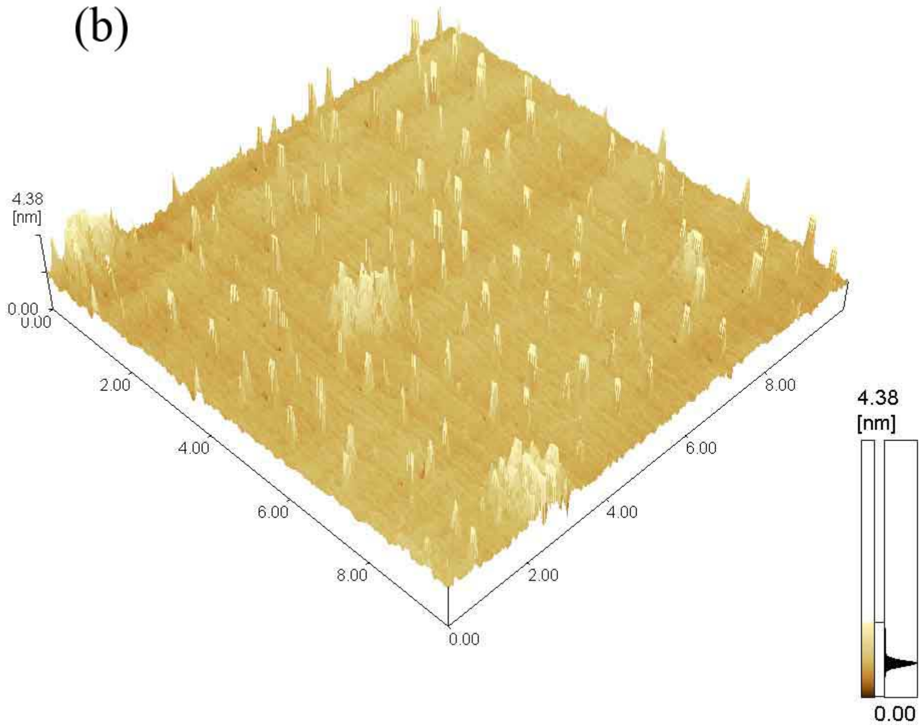


Figure 4.4 AFM (a) height image and (b) 3D image of thin-layer deposits of 20b from acetonitrile on mica

The deposits of polymer **20b** on a mica surface showed a microscopic morphology of small rods standing on the substrate (Figure 4.3a). The diameter of those aggregates (obtained from an analysis of 30 objects) was in the range of 1.7-6.2 nm. The maximum height observed was about 3.2-3.3 nm that is very close to the length of a conjugated unit (about 3.1 nm) ignoring the length of ethylene oxide at terminals. That suggests that the polymer formed folded structure in solution and the folded conjugated segment was perpendicular to the substrate plane after deposition. These structures are likely to be related to the aggregates whose formation is deduced from solution spectroscopic studies.

The stages of growth involved aggregation and formation of islands. The polymer formed aggregation resembling folded rods. With slow evaporation of solvent, the rods stood upright on the substrate through the interaction between hydrophilic mica and ethylene oxide units. Thus it is evident that the polymer already forms aggregation in polar solvent before deposition. After that, its conjugated segments orientates perpendicularly to the substrate plane while its ethylene oxide segments interacts with the mica surface.

4.4. Conclusion

We investigated the aggregation conformation of block polymers. The flexible ethylene oxide chain was indtrouced into rigid backbone to form rod-coil block polymer. Because of the distinctive properties of rigid chains and soft chains, these type of polymers present unique self-assembly behavior in system. Therefore, we could control their microstructure in solution through change of the polarity of solution. As the percentage of methanol in chloroform was more than 50%, it showed an obviously decreased intensity of maximum emission and maximum absorption with the concomitant emergence of a new shoulder peak. The observed changes can be rationalized on the basis of the solvent-induced folding of the chromophore to form a face-to-face stacked foldamer. For this type of face-to-face stacked structure, fluorescence of polymers became weaker compared with unfolded polymers, because the internal conversion from an upper excited state into a lower one occurs immediately, and the emission from a lower excited state is theoretically forbidden.[21]

We also deposited polymer solutions on mica surface and used scanning probe microscopy to study their nano-scale structure in solid. It was interestingly found that the polymer molecule could stand up on the substrate surface. The stages of formation involved aggregation in solution and growth in solid. The polymer formed aggregation of folding structure, for the corporation of π-π stacking and solvophobic effect together in solution. The shape of these aggregations was analogous to stick. With slow evaporation of solvent, the “stick” was standing upright on the substrate through the interaction between hydrophilic mica and ethylene oxide unites. The intra-molecular and inter-molecular interactions can play a key role in molecule self-assembly as well as have a major impact on the polymer’s performances in manufacturing photoelectric devices.

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Chapter 5 Conclusion and Future Work

In the thesis, ethylene oxide with ability to recognize metal ion were introduced into conjugated backbone to form alternating oligo-(*p*-phenylene ethynylene) and flexible oligo-(ethylene oxide) structure. The fluorescence chemosensor with special selectivity towards Ca^{2+} were synthesized successfully and their aggregation behavior in solution was investigated. Our work focused mainly on the following three aspects:

First of all, the PPE-based fluorescence chemosensors were synthesized and characterized. For the chemosensor's signal amplify unit oligo-(p-phenylene ethynylene) and signal recognition unit oligo-(ethylene oxide), we synthesized them via Sonogashira coupling reaction and toluenesulfonyl chloride reaction respectively. After that, polymers were synthesized successfully by Sonogashira polymerization. Their basic chemical structure and properties were characterized by NMR, UV-vis, FL and GPC. By analyzed ^{1}H NMR and ^{13}C NMR spectroscopy, it was also confirmed that the formation of alternating oligo-(*p*-phenylene ethynylene) and flexible oligo-(ethylene oxide) in ratio 1:1 structure. According to GPC analysis, their molecular weights were controlled below 140 000 and the polydispersity was below 1.7. So the preconceived polymers were acquired successfully.

Secondly，we employed the synthesized polymers to detect alkaline metal ions and alkaline earth metal ions in solution. We added different metal ions into dilute solutions of synthesized polymers. Since the coordination effect between metal ion and ethylene oxide, metal ion was embedded into flexible chain in order to restrict polymers loose conformation. Moreover, polymers in solution were able to form layer-by-layer folding structure by the solvophobic effect of ethylene oxide and the aggregation speciality of phenylene ethynylene. Accordingly, this π-π folding structure caused polymer's fluorescence quenching and the aim of detecting metal ion was achieved. From our titration experiments, we found that the polymer **20c** specially responded towards Ca^{2+}, while it showed weak or no response towards other metal ions. The responding properties in such cases depended mainly on the number of oxygen atoms, the size of the pseudo crown cavity, the charge density, and the coordination number of the cation, which might be the reasons for the specific recognition of Ca^{2+} ions with **20c**. We also investigated the changes in ^1H NMR of polymers with addition of metal ions to further confirm the coordination effect between polymer and metal ion. In the ^1H NMR spectrum, all the chemical shifts of proton in benzene, side chain of benzene and ethylene oxide chain shifted from low magnetic field to high magnetic field to some extent. This result can be explained by deshielding effect due to conjugated π-π stacking of the benzene after metal ion coordinated with atom O. The interaction between polymer and metal ion and the π-π aggregation structure formed by conjugated OPE were identified as well. Though the above investigation, a novel fluorescence chemosensor **20c** specially responding towards Ca^{2+} was acquired.

Finally，we studied the self-assemble behavior of well defined π-conjugated polymer. We have investigated on the conformation of polymers in solution through solvent-induced methods which could change the polarity of solution. Changes in absorbance and emission spectra indicated the changes of polymer conformation with increased methanol in chloroform solution. This increased methanol caused π-π aggregation of conjugated unit. This result proved that using change of the polarity of solution to control self-assembly behavior of polymer in solution was an effective method. AFM studies also revealed self-assembly behavior of polymers in solution and in solid status. These polymers could stand upright on the mica surface as a result of the interaction among polymer, solvent and surface.

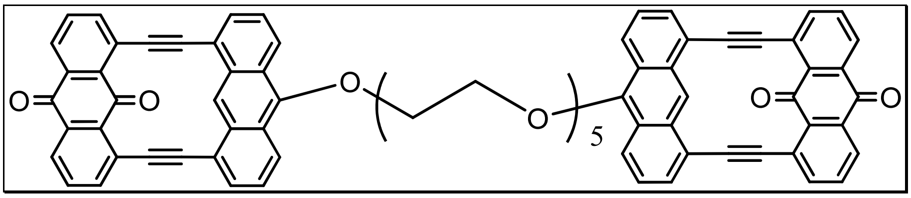

Figure 5.1 Proposed new chemosensor molecule

In conclusion, a novel fluorescence chemosensor **20c** specially responding towards Ca^{2+} was acquired, and its self-assembly behavior was studied as well. Based on current studies, we can design different recognition units with stronger transannular π-π interaction to further improve our chemosensor's sensitivity in the future. These anthraquinone cyclic analogues show a larger and two-dimensional conjugated structure. We proposed this new chemosensor molecule with two anthraquinone cyclic analogues chromophore and one penta(ethylene oxide) linkers (Figure 5.1). This compound might have promising applications in detecting Ca^{2+} with high selectivity and sensitivity. Moreover, interesting of this larger conjugated structure is not only from a structural aspect but also from aspects of electronic spectra and aggregation properties.