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Synthesis of Conjugated Polymer Containing Bipyridine and Oxadiazole Groups and Its Metal Ion Sensing Property

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A new polybipyridine linked with oxadiazole and 2,5-didecyloxybenzene was prepared via simple condensation and ring closing reaction. The polymer ***P2*** *is basically an amorphous material with thermal decomposition temperature greater than 500°C. Introduction of didecyloxy group into the rigid oxadiazole backbone resulted in better solubility in common organic solvents such as THF, chloroform, and DMF. UV-vis and fluorescence spectroscopy were employed to investigate the optical properties both solution in the presence of a variety of metal cations, in which the polymer would be a good candidate for optical sensory material for metal ion.*

Keywords Bipyridine; conjugated polymers; metal ion; sensors

Introduction

Conjugated polymers with fluorescent properties are highly recognized as functional organic materials due to the advantage with which the substance is able to integrate its electronic and optical characteristics. Therefore, these materials are frequently

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Address correspondence to Taek Seung Lee, Organic and Optoelectronic Materials Laboratory, Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 305-764, Korea. Tel.: +82-42-821-6615; Fax: +82-42-823-3736; E-mail: tslee@cnu.kr applied to fields that use electronic properties resulting from π-conjugated structures such as organic light emitting diodes (OLED) and organic solar cells [1–5].

Among the various conjugated polymers the ones with 1,3,4-oxadiazole structures show diverse characteristics such as thermal and chemical stability in addition to mechanical strength and rigidity allowing them to be used in carbon fibers, high-performance fibers, reinforcing materials, and gas separation membranes [6,7]. It is understood that oxadiazole shows such characteristics because it's structures resemble the characteristics of phenyl structures [8]. Hence recently, there has been much study on applying conjugated polymers with oxadiazole structures to eletro-optics. Specifically, related to the development of the multi-level structure of OLED (ITO/HTL/EL/ETL/metal) it is studied and developed widely as ETL [9]. However, multi-layered OLED's have many limitations when selecting materials, like a suitable solvent to produce the multi-layer structure. Many researchers continue to resolve the current limitations and, as a result, researchers are attempting to simplify multi-layered OLED's to single-layered OLED's (ITO/EL/metal) [10,11].

The most important aspect of simulating a single-layered OLED is the hole and electrons provided by the anode and cathode, and the balanced insertion of electrons into the emitting layer. Typical conjugated polymers used as organic emitting materials have better hole transporting abilities than electron transporting abilities due to a high lowest unoccupied molecular orbital (LUMO) energy level. Therefore, in order to increase the efficiency of organic luminescence it is important to design the organic luminescent material to have electron transporting abilities. Thus, it is for this reason, that the introduction of an oxadiazole structure that can give electron transporting abilities to conjugated polymers is so important.

Besides, conjugated polymers have a unique optical property (UV-vis and fluorescence spectra) and signal amplification ability that are advantageous for an analytical tool. An important characteristics is that conjugated polymers and metal ions such as 2,2′-bipyridyl and 4-hydroxybipyridyl can chelate with metal ions, which can lead to conformation changes. This means that the optical properties of conjugated polymers can be altered due to the chelation between the polymer and metal ions. These conjugated polymers, that can form chelation with metal ions, are used as ion-recognizing materials in various studies [12,13].

In this study, we synthesized **P2** containing oxadiazole groups which have an n-type semiconducting property due to electron deficiency and bipyridine groups for chelation with metal ion by means of thermal cyclization of precursor polymer **P1**. We investigated the efficiency of the polymer's ability as an ion-recognition material toward metal ions.

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Experimental

Materials and Reagent

2,5-Dihydroxyterephtalic acid (**1**), 1-bromodecane, hydrazine hydrate, 5,5′-dimethyl-2,2′-dypyridyl used for monomer synthesis were purchased from Aldrich and used without further purification. Sulfuric acid, nitric acid, hydrochloric acid, potassium carbonate, potassium dichromate, potassium hydroxide, magnesium sulfate, triethylamine, and N,N′-dimethylformamide (DMF) were purchased from Duksan Pure Chemicals Co. or Samchun Pure Chemical and used without additional purification procedures. Distilled deionized water was used in polymer synthesis and ion

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recognition experiment. Ethyl ether and thionyl chloride were purified by conventional distillation method.

Instrumentation

^{1}H NMR spectra were collected on a Bruker DRX-300 spectrometer with tetramethylsilane as an internal standard (Korea Basic Science Institute). UV-vis absorption spectra were recorded on a PerkinElmer Lambda 35 spectrometer. Infrared absorption analysis was carried out with the FT-IR Matsson Genesis II. Gel Permeation Chromatography (GPC, solvent: THF, reference material: polystyrene) was used to measure the molecular weight of the polymer. Fluorescence spectrum was recorded in PerkinElmer LS45.

Synthesis

*Diethyl-2,5-dihydroxylterephthalate (**2**) [14].* 5 g (25 mmol) of **1** and 200 mL of ethanol were stirred in a 500 mL 3-neck-round flask. Then, the temperature of the flask was increased to 80°C. After the solid in the flask was completely dissolved, 13 mL (250 mmol) of sulfuric acid was slowly added and the flask was charged with nitrogen. The reaction mixture was stirred vigorously for 24 hr. After the reaction, the flask was cooled to room temperature and the solid precipitate was obtained by filtration. The solid precipitate was then recrystallized in ethanol twice. The solid obtained was vacuum dried at 50°C. The obtained **2** is light green-colored and the yield was 5.9 g (92%). ^{1}H NMR ($CDCl_3$, ppm): 10.2 (s, 2H, OH); 7.5 (s, 2H, aromatic); 4.4 (m, 4H, CH_2); 1.4 (t, 6H, CH_3).

*Diethyl-2,5-didecyloxyterephthalate (**3**) [14].* 5 g (20 mmol) of **2** and 200 mL of DMF were stirred in a 500 mL 3-neck-round flask and heated to 80°C until the solid within the flask was completely dissolved. After the solid was completely dissolved, 13.6 g (100 mmol) of potassium carbonate was put into the flask with 20.5 mL (98.5 mmol) of 1-bromodecane and maintained for 96 hr. After the reaction the flask was cooled to room temperature and the solid precipitate was isolated by filtration. The obtained solution was evaporated in rotary evaporator. The solid **3** obtained after removing the solvent was recrystallized twice in ethanol to obtain a pure substance. The obtained **3** was a white solid (yield 9.0 g (86%)). ^{1}H NMR (DMSO-d_6, ppm): 6.8 (s, 2H, aromatic); 3.7 (m, 4H, $COOCH_2$); 3.3 (t, 4H, OCH_2); 2.4-1.1 (broad, 32H, alkyl); 0.7 (broad, CH_3).

*2,5-Bis(decyloxy)terephthalohydrazide (**4**).* 100 mL of methanol and 16.3 mL (524 mmol) hydrazine hydrate were placed in a 500 mL 3-neck-round flask and the temperature was raised to 65°C. During the vigorous stirring of the solution, 7 g (13.1 mmol) of **3** in 200 mL of methanol was added and reacted for 24 hr. After the reaction, the solvent was removed by evaporation to 50 mL. Then the solution was cooled to room temperature and the solid precipitate was filtered. The solid was recrystallized twice in ethanol. The obtained compound was white and the yield was 6.0 g (91%). ^{1}H NMR ($CDCl_3$, ppm): 9.2 (s, 2H, NH); 7.8 (s, 2H, aromatic); 4.2 (t, 4H, OCH_2); 2.0-1.3 (broad, 36H, alkyl and NH_2); 0.9 (t, 6H, CH_3).

*5,5′-Dicarboxyl-2,2′-bipyridine (**6**) [15].* 125 mL of sulfuric acid was slowly stirred in 500 mL beaker and then 5.0 g (20.5 mmol) of **5** was placed within the beaker.

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The beaker was then heated to 80°C while 24 g (81.5 mmol) of potassium dichromate was added portionwise. After the addition of potassium dichromate, the beaker was cooled to 40°C and then the solution was slowly poured into 800 mL of ice water with vigorous stirring. The solid precipitate was washed with water four times. The solid obtained after the filtration was dried in a vacuum at 60°C. The dried solid and 170 mL of nitric acid (50%) were placed in a 250 mL beaker and heated to 140°C with stirring for 4 hr. After the reaction, the solution was cooled to room temperature and then was slowly added to a 2 L beaker filled with ice. When the ice was completely melted the solution was diluted with 1 L of water. The precipitate was filtered, washed with water 5 times, and finally with acetone twice. The obtained solid was vacuum dried at 40°C to afford white solid (yield 5.6 g (90%)).

5,5′-Dicarbonyl chloride-2,2′-bipyridine (7). 100 mL of distilled thionyl chloride and 2.5 g (10.2 mmol) of **6** were placed in a 250 mL 3-neck-round flask. Three drops of DMF were added and the temperature was raised to reflux and left to react for 24 hr. After the reaction the solution was cooled to room temperature and a needle-shaped precipitate was formed. The solid was filtered using a glass funnel. Then the solid was recrystallized in n-heptane. Finally, it was vacuum dried at room temperature affording **7** as a needle-shaped white crystal (yield 2.3 g (79%)). ^{1}H NMR (DMSO-d_6, ppm): 9.0 (s, 2H, aromatic); 8.4 (d, 2H, aromatic); 8.3 (d, 2H, aromatic).

P1. 10 mL of chloroform and 1.1 g (2.1 mmol) of **4** were stirred in a 100 mL 3-neck-round flask and the solid was completely dissolved. 1.0 mL (7.2 mmol) of triethylamine was added to the flask with vigorous stirring. 0.6 g (2.1 mmol) of **7** dissolved in chloroform was added. The polymerization took place for an hour. After the polymerization, the solution was poured into 700 mL of methanol resulting in a solid precipitate. The solid precipitate was isolated through filtration and washed with water twice and in methanol three times. Then it was dried in a vacuum oven for 24 hours at 50°C. The **P1** was light yellow and the yield was 0.9 g (59%).

P2. 10 mL of phosphorus oxychloride and 0.5 g (0.7 mmol) of **P1** were put into a 50 mL 3-neck-round flask with vigorous stirring. The temperature was raised to 100°C and the reaction was maintained for 24 hr. After the reaction, the flask was cooled to room temperature and the solution was slowly poured into 500 mL of ice water resulting in the formation of a solid precipitate. The solid precipitate was isolated by filtration and washed with water twice and with acetone respectively and dried in vacuum at 50°C. The **P2** was yellow-colored (yield 0.4 g (80%)). ^{1}H NMR (DMSO-d_6, ppm): 8.8-8.5 (d, 4H, aromatic); 7.8 (d, 2H, aromatic); 6.7-6.5 (d, 2H, aromatic); 4.1 (t, 4H, OCH_2); 2.0-1.3 (broad, 32H, alkyl); 0.9 (t, 6H, CH_3).

Ion Recognition Properties

The **P2** was dissolved in chloroform and the concentration was varied depending on the metal ion used. To analyze the polymer solution's light absorption property, 1 cm cuvette cells were used to test for the path length of light. To obtain the absorption spectrum, 3 mL of the polymer solution was used and the measured wavelength range was 250–700 nm. The same cuvette cells and the same volume of solution were used to study the absorption properties of the polymer solution as well as to study the fluorescence properties of the polymer solution.

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The change in optical property due to the formation of a polymer-metal complex compound was measured within the 250–700 mn range for absorption spectrum and 357–700 nm range for fluorescent spectrum. The metal ions used were Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Zn^{2+}, Cd^{2+}, Al^{3+}, and Mg^{2+}.

Results and Discussion

Heterocyclic amines with 2,2′-bipyridine exhibit two important features. The first one is related to the fact that the unshared electron pair can react separately and this is known as 'π-deficiency.' The second feature is that such unshared electron pairs act as ligands that can form chelation with various metal ions [16]. Since the discovery of bipyridyl ligand in the late 19th century, it has been widely used for the coordinate bonding of metal ions. It has been proved that the chelation between metal ions with bipyridyl groups can alter the UV-vis and the fluorescent spectra. Also, theoretically, the two pyridyl rings can form a dihedral angle of 20° near the molecules. However, the chelation between such molecules and metal ions result in more planar bipyridyl ring conformation. It has been found that such chelation will eventually increase the conjugated length of the molecule resulting in red shift within the peak absorption wavelength in the UV-vis spectrum [17].

Regarding the design of the **P2** molecular structure, 2,2′-bipyridyl rings were introduced to give ion recognizing abilities using ionochromic effect. The 2,2′-bipyridyl rings were introduced to make the polymer into a effective conjugated structure thus giving it a signal amplification and therefore increase it's sensitivity towards metal ions. Finally, by incorporating alkoxy groups into the main chain of the polymers, it was possible to enhance the solubility allowing it to be applied to more diverse fields.

In this study, the synthesis of conjugated polymers with 1,3,5-oxydiazoles was achieved through condensation polymerization of dihydrazide radical monomer (**4**) and diacid chloride monomer (**7**) to produce a polymer precursor (**P1**). Then the intermediate polymer was cyclized into **P2**. The general method of cyclization was related to dehydration in hydrazide to form oxydiazole compound using phosphorous oxychloride. The didodecyloxy group present in the side chain improved the solubility and therefore showed complete dissolution of **P2** in chloroform, DMF, and DMSO, on the while **P2** was not soluble in THF and acetone. The synthetic scheme of the monomer for the polymer is described in Scheme 1.

The compounds for monomer synthesis and **P2** were analyzed using ^{1}H NMR and they were in good agreement with our expectation. **P1**, that has a hydrazide structure in the main chain, did not dissolve due to the intermolecular bonding and therefore could not be analyzed by the ^{1}H NMR. The KBr pellet was used to check the cyclization by studying the IR spectrum of precursor polymer **P1** and cyclized polymer **P2**. Figure 1(a) and (b) show the IR spectra of **P1** and **P2** respectively. In the aforementioned IR spectrum, the characteristic band of hydrazide (−CONHNHCO−) was shown at 1680 cm^{-1} (amide C=O) and 3250 cm^{-1} (amide N−H). However, in the spectrum of **P2**, as a result of cyclization, the bands disappeared from the spectrum. This leads to the conclusion that hydrazide in **P1** was successfully cyclized as to give 1,3,4-oxadiazole structures. Also the observation of disappearance of NH proton signals of hydrazide in ^{1}H NMR spectrum of **P2** confirms the aforementioned conclusion.

Thermogravimetric analysis was carried out by heating to 900°C under the nitrogen flow (Fig. 2). Through this thermogram it can be known that compound

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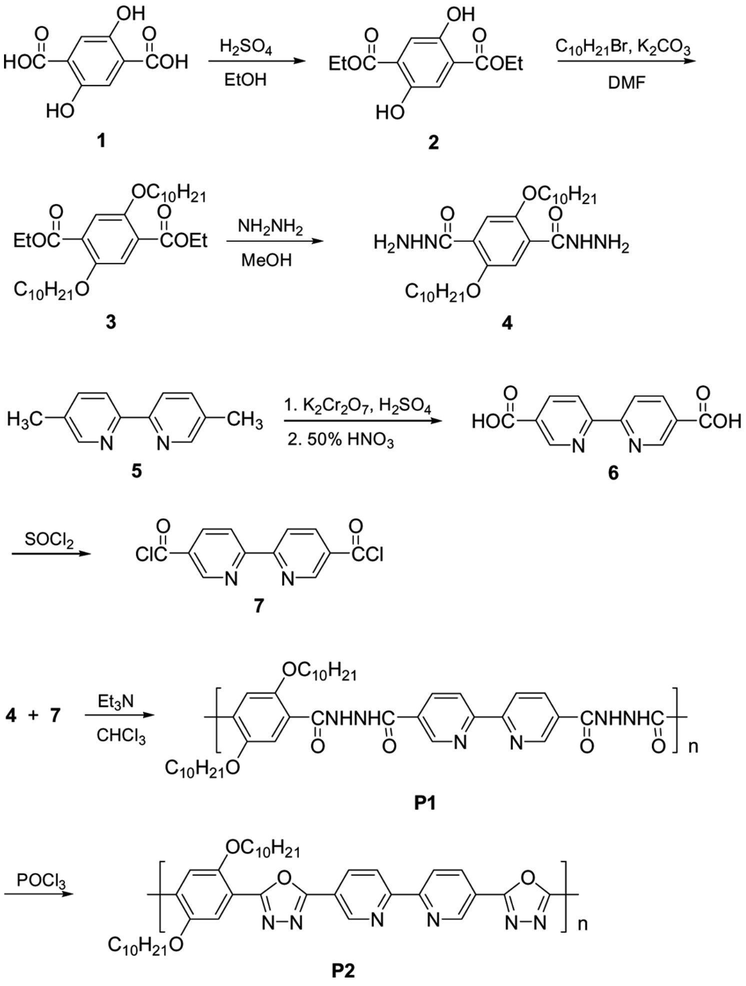

Scheme 1. Synthesis of monomers and polymers.

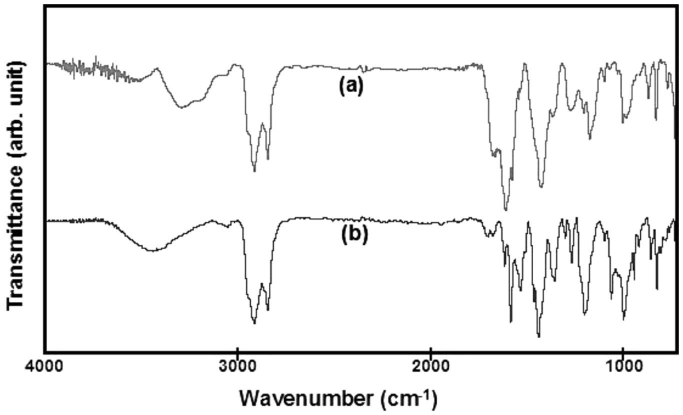

Figure 1. Infrared spectra of precursor polymer (a) **P1** and (b) **P2**.

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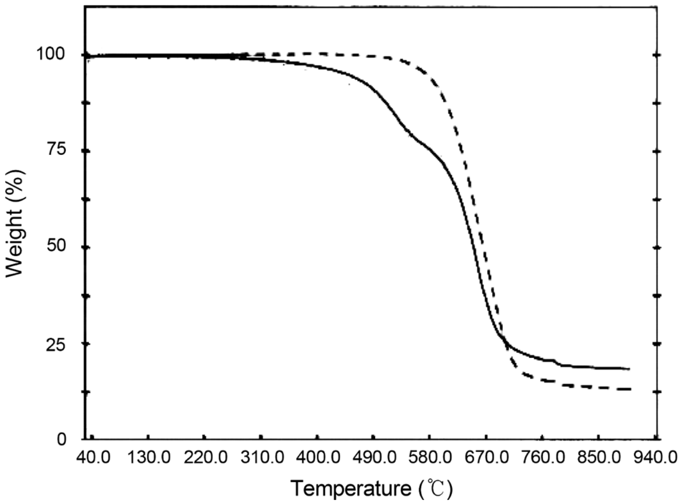

Figure 2. TGA thermograms of the precursor polymer **P1** (solid) and **P2** (dotted) under nitrogen atmosphere.

thermal decomposition temperature (onset T_d) of **P1** was found to be 482.3°C and that of **P2** to be 592.4°C. As can be seen on the TGA thermogram, the polymer with oxadiazole structure showed significantly increased the decomposition temperature. It can be observed that the decomposition temperature **P2** is much higher than that of **P1** and it conforms that the decomposition temperature of main-chain oxadiazole polymers is located between 400–600°C. This predicts that as 1,3,4-oxadiazole polymers can be used as heat-resistant materials. Glass transition temperature (T_g) and melting temperature (T_m) were not found in DSC measurement showing that the polymers are amorphous.

GPC revealed that number-average molecular weight (M_n) of **P1** was found to be 5,210 and weight-average molecular weight (M_w) was 9,330. M_n of **P2** was found to be 4,770 and M_w to be 8,920. Thus, it can be thought that there was a slight decrease in the molecular weight through cyclization.

UV-vis spectrum of **P2** showed absorption maximum (λ_{max}) at 337 nm with a shoulder at approximately 360 nm in the chloroform. When excited at 337 nm, it showed a emission maximum at 425 nm and a band-edge reached to approximately 600 nm. Figure 3 illustrates the absorption and fluorescence spectra of **P2** solution in chloroform.

In order to study the metal-recognition ability of **P2**, various amounts of metal ions were continuously added into the solution to investigate the changes in the absorption and fluorescence spectra. Figure 4 shows the change of the UV-vis spectrum in relation to the addition of ferric nitrate (4.0×10^{-5} M) dissolved in methanol. In the spectrum, as the concentration Fe^{3+} within the polymer solution increased there was no change in the absorption wavelength of **P2**. However, the overall absorption was remarkably increased. This linearly proportional increase in absorbance is due to the increase in the formation of polymer-metal complex with the increase of Fe^{3+} ions within the polymer solution. Therefore, it can be concluded that **P2** is an efficient candidate for an ion-recognizing material quantitatively and qualitatively toward Fe^{3+}.

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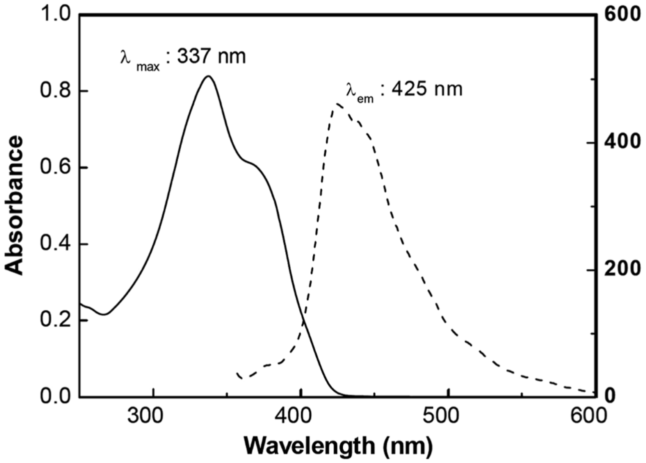

Figure 3. Absorption (solid) and emission spectra (dotted) of the **P2** solution in chloroform (excitation wavelength 337 nm).

Similarly, when Cu^{2+} ion is added to the **P2** in chloroform solution to a variable concentration, the absorption in UV-vis spectrum increases. However, the extent of the increament was smaller compared to that of Fe^{3+}. Figure 5 illustrates the change in UV-vis spectrum of the solution when cupric sulfate (4.0×10^{-5} M) solution dissolved in methanol is added. Similar to the case with Fe^{3+} ion, Cu^{2+} ion can alter the conformation structure of **P2**.

Figure 6 illustrates the change in UV-vis spectrum due to the addition of cobalt (II) chloride hexahydrate (1.0×10^{-6} M) in methanol into **P2** solution. This spectrum shows some difference from those of Fe^{3+} and Cu^{2+} ions in that the absorbance

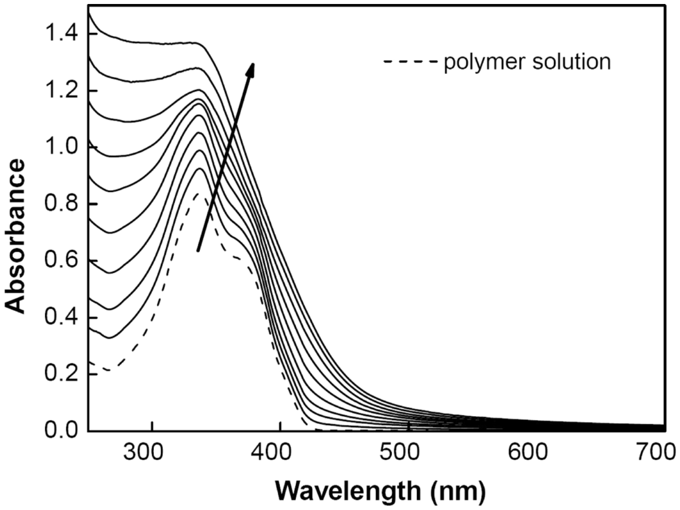

Figure 4. Absorption spectra of the **P2** solution in chloroform (6.0×10^{-4} M) at room temperature upon addition of Fe^{3+}. $[Fe^{3+}] = 0$; 0.40; 0.80; 1.20; 1.60; 2.00; 2.40; 2.80; 3.20; 3.60; 4.00×10^{-4} M.

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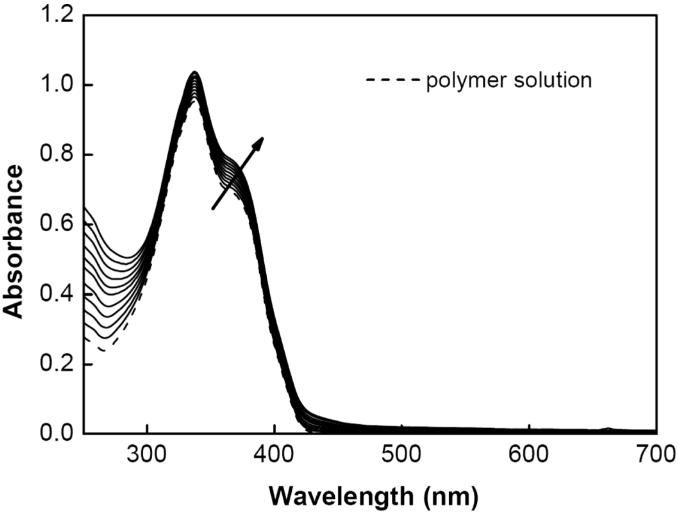

Figure 5. Absorption spectra of the **P2** solution in chloroform (6.0×10^{-4} M) at room temperature upon addition of Cu^{2+}. $[Cu^{2+}] = 0$; 0.40; 0.80; 1.20; 1.60; 2.00; 2.40; 2.80; 3.20; 3.60; 4.00×10^{-4} M.

linearly decreases. This relationship reveals that this polymer solution carries both the selectivity and the sensitivity that is needed for it to be used as an ion-recognition material. Nevertheless, in the case with other metal ions, that is with Ni^{2+}, Cr^{3+}, Zn^{2+}, Cd^{2+}, Al^{3+}, and Mg^{2+} the optical changes were negligible.

For the purpose of diversifying the optical signals in response to molecular recognition, changes in the fluorescent spectrum of the polymer molecule recognition material and metal ion complex compound was measured. Figure 7 compares the

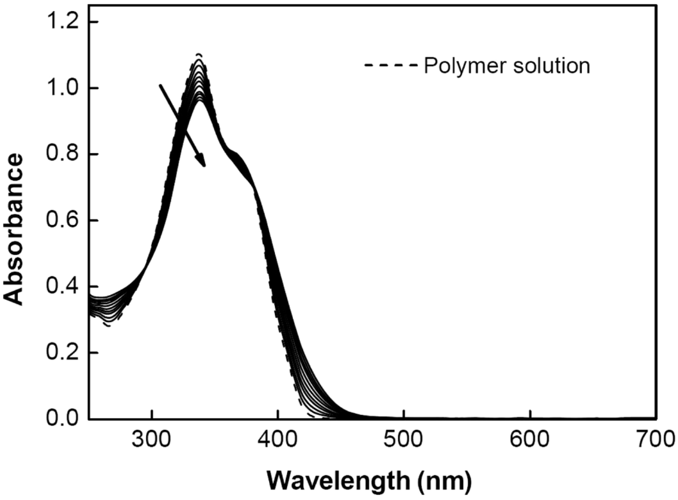

Figure 6. Absorption spectra of the **P2** solution in chloroform (7.0×10^{-4} M) at room temperature upon addition of Co^{2+}. $[Co^{2+}] = 0$; 0.10; 0.20; 0.30; 0.40; 0.50; 0.60; 0.70; 0.80; 0.90×10^{-5} M.

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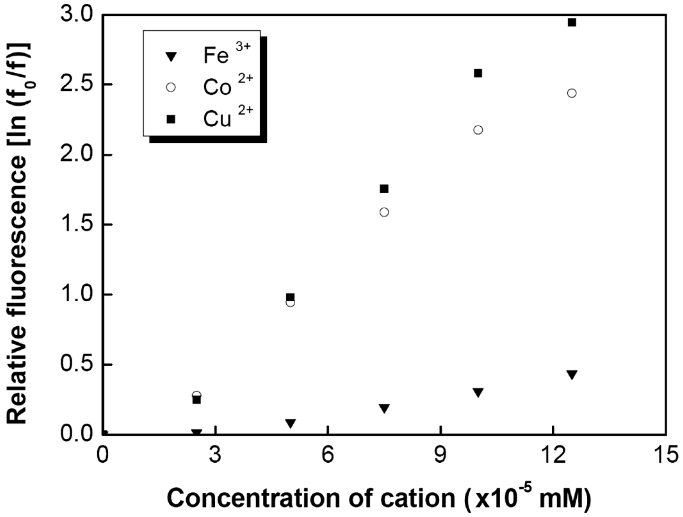

Figure 7. Fluorescence quenching of the **P2** solution in chloroform (8.65×10^{-9} M) by addition of various metal cation. f_0 corresponds to the fluorescence intensity of **P2** solution without metal ion and f corresponds to the fluorescence intensity of the **P2** solution with metal ion.

fluorescence quenching depending on the concentration of various metal ions. Increasing Fe^{3+}, Cu^{2+}, and Co^{2+} ion concentration to **P2** polymer solution it can be seen that the fluorescence quenching took place proportionally. There was no change in the emission wavelength and only the decrease in the fluorescent intensity at 425 nm was observed. It was found that the most significant quenching was observed in the case of copper ion.

Such changes in fluorescence intensity are due to the conformation changes in the bipyridyl groups due to the metal-bipyridyl complex formation in the polymer main chain. Such conformation change in the bipyridyl group is an important feature because when the metal-ligand forms a complex, the electron density in the bipyridyl group as well as the electron conductivity changes. Through the optical characteristics (absorbance and fluorescence) measured through the complex formed between the polymer material and the metal ion, it is confirmed that **P2** is a material that can recognize metal ions such as Fe^{3+}, Cu^{2+}, and Co^{2+} ions.

Conclusion

To obtain a polymer that can recognize ions, a fluorescent conjugated polymer containing bipyridine and oxydiazole was synthesized. Oxadiazole units were introduced by cyclization of their precursot hydrazide group and due to the long alkoxy side chain the solubility was improved. Studying the absorption spectrum of the polymer, there are significant changes in the absorbance depending on the type of metal ion. The polymer has emission wavelength of 425 nm and therefore shows a blue fluorescence. Depending on the concentration of metal ions the level of fluorescence quenching varied, presumably due to metal ion interaction with bipyridine ligand. Therefore, the fluorescent conjugated polymers **P2** can possibly be used as a metal ion-detecting material.

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