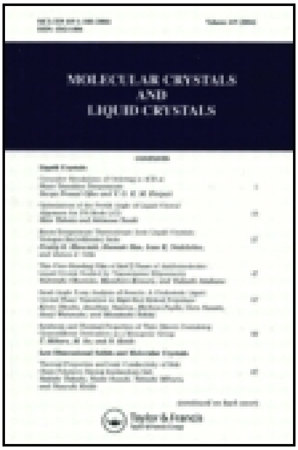

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SYNTHESIS OF CONJUGATED POLYOXADIAZOLE WITH BIPYRIDINE MOIETY FOR OPTICAL SENSING

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SYNTHESIS OF CONJUGATED POLYOXADIAZOLE WITH BIPYRIDINE MOIETY FOR OPTICAL SENSING

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2,2′-Bipyridyl moiety-containing polyoxadiazole was synthesized via cyclodehydration of corresponding polyhydrazide. The polymer solution exhibited absorption maximum at 337 nm and emission maximum at 425 nm. Spectral behaviors from UV-visible and fluorescence spectra were different according to metal cations added. It is presumed that energy transfer between 2,2′-bipyridyl group and metal cation plays a major role in spectral alteration.

Keywords: fluorescence; metal cations; polyoxadiazole; quenching

INTRODUCTION

Recently design and construction of chemosensory systems that are capable of detecting metal cation have attracted considerable interest [1–3]. Enormous potential of optical methods for the analytical detection of clinically, environmentally, and biologically relevant heavy metal cations requires the development of highly selective and highly sensitive chemosensors [4–6].

In particular, researches on design and construction of polymeric chemosensory systems containing molecular recognition site that are capable of detecting metal ions in both a real-time and reversible fashion are performed [7–9]. In recent years conjugated polymers have received a lot of attention as a fluorophore due to delocalized electronic structure, which is responsible for strong absorption and emission. Accordingly, a variety of conjugated polymers with coordination sites for the recognition of metal ion were synthesized, which would show the different absorption and emission

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*Corresponding author. Tel.: +82-42-821-6615, Fax: +82-42-823-3736: E-mail: tslee@cnu.ac.kr characteristics before and after exposure of metal ions with enhanced sensitivity through sensory signal amplification [7–9]. Swager reported that the sensory signal amplification was achieved by the molecular wire approach based on the unique molecular-structure feature of conjugated polymers. Polymers with 2,2′-bipyridyl and terpyridyl group exhibit ion-dependent optical responses toward metal cations [2,3]. Detecting signals of conjugated polymer-based sensory materials for ions are reported by absorption alteration and fluorescence spectral changes (shift, quenching or enhancement), which are caused by conformational changes in the backbone or electronic structure changes upon interaction with metal cations.

We are reporting the synthesis of a conjugated polyoxadiazole containing 2,2′-bipyridyl moiety and investigation on detecting metal cations. As a result different behaviors according to metal cations were observed with spectrometric and fluorometric measurements.

EXPERIMENTAL

Materials and Characterization

2,5-dihydroxyterephthalic acid, hydrazine monohydrate, potassium permanganate, and 5,5′-dimethyl-2,2′-dipyridyl were used as received from Aldrich Chemicals without further purification. Thionyl chloride was distilled just before use.

^{1}H NMR (200 MHz) spectra were recorded on a Varian Gemini 200 spectrometer and chemical shifts are referenced to TMS. Infrared spectra were taken from a MAGNA-IR 560 spectrometer using KBr pellets. Molecular weight was determined with gel permeation chromatography (GPC, Waters 150 C) using chloroform as eluent. Differential scanning calorimetry (DSC) was performed with a Du Pont thermal analyzer Model 2100 equipped with a Model 2910 DSC under nitrogen atmosphere with heating rate of 10°C/min. Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer TGA 7 equipped with 7/3 Instrument Controller with heating rate of 20°C/min under nitrogen.

Synthesis of 2,5-didecyloxyterephthalic Dihydrazide (I)

Diethyl-2,5-didecyloxyterephthalate that was synthesized according to literature method [11] was reacted with excess hydrazine monohydrate in 100 ml of methanol. The mixture was refluxed for 15 hr and was isolated by filtration. The solid was purified by recrystallization from ethanol and dried in a vacuum oven at 80°C for 24 hr affording 6.04 g (yield 91%) of white crystals.

^{1}H NMR ($CDCl_3$): $\delta = 9.28$ (s, 2H), 7.85 (s, 2H), 4.18 (d, 2H), 1.88 (m, 4H), 1.6 (s, 4H), 1.40-1.15 (broad, 24H), 0.88 ppm (t, 6H).

Synthesis of 2,2′-bipyridine-5,5′-dicarbonyl Dichloride (II)

II was prepared by refluxing 2,2′-bipyridine-5,5′-dicarboxylic acid [12] (5 g, 20.48 mmol) in excess thionyl chloride (150 ml) with 3–5 drops of N,N-dimethylformamide. After removal of excess thionyl chloride by evaporation, the solid product was recrystallized from heptane (800 ml) yielding 2.4 g (40.6%) of white crystals.

^{1}H NMR (DMSO-d_6): $\delta = 9.20$ (s, 2H), 8.58 (d, 2H), 8.49 ppm (d, 2H).

Polyhydrazide Precursor (III) Synthesis

0.23 g (0.83 mmol) of **II** in chloroform (50 ml) was added into a solution of 0.42 g (0.83 mmol) of **I** and 0.726 g (7.17 mmol) of triethylamine in 10 ml of chloroform under vigorous stirring. After 0.5 hr stirring, the mixture was poured into methanol. The precipitate was collected by filtration, washed with methanol, water, and acetone, and then dried in a vacuum at 80°C to yield 0.53 g (89%) of product.

Polyoxadiazole (IV) Synthesis

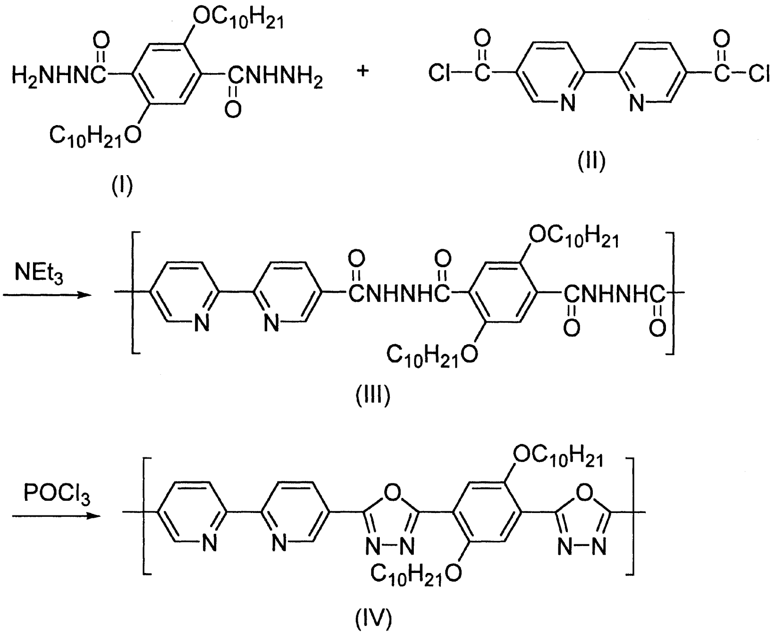
The polyhydrazide (**III**) was refluxed in 30 ml of $POCl_3$ for 5 hr. The mixture was poured into ice water. The yellow precipitate was collected by filtration and washed with water and acetone. After drying in a vacuum oven 80°C yellow powder was obtained.

Spectrometric Measurement and Fluorescence Experiment

The polymer concentration in chloroform used in the experiment was varied according to metal ion used. UV/visible spectroscopy measurement was carried out on a Perkin-Elmer Lambda 35 spectrometer using a 1 cm optical path length cell. Fluorescence measurement was carried out using a Perkin Elmer LS 45 spectrofluorimeter in a similar manner described for UV/visible absorption measurement. The metal salts investigated in this study were cupric sulfate, ferric nitrate, cobalt chloride, lithium hydroxide, magnesium nitrate, and uranyl nitrate.

RESULTS AND DISCUSSION

Polyhydrazide precursor (**III**) was synthesized by reaction of 2,5-didecyloxyterephthalic dihydrazide (**I**) and 2,2′-bipyridine-5,5′-dicarbonyl dichloride (**II**) in the presence of triethylamine (Scheme 1). As shown in Figure 1, FT-IR spectrum of the precursor showed characteristic bands based on the carbonyl group around 1650 cm^{-1}, N-H group of the hydrazide



SCHEME 1 Synthesis of polyhydrazide (**III**) and polyoxadiazole (**IV**).

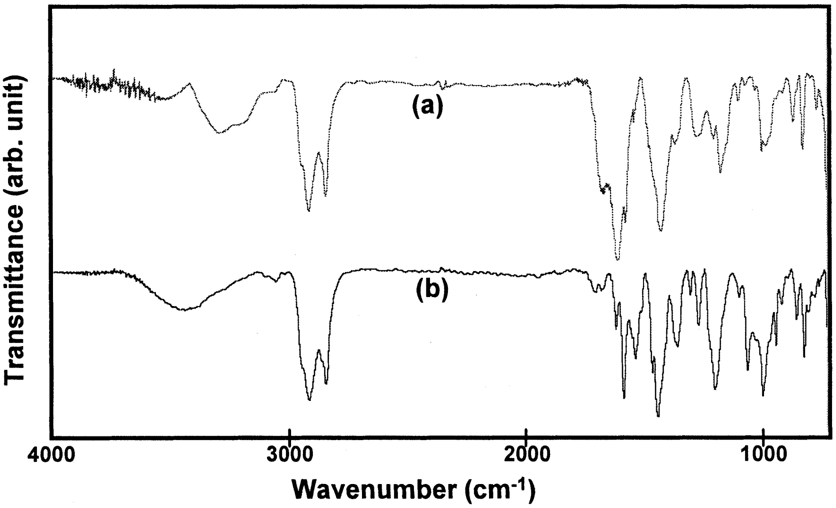


FIGURE 1 FT-IR spectra of (a) **III** and (b) **IV**.

linkage at 3340 cm^{-1}, and C-H group around 2900 cm^{-1}. We carried out conversion into the expected conjugated polyoxadiazole (**IV**) composed of 1,3,4-oxadiazole-2,5-didecyloxybenzene, and bipyridine ring moieties by intermolecular cyclization in the presence of $POCl_3$. The absence of absorption bands in the range of C=O stretching and N-H stretching indicates the complete reaction of cyclohydration. Polymer with number average molecular weight (M_n) of 11,000 was obtained. The polymer is yellowish orange-colored and soluble in chloroform and DMF.

Absorption and emission spectra of polymer were investigated in chloroform solution. The UV-visible spectrum in solution shows the typical absorption of conjugated polymers and absorption maximum around 337 nm with small shoulder absorption at 365 nm. The fluorescence spectrum of polymer in chloroform solution shows blue-emission maximum observed around 425 nm when excited at 337 or 365 nm.

Absorbance changes of solutions containing the polymer in chloroform were investigated by addition of metal cations to measure any possible chromatic changes in the presence of metal ions. Figure 2(a) shows increases in absorption bands (337 nm) in the presence of Fe^{3+} ion, indicating broad hyperchromic shift of λ_{max}. Absorbance was strongly influenced by the amount of Fe^{3+} ion added and increased. On the contrary different effect was observed in the case of Co^{2+} ion. Cobalt ion exhibited substantial decrease in absorption band at 337 nm without significant change at original λ_{max} even in one tenth the concentration of Fe^{3+} shown in Figure 2(a). Absorption increase was also found in the case of Cu^{2+}, which showed much different behavior compared to the case of Fe^{3+} Figure 2(b). Solutions of polymer showed essentially unchanged absorbance spectrum under excess of other metal cations such as Li^+, Mg^{2+}, and $UO_2{}^{2+}$.

It is unusual feature of optical sensory material, which exhibits both absorption increase and decrease according to metal cation added in the same polymer. We believe that 2,2′-bipyridyl units behave as metal cation recognition site and intramolecular electron transfer plays a more important role rather than conformational change of the polymer backbone. Though both of Co^{2+} and Cu^{2+} ions are classified as bivalent ions, absorption behaviors found to be different each other, that is Co^{2+} induced absorption increase, on the while Cu^{2+} affected decrease in absorption. Subsequent study on fluorescence quenching of the polymer solution reveals the consistency of the above observation that it was most likely caused by energy or electron transfer reactions between the oxadiazole and 2,2′-bipyridine complexes.

We investigated the degree of fluorescence quenching by addition of metal ions in terms of monitoring of fluorescence intensity of a polymer solution or film Figure 3. The polymer solution exhibited broad emission band with emission maximum (λ_{em}) at 425 nm, and the resulting emission

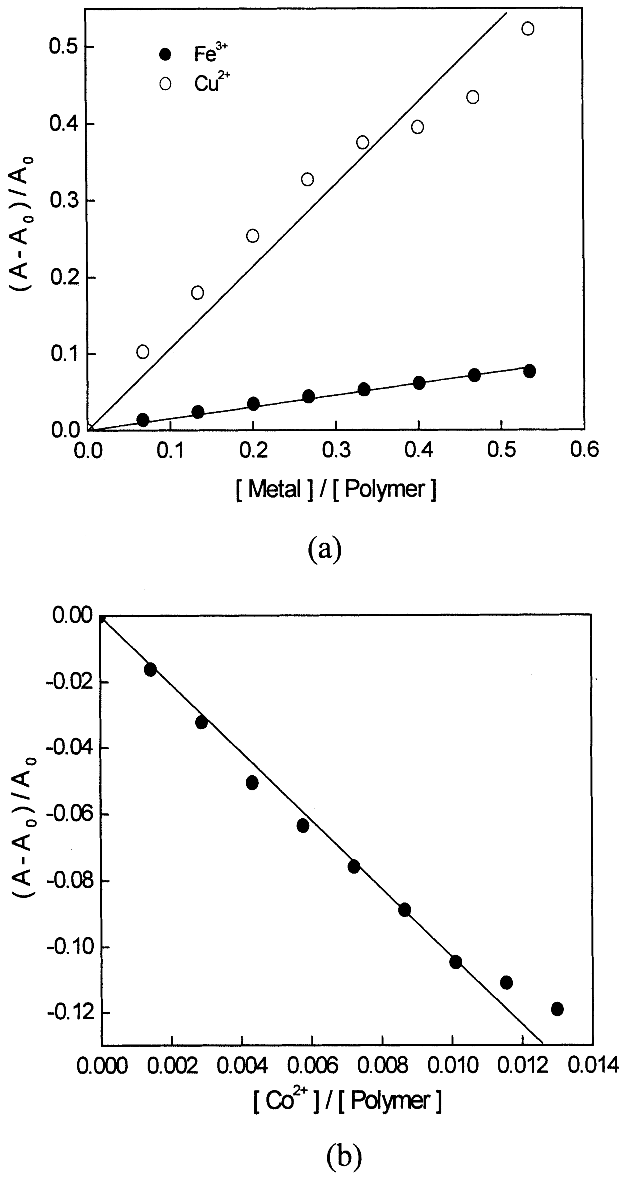


FIGURE 2 Effect of (a) Fe^{3+} and Co^{2+}, (b) Cu^{2+}concentration on the absorption spectrum of polymer (5.26×10^{-4} M corresponding to monomer unit) in chloroform. A$_0$ corresponds to the absorbance of polymer solution without metal ion and A to the absorbance of polymer solution with metal ion.

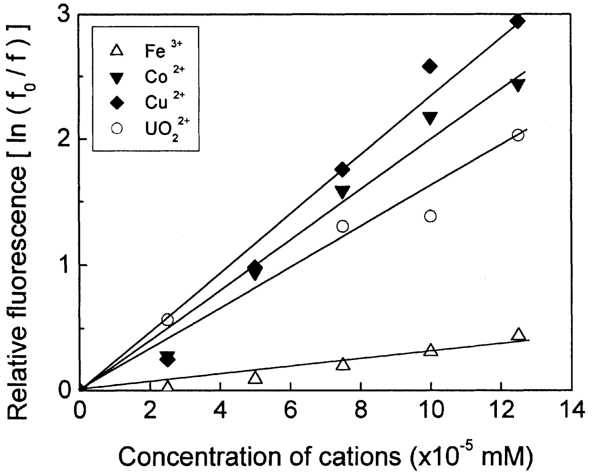


FIGURE 3 Fluorescence quenching of polymer solution (8.65×10^{-9} M) by addition of various metal cations. f_0 corresponds to the absorbance of polymer solution without metal ion and f to the absorbance of polymer solution with metal ion.

was blue in color. Photoluminescence intensity of the polymer solution in chloroform decreased upon exposure to various metal cations. The degree of fluorescence quenching is directly proportional to the concentration of ions. Addition of Co^{2+} or Cu^{2+} to the polymer solution induces efficient quenching of fluorescence compared Fe^{3+}. Especially, $UO_2{}^{2+}$ also acts as a quencher, which did not induce ionochromic changes in spectrometric measurement. Therefore we can concluded that selective interaction between 2,2′-bipyridine group and metal cation was not accomplished in this system, though the degree of quenching was different according to metal cations.

CONCLUSION

We have synthesized bipyridyl-oxadiazole-based polymer (**IV**) for metal ion sensor studies. The polymer was found to be ionochromic to a variety of transition metal cations. The sensing properties of polymer arise from ion-recognition-induced electron transfer resulting in electron density changes rather than conformational alteration resulting in conjugation enhancement on the polymer backbone. The observed optical property change is ion-dependent to a certain degree, that is absorption enhancement was observed in cobalt ion, while absorption decrease was found in ferric and copper ion with different feature of spectra. Unfortunately sensory response from emission maximum was not distinguishable among metalcations, though degree of quenching enables to differentiate each metalcation.

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