

〈Research Paper〉

Preparation of Polymeric Metal Complex Containing Azo Dye Rotaxane

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Abstract— In this article, we synthesized an azo dye rotaxane containing bis(8-hydroxyquinoline) group and its polymeric metal complex with zinc. The azo dye rotaxane exhibits high pH sensitivity, solvatochromism and zinc (II) ion sensings in aqueous solution. These behaviors came from the tautomeric equilibrium between azo-hydrazone tautomers and the formation of extended conjugation. The structure of polymeric zinc complexed dye rotaxane was confirmed with NMR and FT-IR measurements. The existence of CD rings, provided by dye rotaxane formation, was found to be very beneficial in improving aqueous solubility of polymeric metal complex.

Keywords: cyclodextrin, azo dye, dye rotaxane, pseudorotaxane, polymeric metal complex, 8-hydroxyquinoline

1. Introduction

8-hydroxyquinoline (8-HQ) is being widely used in inorganic analysis for the identification and separation of various metal ions¹⁾. 8-HQ is well-known as a ligand with reactivity toward metal (II) ions²⁾, and its products with two coplanar N, O metal-chelate forms in an N, N, (O, O) trans geometry³⁾. Recently, its complexes with metals, such as aluminum, Alq₃, and zinc, Znq₂, have been important as the emissive and electron transporting material in organic light-emitting devices (OLEDs)^{4,5)}. However, these metal complexed light emitters are poorly soluble in all the common solvents, and to overcome this limitation, investigations of substituted 8-HQs have been performed⁶⁾.

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six (α -CD), seven (β -CD), or eight (γ -CD) glucose units, and they provide a hydrophobic cavity in a hydrophilic environment due to the existence of numerous hydroxyl groups all pointing out of the outside wall⁷⁾. A rotaxane is a supramolecular assembly of a dumbbell-like component that has macrocycle around the molecular axis⁸⁻¹⁰⁾. The formation of polymer-CD inclusions consists of CD molecules threading

onto a polymer chain from the end toward the center of the macromolecules, and some of them successfully described the formation of polymer-CD inclusion complexes¹¹⁻¹³⁾. However, most of their attempts are based on the pseudorotaxane structure which can associate and dissociate depending upon the given experimental conditions. It's been tried to make true polyrotaxane, but only a few successes have been reported in the synthesis. The conjugated polymers are threaded through CDs in order to form conjugated polyrotaxanes as a form of "insulated molecular wire"¹⁴⁾. Suzuki coupling was employed in water in order to facilitate the formation of stable rotaxane structure^{15,16)}.

In this paper, we synthesize azoxine dye rotaxane by coupling 8-HQs with diazo components in the presence of α -CD. 8-HQ has been used as coupling component in a series of azo dyes named "azoxines"¹⁷⁾. The ability of 8-HQ to behave as a bidentate ligands was used to form metal chelates. Through the reaction with Zn²⁺ ions, polymeric metal complexed dye rotaxane is achieved.

With this approach, it is expected to provide a CD ring per each dye molecule in a regular way throughout extended chains. The presence of CDs is able to bring several advantages of rotaxanation, including increased aqueous solubility.

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Their structures are characterized by measuring NMR, IR and MALDI-TOF spectra. Property changes are examined and compared in terms of UV-Vis spectra.

2. Experimental

2.1 Materials

The chemicals used in the synthesis and purification of the rotaxane dye were 4,4'-diaminoazobenzene, 8-hydroxyquinoline, sulfanilic acid, α -CD, HCl (37%), NaNO_2 , sodium acetate, methanol, ethanol, silica, and DMSO-d_6 . All chemicals used in the syntheses were of laboratory reagent grade.

2.2 Synthesis of dye rotaxane

4,4'-diaminoazobenzene (480 mg, 2.24 mmol) was dissolved in water (10 ml). 1 N HCl (13.6 ml) and 10% NaNO_2 aqueous solution (3.1 ml) was added, and the solution was stirred at 0–5 °C for 1 hr to complete diazotization. α -CD (9.336 g, 9.6 mmol) in water (15 ml) was added to above mixture and stirred for another 1 hr at 0–5 °C. 8-HQ (0.976 mg, 6.72 mmol) in 2 N NaOH (4 ml) was added dropwise for 30 minutes and stirring continued at room temperature overnight (Scheme 1). After reaction, pH was adjusted to 8.5–9.0 and dye precipitate was collected by filtration and dried under vacuum. It was dissolved in aqueous alkaline solution (pH 11 by NaOH), and then free dye was removed by filtration. The pH of the filtrate was then adjusted to neutral condition, and the residue was collected.

Dissolving and precipitating were repeated twice to ensure the purity of the rotaxane dye (RD, yield 40%). Free dye was synthesized following the same routes, but without the addition of α -CD (FD, yield 55%).

δ_{H} for FD (300 MHz, DMSO-d_6 with NaOH) 9.1 (d, 2H, $J=8.1$ Hz), 8.5 (d, 2H, $J=5.7$ Hz), 8.1 (d, 2H, $J=9.3$ Hz), 7.9 (d, 4H, $J=9.0$ Hz), 7.8 (d, 4H, $J=8.7$ Hz), 7.5 (q, 2H, $J=4.2$ Hz), 6.4 (d, 2H, $J=9.3$ Hz); δ_{H} for RD (300 MHz, DMSO-d_6) 9.6 (d, 1H, $J=8.4$ Hz), 9.5 (d, 1H, $J=8.7$ Hz), 9.0 (d, 2H, $J=8.4$ Hz), 8.6 (d, 2H, $J=8.4$ Hz), 8.2 (m, 6H), 8.0 (d, 2H, $J=8.4$ Hz), 7.9 (q, 2H, $J=8.7$ Hz), 7.3 (d, 2H, $J=8.1$ Hz).

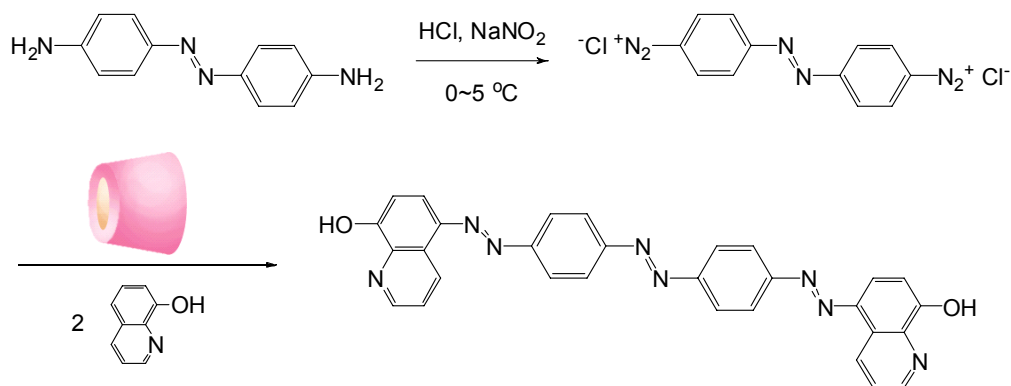
2.3 Preparation of polymeric metal complex

Polymeric metal complexed dye rotaxane (Zn-RD hereafter) was prepared by slowly mixing RD (0.2245 g, 0.15 mmol) in hot methanol (10 ml) with ZnCl_2 (0.0137 g, 0.1 mmol) in hot aqueous solution (10 ml). The molar ratio added was maintained at 2:3 (Zn^{2+} :RD), according to previous report of polymeric metal complex¹⁸⁾.

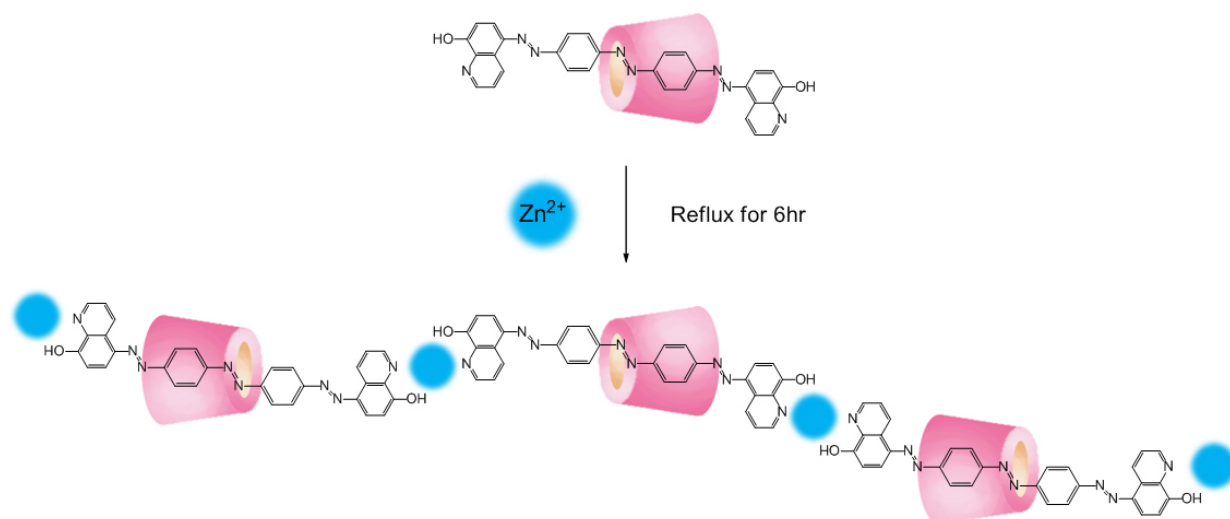
The mixed solution was stirred for another 6 hrs under reflux (Scheme 2). After reaction, the solvent was removed to a half volume of the original and cooled down to room temperature.

Dye precipitates was collected by filtration and washed with a cold water-methanol mixture, followed by overnight vacuum drying.

For comparison, metal complex of free dye (Zn-FD) was synthesized following the same way.



Scheme 1. Synthesis of an azo dye rotaxane with 8-HQs as a coupling component.



Scheme 2. Schematic synthetic representation of polymeric metal complex of the azo dye rotaxane with zinc ion.

2.4 Property investigation

The ^1H -NMR spectra were measured in solvents of DMSO-d_6 using Mercury VXx 300 (Varian, 300MHz). The structure of dyes was characterized using MALDI-TOF measurements. α -Cyano-4-hydroxy cinnamic acid was used as matrix and equal volume mixture of acetonitrile and water was used as solvent. IR spectra were collected on a Perkin Elmer FT-IR microscope. All samples were prepared into KBr pellets for the measurements. Absorption spectra were measured at room temperature on a Lambda 7 (Perkin Elmer) in 1 cm cuvette. The fluorescent spectra were collected using Shimadzu RF-5300PC spectrofluorophotometer with excitation at 353nm.

3. Results and Discussion

The structure of dyes is confirmed by ^1H -NMR spectroscopy. Due to the presence of inter- and intra-molecular hydrogen bonding of 8-HQs¹⁹⁾, it is extremely difficult to dissolve FD in DMSO-d_6 . Small amount of alkali (NaOH) was added to make it soluble. As for RD, due to the existence of hydroxyl groups in α -CD, it readily dissolved in the solvent. The polymeric metal complexes have been reported before^{20,21)}. However, as far as we know, this is the first attempt of making polymeric dye molecules through the formation of metal-ligand

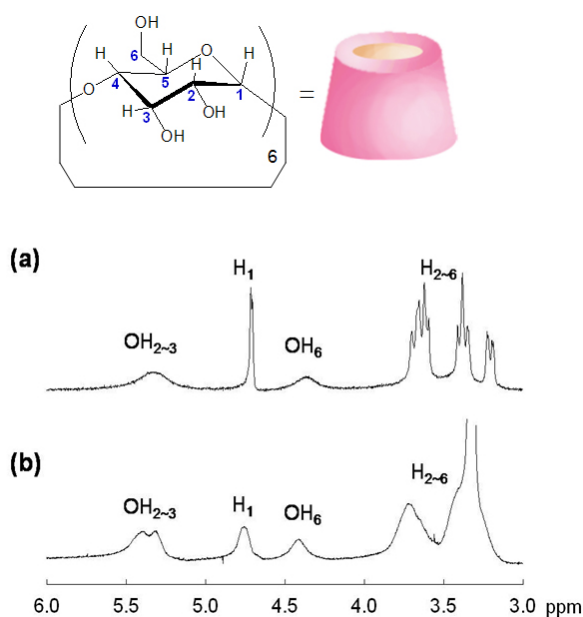


Fig. 1. ^1H -NMR of α -CD in (a) an azo dye rotaxane (RD), and (b) its polymeric metal complex with zinc ion (Zn-RD).

bonds. Moreover, in this case, each dye molecule is locked within α -CD cavity to form stable rotaxane structure. CD rings exist uniformly throughout the polymeric chains. The presence of CD is beneficial in overcoming the poor solubility of polymeric metal complexes. The formation of metal-ligand is readily manifested. ^1H -NMR spectra of CD parts are shown (Fig. 1). The peaks of CDs are found to be even broader when metal complexed with Zn^{2+} . It is attributed to the fact

that upon metal coordination, the conformational flexibility of CDs is much reduced in the extended structure. This agrees to the previous report²²⁾, from which we see that polymeric structure of metal complexed dye rotaxane was successfully made.

Several important FT-IR peaks are shown (Fig. 2). Three major peaks appear in the regions 1130, 1400 and 1573 cm^{-1} , corresponding to $\nu(\text{C-O})$, $\nu(\text{N=N})$ and $\nu(\text{C=N})$ respectively²³⁾. These peaks are shifted to higher wavenumbers by coordination bonding with Zn^{2+} ion (to 1151, 1410, 1597 cm^{-1}). This shift is consistent with metal coordination. The formation of Zn-nitrogen and Zn-oxygen bonds are confirmed by the appearance of two splitted peaks in 434 and 474 cm^{-1} , respectively. These are clear evidence of metal coordination through oxygen and nitrogen atoms of the 8-HQs.

The absorption spectra of RD and Zn-RD were compared (Fig. 3). In a given condition, Zn-RD exhibits slight red shift as expected, which is due to the incorporation of Zn^{+} ions in the extended structure. The shift is attributed to the complex formation between HQs and Zn^{2+} ion, which extends chromophore conjugation to adjacent molecules. This result well agrees to the previous report that the LUMO energy of azo dye is lowered upon zinc coordination, leading to red shift²⁴⁾.

The DSC measurement of α -CD agrees to previous report that α -CD hydrate showed three endothermic peaks (Fig. 4)²⁵⁾.

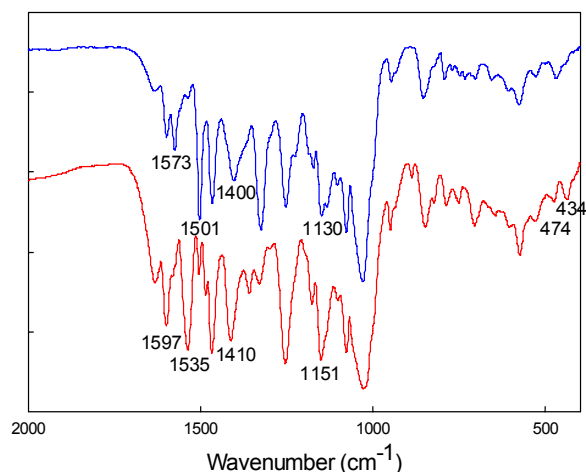


Fig. 2. FT-IR spectra of RD (upper) and Zn-RD (lower).

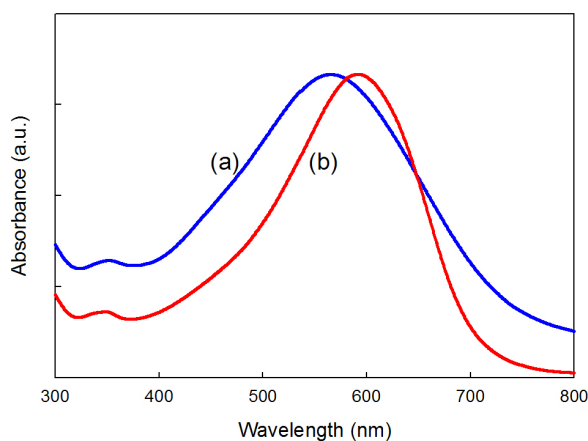


Fig. 3. Absorption spectra of (a) RD and (b) Zn-RD. Mixed solvent (DMF / pH 9.5 Buffer, 8:2, v/v) was used. $[\text{RD}] = 2.0 \times 10^{-5}\text{M}$, $[\text{Zn-RD}] = 30 \text{ mg/L}$. Absorbance intensities are normalized.

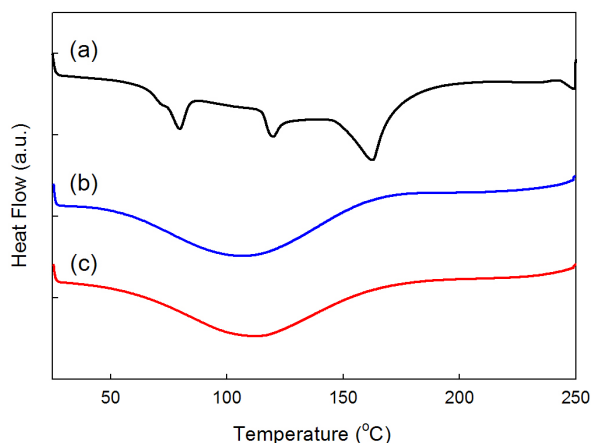


Fig. 4. DSC diagrams of (a) α -CD, (b) RD, and (c) Zn-RD.

It came from the existence of different types of water in the crystal structure of CD hydrate, included water and interstitial water²⁶⁾. A broad endothermic peak is observed for RD and Zn-RD, which is considered to the release of included water from CD cavity on heating. Negligible change was observed in the thermodiagrams of RD and Zn-RD, except for slight shift to higher transition temperature in case of Zn-RD.

4. Conclusion

We successfully synthesized an azo dye rotaxane containing bis(8-hydroxyquinoline) group and its polymeric metal complex with zinc. Azoxine dye rotaxane exhibits high pH sensitivity, solvatochromism and zinc (II) ion sensings in aqueous

solution. These behaviors came from the tautomeric equilibrium between azo-hydrazone tautomers and the formation of extended conjugation. The structure of polymeric zinc complexed dye rotaxane was confirmed with NMR and FT-IR measurements. The existence of CD rings, provided by dye rotaxane formation, was found to be very beneficial in improving aqueous solubility of polymeric metal complex.

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