

# Synthesis of azo dye rotaxane and its colorimetric sensing of metal ions

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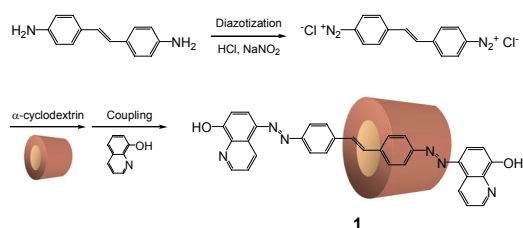
## 1. INTRODUCTION

A rotaxane is a supramolecular assembly with a macrocycle around the molecular axis. Cyclodextrins (CDs) are conically shaped cyclic oligosaccharides with the primary hydroxyl groups on the narrow side of torus glucose residues and the secondary hydroxyl groups on the wider side [1,2].

This study introduces a dye rotaxane that exhibits high selectivity and sensitivity for  $\text{Cu}^{2+}$ . This is made possible by adopting 8-hydroxyquinoline (8-HQ) as the blocking groups. 8-HQ is a well-known ligand with high reactivity toward metal ions [3]. Previously, several azo dyes with 8-HQs, collectively termed azoxine, were reported, but none were rotaxanated. Once rotaxanated, the dye shows a colorimetric response to copper ions. This color change can be identified easily by the naked eye, which mitigates the need for an instrumental set-up.

## 2. EXPERIMENTALS

Dye rotaxane **1** and its unrotaxanated dyes were prepared by following known methods [4,5]. Their synthetic scheme is shown in Scheme 1.



**Scheme 1.** Synthesis of dye rotaxane **1**.

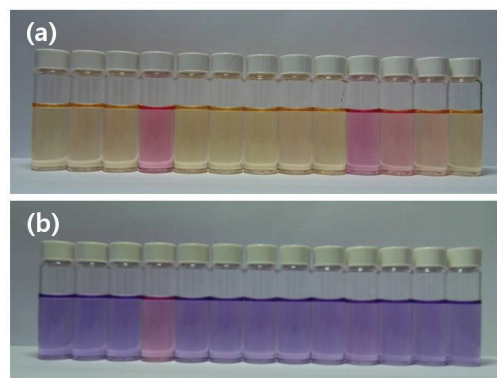
The absorbance spectra of dye **1** were measured using a UV-Visible spectrophotometer for metal ion screening, and compared to those of unrotaxanated analogues.

## 3. RESULTS AND DISCUSSION

The influence of metal ions is easily recognized by inspecting the dye solutions. Dye **1** exhibits a color change upon the addition of metal ions (Fig. 1).

Among them, its response to  $\text{Cu}^{2+}$  is characteristic, showing that the color shift depends on the pH. It shows a red shift from orange to red (pH 7.5) as well as a blue shift from blue to red (pH 11). Moreover, its sensitivity to  $\text{Cu}^{2+}$  was estimated to be very high. A complex color was noted upon the addition of much less than  $1 \mu\text{mol}$  of  $\text{Cu}^{2+}$ , which is 10 times more sensitive than EPA regulations regarding the copper content in drinking water.

Besides, all other detailed results will be given in this poster presentation.



**Fig. 1.** Colors of dye rotaxane **1** after an addition of equivalent metal ions under different pHs (DMF : water = 80 : 20, wt %): (a) pH 7.5, (b) pH 11. The order of the metal cations added was as follows: none,  $\text{Al}^{3+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Li}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$  (left~right).

## 4. REFERENCES

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