8-Hydroxyquinoline Ligands as Fluorescent Chemosensors for Zinc and Cadmium Ions

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8-Hydroxyquinoline ligands 1 and 2 as fluorescent chemosensors for zinc or cadmium ions were synthesized. It is generally difficult to selectively respond to Za2+ over Cd2+ or Cd2+ over Zn2+. However, ligand 1 selectively responded to Zn2+ over Cd2+, and ligand 2 selectively responded to Cd2+ over Zn2+. Key words: 8-Hydroxyquinoline, Fluorescent chemosensors, Zinc ion, Cadmium ion

1. INTRODUCTION

The development of selective and sensitive chemosensors for the quantitative analysis of Za2+ has become extremely important for environmental and biological applications [1, 2]. While remarkable development has been made for other biologically important divalent metal ions such as Ca2+, which has a few selective fluorophores (e.g., FurA-2, Quin-2) [3], there are few Za2+ or Cd2+-selective analytical reagents available. The reported Za2+ or Cd2+ chelating fluorophores use a variety of strategies for binding and responding to their target metal ion [4]. Because Cd2+ is often found with Za2+ in the environment [5] and can form fluorescent complexes with chelating fluorophores [6], a potentially important property of chemosensors for Za2+ or Cd2+ is their selectivity for Za2+ over Cd2+ or Cd2+ over Za2+. Ion selectivity can originate through selective association with the target analyte and/or selective response to the target analyte. We synthesized a new fluorescent chemosensor for Za2+ and Cd2+. We now wish to report the results of our study on zinc ion recognition by the 8-hydroxyquinoline ligand 1 and cadmium ion recognition by the 8-hydroxyquinoline ligand 2. The structural formulas of the ligands 1 and 2 are shown in Fig. 1.

![Figure 1. The structural formulas of the ligands 1 and 2.](image)

2. EXPERIMENTAL

Ligand 1 was prepared from 8-hydroxy quinolinecarboxaldehyde and 1,2-bis (2-benzyl aminoethoxy)ethane [7]. 8-Hydroxyquinolinecarboxaldehyde was prepared by the oxidation of commercially available 5-methyl-8-hydroquinoline with selenium dioxide in dioxane [8]. Ligand 2 was prepared from 5-chloro-8-hydroxyquinoline and 1,2-bis (2-benzyl aminoethoxy)ethane [7]. The MS spectra of ligands 1 and 2 showed corresponding molecular ion peaks and the NMR spectra were suitable for structures [9, 10]. The ligand stock solutions were prepared by the dissolution of a weighed amount of the ligand in methanol. Titrations were done using a Hitachi F-4500 fluorometer. Fluorescence intensities of the ligands (10 μM, M = mol dm−3) by metal ion solutions were directly performed in a spectrophotometric cell of 1 cm path length. The resulting spectra were recorded from 200 nm to 600 nm at room temperature using a Hitachi U-2001 spectrophotometer after each addition of the metal salts. The ionic strength was kept constant at 0.01 M by the addition of sodium acetate. The fluorescence spectra were measured using 252 nm or 256 nm as excitation wavelength at a wavelength between 400 and 800 nm with a measurement in methanol containing 0.01 M NaOAc. The titrations were performed with a titrant (metal ions; 1-100 μM) and titrate (ligand; 10 μM). The metal ion sources were identical to those used to perform the UV-vis studies.

3. RESULTS AND DISCUSSION

We examined the change in the absorption spectra after adding Za2+ or Cd2+ to the solution of ligands 1 and 2. The addition of Za2+ or Cd2+ to 1 and 2 resulted in a red shift of the quinoline absorption. The absorption spectra of 1 in the presence of several concentrations of Za(CIO4)2 are shown in Fig. 2 as a typical example. An isosbestic point at 252 nm was observed. The titration curves by absorbance at 244 nm and 266 nm indicate a sharp endpoint for 1 at a 1:1 ligand:ion ratio for Za2+. (Inset of Fig. 2) Similar results were also observed for ligand 1 with Cd2+ and for ligand 2 with Za2+ or Cd2+. The fluorescence spectra of 1 and 2 in the presence of several concentrations of Za(CIO4)2 or Cd(CIO4)2 are shown in Fig. 3. The Za2+ or Cd2+ complex of 1 and 2
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Figure 2. Spectral changes in the UV-vis absorption of 1 (10 μM) upon the addition of Zn(Cl)₂ in MeOH.

Figure 3. Fluorescence spectra of a titration of a) 1 with Zn²⁺ or Cd²⁺ when excited at 252 nm: [1] = 10 mM, Zn²⁺ or Cd²⁺ = 0.1-10 equiv and b) 2 with Zn²⁺ or Cd²⁺ when excited at 256 nm: [2] = 10 mM, Zn²⁺ or Cd²⁺ = 0.1-10 equiv. Inset is the fluorescence of the 1–Zn²⁺ complex.

The selectivity of Zn²⁺ and Cd²⁺ was completely reversed. Ligand 1 selectively responded to Zn²⁺ over Cd²⁺, and ligand 2 selectively responded to Cd²⁺ over Zn²⁺. These results are very interesting. The difference in the selectivity will be due to the difference in the binding site with the spacer, namely the spacer of ligand 1 attached to the two quinoline rings through the quinoline C-2 position. On the other hand, the spacer of ligand 2 is attached to the two quinoline rings through its C-7 position (Fig. 4).

There are few Zn²⁺ or Cd²⁺-selective analytical reagents available. Especially, it is difficult to selectively respond to Zn²⁺ over Cd²⁺ or Cd²⁺ over Zn²⁺. However, ligand 1 selectively responded to Zn²⁺ over Cd²⁺, and ligand 2 selectively responded to Cd²⁺ over Zn²⁺.

4. CONCLUSIONS
8-Hydroxyquinoline ligands 1 and 2 as fluorescent chemosensors for zinc or cadmium ions were synthesized. It is generally difficult to selectively respond to Zn²⁺ over Cd²⁺ or Cd²⁺ over Zn²⁺. However, ligand 1 selectively responded to Zn²⁺ over Cd²⁺, and ligand 2 selectively responded to Cd²⁺ over Zn²⁺.

5. ACKNOWLEDGMENTS
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6. REFERENCES
[10] The MS spectra of 2 showed a corresponding molecular ion peak. (m/z: 711); 1H NMR(CDCl₃) δ 2.77 (4H, t, J = 5.5 Hz, -CH₂-N), 3.49-4.00 (16H, m, -CH₂-), 7.00-9.00 (18H, m, quinoline and benzene rings).

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Figure 4 C-2 and C7 positions of quinoline ring.

Zn²⁺. Ligands 1 and 2 will become good fluorescent chemosensors for Zn²⁺ or Cd²⁺.