Fluorescence property studies of dibenzo-dithiazole crown ether as ion sensors

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Novel fluoroionophores of dibenzo dithiazol 18 crown 6 has been successfully synthesized from diformal dibenzo 18 crown 6 with 2 aminothiophenol. The newly synthesized dibenzo dithiazol 18 crown 6 was characterized by $^1$H NMR, $^{13}$C NMR, IR spectrum, Mass spectrum, elemental analyses, respectively. Its fluorescence properties was investigated via different alkali metal cations. The results indicated that with the increase of the concentration of the alkali cations, the fluorescence intensity increased very fast. The absorption spectrum also showed interesting changes.

1. Introduction

The application of synthetic fluoroionophores which based on crown ethers have drawn considerable attentions recently. The fluoroionophores is one of the most sensitive detection techniques for the recognition. The fluoroionophores give rise to a specific emission spectral change upon selective complexation with metal cations. As the synthesis and investigations of the fluoroionophores have gone so far, most of the reported fluoroionophores were derived from a combination of fluorophore such as coumarins, naphthalene, anthracenes and pyrene function groups with receptors like crown ethers, cryptands, calixarenes. In this letter, we report the synthesis and fluorescence property investigations about dibenzo dithiazol 18 crown 6 with different alkali metal cations.

2. Experiment

Diformal dibenzo 18 crown 6 was synthesized from 3,4 dihydroxy benzaldehyde with diethylene glycol ditosylate similar to the method described in the literature [1]. Dibeno dithiazol 18 crown 6 was prepared from diformal dibenzo 18 crown 6 with 2 aminothiophenol in ethanol with the method similar to [1,2]. The newly synthesized fluoroionophore was well
characterized by $^1$H NMR, $^{13}$C NMR, IR spectrum, Mass spectrum, elemental analyses. The absorption spectrum were taken on Hewlett Packard UV visible spectrophotometer UV 8453. The fluorescence properties were recorded on a JASCO Spectrofluorometer FP 6300. Fluorescence spectral data of diformal dibenzo 18 crown 6 recorded in chloroform at room temperature, different alkali metal cations such as Na', K', Rb', Cs' and NH$_4$' were added to the solution to record the changes of fluorescence intensity, repectively.

3. Results and Discussion

The absorption spectrum of dibenzo dithiazol 18 crown 6 changed with the addition of different alkali metal cations and NH$_4$'. Figure 1 shows the absorption spectral changes of dibenzo dithiazol 18 crown 6 in chloroform with the addition of K'. The absorption maximum appeared at 324 nm. With the addition of K', the absorption at 324 nm increased, and the absorption at 370 nm region decreased. Similar changes were observed with the addition of other alkali metal cations, but the changed values were different with the addition of different alkali metal cations and NH$_4$'. The absorption behavior reflects the manner of complexation. Because the metal cation withdraw the nonbonding electrons of the oxygen atoms connected to the benzene ring upon complexation.

![Fig. 1. UV spectra of dibenzo-dithiazol 18 crown 6 with the addition of K'.](image1)

![Fig. 2. Fluorescence spectral change of dibenzo dithiazol 18 crown 6 with the addition of K'.](image2)

In the Figure 2 is illustrated the fluorescence spectral behavior of dibenzo dithiazol 18 crown 6 in chloroform at room temperature. The fluoroionophore
(when excited at 324 nm) gave a broad emission band with a maximum at 384 nm with the addition of K⁺. The fluorescence intensity increased with the addition of K⁺. The case of fluorescence behaviour changed very similar when other alkali metal cations and NH₄⁺ were added. The fluorescence intensity increased as the concentration of alkali metal cations increased. The fluorescence of the fluoroionophore illustrated the complexing difference between different alkali metal cations, which can not be distinguished via absorption.

References