Synthesis and fluorescent property investigation of novel fluoroionophores

Zhi Bin Huang[1], Zhi Ping Wang[1], Tai Jong Kang[1], Young Hwan Kwon[2],
Sung Nam Kim[1] and Seung Hyun Chang[1]*
1. Department of Chemistry, Daegu University, Kyongbuk, 712-714, Korea
2. Department of Chemical Engineering, Daegu University, Kyongbuk, 712-714, Korea

Abstract: Novel fluoroionophore of dibenzothiazolyl-dibenzo-crown ethers were synthesized from diformal-dibenzo 18-crown-6 (24-crown-8) with 2-aminothiophenol, and they were characterizated by ^{1}H-NMR, ^{13}C-NMR, IR spectrum, Mass spectrum, elemental analyses, respectively. The fluorescent properties of the newly synthesized crown ether were examined with Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+ and CF_3COOH, respectively. With protonation using CF_3COOH, the absorption bands of the new crown ethers are further blue shifted, the maximum emission wavelengths further red shifted.

Keywords: Crown ether; Benzothiazole; Absorption spectra; Fluorescence spectra.

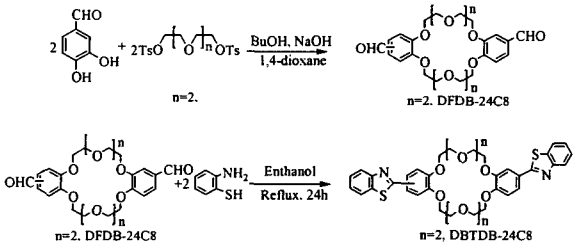
1. Introduction

Crown ether and its derivatives have attracted considerable attentions since it was introduced by Pedersen in 1967 [1]. The design and synthesis of crown ether derivatives combining more than one fluoroionophore with crown ether moieties, which are able to give rise to a specific emission spectral change upon selective complexation with metal cations is one current interest in this area [2-8]. The benzothiazole group contains excellent fluorescent properties.

In this paper, we report the design, synthesis, characterization and fluoresence porperties of dibenzothiazolyl-dibenzo dibenzothiazolyl-dibenzo 24 crown 8 (DBTDB 24C8), which are characterized by the linkage of benzothiazole to the dibenzo-crown ether. The absorption and fluorescence properties of DBTDB24C8 in chloroform solutions and the effect of complexation on these properties have been investigated and compared with the Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+ and CF_3COOH, respectively. It is very interesting that with protonation using CF_3COOH, the absorption bands of the new crown ethers are further blue shifted, the maximum emission wavelengths further red shifted.

2. Experimental

Reagents and Syntheses: All the reagents were purchased from Aldrich Company and used as received. The synthetic approach to DBTDB24C8 are outlined in Scheme 1.



Scheme 1. The synthetic approach of DBTDB24C8

The DBTDB24C8 were dissolved in chloroform to make 2×10^{-6} M solution. The alkali metal salts of LiSCN, NaSCN, KSCN, RbSCN, CsSCN and NH_4SCN were made into 1×10^{-4} M solutions in methanol. The titrations were conducted by adding the metal salt into the solution. CF_3COOH was used to check the absorption and fluorescence spectra and compared with the case of metal cations.

3. Result and discussion

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 of the dibenzo crown ether center upon complexation, this process reduced to electron-donating character of the oxygen to the benzene ring. With the addition of the metal cations of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+ and CF_3COOH into the DBTDB24C8, the absorption spectra all changed, respectively. As shown in Figure. 1, for example, with an addition of LiSCN into the DBTDB24C8 solution, the absorption maximum blue shifted from 324nm to 316 nm.

Meanwhile, with the addition of CF_3COOH into the DBTDB24C8 solution, caused the absorption maximum blue shifted from 324nm to 307 nm. absorbance intensity increased. Then added CF_3COOH, the absorption maximum shifted from 318 nm to 309 nm, and the absorbance intensity decreased.

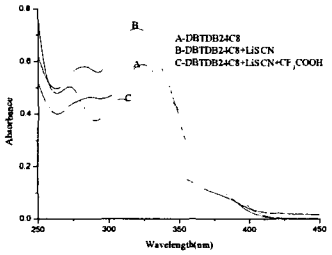


Fig.1. The abosrption spectra of DBTDB24C8 after added LiSCN and CF_3COOH

Figure. 2. gives emission spectra of DBTDB24C8 with LiSCN in chloroform solution. The fluorescence intensity of DBTDB24C8 reached its maximum at 383 nm with the excitation of 324 nm, and it increased with the addition of Li^+.

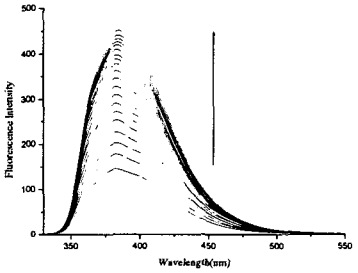


Fig. 2. The emission spectra of DBTDB24C8 with the addition of LiSCN in chloroform.

It can be found that the increased ratio of fluorescence intensity of Li^+ is the best in DBTDB24C8. Since 24 crown 8 cavity size can form a *stoichiometaic* 1:2 *complex with* Li^+. *The ability of* DBTDB24C8 binding with Li^+ cooperatively and selectively over other alkali metal ions such as Cs^+, Rb^+, K^+, Na^+ and NH_4^+.

From the results of comparsion, we think that when added metal cations, the interaction between crown ether cavity with the cation took place, it leads to the intramolecular charge transfer from the benzothiazole group to the crown benzene ring. When CF_3COOH was added, the protonation of the two benzothiazole nitrogens with CF_3COOH and cause enhancement of the π-acceptor properties of the hetero-rings . Because the interaction of metal cations with the fluorophone is indirect, and the proton bind with the nitrogen atom directly, that resulted the effect was different. When the DBTDB crown ether solution only added metal cations, it mainly caused the increase of fluorescence of the excitation of the benzene ring which were observed at 384 nm. With the addition of CF_3COOH, the protonation mainly caused the fluorescence intensity increase of benzothiazole group which was observed at 433 nm. Due to the charge transferred from the crown ether ring to the benzothiazole, the fluorescence intensity at 384 decreased.

4. Conclusions

A new crown ether carrying two fluoroionophores have been synthesized and characterizated. The fluorescent properties were investigated by using alkali metal cations, NH_4^+ and CF_3COOH. The results showed that Li^+ was very effective to enhance the fluorescence properties of DBTDB24C8. CF_3COOH can cause great enhancement of the DBTDB24C8, this enhancement of the fluorescent properties owing to the protonation.

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