Synthesis and property of Functionalzed quinoxaline colorants and those containing electrospun nanofiber

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Introduction

There are many researches of fluorescent heterocyclic compounds for application to emitters of electroluminescence devices and in the molecular probes used for biochemical research, as well as in the traditional textile and polymer fields. Especially, fluorescent dye materials which of fluorescence emission occurs at a longer wavelength in the red light region are expected to play a leading role in full color electroluminescence displays. [1-4]

Heterocyclic fluorophores are useful materials in search for new biologically active compounds and diagnostic methods. Fluorescent chromophores are generally known to have planar and rigid π-conjugation systems, and many fluorescent chromophores are based on rigid ring systems such as stilbene, coumarin, naphthalimide, perylene and rhodamine. Our research group has been interested in the chemistry of nitrogen-containing heterocyclic molecules for many years. Quinoxaline was the representative fluorophore, and reported several quinoxaline derivative compounds recent years. [5]

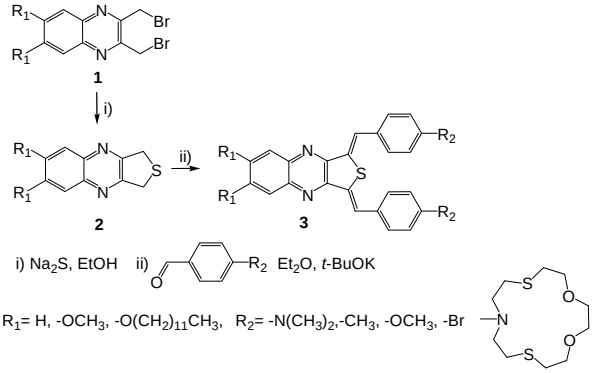
The fluorescent optical change due to the circumstance of fluorephore is very important ability to the colorants have application to chmosensors. Quinoxaline can easily change their absorption or emission wavelength by oxidation with proton base in the nitrogen of the quinoxaline ring. In addition, it was proved many types of metal chelating ligand substituents such as dipyrrole, terpyridine, and crown-ether rings can control electronic levels of those fluorephores. [6-7]

In this study, we designed and synthesized with several thieno[3,4-b]quinoxaline derivatives each have different electron-donating abilities. The chromophoric systems of these compounds, and the substituent effects on their absorption spectra in solution, were studied. And we groped the application to the fabrication of films, and nanofibers by electrospinning which containing those synthesized colorants.

Result and discussion

1. Synthesis

1,3-dihydrothieno[3,4-b]quinoxaline and its 6,7-bis(dodecyloxy) substituted derivative was refered to the previous literature.[8] Scheme 1 shows the synthetic method of the The two α-positions to the S-atom are acidic, hence the condensation can occurs both position when excess aldehydes added in a small amount of diethyl ether of basic condition. The compounds was reacted various types of benzaldehydes by knoevanagel condensation reaction. The special reactivity of **2** is therefore due to the electron-withdrawing effect of the pyrazine ring condensed to the 3 and 4 positions of the thiophene ring. The Z,Z'-configuration was prefered for diethyl ether as the solvent and potassium *tert*-butoxide as the catalyst.



Scheme 1.

2. Absorption & Emission Properties

The dodecyloxy group substituted quinoxalines were more soluble and have lower melting temperature than the original back-bone quinoxaline.

The compounds have a different solubility as to several organic solvents and UV-visible absorption which changes the alkyl group of para- position of aromatic aldehyde. In addition, solvatochromic effects were observed for these

chromophores due to the difference of polarity and protic ability of each solvents. Figure 1 shows the absorption spectra of these various compounds in $CHCl_3$.

In particular, *N,N*-dimethylaminophenyl substitued quinoxaline (**3a**) has unique absorption change between different solvents. It shows significantly bathochromic shift on protic solvents such as methanol and also shows different emission properties as shown in Fig 2. It's assumed that photoinduced charge tranfer from the dimethyl amino group to pyrazine rings was influenced by the polarity and protic ability of solvent. Futhermore the emission intensity also shift to longer wavelength, however, the intensity was reduced.

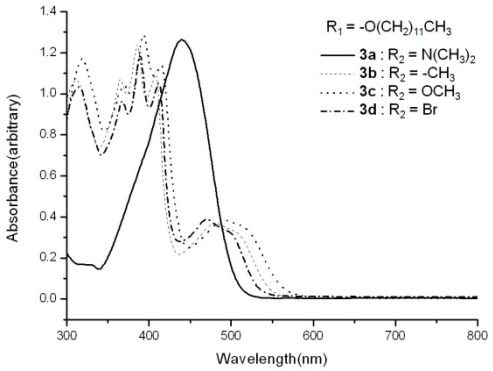


Fig 1. UV-Vis spectra of quinoxalines in $CHCl_3$

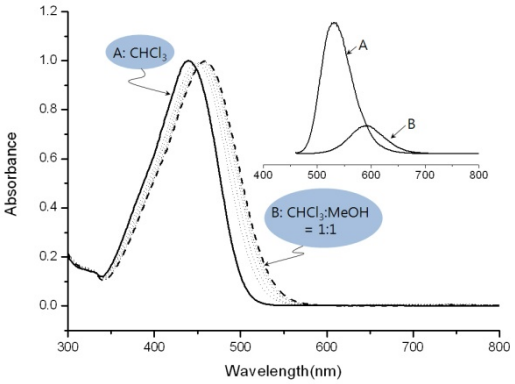


Fig 2. Absorption and Emission change of **3a** from $CHCl_3$ to $CHCl_3$:MeOH=1:1

Electrospun nanofibers which containing those synthesized quinoxalines, have also fluroscent change when the acid vapor gas were passing through the web as shown in Fig 3. The bright yellow fluorescence were changed to red color, and the strength was reduced as those fluorescent spectra in organic solvent.

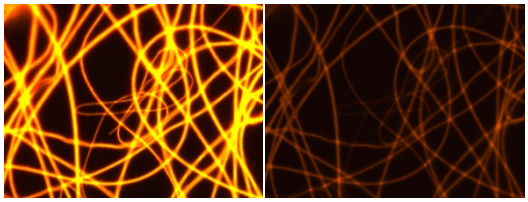


Fig.3 fluorescent change of electrospunfiber in acid vapor gases

3. Conclusion

Demands of chemosensors for sensitizing pH, metal ions are growing much more, and It's very important technology to analysing the heavy metal ions such as mercury in aqueous solution. In this study, we attempted quinoxaline based compounds which contain various functional groups to sensitize such cationic condition. And it is also attempted to confirm the possibility of sensing ability of nanofiber which containing those materials.

4. Reference

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