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The Synthesis and Optical Properties of Fluorescent Quinoxalines and of Electrospun Fibers Containing Fluorescent Quinoxaline

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Heterocyclic fluorophores are useful materials in the search for new biologically active compounds and diagnostic methods. We have been interested in the chemistry of nitrogen-containing heterocyclic molecules for many years. Quinoxaline is a representative fluorophore. We have reported on several quinoxalines in recent years. Quinoxaline can easily change its absorption and emission wavelength by oxidation with the proton base in the nitrogen of the quinoxaline ring. In this study, we designed and synthesized several 2,3-distyrylquinoxaline and thieno[3,4-*b*]quinoxaline derivatives, Each with different electron-donating capabilities. The designed quinoxalines were substituted for the dodecyloxy groups on the benzene ring and stillbene groups were attached by knoevenagel reaction or Hornor-Wadsworth-Emmons (HWE) reaction on the 2,3-positions of the pyrazine ring. They amplified the electron donating capability of the quinoxaline structure. Thus, the weak base property of nitrogen in the heterocyclic ring was increased, especially in a protonic condition. The property in an acidic condition was revealed by fluorescence quenching. However, fluorescent spectral change was observed, especially when the *N*,*N*-dimethylamino group was attached to the stillbene group. These properties were also observed in electrospun fibers containing those synthesized compounds. Electrospun fibers contained quinoxaline colorants are expected to have various applications in chemosensors.

Keywords: Quinoxaline, Chemical Sensor, Fluorescence.

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1. INTRODUCTION

There has been much research done into fluorescent heterocyclic compounds for application to emitters in electroluminescent devices and to the molecular probes used in biochemical research, as well as in the traditional textile and polymer fields.[1–4] Heterocyclic fluorophores are useful materials in the 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 is a representative fluorophore. We have reported on several quinoxaline derivative compounds in recent years.[5]

The fluorescent optical change due to the circumstance of fluorophores should be apparent for them to have an application to chemosensors. Quinoxaline itself has a weak base, and it can easily change its absorption or emission wavelength by oxidation with the proton analyte in the nitrogen of the quinoxaline ring when electron-donating substituents are attached in its heterocyclic ring. In addition, it has been proven that many types of metal chelating ligand substituents, such as dipyrrole, terpyridine, and crown-ether rings, can control electronic levels of the fluorephores.[6–7]

In this study, we designed and synthesized several 2,3-distyrylquinoxalines and thieno[3,4-*b*]quinoxaline derivatives, each with different electron-donating substituents. The chromophoric systems of these compounds were studied, along with the substituent affects on their absorption and emission spectra in solution. And recently, there are approaches for electrospun fibers containing various luminescent materials with substrate polymer.[8–9] Thus we fabricated to electrospun fibers contained these synthesized colorants and analyzed structure and optical properties for chemical sensor.

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2. EXPERIMENTAL DETAILS

Flash chromatography was performed with Merck-EM Type 60 (230–400 mesh) silica gel (flash). ^{1}H-NMR spectra were recorded using a VARIAN UnityInova 300 MHz FT-NMR Spectrometer. The UV-visible and fluorescence spectra were measured using SCINCO S-4100 and SHIMADZU RF-5301PC spectrophotometers, respectively. The reagents and solvents used for the syntheses were all synthetic grade, used as received. The chemicals used for the spectroscopic analysis were all analytical reagent grade.

2.1. Typical Procedure to Synthesize 3a

The mixture of 6,7-bis(dodecyloxy)-1,3-dihydrothieno [3,4-*b*]quinoxaline (**2**, 500 mg, 0.90 mmol), *N*-dimethylaminobenzaldehyde 1.34 g (9.0 mmol) in 25 ml of diethyl ether was refluxed in the presence of a catalystic amount of potassium *t*-butoxide. After 18 hr, the solvent was removed under reduced pressure and the residue was filtered off and washed with methanol. The crude product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/2 as the eluant). **3a** (orange crystal, 24%): m.p 118 °C, ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.89 (s, 2H, quinoxaline), 7.71 (d, 4H, $J = 9.0$ Hz, Ar-H), 7.34 (s, 2H, ethene), 6.85 (d, 4H, $J = 9.0$ Hz, Ar-H), 4.22 (t, 4H, $J = 6.0$ Hz, OCH_2), 3.04 (s, 12H, NCH_3), 1.97–1.92 (m, 4H, CH_2), 1.54–1.28 (m, 36H, methylene), 0.89 (t, 6H, $J = 6.0$ Hz, CH_3) $C_{52}H_{74}N_4O_2S$ Calcd. C, 76.24; H, 9.10; N, 6.84; O, 3.91; S, 3.91 Found. C, 75.38; H, 8.97; N, 6.81.

2.2. Typical Procedure to Synthesize 5a

Potassium *t*-butoxide (4eq.) was added to the stirring mixture of diphosphonate (**4**, 1.18 g, 1.47 mmol), *N*-dimethylaminobenzaldehyde 2.2 g (14.7 mmol) in 30 ml of THF at room temperature. The mixture was stirred for 3 hr. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/1 as the eluant). **5a** (yellow crystal, 48%): m.p 107 °C, ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.97(d, $J = 15.6$ Hz, 2H, ethene), 7.87 (s, 2H, quinoxaline), 7.74 (d, 4H, $J = 9.0$ Hz, Ar–H), 7.51 (d, $J = 15.6$ Hz, 2H, ethene), 7.02 (d, 4H, $J = 9.0$ Hz, Ar–H), 4.23 (t, 4H, $J = 6.0$ Hz, OCH_2), 3.04 (s, 6H, NCH_3), 1.97–1.92 (m, 4H, methylene) 1.54–1.28 (m, 36H, CH_2), 0.88 (t, 6H, $J = 6.0$ Hz, CH_3); $C_{52}H_{76}N_4O_2$ Calcd. C, 79.14; H, 9.71; N, 7.10; O, 4.05 Found. C, 78.79; H, 9.56; N, 7.03.

2.3. Electrospinning Materials and Set-Up

Polystyrene (PS, Mn = 140,000) and Polycarbonate (PC, Mn = 100,000) were purchased from Sigma Aldrich, and *N*,*N*-dimethylformamide (DMF), methyl ethyl ketone (MEK), and chloroform were purchased from Samchun Pure chemical Co. and used without further purification.

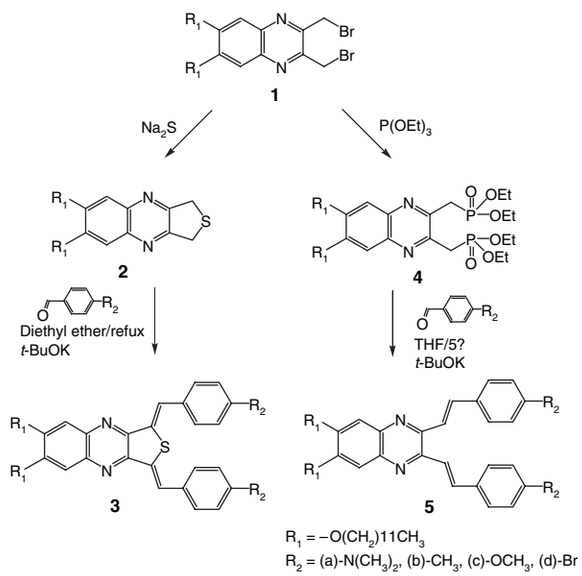
In a typical procedure, the solution was loaded into a plastic syringe equipped with a 30 gauge needle made of stainless steel. The needle was connected to a high voltage power supply capable of generating DC voltage up to 30 kV. The solution was continuously supplied using a syringe pump (KDS-200, Stoeling, Wood Dale, IL) at a rate of 0.005 ml/h–0.01 ml/h. A positive voltage of 15 and 20 kV was applied to the solution and the distance between the needle tip and the collector (TCD) was between 15 and 30 cm. The needle, electrode, and grounded target were all enclosed in order to reduce the effect of air currents on the trajectory of the electrospun jet. The collected fiber was dried at 80 °C for one day to evaporate any remaining solvents.

3. RESULTS AND DISCUSSION

3.1. Synthesis

1,3-dihydrothieno[3,4-*b*]quinoxaline derivatives and diphosphonates were prepared, referring to previous literature.[7, 10] Long linear alkyl ether moiety was chosen to improve the solubility of the resulting quinoxaline fluorescent compounds in common organic solvents. Scheme 1 shows the synthetic methods of the quinoxaline compounds.

In the case of **3**, condensation occured on two α-positions to the S-atom when an excess amount of aldehydes was added to diethyl ether under basic conditions. The compounds reacted with various types of benzaldehydes using the Knoevenagel condensation reaction. The special reactivity of **2** is therefore due to an



Scheme 1. Synthetic route of quinoxaline derivatives.

electron-withdrawing effect of the pyrazine ring condensed to 3 and 4 positions of thiophene ring. Z,Z'-configuration was preferred for diethyl ether with solvent and potassium *tert*-butoxide as a catalyst.

The Horner-Wadsworth-Emmons (HWE) reaction in THF yielded compound **5**. The reaction of compound **4** with 10 equivalents of a 4-substituted benzaldehyde, in the presence of potassium *tert*-butoxide, gave mono and di-substituted quinoxaline by controlling the specific reaction time. These products can be easily separated by liquid column chromatography (using ethyl acetate/*n*-hexane = 1/1 as the eluant).

^{1}H-NMR spectroscopy of compounds was used in $CDCl_3$ at 20 °C, which provides structural information. In the aliphatic region, a sharp triplet resonance corresponding to the O-methylene proton was observed. The ethylene protons of **5a** appeared as a doublet at 7.97 and 7.51 ppm revealed a *trans*-configuration with coupling constants of 15.6 Hz. In addition, the protons of terminal N-CH_3 were singlet at 3.04 respectively.

3.2. Absorption and Emission Properties

Synthesized compounds have different solubility as to many organic solvents and UV-visible absorption which changes the alkyl group of the *p*-position of aromatic aldehyde. Table I shows the maximum absorption and emission wavelength of these synthesized compounds. They had a solvatochromic effect. In particular, *N*,*N*-dimethylaminostyryl substituted for quinoxaline (**3a**) has a unique absorption change by different solvents as shown in Figure 1. It shows a bathochromic shift by increasing the ratio of methanol, and the emission was reduced showing a red shift. It seems to be caused by an aggregation-induced red shift because of the different solubility between chloroform and methanol. Other compounds show their emission quenched significantly.

The emission change under an acidic condition was tested by adding *p*-toluenesulfonic acid (PTC) to the $CHCl_3$:MeOH = 9:1 solution. The solvent combination was considered and selected for PTC to be more soluble than $CHCl_3$.

In the case of compound **3, 3a** shows its emission spectra from greenish-yellow to red (F_{max} = 659 nm), but the intensity was reduced as shown in Figure 2. In contrast to other compounds, including **3b**, the emission spectra were directly quenched. Quinoxaline itself is a weak base, while

Table I. Absorption and emission wavelength of synthesized compounds **3** and **5** in $CHCl_3$.

	λ_{max}	F_{max}		λ_{max}	F_{max}
3a	438	538	**5a**	417, 447	527
3b	387	483	**5b**	417	459
3c	394	474	**5c**	423	476
3d	390	476	**5d**	416	453

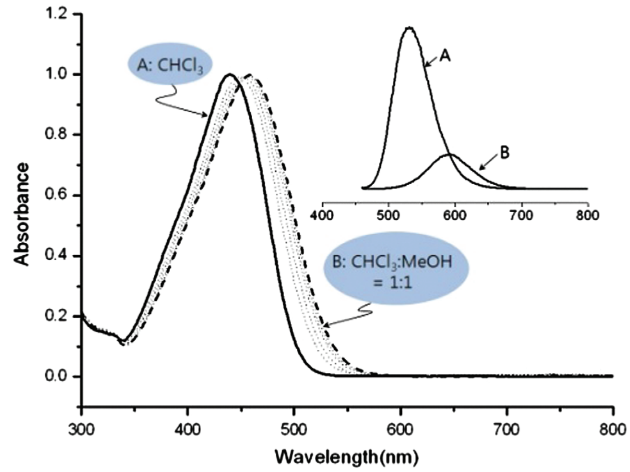


Fig. 1. Absorption and Emission change of **3a** and from $CHCl_3$ to $CHCl_3$:MeOH = 1:1.

quinoxalines onto which electron-donating substituents have been introduced are protonated easily at the 1,4-positions. In addition, the substituent in the stillbene group also affects especially the *N*-dimethylamino group. It is assumed that the amino group can be also protonated under an acidic condition. Therefore the electronic level change of LUMO of the amino group induced the red-shift of the emission spectra. In contrast, the methyl group of stillbene substituents has no electronic level change under a protic condition. **3b** thus only has one of the protonations of quinoxaline backbone, showing direct quenching of its emission spectra.

In the case of compound **5**, there was a different emission change among each substituent as shown in Figure 3. The original orange-yellow solution of **5a** became greenish blue as the concentration of PTC was increased. The absorption maximum of **5a** at 417 nm decreased, while that of a new absorption band which appeared at 597 nm increased. No fluorescence was observed when the excitation wavelength was 597 nm, and the emission showed less intense, blue-shifted color under excitation at 417 nm. On the other hand, other compounds including **5c** show another optical change as shown in Figure 4. They show a bathochromic shift of absorption and emission spectra and their intensity was slightly increased. The original yellow color (λ_{max} = 423, F_{max} = 476) was changed to an orange color (λ_{max} = 502 nm, F_{max} = 573). The protonation of the imine nitrogen of **5** seems to change the electronic state of the dyes and the process by which the fluorescence is generated. It has been reported that the protonation of the nitrogen atom of heteroaromatic poly(arylene) in acidic media leads to a bathochromic shift of the absorption peak.[11–12]

3.3. Electrospun Fiber and Its Sensor Ability

The synthesized quinoxalines have an optical change, notably a fluorescent change under a protic condition.

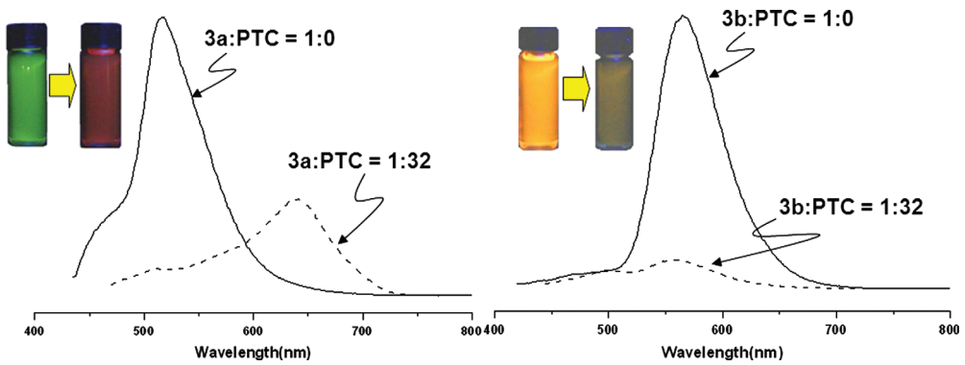


Fig. 2. PL spectral change of **3a** and **3b** by adding PTC.

Electrospun fibers containing synthesized quinoxaline fluorophores also show an optical change under acidic conditions.

Figure 5 contains microscopic pictures of electrospun polystyrene (PS) (a) and polycarbonate (PC) (b) fibers containing **3a**. They show a uniform emission and have a 700∼1000 nm diameter under specific spinning conditions as shown in Table II.

The acid sensitivity of these fibers was tested under nitric acid vapors and liquid conditions. In the case of the polystyrene fibers, fluorescence significantly changed under acid vapor condition for 60 seconds as shown in Figure 6. They changed from bright yellow to dark red, with the critical time to complete the spectral change being about 60–90 sec.

However, polycarbonate fibers show less sensitivity than polystyrene fibers. They also changed to a dark red color, but not significantly, and the critical time to complete the change was 10–15 min.

The relatively slow change of PC fibers is assumed to be due to the morphology of polymer substrates and the inner position of quinoxaline colorants. It is assumed that the quinoxaline chromophores slowly moved nearer to the surface of the fiber because PS fibers used DMF/MEK—a relatively slower vaporized solvent than chloroform—for

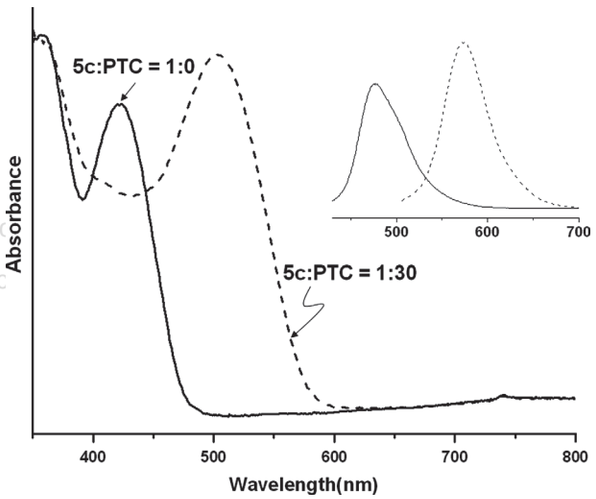


Fig. 4. Spectral change of **5c** by adding PTC.

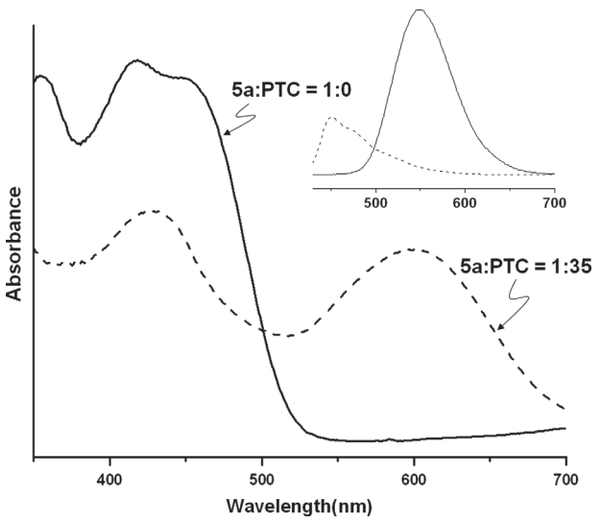


Fig. 3. Spectral change of **5a** by adding PTC.

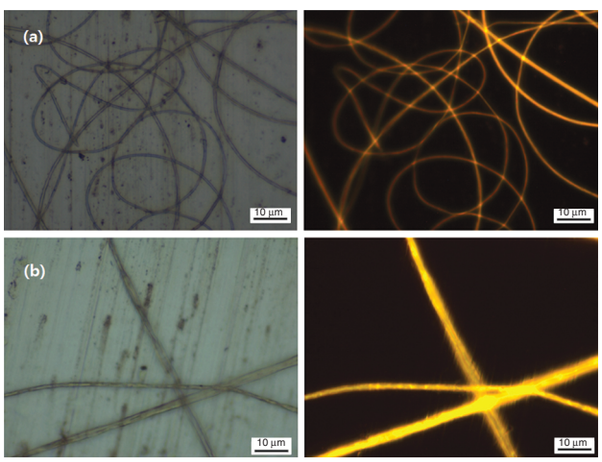


Fig. 5. Electrospun polystyrene (a) and polycarbonate (b) fibers containing **3a**.

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Table II. Specific electrospinning condition of the resulting fibers.

	Solvent	Voltage (kV)	Tip to collector distance (cm)	Flow rate (mL/h)
PS	DMF/MEK	15	20	0.005
PC	Chloroform	20	15	0.005

Concentration of Polymer: 15 wt%. Concentration of dye: 0.130 wt%.

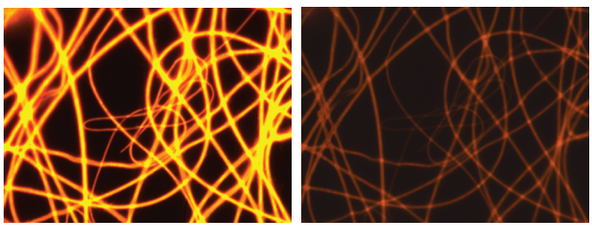

Fig. 6. Emission change of **3a** containing PS fiber (HNO_3 vapor exposure for 60 s).

the solvent, and this resulting in higher sensitivity than that of PC fibers.[13]

4. CONCLUSIONS

In this study, we attempted to create quinoxaline based compounds which contain various functional groups that are sensitive in a protic condition. We also attempted to confirm the possibility of applying electrospun fibers containing these fluorescent materials to chemical sensors.

The proton sensor ability of these fibers will be improved by controlling their diameters from the changing spinning condition and solvents. The progress of further researches will be reported elsewhere.

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