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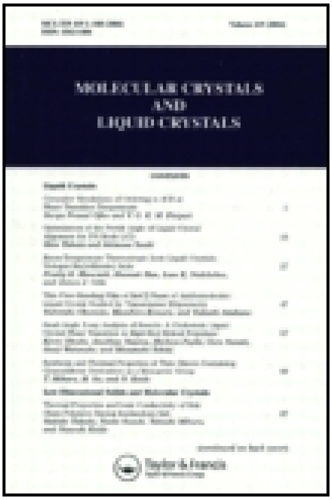

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Synthesis of Fluorescent Probe Sensitive to Amine

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SYNTHESIS OF FLUORESCENT PROBE SENSITIVE TO AMINE

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5-Bromo-2-(5′-bromo-2′-hydroxyphenyl)benzoxazole ***4*** *is prepared from the Sandmeyer reaction of 5-amino-2-(5′-amino-2′-hydroxyphenyl)benzoxazole* ***3*** *with copper bromide. Two kinds of the (hydroxyphenyl)benzoxazole compounds are investigated for application in fluorescent probe sensing amino compounds and compound* ***4*** *is proved to be more suitable for sensing hexamethylenediamine and hydrazine with different fluorescent colors.*

INTRODUCTION

The sensitive and selective binding of chemical species upon molecular recognition has received considerable attention in applications for sensors, switches, triggers, logic gates, and molecular level machines [1–3]. The enormous potential of fluorometric methods for the analytical detection of environmentally and biologically relevant organic species requires the development of highly selective and highly sensitive fluorescent probes. Due to the sensitivity reasons, probes showing fluorescence enhancement as a result of binding event are to be favored over those which exhibit fluorescence quenching upon binding [4,5].

It is well-known that 2-(2′-hydroxyphenyl)benzoxazole has been widely studied from the viewpoint of photophysics because of its high Stokes shift

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and dual emission via the excited-state intramolecular proton transfer (ESIPT) for use as laser dyes, polymer UV stabilizers, and organic NLO materials [6–8]. In nonpolar solvent, it emits long-wavelength fluorescence ($\sim$500 nm) exclusively via the ESIPT process of the excited state of the intramolecularly hydrogen-bonded keto form, and the intensity of short wavelength fluorescence ($\sim$360 nm), which arises from the excited state of the intramolecularly hydrogen-bonded enol form [9]. Several investigations on probe or chemosensor with 2-(2′-hydroxyphenyl)benzoxazole have been reported for metal cations and anions [9–11]. However, to our knowledge, description on sensing other organic compounds such as amines is rare.

Therefore, in this paper we are reporting newly synthesized fluorescent chemosensors composed of 2-(2′-hydroxyphenyl)benzoxazole, **3** and **4**, which demonstrate selective fluorescence enhancing effects with specific amines.

EXPERIMENTAL

Reagents and Measurements

2,4-Diaminophenol dihydrochloride and 5-aminosalicylic acid were purchased from Aldrich Chemical and used without further purification. Tetrahydrofuran (THF) was purified via conventional sodium/benzophenone method.

^{1}H NMR spectra were obtained on a Bruker ARX-300 spectrometer. UV-visible spectra were recorded on a Perkin Elmer Lambda 35 spectrometer. Steady-state fluorescence measurement was carried out using a Perkin Elmer LS 45 spectrofluorimeter.

Synthesis of 5-amino-2-(5′-amino-2′-hydroxyphenyl) benzoxazole 3

A solution of 2,4-diaminophenol dihydrochloride **1** (6.43 g, 32.65 mmol) and 5-aminosalicylic acid **2** (5.0 g, 32.65 mmol) in polyphosphoric acid (150 ml) was heated under reflux for 15 hr. The reaction mixture was cooled to room temperature and poured into ice water. The mixture was controlled to pH 7 by addition of sodium bicarbonate. The precipitate was isolated by filtration and the brown solid was recrystallized in ethanol. The product was further purified by flash column chromatography on silica gel with acetone. Yield (4.10 g, 52%).

^{1}H NMR (acetone-d_6): 10.7 (s, hydroxyl), 7.66, 7.45, 7.38, 7.02, 6.85 (m, aromatic), 4.80 (s, amine), 4.47 (s, amine) ppm.

Synthesis of 5-bromo-2-(5′-bromo-2′-hydroxyphenyl) benzoxazole 4

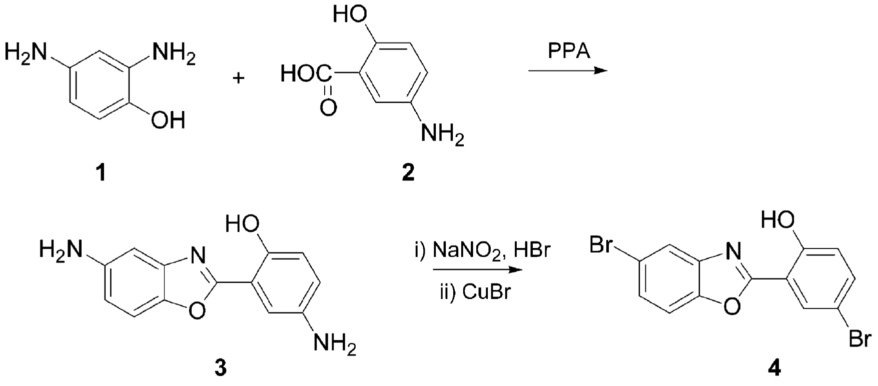
Three-necked round-bottomed flask was charged with 2.4 g (10 mmol) of **3** and 32% hydrobromic acid (50 ml) at 0°C. Aqueous solution (5 ml) of sodium nitrate (1.73 g, 25 mmol) was slowly added into the flask and mixture was stirred for 10 min. During the stirring, 11.48 g (40 mmol) of copper bromide dissolved in 48% hydrobromic acid was added dropwise with dropping funnel. After 10 min stirring at 0°C, the mixture was allowed to raise 100°C and was further stirring for 5 hr. The mixture was extracted with chloroform (1:1 by volume) four times and dried over magnesium sulfate. The crude product was purified by flash column chromatography on silica gel with *n*-hexane and ethyl acetate (2:1 by volume) yielding 2.10 g (57%).

^{1}H NMR (DMSO-d_6): 11.1 (s, hydroxyl), 8.11, 7.82, 7.69, 7.13 (m, aromatic) ppm.

RESULTS AND DISCUSSION

For the synthesis of 5-bromo-2-(5′-bromo-2′-hydroxyphenyl)benzoxazole **4**, 5-amino-2-(5′-amino-2′-hydroxyphenyl)benzoxazole **3** was first synthesized following the procedure of well-known ring closure reaction in the presence of polyphosphoric acid. Treatment of **3** with sodium nitrate and HBr followed by reaction with CuBr known as Sandmeyer reaction allows yielding dibromo-compound **4**. The compound 4 was obtained in 57% yield (Scheme 1). Conversion from amine to bromine was confirmed with NMR spectrum, which exhibited disappearance of amine contribution at 4.47 and 4.80 ppm.

Absorption spectra of **3** and **4** in chloroform solutions are essentially different, as that of **3** is red-shifted as shown in Figure 1(a). The origin



SCHEME 1 Synthesis of **3** and **4**.

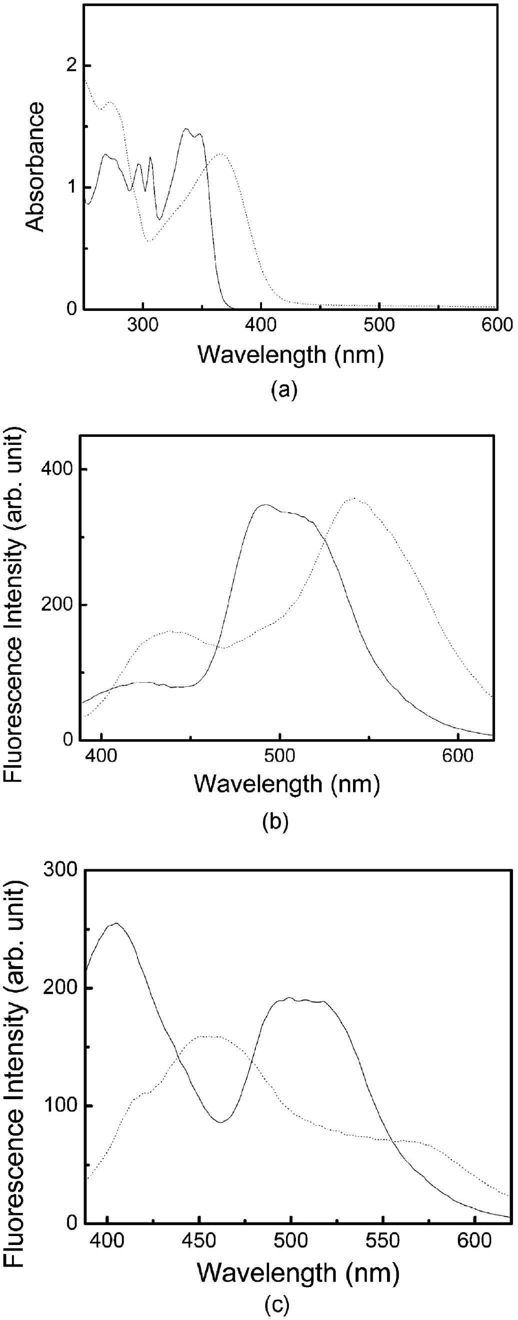


FIGURE 1 (a) Absorption spectra of **3** and **4** in chloroform solution and fluorescence spectra in chloroform (b) and in THF (c) solution; **3** (dotted line), **4** (solid line).

of red-shift of absorption in diamino compound **3** is attributed to the fact that electron-donating and withdrawing properties of substituents (amines and bromines) play a decisive role in structural planarization or conjugation *via* electron movement. Fluorescence spectra of **3** in chloroform solution show appreciable two emissions at 438 and 546 nm resulted from enol and keto form by ESIPT, respectively (Fig. 1(b)). However, only single broad emission centered at 489 nm was observed in the case of **4** in chloroform solution, which is an intermediate emission wavelength of **3** and implying ESIPT in **4** was not brought out in chloroform. On the contrary, two emissions by means of ESIPT can be observed in fluorescence spectra of **4** in THF solution at 405 and around 500 nm, but the same result could not be drawn in **3** in THF, which shows a strong emission at 455 nm and a weak shoulder at around 580 nm as shown in Figure 1(c). Fluorescence intensity of **4** in chloroform or THF solution is much stronger than **3** at the same concentration and the solvents effects on the fluorometric behaviors such as ESIPT seems to be tremendous. It is presumed that the solvent interaction as well as substituents on each end affect the hydroxyl group of **3** and **4**, which is strongly related to ESIPT.

We investigated the effect of amines on the emission of **3** and **4** in THF and the change in the luminescence intensity in the presence of an amine is summarized in Figure 2. Compared to **3**, dibromo-terminated (hydroxyphenyl)benzoxazole **4** recognizes hexamethylenediamine (HMDA) and hydrazine to bring about considerable fluorescence enhancement and recognizes triethylamine (TEA) to cause negligible fluorescence enhancement. Along with fluorescence intensity increase, emission from keto form (from around 500 nm to 466 nm) was much more affected by hydrazine rather than that from enol form (403 nm). For the case of **3**, a meaningful luminescence change is not detected for three amines such as HMDA, hydrazine, and TEA as shown in Figure 2(a). From the observation described above, **4** can be regarded as a probe sensing HMDA sensitively and selectively. Noticeable fluorometric changes of **3** and **4** by addition of amines were not observed when chloroform was used as a solvent.

It is generally accepted that dramatic fluorescence enhancement of (hydroxyphenyl)benzoxazole compound with interacting chemical species was considered by the formation of a complex, where the benzoxazole and phenolate ring lies on the same plane by the bridging, and this coplanarity and the anionic property of the phenolate ring bring about large fluorescence enhancement [12,13].

CONCLUSION

We have synthesized (hydroxypheyl)benzoxazole-based molecules **3** and **4** for amine sensing measurement. The substituents (amine and bromine) in

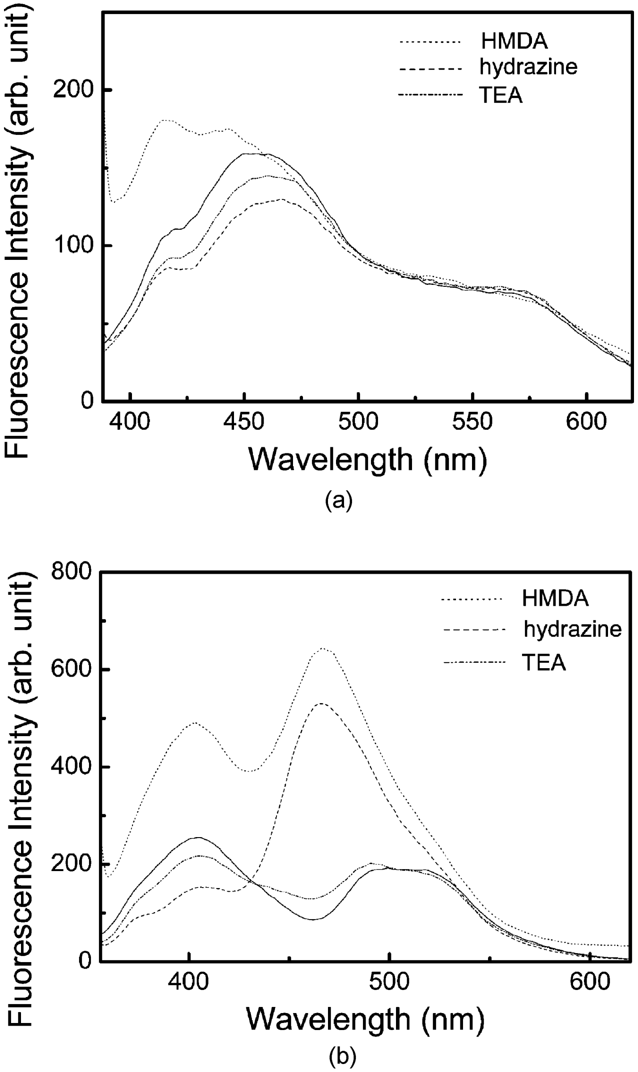


FIGURE 2 Fluorescence spectra of (a) **3** and (b) **4** in THF solution with addition of amines; original polymer solution (6.94×10^{-4} μM, solid line); HMDA (4.3×10^{-1} M); hydrazine (0.10×10^{-1} M); TEA (3.6×10^{-1} M).

3 and **4** as well as solvent used have considerable effects on ESIPT behavior and interaction with amines which will be transduced into optical signals. Generally dibromo-terminated compound **4** exhibited noticeable and appreciable fluorometric changes such as fluorescence enhancement and emission shift compared to amino-terminated compound **3**. Presumably this resulted from electron density increase in electron-poor benzoxazole ring by electron-donating property of the amines.

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