

Photostable BF₂-Chelated Fluorophores Based on 2-(2'-Hydroxyphenyl)benzoxazole and 2-(2'-Hydroxyphenyl)benzothiazole

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Received August 27, 2009, Accepted October 6, 2009

Key Words: Blue luminescent materials, Boron complex, Photostability, Fluorophore, High fluorescence efficiency

Organic chromophores based on small molecules have attracted considerable attention over the past decades due to their potential applications including organic light-emitting diodes (OLEDs), solar cells, dye lasers, photosensitizers and molecular probes.¹ A great variety of organic and organometallic luminescent molecules with different chemical/photophysical properties adapted to specific needs have been reported, and a number of those are also commercially available.²

Metal complexes based on the N- and/or O-donor ligands, have shown promising luminescent properties as efficient EL emitters. Among them, aluminum (III) complex of 8-hydroxyquinoline (Alq₃) has been used as a green emitter and one of the stable electron transport materials with high emission efficiency.³ Similarly, zinc (II) complex⁴ and boron (III) complex⁵ of 8-hydroxyquinoline have been investigated as an EL materials in vapor-deposited films. In general, boron compounds are more stable than corresponding aluminum compounds, and boron difluoride dyes such as boron dipyrromethene (BODIPY) and boron diketonates possess remarkable properties such as large molar extinction coefficients, high fluorescence quantum yields and excellent photostability.⁶

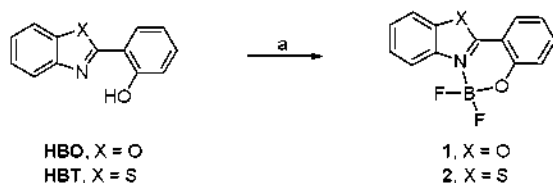
2-(2'-Hydroxyphenyl)benzoxazole (**HBO**) and 2-(2'-hydroxyphenyl)benzothiazole (**HBT**) are widely studied fluorescent compounds for their fundamental photophysics and as optical probes due to their dual emission *via* excited state intramolecular proton transfer (ESIPT).⁷ For example, in nonpolar solvent, absorption and emission peaks of **HBT** are observed at approximately 350 and 530 nm, respectively. This large Stokes shift is due to ESIPT process that occurs when **HBT** is photoexcited. We recently reported ESIPT-based optical probe, showing that inhibition of intramolecular hydrogen bond of **HBT** resulted in preventing ESIPT process, and hypsochromic shift.⁸ We reasoned that this unique optical change could be applied to construct blue emitting dye compound, which might have high quantum yield by blocking less efficient ESIPT process. Herein,

we report the synthesis and characterization of two new boron complexes, **1** and **2**, based on **HBO** and **HBT** as potential blue luminescent materials.

Boron complexes **1** and **2** were synthesized in one step according to Scheme 1. Commercially available **HBO** and **HBT** were reacted with boron trifluoride etherate (BF₃·OEt₂) in dichloromethane at room temperature to give dyes **1** and **2**, in 50% and 92% isolated yields. Boron complexes **1** and **2** exhibited good solubility in common organic solvents such as THF, CH₂Cl₂, CHCl₃, toluene, dichloroethane and DMSO. Their structure and purity were confirmed by ¹H and ¹³C NMR spectroscopy and HR-MS.

Boron complexes **1** and **2** emit an intense deep blue light upon being irradiated by UV light in solution and in the solid state. The excitation and emission maxima for **1** and **2** in solution and in the solid state are listed in Table S1. Figure 1 illustrates the absorption and emission spectra of **1**, **2**, **HBO**, and **HBT** in CH₂Cl₂. The UV-visible absorption spectra of dyes **1** and **2** display maxima at 344 and 364 nm, respectively and their emission maxima are observed at 408 nm and 433 nm, respectively. As revealed by the absorption and emission spectra, BF₂ chelation of ligands **HBO** and **HBT** leads to bathochromic shifts in absorption spectra (24 - 32 nm) and hypsochromic shifts in emission spectra (92 - 97 nm), in comparison with those of the corresponding ligands **HBO** and **HBT**. The extinction coefficient of dyes **1** and **2** in CH₂Cl₂ are of 21,200 and 23,000 M⁻¹cm⁻¹, respectively. The emission quantum yields for compounds **1** and **2** in CH₂Cl₂ were determined to be 0.20 and 0.23, respectively, relative to that of quinine sulfate in 0.1 N H₂SO₄, confirming that the boron complexes **1** and **2** are potent emitters. These enhanced quantum yields of **1** and **2**, compared to those of **HBO** (Φ_F = 0.02) and **HBT** (Φ_F = 0.006), might be originated from the interruption of ESIPT process as well as a rigidification of the aromatic ligand occurring upon coordination to boron, thus increasing its emission efficiency by decreasing the loss of energy *via* thermal vibrational modes.

The excitation and emission spectra of **1** and **2** in thin solid films and powder were also investigated (See SI). The excitation spectra of **1**, **2**, **HBO** and **HBT** in thin solid films and powder were observed as broad bands around at 350 - 420 nm. The emission spectra of **1** and **2** in thin film display their maxima at 428 nm and 466 nm, respectively, which are around 20 - 33 nm red-shifted with respect to those of their solutions. Meanwhile their corresponding ligands, **HBO** and **HBT** in thin films show emission maxima at 505 and 527 nm, respectively, which are



Scheme 1. Reagents and conditions: a. BF₃·OEt₂, TEA, CH₂Cl₂, r.t., 48 h, 50% (**1**), 92% (**2**)

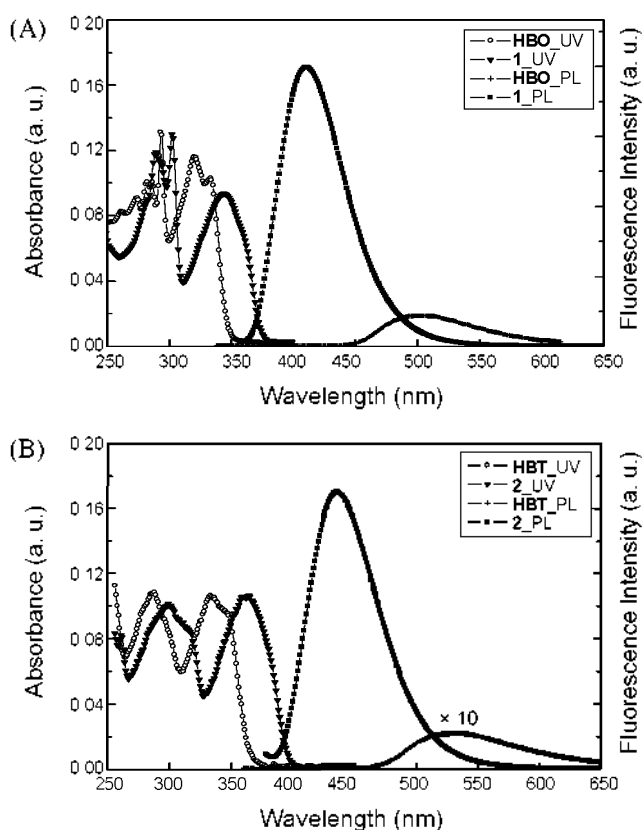


Figure 1. Absorption and emission spectra of (A) dye **1** and **HBO** (B) dye **2** and **HBT** in CH_2Cl_2 at 25 °C. Excited at 320 (**HBO**), 340 (**HBT**, **1**), 360 nm (**2**). Concentrations of all compounds are adjusted to $5.2 \pm 0.2 \mu\text{M}$. Ten-fold increased emission spectrum of **HBT** is shown.

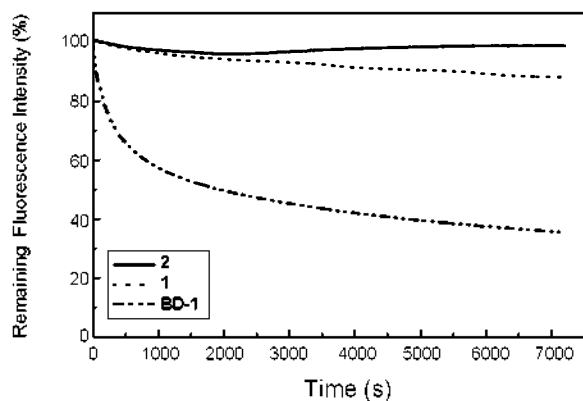


Figure 2. Photostability of dye **1**, **2**, and **BD-1** thin films. The remaining fluorescence emission intensities of the dye thin films as a function of irradiation time. Irradiated at 340 (**1**), 360 (**2**), 380 nm (**BD-1**). Thin films were prepared by drop-casting of dyes dissolved in CHCl_3 ($7.0 \text{ mg} \pm 0.2/\text{mL}$).

near identical with those in diluted solution (Fig. S1). These might be due to the relative suppression of intermolecular π - π^* stacking of **HBO** and **HBT**. The emission spectra of **HBO**, **1** and **2** in powder showed slight red shifts compared with those of thin films. In addition, the full width at half maximum

(FWHM) for both solution and solid emission spectra are as narrow as 63 - 74 nm for **1** and **2**. Both boron complexes **1** and **2** are deep blue emitting materials while the ligands, **HBO** and **HBT** are green emitters.

We have investigated photostabilities of solid thin films **1**, **2**, and **BD-1**. **BD-1** is one notable example, styrylamine-based blue fluorescent dopant in OLED devices.⁹ The photooxidation studies were performed by continuous UV irradiation of dye thin films using a 150 W steady-state Xe lamp as the irradiation source under aerobic conditions. The photoinduced degradation was quantified by monitoring the decrease of fluorescence intensity of **1**, **2**, and **BD-1** thin films as a function of elapsed photolysis time (Figure 2). The fluorescence intensity of **1** and **2** thin films was only slightly attenuated after 2 hours of irradiation even with the strongest light: about 88% (for **1**) ~ 98% (for **2**) of initial fluorescence intensity remained. However, fluorescence intensity of **BD-1** film decreased rapidly as indicated by the fact that only 35% fluorescence intensity remained after irradiation of 2 hours. As indicated by photolysis experiments, deep blue luminescent boron complexes **1** and **2** demonstrated high photostability, which might be an advantage in various applications which involve high intensity light source or during prolonged operation period.

In summary, the preparation and properties of new boron complexes based on a N,O-ligated **HBO** and **HBT** ligands, **1** and **2**, were investigated as candidates for blue luminescent materials. Dyes **1** and **2** show good fluorescence efficiency and high photostability.

Acknowledgments. This work was supported by the Korea Research Foundation Grant (KRF-2008-331-C00173) and by the GRRC program of Gyeonggi province (GRRC dankook 2008-A01).

Supporting Information Available. Experimental procedures and full spectroscopic data.

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