



Efficient luminescence from easily prepared fluorine–boron core complexes based on benzothiazole and benzoxazole



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ABSTRACT

A series of brightly luminescent fluorine–boron cored complexes were synthesized from readily available precursors in high yield and were structurally characterized. The molecular structures were based on the benzothiazole and benzoxazole frameworks. The emission maxima of these fluorine–boron cored complexes spanned 70 nm in the visible spectrum from 450 nm (blue) to 520 nm (green). The photoluminescence quantum yields ranged from 0.16 to 0.8 in dichloromethane at room temperature. Altering the chelating position on the naphthalene ring provides a means to tailor the optical properties of the complexes.

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1. Introduction

Synthetic simplicity is a desirable property for luminescent molecular systems because it can facilitate the rapid expansion and tuning of photophysical properties for targeted functions. The development of colorful high-efficiency fluorophores is essential for fluorescent sensors [1–3], switches [4–7], molecular motors [8,9], logic gates [10], and organic-light-emitting devices (OLED) [11,12]. In particular, luminescent organoboron molecular systems are currently one of the most intriguing families of molecules due to their unique optical properties [13–18]. Small molecules with a built-in fluorine–boron core architecture as the key emissive elements have attracted considerable attention due to their excellent properties, such as bipolar charge (electron and hole) transport and high photo efficiency. Recent research has focused on the design and synthesis of new types of fluorine–boron (F–B) complexes to explore their applications as photoelectric functional materials. For example, 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (**BODIPY**) is a typical fluorine–boron complexes that has been intensively studied

and exhibits strong UV absorption, narrow emission bands, large molar absorption coefficients, and a high fluorescence quantum yield [19–21]. In addition, the majority of F–B complexes, including **BODIPY** derivatives, are relatively insensitive to the solvent polarity and the pH of their environment and are stable under physiological conditions. They are widely regarded as promising candidates for fluorescent labels and probes. However, **BODIPY** and the majority of its analogs emit relatively sharp fluorescence in the wavelength range from 500 to 800 nm. Only a few F–B complexes emit intense blue fluorescence with high efficiency. Therefore, it remains a challenge to develop novel F–B complexes with strong or narrow emission bands.

In this context, a series of fluorine–boron cored fluorescent compounds that are structurally related but are predicted to display different optical properties were designed and synthesized. *Ortho*-hydroxyl aromatic acids were condensed with 2-aminothiophenol or 2-aminophenol to generate benzothiazole or benzoxazole derivatives. The compounds 2-(2-hydroxyphenyl)benzothiazole and 2-(2-hydroxyphenyl)benzoxazole are interesting fluorescent molecules that exhibit large Stokes shifts and thermal and photophysical stability due to their excited state intramolecular proton transfer mechanism (**ESIPT**). Upon binding of the boron atom to the hydroxyl and the nitrogen groups of the azole moiety, the **ESIPT** will be inhibited, and longer emission wavelengths will be lost [22–

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25]. It can be anticipated that the emission maxima of these F–B complexes will therefore be blue-shifted. Due to intramolecular steric hindrance, the molecular structure will be twisted, leading to altered emission characteristics. Additionally, the emission efficiency will be enhanced by the strengthened molecular framework.

2. Experimental

2.1. Materials and equipment

The solvents used in the reactions were carefully dried according to the standard procedure. All the reagent-grade chemicals were purchased from Sigma–Aldrich CO. LLC. (South Korea) and used without further purification. Melting points were determined in open capillaries and are uncorrected. IR spectra were run for KBr on a FTS-175C IR spectrometer (ν_{\max} in cm^{-1}). All synthesized compounds were routinely characterized by TLC (Merck DC. Alufolien Kieselgel 60 F254) and nuclear magnetic resonance (NMR). The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer operating at frequencies of 400 MHz (H) and 100 MHz (C). The masses and high-resolution mass spectra were recorded on an LC-MS (Waters UPLC-TQD) and a Bruker micro-TOF II Focus, respectively.

2.2. X-ray data collection and structure determination

The crystal of **1** was covered with a layer of hydrocarbon oil and mounted on a cryo-loop. The data for crystal **1** were collected on a Bruker SMART APEX CCD area detector system with a graphite monochromator and a Mo K α fine-focus sealed tube ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97 and refined against F^2 for all data by full-matrix least-squares with SHELXS-97. The absorption corrections were applied by using SADABS. The CCDC files 977977 contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK. <http://www.ccdc.cam.ac.uk/conts/retrieving.html>

2.3. Absorbance, emission, and luminescence quantum yield

The solvents used in the photochemical measurements were spectroscopic grade. The absorption spectra were measured with an Agilent 8453 spectrophotometer. The emission spectra were measured with a Shimadzu RF-5301PC fluorescence spectrophotometer. All the experiments were performed repeatedly, and reproducible results were obtained. Prior to the spectroscopic measurements, the solutions were deoxygenated by bubbling with nitrogen through them. The \tilde{O}_F values in solution were measured following a general method with quinine sulfate ($\tilde{O} = 0.55$ in 50 mM H_2SO_4 solution) as a standard. Dilute solutions of the compounds in DCM were used. The sample solutions were placed in quartz cuvettes and degassed for ~ 15 min. The degassed solution exhibited an absorbance of 0.05–0.09 at the absorbance maxima. The fluorescence spectra were recorded 3–4 times and the average values of the integrated areas of fluorescence were used to calculate \tilde{O}_F in solution. The solid emission spectra were measured by attaching the solid samples on a black support on an Agilent 8453 spectrophotometer.

2.4. Theoretical calculations

For the theoretical study of the excited state photo-physics of the complexes, the *DMol³* program packaged in *Material Studio* (Accelrys Software Inc., United States) was used. The ground state

geometries and the frontier molecular orbital of the compound were calculated using density function theory (DFT) with the B3LYP hybrid functional and the double numerical plus *d*-functions (DND) atomic orbital basis set.

2.5. General procedure for the preparation and characterization of F–B complexes

The synthetic routes for these F–B complexes are depicted in **Scheme 1**. The corresponding 2-hydroxybenzothiazole and 2-hydroxybenzoxazole were synthesized following the literature methods [26,27]. **R1–R3** have been previously reported, and here they were synthesized as reference complexes for comparison with the optical properties of the structurally related F–B complexes [23,25,28].

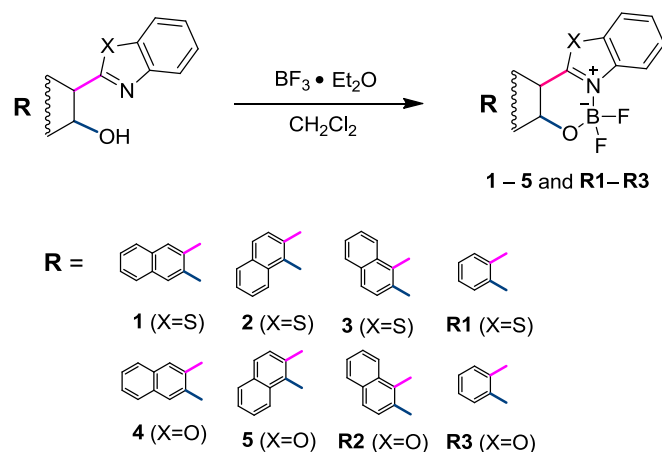
Portions of 2-hydroxybenzothiazole or 2-hydroxybenzoxazole (2.0 mmol) and *N,N*-diisopropylethylamine (DIEA) (0.5 mL) were dissolved in 20 mL of dichloromethane. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.0 mL) was added dropwise at room temperature. A yellowish precipitate formed immediately. After the disappearance of the 2-hydroxybenzothiazole or 2-hydroxybenzoxazole, as monitored by TLC, the yellowish solid was filtered and washed thoroughly with dichloromethane. The crude product was purified by silica gel (200–300 mesh) column chromatography (eluent: CH_2Cl_2 and hexane).

2.5.1. **1**, yellow solid, 92% yield

Mp: 277–281 °C; IR (KBr, ν , cm^{-1}): 747, 867, 904, 954, 1003, 1065, 1098, 1140, 1213, 1290, 1336, 1459, 1501, 1601, 1631; ^1H NMR (DMSO- d_6 , 400 MHz) δ : 8.90 (1H, s); 8.17 (1H, d, $J = 11.0$ Hz); 8.11 (1H, d, $J = 8.0$ Hz); 8.04 (1H, d, $J = 8.0$ Hz); 7.78 (1H, d, $J = 8.0$ Hz); 7.58 (1H, t, $J = 8.0$ Hz); 7.58 (2H, m); 7.41 (1H, s); 7.36 (1H, t, $J = 8.0$ Hz); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 164.5, 152.9, 151.5135.3, 134.9, 129.1, 128.8, 128.0, 127.4, 126.6, 125.8, 125.3, 123.9, 122.3, 122.0, 121.0, 110.5. MS (70 eV, EI): 325 (M^+). HRMS (70 eV, EI): $\text{C}_{17}\text{H}_{10}\text{BF}_2\text{NOS}$ requires 325.0544; found: 325.0544.

2.5.2. **2**, pale-yellow solid, 85% yield

Mp: 252–255 °C; IR (KBr, ν , cm^{-1}): 629, 686, 756, 799, 827, 860, 899, 971, 1043, 1097, 1255, 1298, 1325, 1416, 1456, 1480, 1523, 1567, 1617; ^1H NMR (DMSO- d_6 , 400 MHz) δ : 8.45 (1H, d, $J = 8.0$ Hz); 8.41 (1H, d, $J = 8.0$ Hz); 8.21 (1H, d, $J = 8.0$ Hz); 8.03 (1H, d, $J = 8.0$ Hz); 7.88 (1H, d, $J = 8.0$ Hz); 7.82–7.76 (2H, q); 7.71–7.68 (4H, t, $J = 7.6$ Hz, 8.8 Hz); 7.65 (1H, d, $J = 8.8$ Hz). ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 169.3, 153.7, 142.6, 142.0, 137.2, 130.5, 129.6, 128.9, 128.2, 127.2.



Scheme 1. Synthesis of F–B complexes **1–5** and reference complexes (**R1–R3**).

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