

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

Min Jung Kwak and Youngmi Kim*

Department of Chemistry, Dankook University, Gyeonggi-do 448-701, Korea. *E-mail: youngmi@dankook.ac.kr
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Key Words:

General procedure: To a solution of 2-(2'-hydroxyphenyl)benzothiazole, **HBT**, (3.18 g, 14.0 mmol) in CH₂Cl₂ (200 mL) under argon atmosphere were added BF₃·Et₂O (5.8 mL, 46.2 mmol) and triethylamine (11.69 mL, 83.2 mmol) at room temperature. The resulting solution was stirred at room temperature for 48 hr. The solvent was removed, and the resulting residue was purified by silica gel column chromatography using hexanes and dichloromethane (1:2) as an eluent. The product was further purified by recrystallization from hexanes and dichloromethane to yield dye **2** as a yellowish solid. **1**: (50%). m.p. 209 ~ 210 °C; ¹H-NMR (500 MHz, CDCl₃): δ = 7.95 (m, 2H), 7.73 (m, 1H),

7.64 (t, 1H, *J* = 8.0 Hz), 7.57 (t, 2H, *J* = 8.5 Hz), 7.22 (d, 1H, *J* = 8.5 Hz), 7.08 (t, 1H, *J* = 8.0 Hz); ¹³C-NMR (125 MHz, CDCl₃): δ = 162.0, 159.8, 149.1, 138.2, 130.9, 127.8, 127.7, 125.8, 120.7, 120.5, 117.2, 120.0, 106.2; HR-MS (ESI): calcd. for C₁₃H₈BF₂NO₂ [M+H]⁺ 260.0616, found 260.0704. **2**: (92%). m.p. 244 ~ 247 °C; ¹H-NMR (500 MHz, CDCl₃): δ = 8.41 (d, 1H, *J* = 8.5 Hz), 7.91 (d, 1H, *J* = 8.5 Hz), 7.67 (t, 2H, *J* = 8.0 Hz), 7.58 (m, 2H), 7.22 (d, 1H, *J* = 8.5 Hz), 7.03 (t, 1H, *J* = 8.0 Hz); ¹³C-NMR (125 MHz, CDCl₃): δ = 169.1, 156.3, 143.6, 137.1, 129.2, 128.8, 127.4, 126.9, 122.1, 120.6, 120.5, 120.4, 113.1; HR-MS (ESI): calcd. for C₁₃H₈BF₂NOS [M+H]⁺ 276.0388, found 276.0407.

Table S1. UV-Vis absorption and emission data.

compound	$\lambda_{\text{abs}}/\text{nm}^a$ (log ϵ)	$\lambda_{\text{em}}/\text{nm}^b$ (Φ_F)	FWHM (nm)
HBO (CH ₂ Cl ₂)	320 (4.40)	500 (0.02)	91
HBO (film)	broad (~ 350)	505	86
HBO (powder)	broad (~ 360)	511	97
HBT (CH ₂ Cl ₂)	332 (4.39)	530 (0.006)	107
HBT (film)	broad (~ 365)	527	81
HBT (powder)	broad (~ 375)	527	81
1 (CH ₂ Cl ₂)	344 (4.32)	408 (0.20)	63
1 (film)	broad (~ 385)	428	74
1 (powder)	broad (~ 390)	432	71
2 (CH ₂ Cl ₂)	364 (4.36)	433 (0.23)	63
2 (film)	broad (~406)	466	74
2 (powder)	broad (~420)	473	64

^aAbsorption maximum, ^bEmission maximum, Excited at 320 (**HBO**), 340, (**HBT**, **1**) 360 nm (**2**).

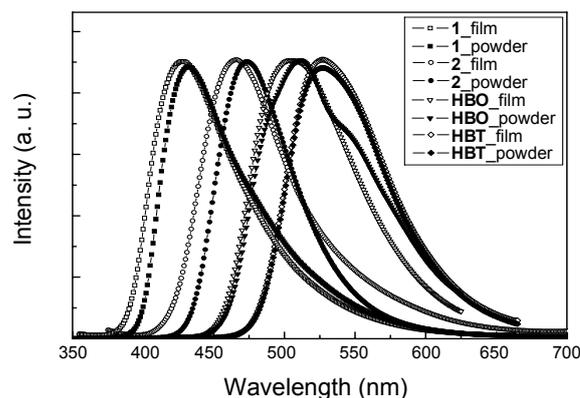


Figure S1. Normalized fluorescence emission spectra of dye **1**, **2**, **HBO** and **HBT** in thin film and powder at 25 °C. Excited at 320 (**HBO**), 340, (**HBT**, **1**) 360 nm (**2**). The thin films were prepared by drop-casting of dyes dissolved CHCl₃ (7.0 mg ± 0.2/mL).