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Supporting Information

for

Benzothiazole-enamide-based BF2 Complexes: Luminophores Exhibiting Aggregation-induced

Emission, Tunable Emission and High Efficient Solid-State Emission

Qingsong Liu,^[a] Xiaoqing Wang, *^[a] Hui Yan,^[b] Yanping Wu,^[a] Zhenyu Li,^[a] Shuwen Gong,*^[a]

Peng Liu,^[c] and Zhipeng Liu*^[a]

^[a] Institute of Organic Functional Molecules and Materials, School of Chemistry and Chemical Engineering, and

School of Material Science and Engineering, Liaocheng University, No.1, Hunan road, Liaocheng, Shandong, P.R.

China, E-mail: chiuzp@163.com; wangxiaoqing@lcu.edu.cn; Gongshw@lcu.edu.cn.

^[b] School of Pharmacy, Liaocheng University, No. 1, Hunan road, Liaocheng, Shandong, P.R. China.

^[c] School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, Shandong, P.R. China.

Materials and instrumentations.

All reactions and manipulations of air-sensitive compounds were carried out under dry argon by using Schlenk techniques and/or vacuum line techniques. Solvents were dried prior to use by common methods in organometallic chemistry. Chemicals were commercially obtained and used as received. ¹H, ¹¹B and ¹³C NMR spectra were recorded using Varian Mercury-plus 400M spectrometer instrument. Chemical shifts were reported in ppm relative to Si(CH₃)₄ (¹H, ¹³C), and coupling constants (*J*) were given in Hz. Mass spectra were obtained on a LCQ (ESI-MS, Thermo Finnigan) mass spectrometer. Thin layer chromatography (TLC) was performed on plates coated with thick silica gel GF254 (Qingdao Haiyang Chemical Co., Ltd). Column chromatography was performed using silica gel (200 mesh, Qingdao Haiyang Chemical Co., Ltd).

Synthesis

Synthesis of compound 2. 2-Methylbenzothiazole (2.5 g, 16.7 mmol) was added to a mixture of THF (15 mL) and NaH (60w% in oil, 2 g, 50 mmol) at room temperature, after stirred for 20 minutes, methyl 4-(dimethylamino)benzonate (3.9 g, 21.8 mmol) was added, and the resulting mixture was heated at reflux for 10 h. After cooling down to room temperature, 2 M HCl aq. was slowly added, and the yellow precipitate was filtered and washed with water. After drying, the desire product was obtained as yellow solid. Yield: 90% (4.45 g), ¹H NMR (400 MHz, CDCl₃): δ /ppm = 8.00 (d, *J* = 8.7, 3H), 7.86 (d, *J* = 8.0, 1H), 7.45 (t, *J* = 7.7, 1H), 7.36 (t, *J* = 7.5, 1H), 6.67 (d, *J* = 8.9, 2H), 4.73 (s, 2H) 3.07 (s, 6H).

General procedure for the synthesis of compound 3–8. Corresponding ketone (4 mmol), aniline (8 mmol) and toluene (15 mL) were added to a round bottom flask equipped with a Dean-Stark trap, condenser and magnetic stirring bar, and then 2 drops of trifluoroacetic acid (cat. amount) was added. The resulting solution was heated to reflux

for 12 h. After cooling down to room temperature, toluene was removed in vacuo. Column chromatography of the residue on silica gel gave desired product as yellow solid.

Compound 3: Yield: 66%, ¹H NMR (400 MHz, CDCl₃) δ /ppm = 11.31 (s, 1H), 7.87 (d, *J* = 8.1, 1H), 7.78 (d, *J* = 7.9, 1H), 7.51–7.20 (m, 7H), 7.13 (t, *J* = 7.8, 2H), 6.91 (t, *J* = 7.3, 1H), 6.78 (d, *J* = 7.8, 2H), 5.74 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ /ppm = 167.15, 153.98, 150.86, 141.47, 136.81, 133.13, 129.16, 128.67, 126.11, 123.87, 122.57, 122.07, 121.29, 96.59. ESI-Ms: calcd., [M+H]⁺ = 329.1, found: [M+H]⁺ = 329.2.

Compound 4: Yield: 51%, ¹H NMR (400 MHz, CDCl₃) δ /ppm = 11.01 (s, 1H), 7.77 (d, *J* = 8.2, 2H), 7.38 (t, *J* = 7.7, 2H), 7.23 (m, 8H), 5.66 (s, 1H), 2.26 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ /ppm =167.87, 154.65, 154.15, 138.79, 137.00, 135.36, 132.94, 128.99, 128.39, 127.98, 127.92, 126.08, 125.91, 123.35, 121.16, 120.86, 92.21, 19.24; ESI-Ms: calcd., [M+H]⁺ = 357.1, found: [M+H]⁺ = 357.2.

Compound 5: Yield: 74%, ¹H NMR (400 MHz, CDCl₃) δ /ppm = 11.21 (s, 1H), 7.81 (d, *J* = 8.1, 1H), 7.76 (d, *J* = 7.9, 1H), 7.44 (dd, *J* = 6.2, 2.6, 2H), 7.38 (t, *J* = 7.7, 1H), 7.34–7.26 (m, 2H), 7.25 (d, *J* = 3.7, 1H), 7.21 (d, *J* = 7.7, 1H), 6.74 (d, *J* = 8.8, 2H), 6.54 (d, *J* = 8.8, 2H), 5.62 (s, 1H), 2.85 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ /ppm =167.37, 154.04, 152.04, 147.15, 136.94, 132.91, 131.17, 128.78, 128.62, 128.39, 125.90, 124.26, 124.21, 123.39, 121.19, 121.08, 120.90, 120.80, 113.22, 113.12, 94.21, 94.16, 41.07. ESI-Ms: calcd., [M+H]⁺ = 372.1, found: [M+H]⁺ = 372.2.

Compound 6: Yield: 52%, ¹H NMR (400 MHz, CDCl₃) δ /ppm = 11.21 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.43 (dd, *J* = 6.3, 2.8 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.22 (dd, *J* = 12.2, 4.0 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 8.9 Hz, 2H), 5.62 (s, 1H), 2.84 (s, 6H); ¹³C NMR (100 MHz, CDCl3): δ /ppm = 167.38, 154.07, 152.07, 147.18, 136.98, 132.93, 131.20, 128.70, 128.38, 125.90, 124.22, 123.39, 121.13, 120.86, 113.20, 94.20, 41.07; ESI-MS: calcd., [M+H]⁺ = 372.1, found: [M+H]⁺ = 372.2.

Compound 7: Yield: 45%, ¹H NMR (400 MHz, CDCl₃) δ /ppm = 10.97 (s, 1H), 7.75–7.70 (m, 2H), 7.35 (t, *J* = 7.7, 1H), 7.20–7.14 (m, 4H), 6.99 (s, 3H), 6.49 (d, *J* = 4.0, 2H), 5.63 (s, 1H), 2.92 (s, 6H), 2.24 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ /ppm = 155.22, 154.29, 150.73, 139.37, 135.31, 132.73, 128.89, 128.35, 125.73, 125.69, 124.16, 122.87, 121.02, 120.44, 111.29, 90.68, 40.25, 19.22; ESI-MS: calcd., [M+H]⁺ = 372.1, found: [M+H]⁺ = 372.2.

Compound 8: Yield: 79%, ¹H NMR (400 MHz, CDCl₃) *δ*/ppm = 10.98 (s, 1H), 7.74 (t, *J* = 8.5 Hz, 2H), 7.41–7.31 (m, 1H), 7.24–7.11 (m, 4H), 7.00 (s, 3H), 6.50 (d, *J* = 8.9 Hz, 2H), 5.64 (s, 1H), 2.92 (s, 6H), 2.25 (s, 6H).; ¹³C NMR (100 MHz, CDCl₃): *δ*/ppm =168.18, 155.23, 154.32, 150.76, 139.37, 135.32, 132.75, 128.90, 128.35, 125.71, 124.20, 122.87, 121.02, 120.45, 111.31, 90.70, 40.26, 19.20.; ESI-MS: calcd., [M+H]⁺ = 415.1, found: [M+H]⁺ = 415.2.

General procedure for the synthesis of Borebt1–6. Corresponding enamide (**3–8**, 1 equiv.) was dissolved in dry toluene. DBU (3 equiv.) was added to the solution and stirred for 10 minutes at room temperature. A solution of toluene containing of boron trifluoride diethyl ether complex (5 equiv.) was slowly added to the mixture via syringe. The resulting mixture was heated to reflux for 1 h. After cooling to room temperature, the solution was extracted with dichloride methane. The organic layer was washed with water and brine, and dried over anhydrous magnesium sulfate. The dried organic layer was filtrated though a short pad of silica gel. Removing the solvent yielded the **Borebt1–6** with high purity.

Borebt1: Yield: 86%, ¹H NMR (400 MHz, CDCl₃) δ /ppm = 8.08 (d, *J* = 8.3, 1H), 7.67 (d, *J* = 7.9, 1H), 7.46 (t, *J* = 7.8, 1H), 7.32 (t, *J* = 7.7, 1H), 7.28 – 7.13 (m, 9H), 7.11 (d, *J* = 6.5, 1H), 5.87 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ /ppm = 164.31, 161.46, 143.43, 142.12, 136.72, 129.23, 129.00, 128.45, 128.15, 127.85, 127.64, 127.28, 126.21, 124.88, 121.66, 118.07, 90.70; ¹¹B NMR (128 MHz, CDCl₃): δ /ppm = 2.29 (t, *J* = 30.9 Hz). ESI-MS: calcd., [M+H]⁺ = 377.23, found: [M+H]⁺ = 377.42; Elemental analysis (%) calcd for C21H15BF2N2S: C, 67.04; H, 4.02; N, 7.45. Found, C, 67.12; H, 4.45; N, 7.86.

Borebt2: Yield:76%, ¹H NMR (400 MHz, CDCl₃) δ /ppm = 8.03 (d, *J* = 8.4, 1H), 7.66 (d, *J* = 8.0, 1H), 7.45 (t, *J* = 7.8, 1H), 7.31 (t, *J* = 7.7, 1H), 7.28–7.21 (m, 4H), 7.21–7.13 (m, 2H), 6.96 (dt, *J* = 15.2, 6.0, 3H), 5.84 (s, 1H), 2.28 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ /ppm = 164.40, 163.02, 143.60, 139.45, 136.74, 136.46, 129.52, 128.28, 127.81, 127.69, 127.62, 127.16, 124.77, 121.63, 118.04, 89.91, 19.30; ¹¹B NMR (128 MHz, CDCl₃): δ /ppm = 2.20 (t, *J* = 30.8 Hz). ESI-MS: calcd., [M+Na]⁺ = 427.26, found: [M+Na]⁺ = 427.42; Elemental analysis (%) calcd for C23H19BF2N2: C, 68.33; H, 4.74; N, 6.93. Found, C, 68.22; H, 4.82; N, 6.81.

Borebt3: Yield: 90%, ¹H NMR (400 MHz, CDCl₃) δ /ppm = 8.05 (d, *J* = 8.2, 1H), 7.64 (d, *J* = 7.9, 1H), 7.44 (t, *J* = 7.8, 1H), 7.37–7.15 (m, 6H), 7.02 (d, *J* = 8.6, 2H), 6.58 (d, *J* = 8.7, 2H), 5.82 (s, 1H), 2.89 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ /ppm = 166.67, 163.85, 161.70, 148.34, 143.53, 137.01, 132.00, 129.01, 128.95, 128.76, 128.13, 127.79, 127.51, 124.64, 121.58, 117.89, 112.84, 90.22, 41.11; ¹¹B NMR (128 MHz, CDCl₃): δ /ppm = 2.28 (t, *J* = 31.5 Hz). ESI-MS: calcd., [M+Na]⁺ = 442.28, found: [M+Na]⁺ = 442.50; Elemental analysis (%) calcd for C23H20BF2N3S: C, 65.88; H, 4.81; N, 10.02. Found, C, 65.45; H, 4.65; N,10.26.

Borebt4: Yield: 89%, ¹H NMR (400 MHz, CDCl₃) δ /ppm = 8.03 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.30–7.23 (m, 1H), 7.21 (d, *J* = 6.5 Hz, 4H), 7.11 (d, *J* = 8.7 Hz, 3H), 6.46 (d, *J* = 8.7 Hz, 2H), 5.87 (s, 1H), 2.92 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ /ppm = 163.82, 161.76, 150.84, 143.62, 143.06, 130.64, 128.47, 128.23, 127.41, 125.73, 124.40, 123.41, 121.52, 117.70, 111.09, 90.35, 40.11; ¹¹B NMR (128 MHz, CDCl₃): δ /ppm = 2.25 (t, *J* = 30.5 Hz). ESI-MS: calcd., [M+Na]+ = 442.12, found: [M+Na]+ = 442.50; Elemental analysis (%) calcd for C23H20BF2N3S: C, 65.88; H, 4.81; N, 10.02. Found, C, 65.58; H, 4.73; N, 10.12.

Borebt5: Yield: 80%, ¹H NMR (400 MHz, CDCl₃) δ /ppm = 7.97 (d, *J* = 8.3, 1H), 7.60 (d, *J* = 8.0, 1H), 7.39 (t, *J* = 7.8, 1H), 7.25 (t, *J* = 7.6, 1H), 7.13 (d, *J* = 8.8, 2H), 7.05–6.91 (m, 3H), 6.43 (d, *J* = 8.8, 2H), 5.85 (s, 1H), 2.90 (s, 6H), 2.26 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ /ppm = 163.79, 163.26, 150.99, 143.66, 140.18, 136.81, 129.56, 128.29, 127.66, 127.39, 126.84, 124.28, 123.17, 121.53, 121.50, 117.55, 110.78, 89.52, 40.07, 19.28; ¹¹B NMR (128 MHz, CDCl₃): δ /ppm = 2.14 (t, *J* = 30.9 Hz). ESI-MS: calcd., [M+Na]⁺ = 470.16, found: [M+Na]⁺ = 470.42; Elemental analysis (%) calcd for C25H24BF2N3S: C, 67.12; H, 5.41; N, 9.39. Found, C, 67.36; H, 5.65; N, 9.86.

Borebt6: Yield: 54%, ¹H NMR (400 MHz, CDCl₃) δ /ppm = 8.00 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 8.7 Hz, 2H), 5.81 (s, 1H), 2.93 (s, 6H), 2.89 (s, 6H).; ¹³C NMR (100 MHz, CDCl₃): δ /ppm = 163.22, 161.86, 150.65, 148.66, 143.71, 132.27, 130.59, 128.49, 127.64, 127.29, 124.13, 123.85, 121.42, 117.52, 112.65, 111.14, 89.84, 40.87, 40.18; ¹¹B NMR (128 MHz, CDCl₃): δ /ppm = 2.25 (t, *J* = 30.3 Hz). ESI-MS:

calcd., [M+Na]⁺ = 485.17, found: [M+Na]⁺ = 485.50; Elemental analysis (%) calcd for C25H25BF2N4S: C, 64.94; H, 5.45; N, 12.12. Found, C, 64.79; H, 5.85; N, 12.81.



Figure S1. Absorption spectra of **Borebt1** (a), **Borebt2** (b), **Borebt3** (c), **Borebt4** (d), **Borebt5** (e) and **Borebt6** (f) (10 μ M) in various solvents (CH₃CN (ACN), dichloromethane (DCM), dimethylformamide (DMF), tetrafuran (THF), ethylene glycol (glycol), ethanol, hexane and toluene.



Figure S2. Emission spectra of **Borebt1** (a), **Borebt2** (b), **Borebt3** (c), **Borebt4** (d), **Borebt5** (e) and **Borebt6** (f) (10 μ M) in various solvents such as hexane, toluene, dichloromethane (DCM), tetrahydrofuran (THF), acetonitrile (ACN), dimethylformamide (DMF), ethanol, ethylene glycol (glycol) and glycerol, respectively.



Figure S3. Absorption and emission spectra of Borebt1 (a), Borebt2 (b), Borebt3 (c), Borebt4 (d), Borebt5 (e) and Borebt6 (f) in the solid state.



Figure S4. Changes in the quantum yields of Borebt1 (a), Borebt2 (b), Borebt3 (c), Borebt4 (d), Borebt5 (e) and Borebt6 (f) in THF/water mixtures (10 μ M) with varied volumetric fractions of water (f_w).



Figure S5. Molecular structures of Borebt1–6 (50% probability for thermal ellipsoids). H atoms are omitted for clarity.



Figure S9. Calculated absorption spectra of Borebt3.

S8 /S20



Figure S10. Calculated absorption spectra of Borebt4.



Figure S11. Calculated absorption spectra of Borebt5.



Figure S12. Calculated absorption spectra of Borebt6.



Figure S13. (a) Emission spectra of initial, HCl (g) and NH₃ (g) fumed powders of **Borebt4**; (b) Reversible switching of the emission of **Borebt4** by HCl/NH₃ fuming cycle; (c) Fluorescent pictures of HCl (g) and NH₃ (g) fumed powders of **Borebt4**.



Figure S14. (a) Emission spectra of initial, HCl (g) and NH₃ (g) fumed powders of **Borebt5**; (b) Reversible switching of the emission of **Borebt5** by HCl/NH₃ fuming cycle; (c) Fluorescent pictures of HCl (g) and NH₃ (g) fumed powders of **Borebt5**.



Figure S15. (a) Emission spectra of initial, HCl (g) and NH₃ (g) fumed powders of **Borebt6**; (b) Reversible switching of the emission of **Borebt6** by HCl/NH₃ fuming cycle; (c) Fluorescent pictures of HCl (g) and NH₃ (g) fumed powders of **Borebt6**.



Figure S16. ¹H NMR of Borebt1 in CDCl₃.



Figure S18. ¹¹B NMR of Borebt1 in CDCl₃.



-2.44 -2.20 -1.96









Figure S24. ¹¹B NMR of Borebt3 in CDCl₃.





-2.49 -2.25 -2.02











--2.48 --2.25 --2.01



Figure S33. $^{11}\mbox{B}$ NMR of Borebt6 in CDCl3.