

Supporting Information for

Film-Type Chemosensors Based on Boron Diiminate Polymers Having Oxidation-Induced Emission Properties

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Synthesis of Boron diiminate derivatives

Scheme S1. Synthetic routes of M1, M2 and M3

1. Reaction of 2-aminothiophenol and 4-iodocacetophenone in toluene, MS to form 1.
2. Reaction of 2-aminothiophenol and benzoyl chloride in THF, NEt₃ to form 2.
3. Conversion of 1 to 3 by treatment with LDA and 2 in THF.
4. Reaction of 3 with BF₃·Et₂O in toluene to form M1.
5. Treatment of M1 with MCPBA and CHCl₃ to form M2 and M3.
Scheme S2. Synthetic routes of M-SMe

1. LDA
2. THF

43%  39%

5

BF₃ •Et₂O
toluene

39%
Experimental Section

Measurements: $^1$H (400 MHz), $^{13}$C (100 MHz), and $^{11}$B (128 MHz) NMR spectra were recorded on JEOL JNM-EX400 spectrometers. In $^1$H and $^{13}$C NMR spectra, tetramethylsilane (TMS) was used as an internal standard in CDCl$_3$, and $^{11}$B NMR spectra were referenced externally to BF$_3$·OEt$_2$ (sealed capillary). The number–average molecular weight ($M_n$) and the molecular weight distribution [weight-average molecular weight/number-average molecular weight ($M_w/M_n$)] values of all polymers were estimated by size-exclusion chromatography (SEC) with a TOSOH G3000HXL system equipped with three consecutive polystyrene gel columns [TOSOH gels: $\alpha$–4000, $\alpha$–3000, and $\alpha$–2500] and ultraviolet detector at 40 °C. The system was operated at a flow rate of 1.0 mL/min with CHCl$_3$ as an eluent. Polystyrene standards were employed for the calibration. UV–vis spectra were recorded on a SHIMADZU UV–3600 spectrophotometer, fluorescence emission spectra were measured with a HORIBA JOBIN YVON Fluoromax–4P spectrofluorometer. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Materials: 4-(Methylthio)aniline (Wako Chemical, Co.), 1-(4-iodophenyl)ethan-1-one (Tokyo Chemical, Co.), sodium tungstate(VI) dihydrate (Wako Chemical, Co.), hydrogen peroxide (30 wt%, Wako Chemical, Co.), acetic acid (Wako Chemical, Co.), [9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl]bisboronic acid (Aldrich Chemical, Co.), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-Phos, Aldrich Chemical, Co.), tris(dibenzylideneacetone dipalladium(0)) (Pd$_2$(dba)$_3$, Tokyo Kasei Kogyo, Co.), lithium diisopropylamide (1 mol/L in mixed solvent of hexane and THF (= 70% : 13%), Kanto Chemical, Co., Inc.) and boron trifluoride diethyl etherate (BF$_3$·OEt$_2$, Aldrich Chemical, Co.) were used as received. Tetrahydrofuran (THF) and triethylamine were purified using a two-column solid-state purification system (Glasscoutour System, Joerg Meyer, Irvine, CA).

Synthesis of 1. In a round bottom flask, $p$-iodoacetophenone (18.0 g, 73.1 mmol) and molecular sieves 3A (40 g) were placed under nitrogen atmosphere. Toluene (200 mL) and 4-(methylthio)aniline (13.2 g, 11.6 mL, 95.0 mmol) were added to the flask.
The reaction mixture was refluxed under argon atmosphere at ambient temperature for 2 d. After the sieves were removed by filtration using celite, the solvent was removed by a rotary evaporator. The obtained product was recrystallized from ethyl acetate. The precipitate collected by filtration was dried in vacuum to give pure 1 as a yellow crystal (20.4 g, 76%). $^1$H NMR (CD$_2$Cl$_2$): $\delta = 7.81$ (2H, d, $J = 11.0$ Hz), 7.72 (2H, d, $J = 10.7$ Hz), 7.29 (2H, d, $J = 8.5$ Hz), 6.74 (2H, d, $J = 11.2$ Hz), 2.49 (3H, s), 2.20 (3H, s) ppm. HRMS (ESI): Calcd for [M+H]$^+$, 367.9964; found, m/z 367.9952.

**Synthesis of 2.** Compound 2 was synthesized according to our previous report.[1]

**Synthesis of 3.** Lithium diisopropylamide (30.0 mL, 30.0 mmol, 1.0 mol/L in hexane) was added dropwise to the solution of 1 (10.0 g, 27.2 mmol) in THF (100 mL) at $-10$ °C. Then, 2 (10.2 g, 30.0 mmol) in THF (60 mL) was added to the solution at $-10$ °C. After stirred the solution at ambient temperature for 15 h, the solution was poured into a large amount of CPME. The solution was washed with brine three times and dried over anhydrous magnesium sulfate. After the solvent was removed by a rotary evaporator, the product was purified by silica gel column chromatography (eluted with hexane/ethyl acetate = 3/1) to give crude products. The obtained product was dissolved in a small amount of THF, and then the product was reprecipitated from methanol. The solid collected by filtration was dried in vacuum to give pure 3 as a yellow crystal (8.47 g, 46%). $^1$H NMR (CDCl$_3$): $\delta$: 12.9 (1H, br s), 7.8 (1H, d, $J = 8.53$ Hz), 7.7 (1H, d, $J = 8.77$ Hz), 7.6 (2H, d, $J = 8.28$ Hz), 7.4 (2H, d, $J = 8.53$ Hz), 7.3–7.3 (5H, m), 7.1 (3H, dd, $J = 8.53$, 4.26 Hz), 6.7 (1H, d, $J = 8.28$ Hz), 6.7 (2H, d, $J = 8.53$ Hz), 6.5 (2H, d, $J = 8.77$ Hz), 5.3 (1H, s), 2.4 (3H, s). HRMS (ESI): Calcd for [M+H]$^+$, 672.9664; found, m/z 672.9666.

**Synthesis of M1.** BF$_3$·OEt$_2$ (11.7 mL, 13.5 g, 95.2 mmol) was added to the solution of 3 (6.40 g, 9.52 mmol) in toluene (30 mL) at ambient temperature, and the solution was stirred at 100 °C for 16 h. After precipitates were removed by filtration, the solvent was removed by a rotary evaporator. The obtained product was dissolved in a small amount of THF,
and then the product was reprecipitated from methanol. The precipitate collected by filtration was dried in vacuum to give pure **M1** as a yellow crystal (4.60 g, 67%). $^1$H NMR (CDCl$_3$): $\delta$ = 7.6 (2H, d, $J$ = 8.28 Hz), 7.5 (2H, d, $J$ = 8.28 Hz), 7.3–7.3 (3H, m), 7.3–7.2 (2H, m), 7.1–7.0 (6H, m), 6.9 (2H, d, $J$ = 6.21 Hz), 5.6 (1H, s), 2.4 (3H, s). $^{13}$C NMR (CDCl$_3$): $\delta$ = 164.52, 163.35, 141.45, 138.40, 137.53, 137.45, 137.02, 130.54, 129.79, 129.60, 128.96, 128.36, 127.83, 126.45, 125.67, 125.48, 99.63, 96.21, 91.48, 43.90 ppm. $^{11}$B NMR (CDCl$_3$): $\delta$ = 1.42 (t, $J$ = 31.30 Hz) ppm. HRMS (ESI): Calcd for [M+H]$^+$, 720.9649; found, m/z 720.9633. Anal. Calcd for C$_{28}$H$_{21}$BF$_2$I$_2$N$_2$: C, 46.70; H, 2.94; N, 3.89. Found: C, 46.51; H, 3.19; N, 3.66.

**Synthesis of M2 and M3.** $m$-Chloroperoxybenzoic acid (0.34 g, 1.4 mmol) was added to the solution of M1 (0.50 g, 0.69 mmol) in CHCl$_3$ (15 mL) at 0 °C. Then, the reaction mixture was stirred at room temperature for 20 min. The solution was washed with water. The organic layer was dried over anhydrous magnesium sulfate. After the solvent was removed by a rotary evaporator, the product was purified by silica gel column chromatography (eluted with hexane/ethyl acetate = 2/1). After M3 was ejected, the solvent component was changed (hexane/ethyl acetate = 1/2). The pure M2 and M3 were obtained as a yellow crystal (M2: 0.14 g, 27%, M3: 0.05 g, 10%).

**M2** $^1$H NMR (CDCl$_3$): $\delta$ = 7.6 (2H, d, $J$ = 8.04 Hz), 7.5–7.5 (4H, m), 7.3–7.3 (7H, m), 7.0 (2H, d, $J$ = 8.04 Hz), 6.9 (2H, d, $J$ = 8.04 Hz), 5.6 (1H, s), 2.6 (3H, s) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ = 165.19, 163.34, 144.02, 143.65, 143.31, 141.11, 140.75, 137.71, 137.56, 130.51, 130.09, 129.43, 128.96, 128.60, 128.49, 123.94, 100.18, 96.73, 91.80, 43.95 ppm. $^{11}$B NMR (CDCl$_3$): $\delta$ = 1.47 (t, $J$ = 31.36 Hz) ppm. HRMS (ESI): Calcd for [M+H]$^+$, 736.9598; found, m/z 736.9584. Anal. Calcd for C$_{28}$H$_{21}$BF$_2$I$_2$N$_2$OS: C, 45.68; H, 2.88; N, 3.81. Found: C, 45.72; H, 2.99; N, 3.72.

**M3** $^1$H NMR (CDCl$_3$): $\delta$ = 7.8 (2H, d, $J$ = 8.28 Hz), 7.6 (2H, d, $J$ = 8.28 Hz), 7.5 (2H, d, $J$ = 8.53 Hz), 7.3 (3H, d, $J$ = 8.04 Hz), 7.3–7.3 (4H, m), 7.0 (2H, d, $J$ = 8.04 Hz), 6.9 (2H, d, $J$ = 8.28 Hz), 5.7 (1H, s), 3.0 (3H, s) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ = 165.63, 163.13, 146.56, 140.95, 138.03, 137.93, 137.64, 135.33, 134.79, 130.50, 130.26, 129.36, 128.96, 128.56, 128.48, 128.00, 97.13, 92.03, 44.60 ppm. $^{11}$B NMR
(CDCl₃): δ = 1.47 (t, J = 31.36 Hz) ppm. HRMS (ESI): Calcd for [M+H]⁺, 786.9157; found, m/z 786.9182. Anal. Calcd for C₂₈H₂₁BF₂₁N₂O₂S: C, 44.71; H, 2.81; N, 3.72. Found: C, 44.70; H, 2.91; N, 3.66.

Synthesis of 4. Compound 4 was synthesized in 48% yield (6.56 g, yellow crystal) according to the same method with 1. ¹H NMR (CDCl₃): δ = 8.0 (2H, d, J = 8.04 Hz), 7.5–7.4 (3H, m), 7.3 (2H, t, J = 8.53 Hz), 6.8 (2H, d, J = 8.53 Hz), 2.5 (3H, s), 2.2 (3H, s). HRMS (ESI): Calcd for [M+H]⁺, 242.0998; found, m/z 242.0994.

Synthesis of 5. Compound 5 was synthesized according to our previous report.[2]

Synthesis of 6. Compound 6 was synthesized in 43% yield (7.20 g, yellow crystal) according to the same method with 3. ¹H NMR (CDCl₃): δ = 13.0 (1H, s), 7.3–7.3 (10H, m), 7.1 (2H, t, J = 7.80 Hz), 7.0 (2H, d, J = 8.28 Hz), 6.9 (1H, t, J = 7.43 Hz), 6.7 (2H, d, J = 7.55 Hz), 6.7 (2H, d, J = 8.28 Hz), 5.4 (1H, s), 2.4 (3H, s). HRMS (ESI): Calcd for [M+H]⁺, 421.1733; found, m/z 421.1720.

Synthesis of M-SMe. M-SMe was synthesized in 39 % (0.87 g, yellow crystal) according to the same method with M₁. ¹H NMR (CDCl₃): δ = 7.3–7.3 (5H, m), 7.2–7.0 (13H, m), 5.6 (1H, s), 2.4 (3H, s) ppm. ¹³C NMR (CDCl₃): δ = 164.45, 164.22, 141.66, 138.98, 136.31, 129.47, 129.42, 129.29, 129.04, 128.27, 128.22, 128.09, 128.05, 127.77, 126.42, 126.31, 99.58, 99.57, 67.97, 15.89 ppm. ¹¹B NMR (CDCl₃): δ = 1.66 (t, J = 27.52 Hz) ppm. HRMS (ESI): Calcd for [M+H]⁺, 469.1716; found, m/z 469.1710. Anal. Calcd for C₂₈H₂₃BF₂₁N₂: C, 71.80; H, 4.95; N, 5.98. Found: C, 71.78; H, 5.04; N, 5.89.

Synthesis of M-SOMe and M-SO₂Me. m-Chloroperoxybenzoic acid (0.53 g, 2.1 mmol) was added to the solution of M-SOMe (0.50 g, 1.1 mmol) in CHCl₃ (10 mL) at 0 °C. Then, the reaction mixture was stirred at room temperature for 20 min. The solution was washed with water. The organic layer was
dried over anhydrous magnesium sulfate. After the solvent was removed by a rotary evaporator, the product was purified by silica gel column chromatography (eluted with hexane/ethyl acetate = 2/1). After M-SO₂Me was ejected, the solvent component was changed (hexane/ethyl acetate = 1/2). The pure M-SO₂Me and M-SOMe were obtained as a yellow crystal (M-SO₂Me: 0.12 g, 23%, M-SOMe: 0.016 g, 30%).

M-SOMe ¹H NMR (CDCl₃): δ = 7.5 (2H, d, J = 8.04 Hz), 7.3–7.3 (9H, m), 7.2–7.2 (2H, m), 7.2 (4H, d, J = 4.39 Hz), 7.2–7.1 (2H, m), 5.7 (1H, s), 2.6 (3H, s) ppm. ¹³C NMR (CDCl₃): δ = 165.81, 164.76, 145.17, 143.78, 142.02, 136.70, 136.48, 130.46, 130.25, 129.65, 129.63, 129.40, 128.98, 128.97, 128.77, 128.29, 127.17, 124.25, 100.65, 44.70 ppm. ¹¹B NMR (CDCl₃): δ = 1.66 (t, J = 31.36 Hz) ppm. HRMS (ESI): Calcd for [M+H]⁺, 485.1665; found, m/z 485.1657.

M-SO₂Me ¹H NMR (CDCl₃): δ = 7.7 (2H, d, J = 6.84 Hz), 7.4 (2H, d, J = 8.31 Hz), 7.3–7.3 (9H, m), 7.2–7.2 (6H, m), 5.7 (1H, s), 3.0 (3H, s) ppm. ¹³C NMR (CDCl₃): δ = 165.64, 163.85, 147.04, 141.18, 137.57, 135.86, 135.51, 130.10, 129.75, 129.01, 128.95, 128.57, 128.53, 128.38, 128.17, 127.64, 127.55, 126.67, 100.50, 44.65 ppm. ¹¹B NMR (CDCl₃): δ = 1.66 (t, J = 27.52 Hz) ppm. HRMS (ESI): Calcd for [M+H]⁺, 501.1614; found, m/z 501.1610. Anal. Calcd for C₂₈H₂₃BF₂N₂O₂S: C, 67.21; H, 4.63; N, 5.60. Found: C, 67.45; H, 4.88; N, 5.35.

**Synthesis of PSMe, PSOMe and PSO₂Me.** Water (1.6 mL) was added to the solution of the boron diiminate monomer (0.16 mmol), [9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl]bisboronic acid (77 mg, 0.16 mmol), Pd₂(dba)₃ (1.4 mg, 1.6 µmol), S-Phos (2.6 mg, 6.4 µmol) and cesium carbonate (0.52 g, 1.6 mmol) in toluene (1.6 mL). The reaction mixture was stirred at 80 °C for 24 h under argon atmosphere. After cooling to room temperature, the reaction mixture was poured into a large amount of methanol to collect the polymer as a precipitate. After the filtration, the product was washed with ethanol and water. The precipitate was dissolved in a small amount of THF, and then the product was reprecipitated from methanol. The polymer collected by filtration was dried in vacuum to give PSMe, PSOMe, PSO₂Me as yellow solids (PSMe: 83%, PSOMe: 83%, PSO₂Me: 92%).
The condition of oxidation of PSMe. The film samples of PSMe were soaked into the H$_2$O$_2$ solution at room temperature (H$_2$O$_2$: 30 mL (30 wt%), Na$_2$WO$_4$·2H$_2$O: 5.0 × 10$^{-3}$ M, AcOH: 1.0 × 10$^{-3}$ M).
Figure S1. a) $^1$H, b) $^{13}$C and c) $^{11}$B NMR spectra of PSMe in CDCl$_3$. 
Figure S2. a) $^1$H, b) $^{13}$C and c) $^{11}$B NMR spectra of PSOMe in CDCl$_3$. 
Figure S3. a) $^1H$, b) $^{13}C$ and c) $^{11}B$ NMR spectra of $\text{PSO}_2\text{Me}$ in CDCl$_3$. 
Figure S4. FT-IR spectra of (a) PSMe, (b) PSOMe and (c) PSO$_2$Me (film on KBr).
Figure S5. a) UV–vis spectra and b) PL spectra of the polymers in THF (1.0 × 10⁻⁵ M, solid line: PSMe, dashed lines: PSOMe, dashed lines: PSO₂Me).
Figure S6. Structures and molecular orbital diagrams for the LUMO and HOMO of the model compounds (B3LYP/6-31G (d)//B3LYP/6-31G (d)).[2]
Figure S7. UV–vis spectra of the synthesized polymers in THF (1.0 × 10^{-5} M) with the oscillator strengths obtained by TD-DFT calculations of the model compounds at the M06-2X/6-31G+(d) level.
Figure S8. UV−vis absorption spectra from the films of PSMe during the incubation in 30 wt% H₂O₂ solution at room temperature for variable time periods.
Figure S9. FT-IR spectra the films of PSMe during the incubation in 30 wt% H$_2$O$_2$ solution at room temperature for variable time periods (film on KBr).
Figure S10. Spectra changes with the films of PSMe before and after 24 h incubation in (a) 15 wt% and (b) 3 wt% H₂O₂ solution at room temperature.
References