

## Electronic Supplementary Information

### Enhanced fluorescence sensing of hydroxylated organotins by a boronic acid-linked Schiff base

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#### 1. Reagents and Syntheses

All the organotin compounds (OTC) and 2,4-dihydroxybenzaldehyde were purchased from Sigma-Aldrich Co., Ltd. 2-aminobenzeneboronic acid was purchased from Tokyo Chemical Industry (TCI) Co., Ltd. They were used without any further purification. All other reagents were of analytical grade or better and used without further purification.

**(2,4-dihydroxybenzylidene) aniline (1)** A mixture of aniline (186 mg, 2 mmol) and 2,4-dihydroxybenzaldehyde (276 mg, 2 mmol) in ethanol (8 mL) was stirred at 80 °C for 2 h. The solvent of the resulting mixture was removed completely under vacuum. The residue was purified by column chromatography (silica gel, eluent: CH<sub>2</sub>Cl<sub>2</sub>) to give **1** as an orange solid. Yield: 332 mg, 78%.

**2-(2',4'-dihydroxybenzylidene)aminobenzeneboronic acid (2)** 2-Aminobenzeneboronic acid (137 mg, 1 mmol) was added to a solution of 2,4-dihydroxybenzaldehyde (276 mg, 2 mmol) in acetonitrile (6 mL). The mixture was stirred and refluxed for 6 h in nitrogen atmosphere to give a yellow solid. The produced solid was collected by filtration, washed with ethanol (10 × 5 mL), and dried under vacuum. Yield: 149 mg, 58%.

#### 2. Characterization of 1

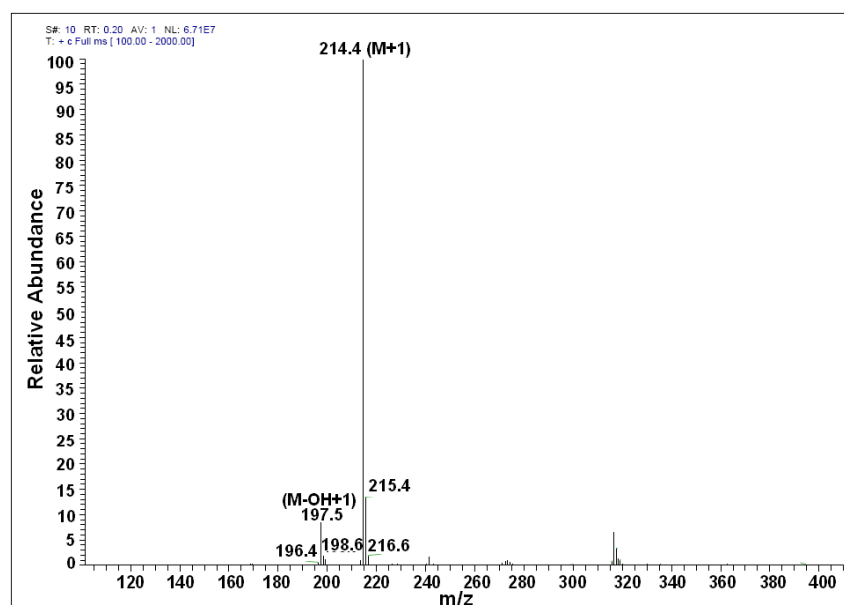
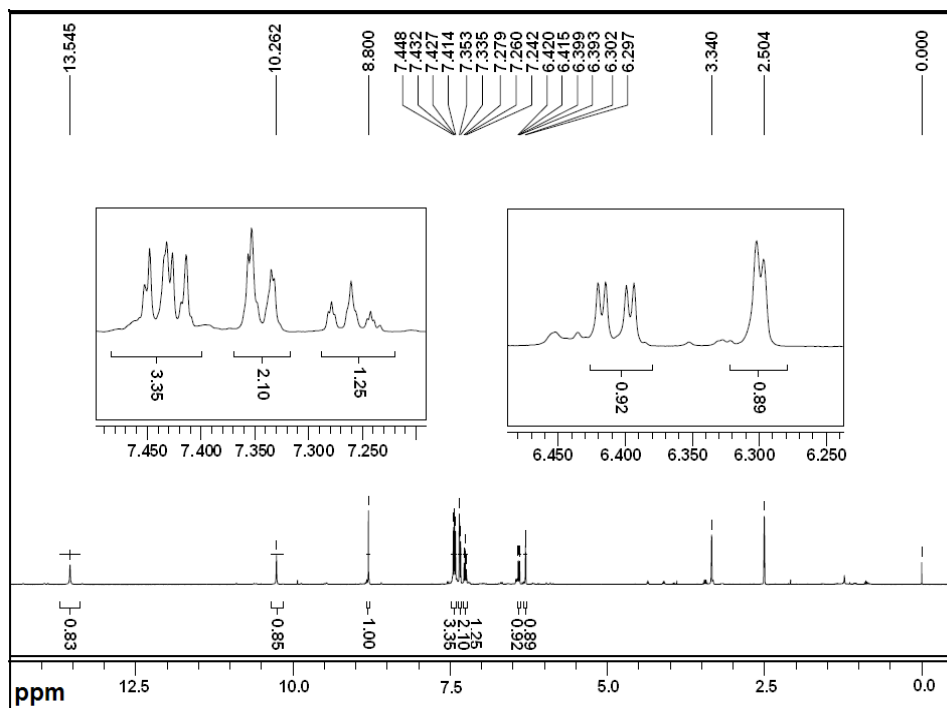
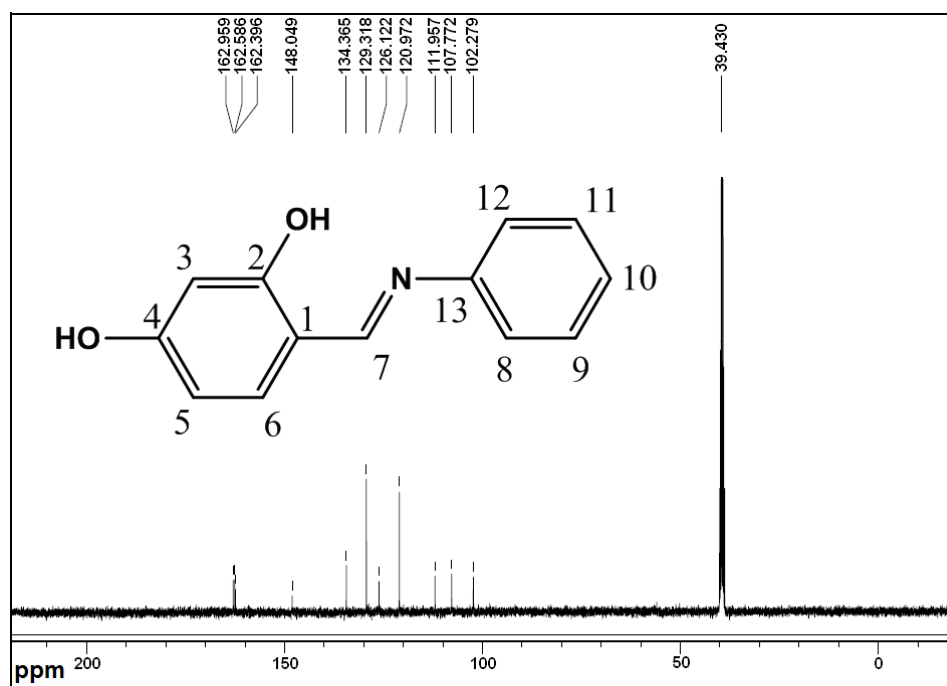


Figure S1(a). ESI-MS spectrum of 1.



**Figure S1(b).**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO-d}_6$ , ppm) of **1**.  $\delta = 13.54$  (s, 1H, -OH, C-2), 10.26 (s, 1H, -OH, C-4), 8.80 (s, 1H, N=CH, C-7), 7.47-7.41 (m, 3H, Ph-H, C-9,11,6), 7.34 (d, 2H,  $J = 7.3$  Hz, Ph-H, C-8,12), 7.26 (t, 1H,  $J = 7.3$  Hz, Ph-H, C-10), 6.41 (dd, 1H,  $J_1 = 2.3$  Hz,  $J_2 = 8.5$  Hz, Ph-H, C-5), 6.30 (d, 1H,  $J = 2.3$  Hz, Ph-H, C-3), 2.50 (DMSO), 3.34 ( $\text{H}_2\text{O}$ ).



**Figure S1(c).**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{DMSO-d}_6$ , ppm) of **1**.  $\delta = 162.96$  (C-2), 162.59 (C-4), 162.40 (C-7), 148.05 (C-13), 134.36 (C-6), 129.32 (C-11,9), 126.12 (C-8,12), 120.97 (C-10), 111.96 (C-1), 107.77 (C-5), 102.28 (C-3).

### 3. Characterization of 2

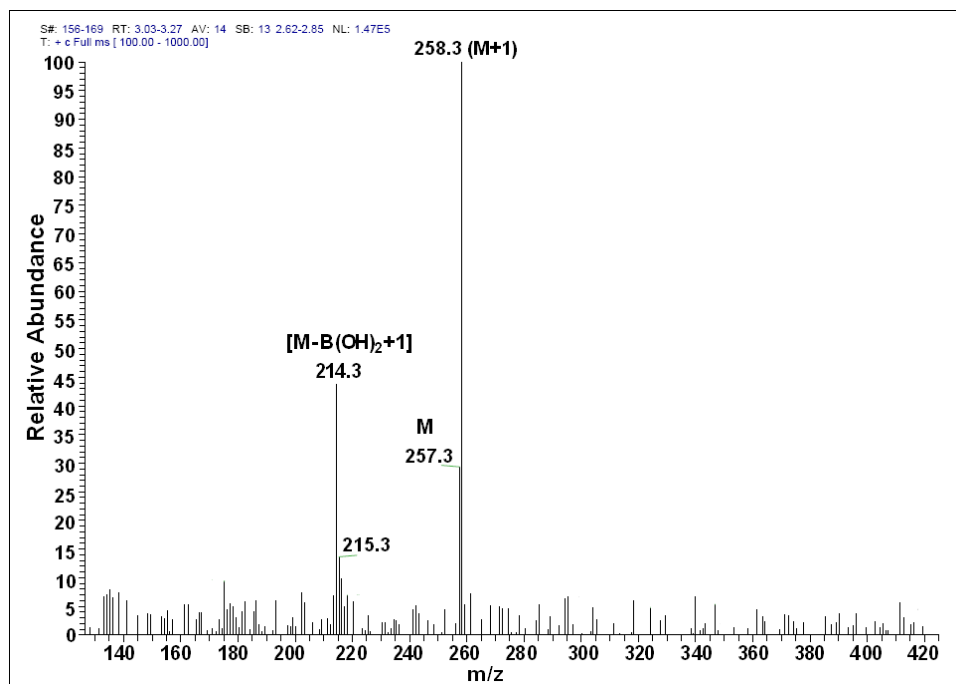


Figure S2(a). ESI-MS spectrum of 2.

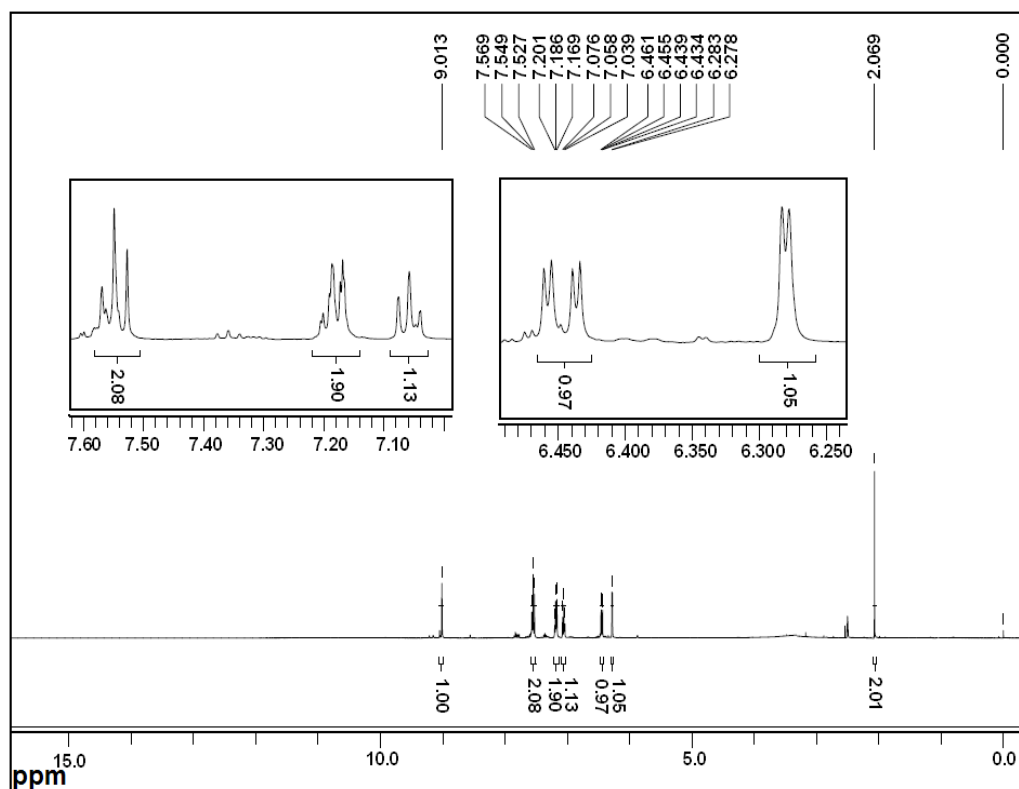
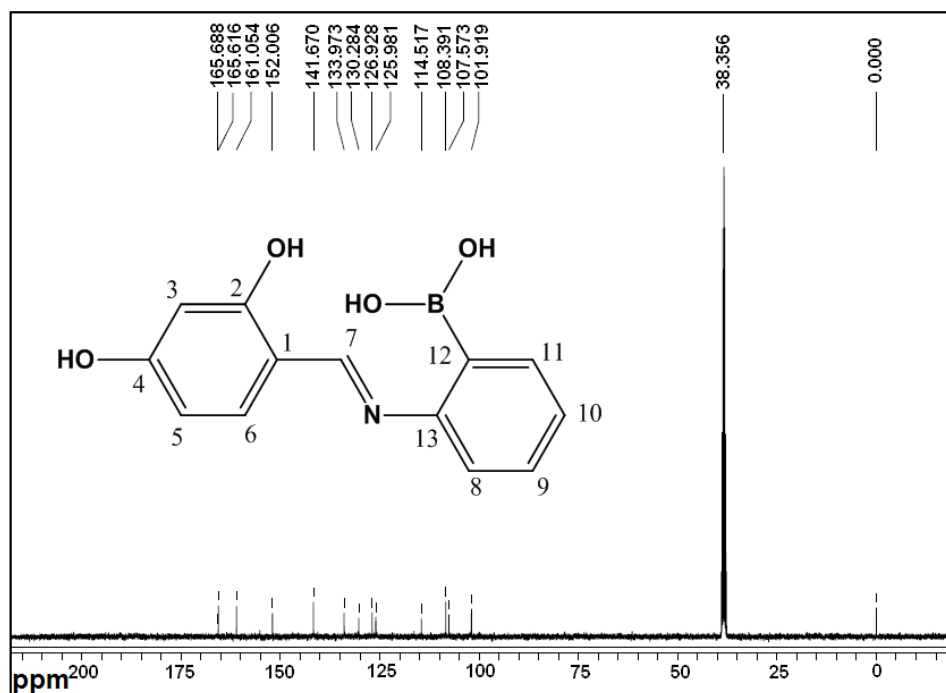
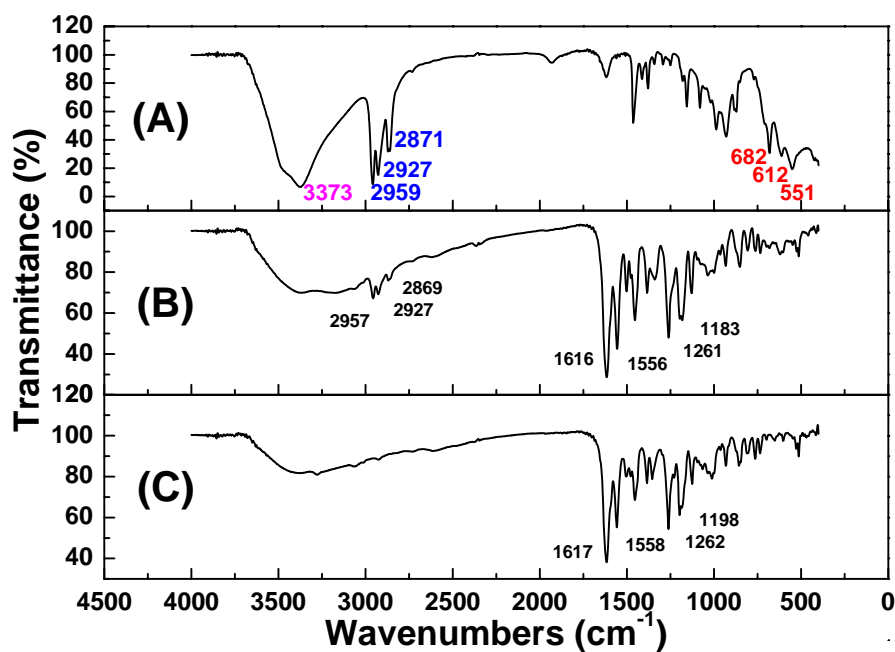


Figure S2(b). <sup>1</sup>H NMR spectrum (400 MHz, DMSO-d<sub>6</sub>, ppm) of 2.  $\delta$  = 9.01 (s, 1H, CH=N, C-7), 7.58-7.53 (m, 2H, Ph-H, C-6,11), 7.22-7.14 (m, 2H, Ph-H, C-8,9), 7.06 (dd, 1H,  $J_1$  = 7.0 Hz,  $J_2$  = 7.0 Hz, Ph-H, C-10), 6.45 (dd, 1H,  $J_1$  = 8.5 Hz,  $J_2$  = 2.2 Hz, Ph-H, C-5) 6.28 (d, 1H,  $J$  = 2.2 Hz, Ph-H, C-3), 2.07 (s, 2H, B-OH).



**Figure S2(c).**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{DMSO-d}_6$ , ppm) of **2**.  $\delta = 165.69$  (C-2), 165.62 (C-4), 161.05 (C-7), 152.01 (C-13), 141.67 (C-6), 133.97 (C-11), 130.28 (C-12), 126.93 (C-9), 125.98 (C-10), 114.52 (C-8), 108.39 (C-1), 107.57 (C-5), 101.92 (C-3).

#### 4. FT-IR absorption spectra of the related complexes



**Figure S3.** FT-IR absorption spectra of the related complexes in KBr. (A)  $\text{BuSn(OH)}_2\text{Cl}$ ; (B) **2** +  $\text{BuSn(OH)}_2\text{Cl}$  (1 equiv); (C) **2**.

## 5. MALDI-TOF-MS and <sup>1</sup>H NMR spectra of the HOT-sensing product

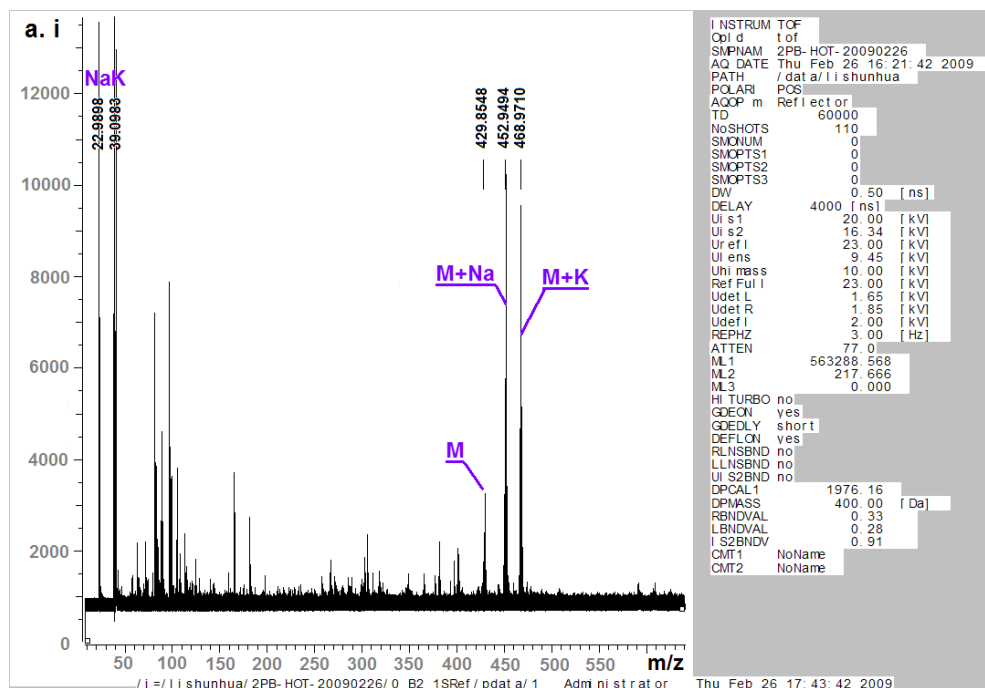


Figure S4(a). MALDI-TOF-MS spectrum of the 2-BuSn(OH)<sub>2</sub>Cl adduct formed in ethanol.

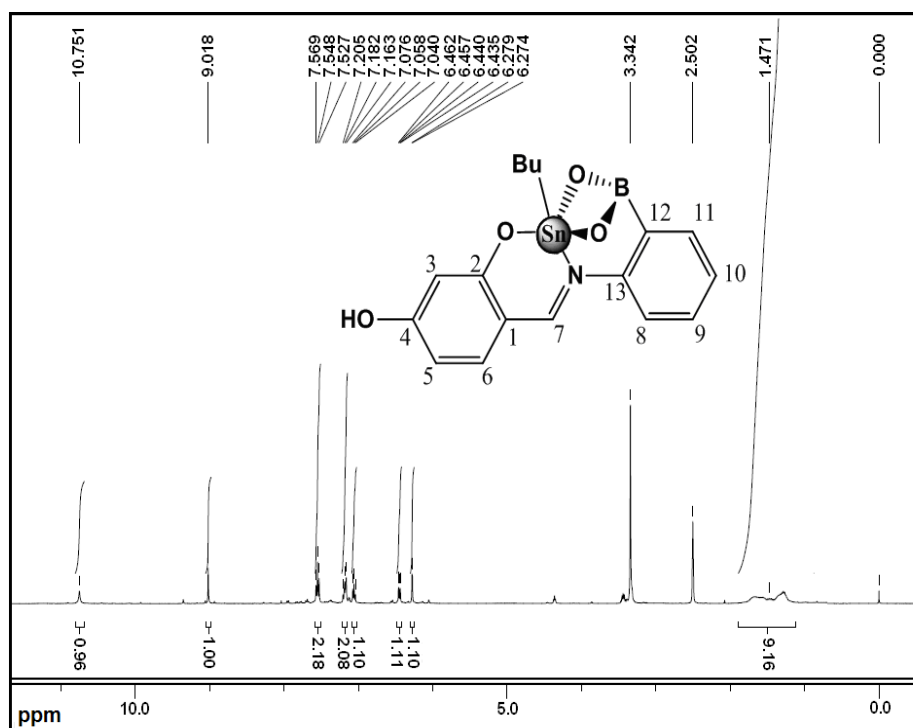
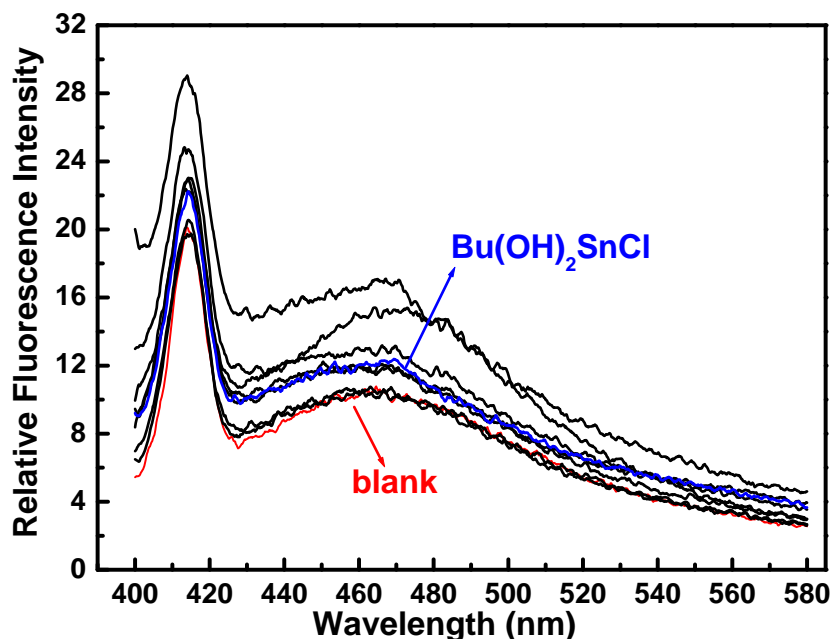


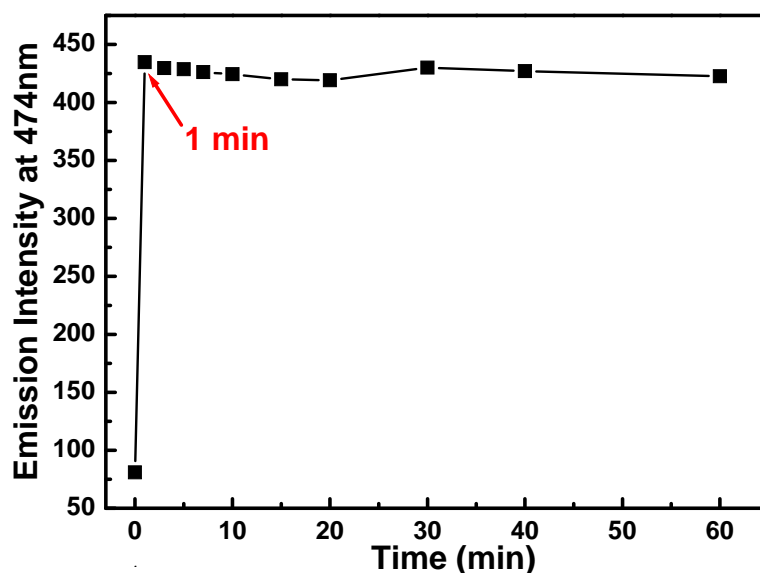
Figure S4(b). <sup>1</sup>H NMR spectrum (400 MHz, DMSO-d<sub>6</sub>, ppm) of the 2-BuSn(OH)<sub>2</sub>Cl adduct.  $\delta$  = 10.75 (s, 1H, Ph-OH, C-4), 9.02 (s, 1H, CH=N, C-7), 7.58-7.50 (m, 2H, Ph-H, C-6,11), 7.22-7.14 (m, 2H, Ph-H, C-8,9), 7.06 (dd, 1H,  $J_1 = 7.0$  Hz,  $J_2 = 7.0$  Hz, Ph-H, C-10), 6.45 (dd, 1H,  $J_1 = 8.5$  Hz,  $J_2 = 2.2$  Hz, Ph-H, C-5), 6.28 (d, 1H,  $J = 2.2$  Hz, Ph-H, C-3), 1.89-1.11 (m, 9H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.50 (DMSO), 3.34 (H<sub>2</sub>O).

## 6. Fluorescence responses of **1** to different metal species



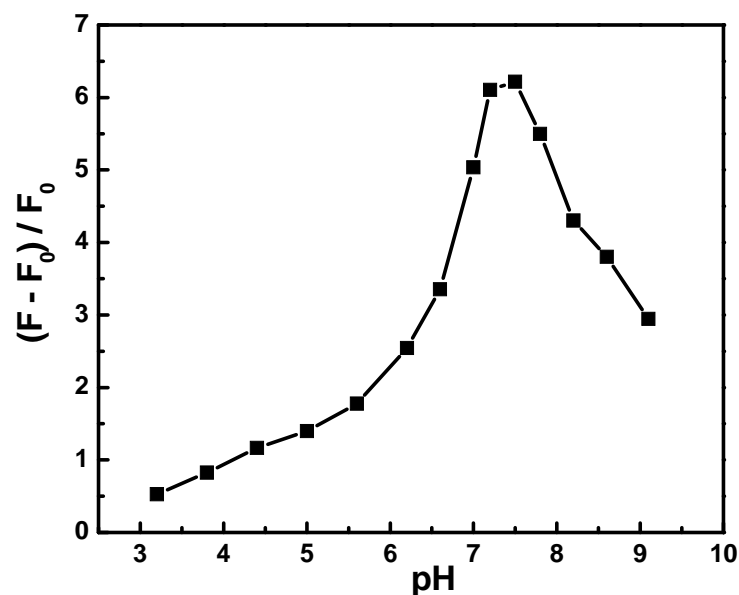
**Figure S5.** Emission spectra of **1** in the presence of different metal species in H<sub>2</sub>O/EtOH (90:10, v/v). **1**:  $1.0 \times 10^{-6}$  M; metal species including K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Al<sup>3+</sup>, Cd<sup>2+</sup>, Ag<sup>+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Hg<sup>2+</sup>, Cu<sup>2+</sup>, BuSn(OH)<sub>2</sub>Cl, Bu<sub>3</sub>SnCl, Bu<sub>2</sub>SnCl<sub>2</sub>, BuSnCl<sub>3</sub>, SnCl<sub>4</sub>, SnCl<sub>2</sub>, Me<sub>2</sub>SnCl<sub>2</sub> and Ph<sub>2</sub>SnCl<sub>2</sub>:  $5.0 \times 10^{-5}$  M; pH: 7.4, buffered by 0.01 M Tris-HCl; Excitation wavelength: 360 nm. The emission peaks at ca. 413 nm are attributed to raman scattering.

## 7. Effect of reaction time on fluorescent sensing of H<sub>2</sub>O<sub>2</sub>



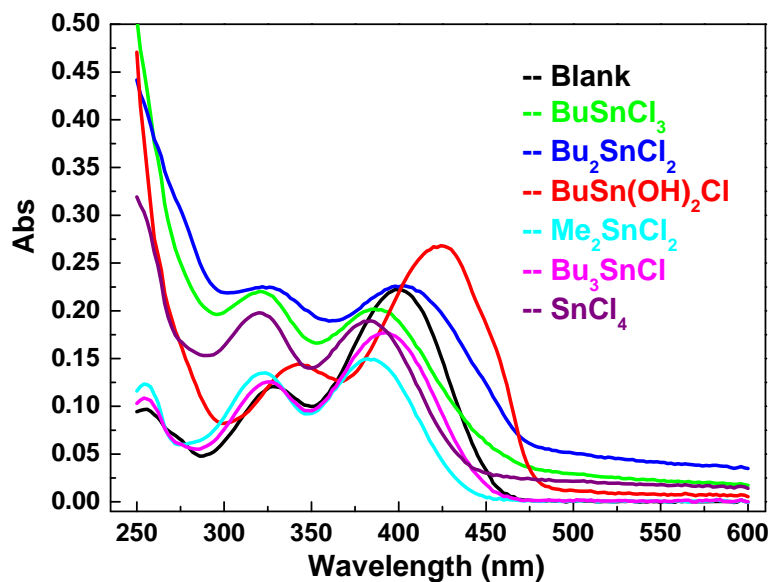
**Figure S6.** Effect of reaction time on fluorescence of **2** upon addition of 50 equiv of BuSn(OH)<sub>2</sub>Cl in H<sub>2</sub>O/EtOH (90:10, v/v). **2**:  $1.0 \times 10^{-6}$  M; pH: 7.4, buffered by 0.01 M Tris-HCl; Excitation wavelength: 403 nm.

## 8. Effect of pH on fluorescent sensing of HOT



**Figure S7.** Effect of pH on fluorescence of **2** upon addition of 50 equiv of  $\text{BuSn}(\text{OH})_2\text{Cl}$  in  $\text{H}_2\text{O}/\text{EtOH}$  (90:10, v/v). **2**:  $1.0 \times 10^{-6}$  M; pH buffer: 0.02 M 3,3-dimethylglutaric acid-NaOH (pH 3.2 - 7.0); 0.01 M Tris-HCl (pH 7.2 - 9.1); Excitation wavelength: 403 nm.

## 9. Absorption spectra of **2** upon addition of TOC species



**Figure S8.** Absorption spectra of **2** upon addition of TOC species in  $\text{H}_2\text{O}/\text{EtOH}$  (90:10, v/v). **2**:  $1.0 \times 10^{-5}$  M; metal species:  $1.0 \times 10^{-3}$  M; pH: 7.4, buffered by 0.01 M Tris-HCl.