Supporting Information

Development of a borondipyrromethene-based Zn\(^{2+}\) fluorescent probe: solvent effects on modulation sensing ability

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Experimental Section

General. All chemicals were purchased from commercial suppliers unless otherwise specified. Et$_3$N, chloroform and 1,2-dichloroethane were used as received without further purification. Anhydrous N,N-dimethylformamide (DMF) and toluene were dried and distilled immediately prior to use. 2-chloro-5-benzoyl-pyrrole$^1$, 2,4-dimethyl-3-ethylpyrrole$^2$ were prepared according to literature procedures.

$^1$H NMR and $^{13}$C NMR spectra were recorded on spectrometer operating at 400 MHz and 100 MHz, respectively. Deuterated chloroform was used as the solvent, TMS as internal standard. Mass spectra were measured on a HP 1100 LC-MS spectrometer. UV-vis spectra were measured using a shimadzu UV-2550 spectrophotometer. Fluorescence spectroscopic measurements were conducted on a Varian Cary eclipse fluorescence spectrophotometer.

For absorption or fluorescence measurements, compounds were dissolved in DMSO to obtain stock solutions (2-5 mM). These stock solutions were diluted with CH$_3$CN or aqueous solutions to the desired concentration.


Figure S1. a) Absorption and b) emission spectra of BODPAQ in aqueous solutions.
Figure S2. Absorption spectra of BODPAQ (5 µm) upon addition of Zn$^{2+}$ (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.6, 2.0 with respect to BODPAQ) in CH$_3$CN. Inset is the titration profile according to the absorbance at 560 nm.

Figure S3. Ratiometric calibration curve $F_{549\text{nm}}/F_{581\text{nm}}$ as a function of Zn$^{2+}$ concentration (BODPAQ 5 µm).
Figure S4. Absorption spectra of **BODPAQ** (5 µm) upon addition of Zn$^{2+}$ (a) 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 equiv with respect to **BODPAQ** in methanol; (b) 1.0, 1.2, 1.4, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 8.0, 14 equiv with respect to **BODPAQ** in methanol.
Figure S5. Emission spectra of BODPAQ (5 µm) upon addition of Zn$^{2+}$ (a) 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 equiv with respect to BODPAQ in methanol; (b) 1.0, 1.2, 1.4, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 8.0, 14 equiv with respect to BODPAQ in methanol.
Figure S6. The HRMS spectrum of BODPAQ$^+$ Zn$^{2+}$ complex.

Figure S7. Benesi-Hildebrand plot for BODPAQ-Zn$^{2+}$ system in CH$_3$CN.
Figure S8. Benesi-Hildebrand plot for BODPAQ-Zn$^{2+}$ system in MOPS buffer.
Figure S9. (a) Absorption spectra of BODPAQ (5 μM) upon addition of Zn$^{2+}$ (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.6, 3.0 equiv with respect to BODPAQ in Methanol/MOPS buffer(50:50); (b) Emission spectra of BODPAQ (5 μm) upon addition of Zn$^{2+}$ (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.6, 3.0 equiv with respect to BODPAQ in Methanol/MOPS buffer(50:50).
$^1$H MNR and $^{13}$C NMR