Electronic Supplementary Information

A boronate hydrogel film containing organized two-component dyes as a multicolor fluorescent sensor for heavy metal ions in water

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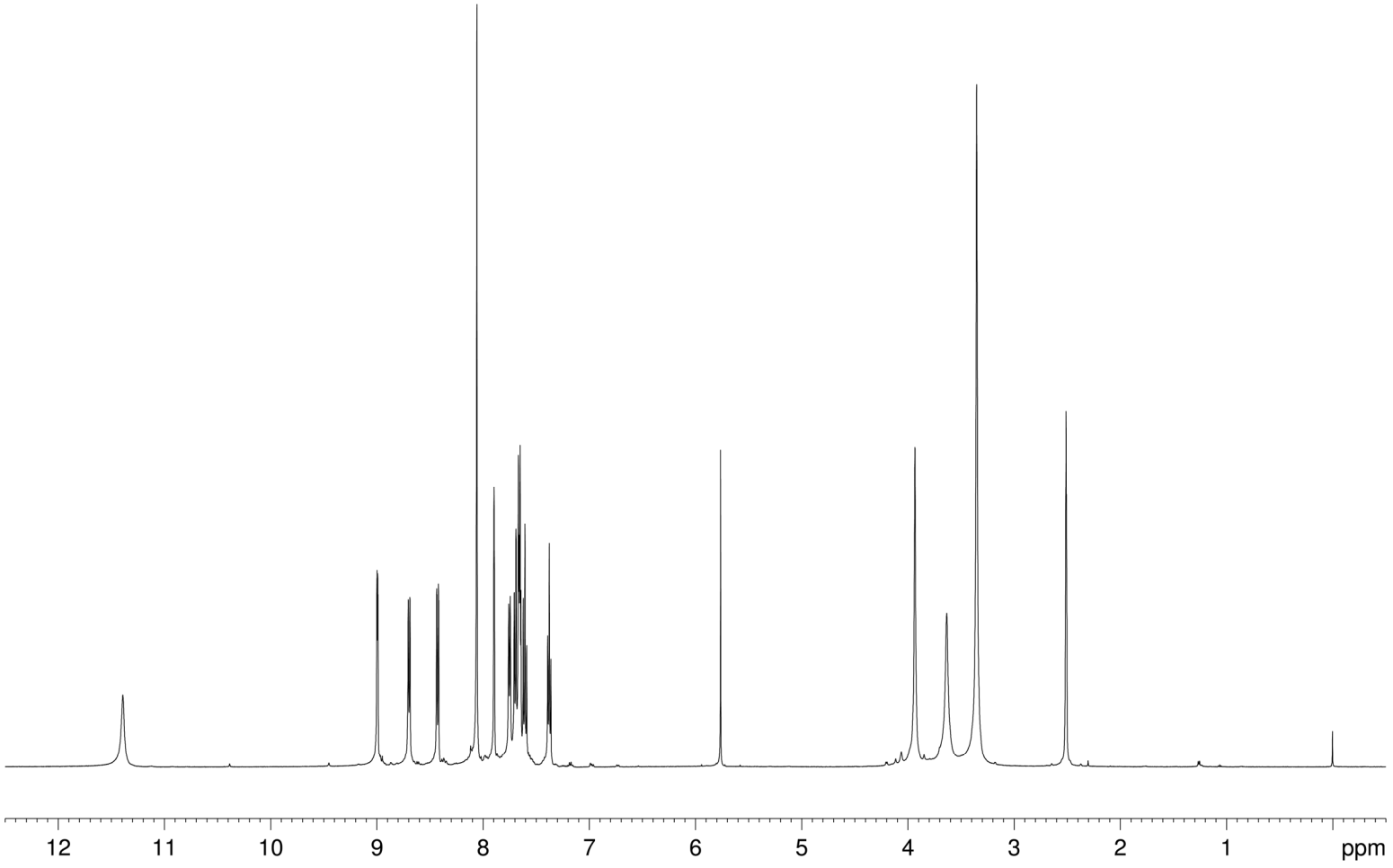

Fig. S1 ^{1}H NMR spectrum of **1** in DMSO-d_6 at 25 °C.

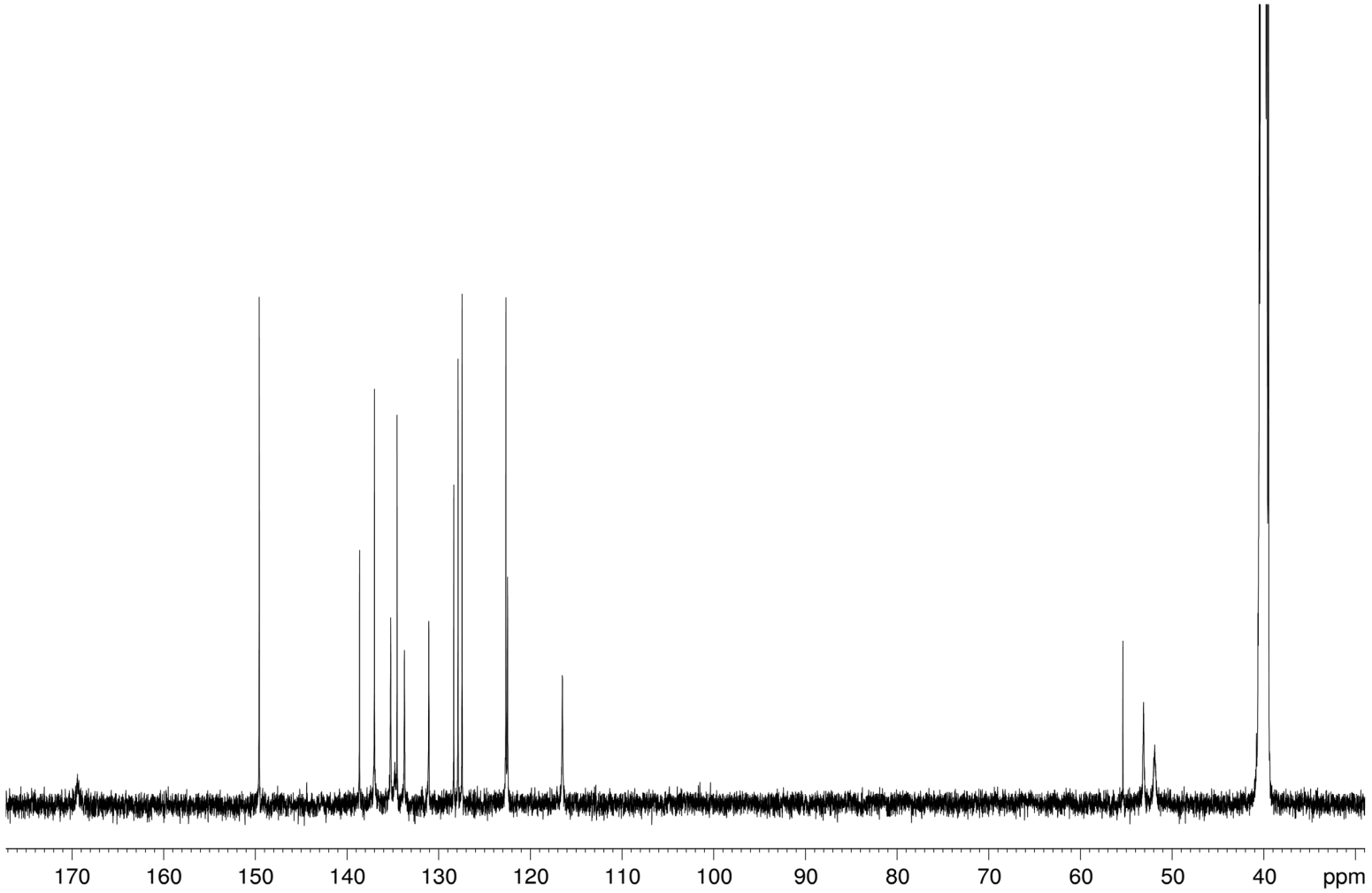

Fig. S2 ^{13}C NMR spectrum of **1** in DMSO-d_6 at 25 °C.

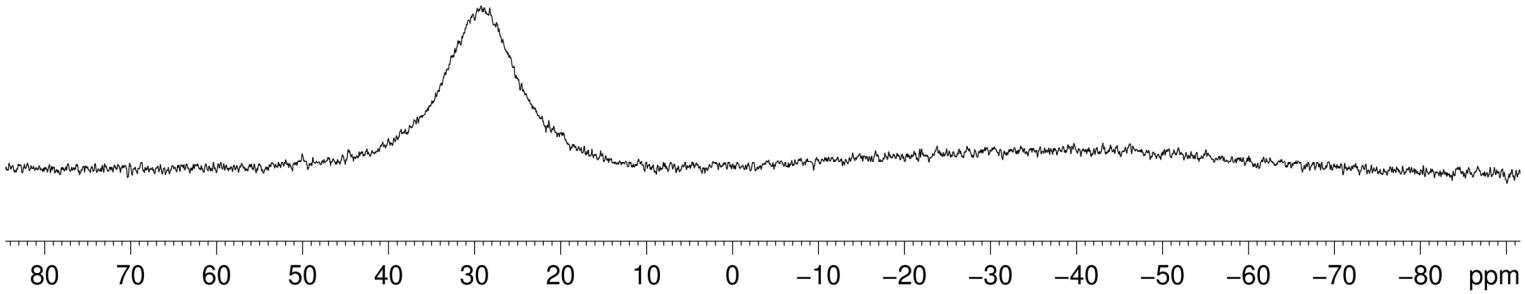

Fig. S3 ^{11}B NMR spectrum of **1** in DMSO-d_6 at 25 °C.

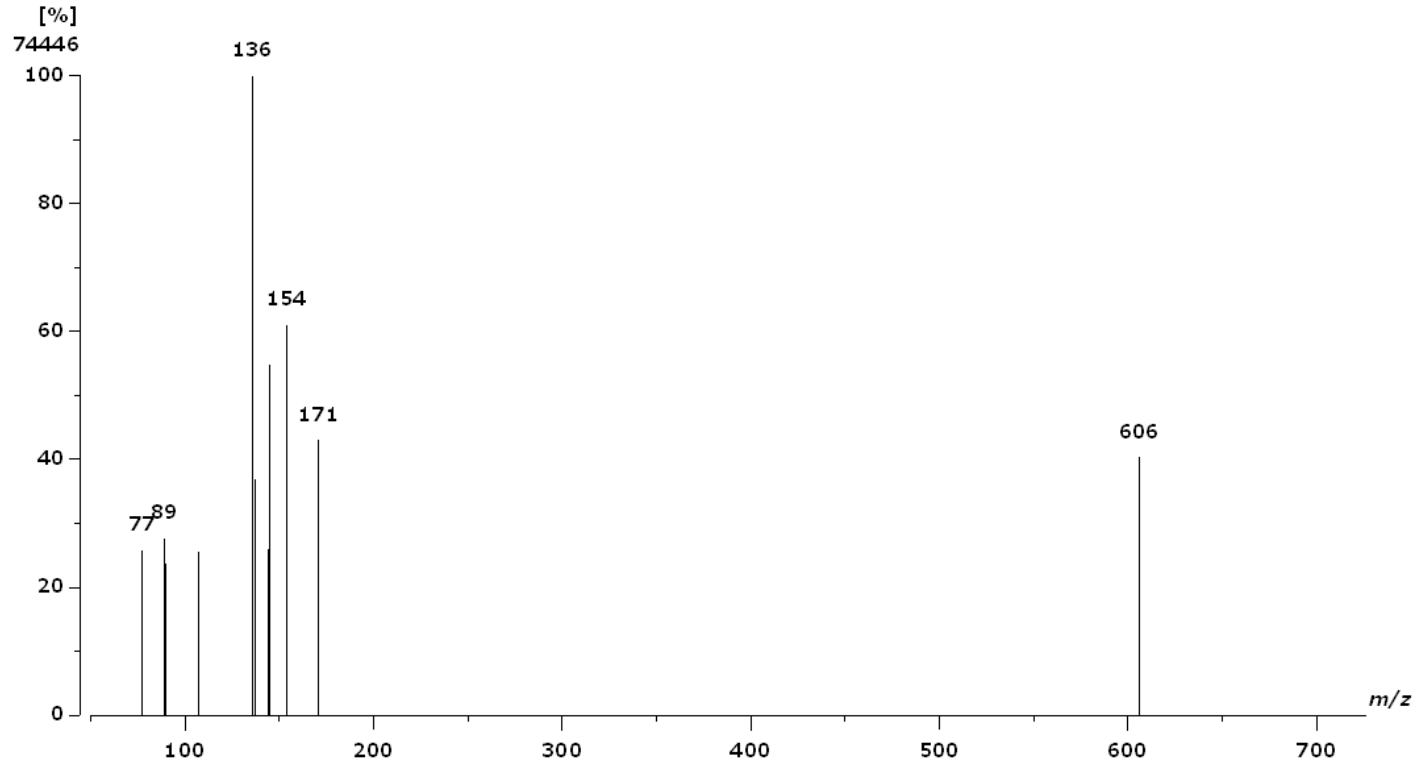

Fig. S4 FAB mass spectrum of **1**. 3-Nitrobenzyl alcohol was used as a matrix.

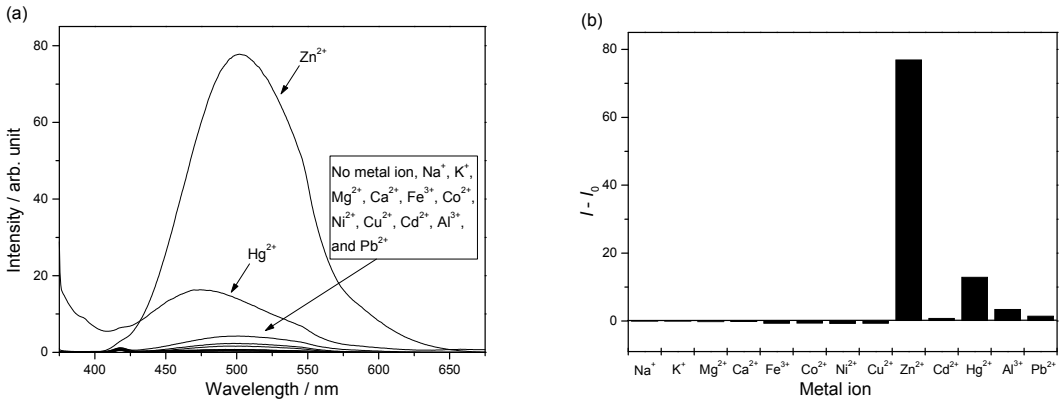

Fig. S5 (a) Fluorescence spectra of **1** in the absence and presence of different metal ions (Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+} and Pb^{2+}) in 5.0 mM HEPES buffer solution (2% DMSO, pH 7.0). (b) Changes in the fluorescence intensities. Conditions: [**1**] = [M^{n+}] = 5.0 × 10^{-5} M, 25 °C, λ_{ex} = 365 nm, λ_{em} = 502 nm.

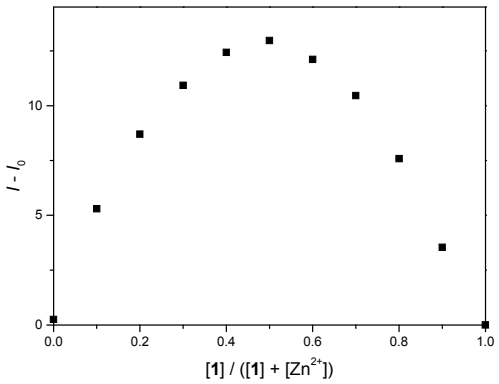

Fig. S6 Job's plot for complexation of **1** with Zn^{2+} ions in 5.0 mM HEPES buffer solution (2% DMSO, pH 7.0). Conditions: [**1**] + [Zn^{2+}] = 2.5 × 10^{-5} M, 25 °C, λ_{ex} = 325 nm, λ_{em} = 502 nm.

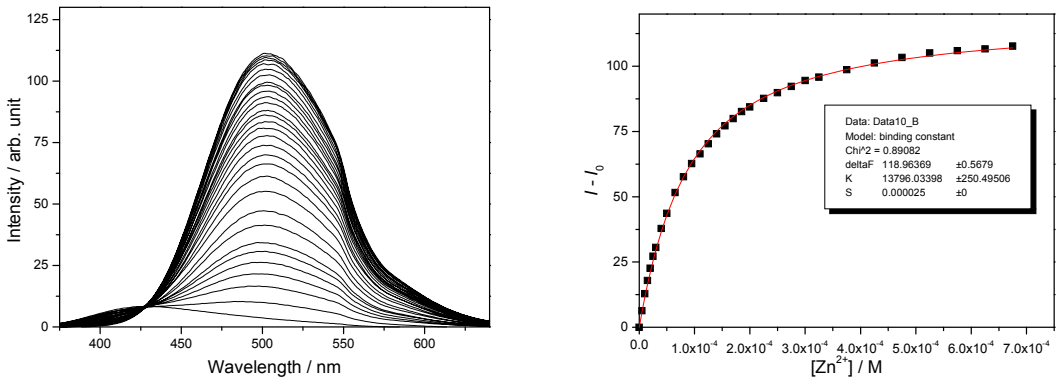

Fig. S7 Fluorescence spectra of **1** (2.5 × 10^{-5} M) in the presence of different concentrations of Zn^{2+} ions (0 – 27 equiv.) in 5.0 mM HEPES buffer solution (2% DMSO, pH 7.0). Conditions: 25 °C, λ_{ex} = 325 nm and λ_{em} = 502 nm.

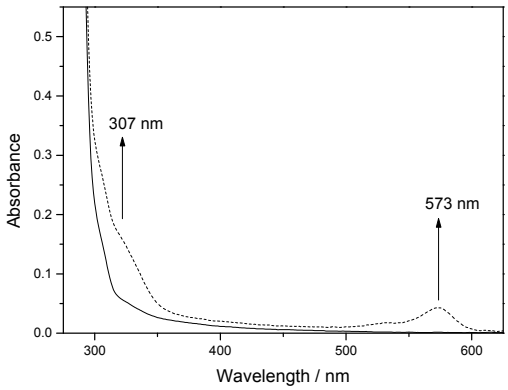

Fig. S8 UV-vis absorption spectra of the boronate hydrogel film functionalized with **1** and **2** (dashed line) and the reference boronate hydrogel film prepared in the absence of **1** and **2** (solid line). The amounts of immobilized **1** and **2** in the film were calculated to be 6.2×10^{-8} mol and 1.3×10^{-9} mol from the absorption intensities at 307 nm for **1** and 573 nm for **2**, respectively. Extinction coefficients of **1** ($\varepsilon = 5.5 \times 10^3$ M^{-1} cm^{-1} at 302 nm) and **2** ($\varepsilon = 1.1 \times 10^5$ M^{-1} cm^{-1} at 573 nm) in DMSO were employed for the calculations, respectively.

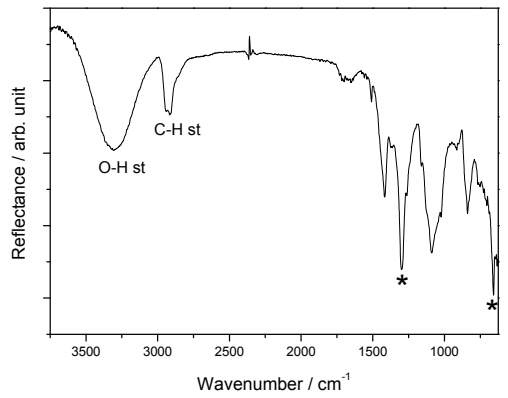

Fig. S9 FT-IR spectrum of the xerogel of the boronate hydrogel film. Characteristic intense peaks (*) at 658 cm^{-1} and 1299 cm^{-1} were assignable to the boronate esters.

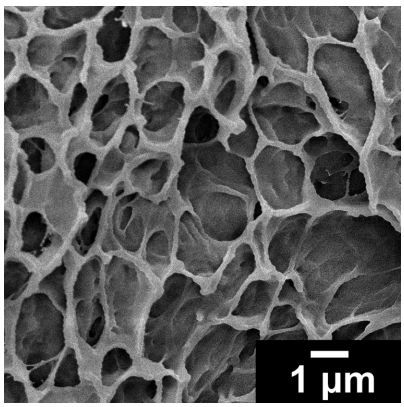

Fig. S10 FE-SEM image of the xerogel of the boronate hydrogel film.

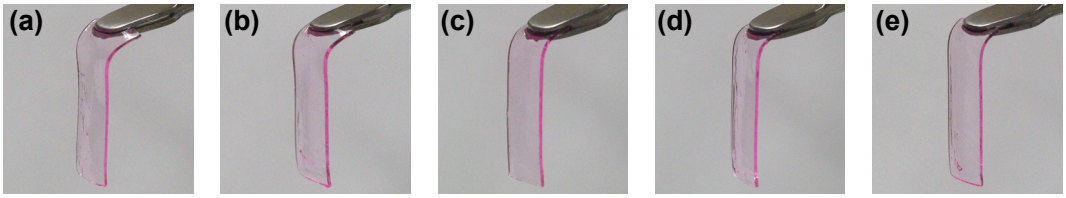

Fig. S11 Photographs of the boronate hydrogels immersed in aqueous solutions at different pH values for 12 h. Conditions: (a) pH 3, (b) pH 6, (c) pH 7, (d) pH 8, and (e) pH 11.

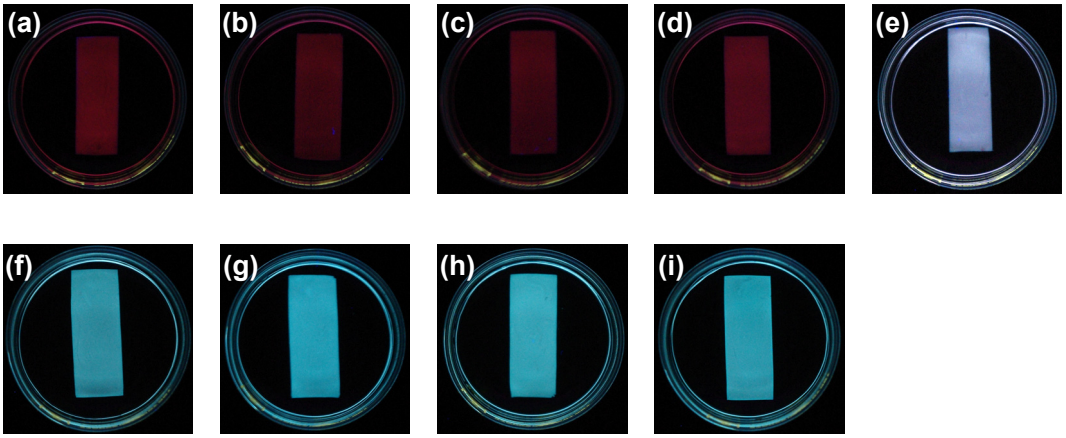

Fig. S12 Photograpsh of the boronate hydrogels in the presence of Zn^{2+} ions ($[Zn^{2+}] = 3.0 \times 10^{-5}$ M) at different pH values (5 mM HEPES, 3 mL). Conditions: (a) pH 3, (b) pH 4, (c) pH 5, (d) pH 6, (e) pH 7, (f) pH 8, (g) pH 9, (h) pH 10 and (i) pH 11. The boronate hydrogels were immersed in the solutions with shaking (125 rpm) at room temperature for 30 min. The photographs were taken under UV light: $\lambda_{ex} = 365$ nm.

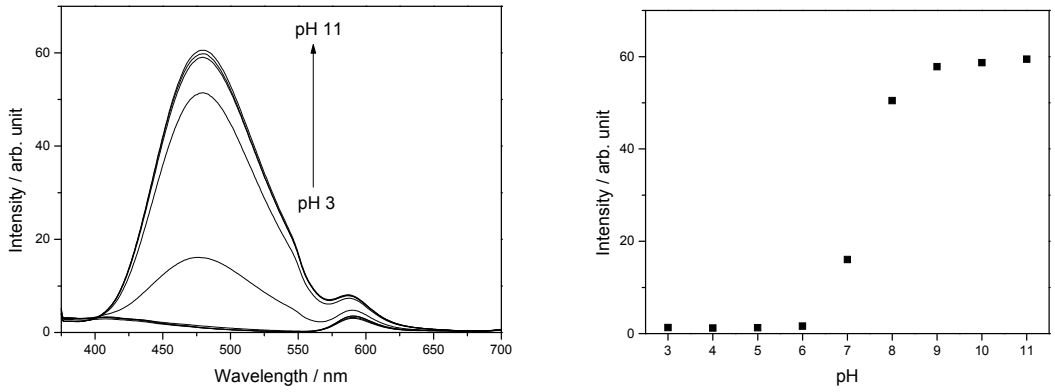

Fig. S13 Fluorescence spectra and intensities of the boronate hydrogels in the presence of Zn^{2+} ions ($[Zn^{2+}] = 3.0 \times 10^{-5}$ M) at different pH values (5 mM HEPES, 3 mL): $\lambda_{ex} = 365$ nm.

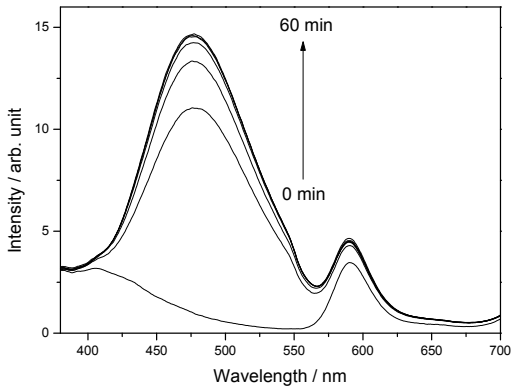

Fig. S14 Fluorescence spectra of the boronate hydrogel film in response to the addition of Zn^{2+} ions (3.0×10^{-5} M) as a function of time (t = 0, 10, 20, 30, 40, 50 and 60 min) in HEPES buffer solution (5.0 mM, pH = 7.0, 3 mL). Conditions: 25 °C, λ_{ex} = 365 nm. The gel film in the solution was shaken (125 rpm) at room temperature before the fluorescence measurements.

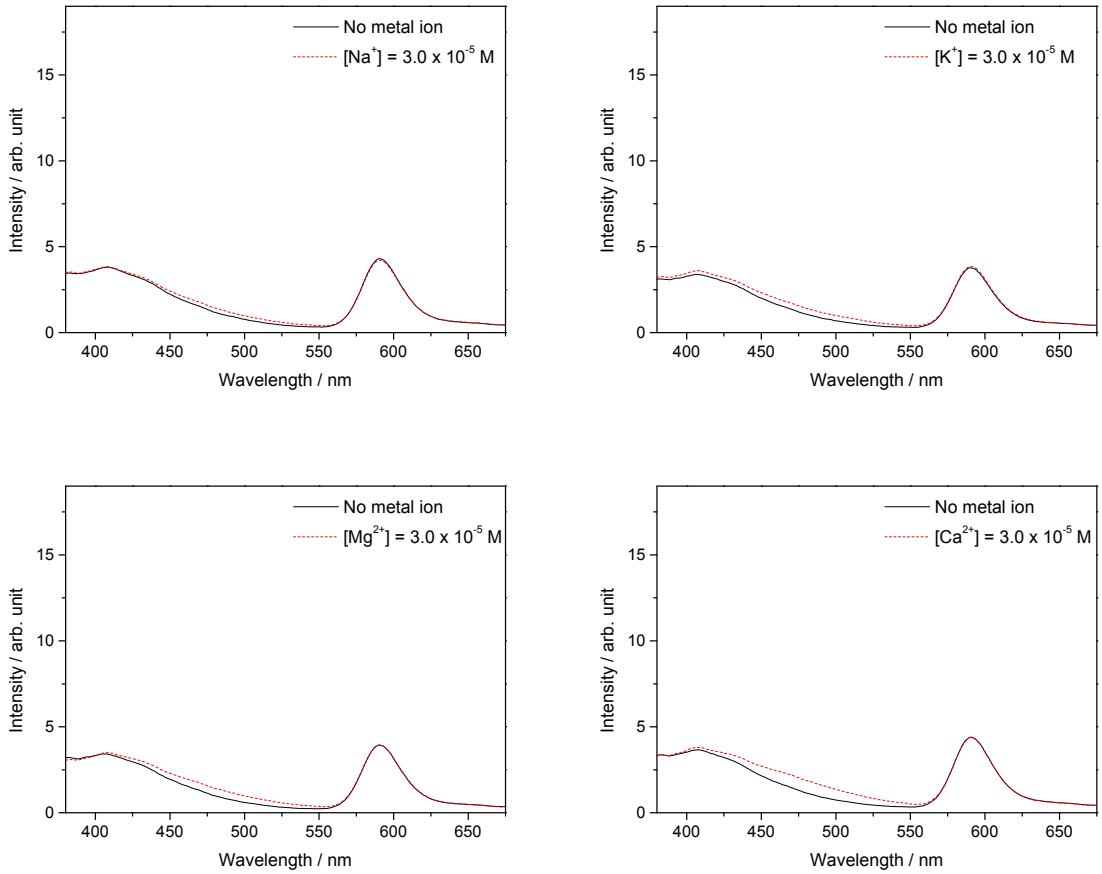

Fig. S15 Changes in the fluorescence spectra of the boronate hydrogel films upon adding Na^+, K^+, Mg^{2+} and Ca^{2+} ions in 5 mM HEPES buffer solution ($[M^{n+}] = 3.0 \times 10^{-5}$ M, 3 mL, pH = 7.0). The films were immersed in the solutions with shaking (125 rpm) at room temperature for 30 min before the fluorescence measurements (λ_{ex} = 365 nm).

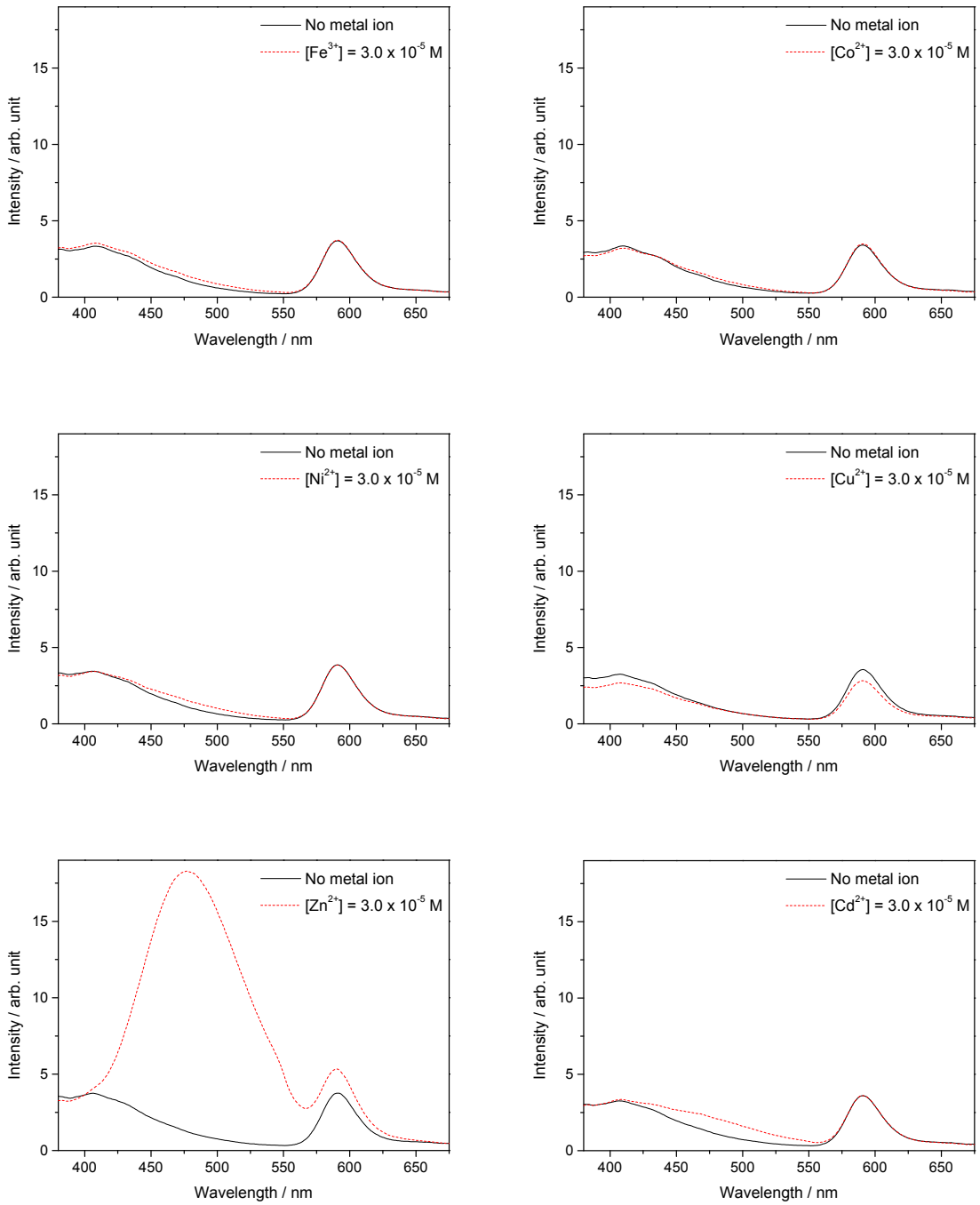

Fig. S16 Changes in the fluorescence spectra of boronate hydrogel films upon adding Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} Zn^{2+} and Cd^{2+} ions in 5 mM HEPES buffer solution ($[M^{n+}] = 3.0 \times 10^{-5}$ M, 3 mL, pH = 7.0). The films were immersed in the solutions with shaking (125 rpm) at room temperature for 30 min before the fluorescence measurements (λ_{ex} = 365 nm).

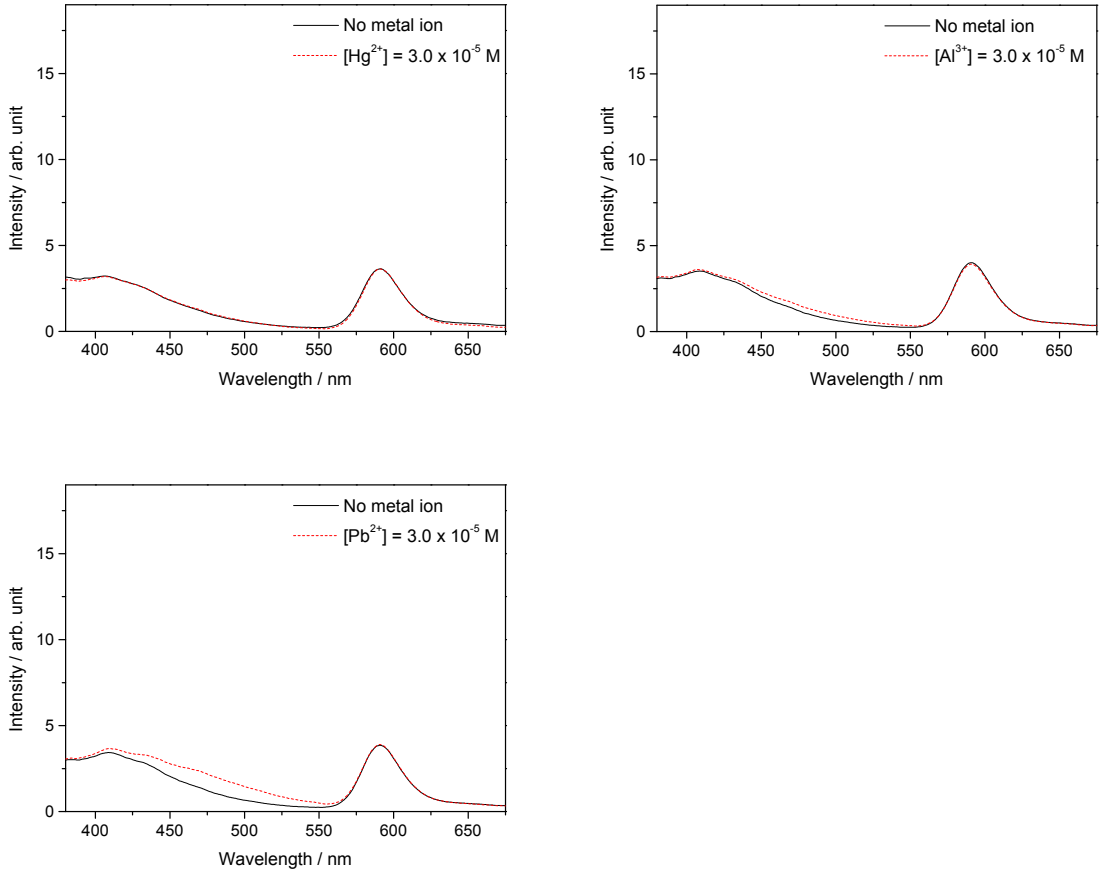

Fig. S17 Changes in the fluorescence spectra of the boronate hydrogel films upon adding Hg^{2+}, Al^{3+} and Pb^{2+} ions in 5 mM HEPES buffer solution ($[M^{n+}]$ = 3.0 × 10^{-5} M, 3 mL, pH = 7.0). The hydrogel films were immersed in the solutions with shaking (125 rpm) at room temperature for 30 min before the fluorescence measurements (λ_{ex} = 365 nm).

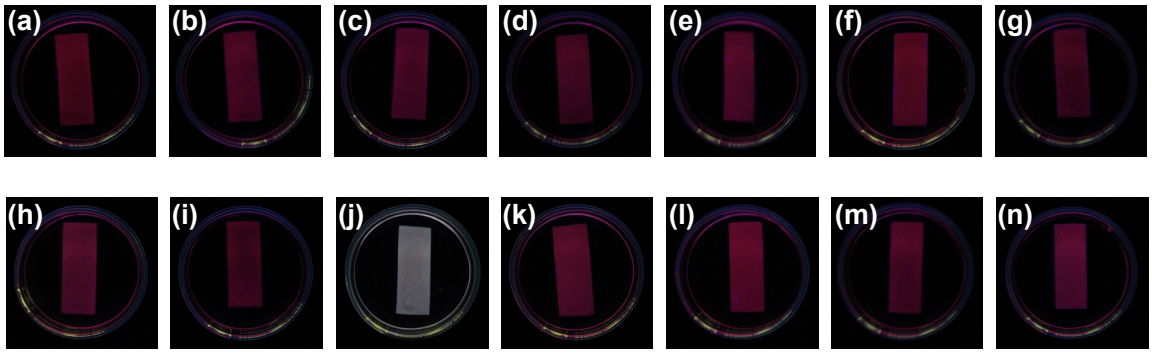

Fig. S18 Photographs of the boronate hydorgel films after immersion in HEPES buffer solutions (5 mM, pH = 7.0, 3.0 mL) of varied metal ions ($[M^{n+}]$ = 3.0 × 10^{-5} M). (a) No metal ion (b) Na^{+}, (c) K^{+}, (d) Mg^{2+}, (e) Ca^{2+}, (f) Fe^{3+}, (g) Co^{2+}, (h) Ni^{2+}, (i) Cu^{2+}, (j) Zn^{2+}, (k) Cd^{2+}, (l) Hg^{2+}, (m) Al^{3+} and (n) Pb^{2+} ions. The photographs were taken under the UV light (λ_{ex} = 365 nm).

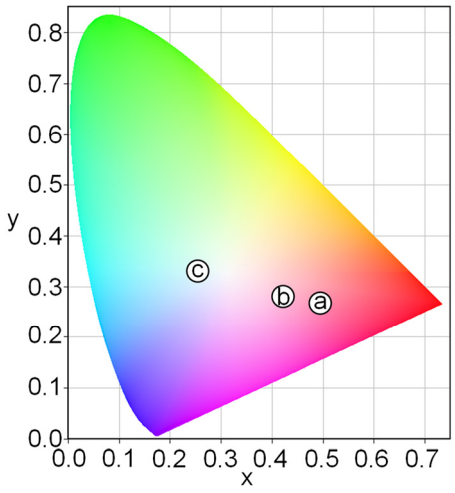

Fig. S19 CIE coordinate diagram of the emission colors of the films in (a) distilled water, (b) tap water and (c) spiked tap water with Zn^{2+} ions (3 ppm). The films were immersed in the solutions (3 mL) with shaking (125 rpm) at room temperature for 30 min.