Electronic Supplementary Information

Dansyl-containing boronate hydrogel films as fluorescent chemosensor of copper ions in water

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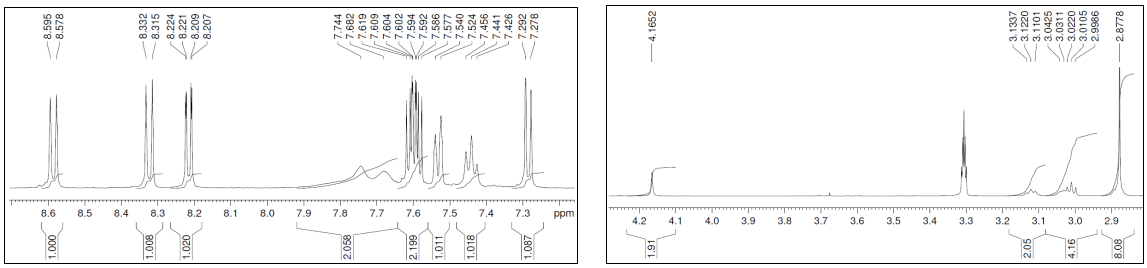
1. Characterization of 3-[({(*N*-dansylamino)ethylamino}ethylamino)methyl]phenylboronic acid (1)



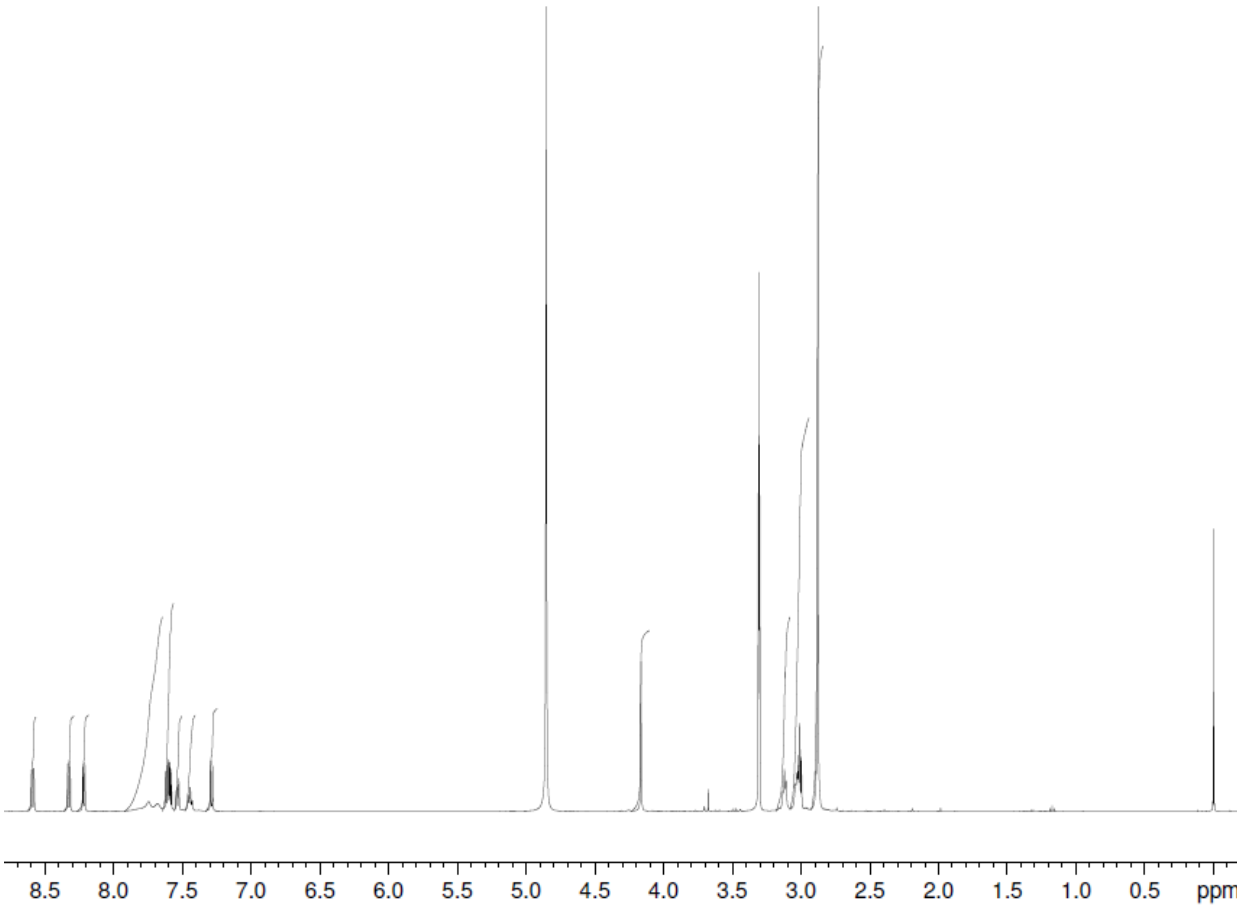


Fig. S1 ^{1}H NMR spectrum of **1** in CD_3OD at 25°C.

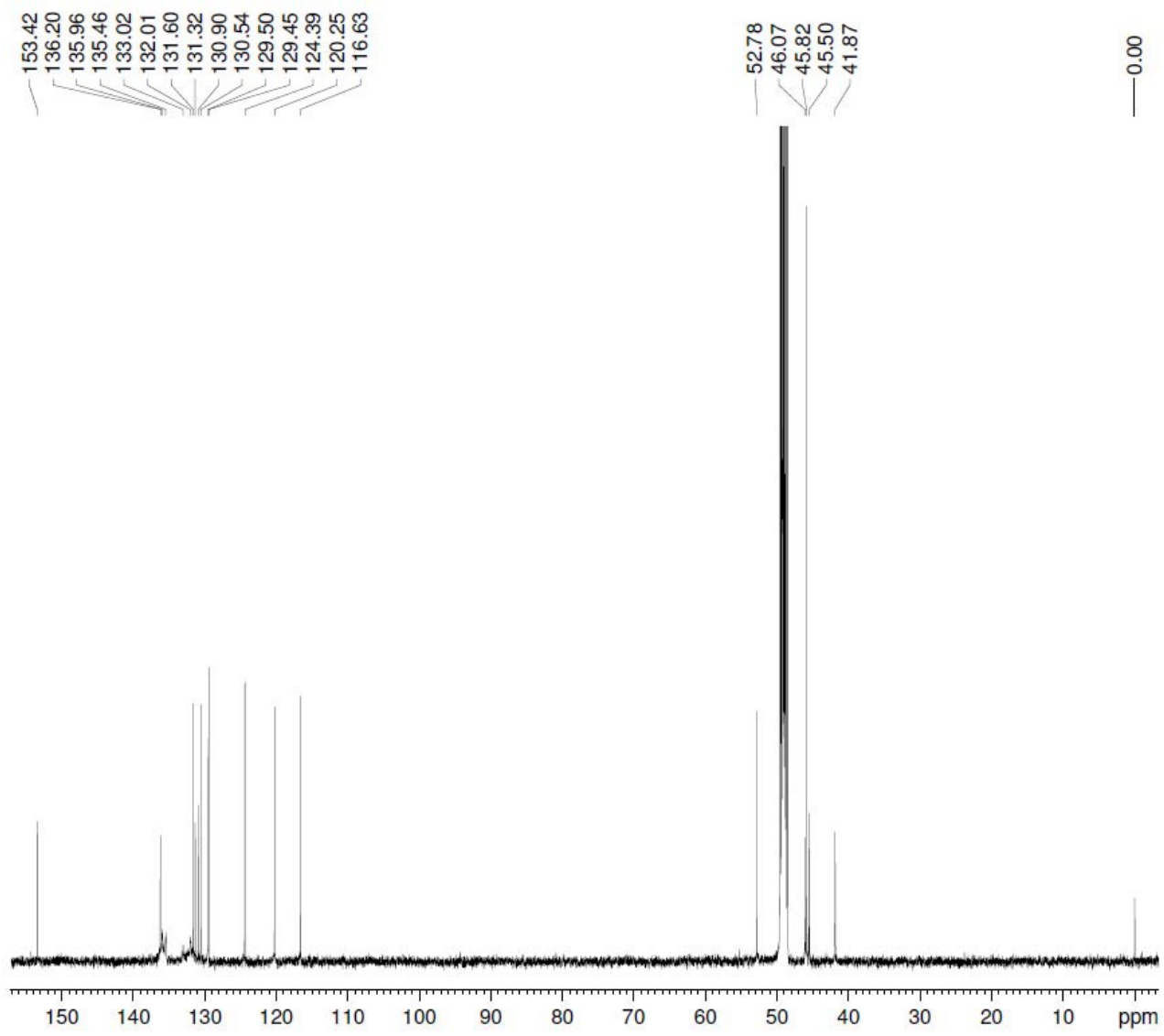


Fig. S2 ^{13}C NMR spectrum of **1** in CD_3OD at 25°C.

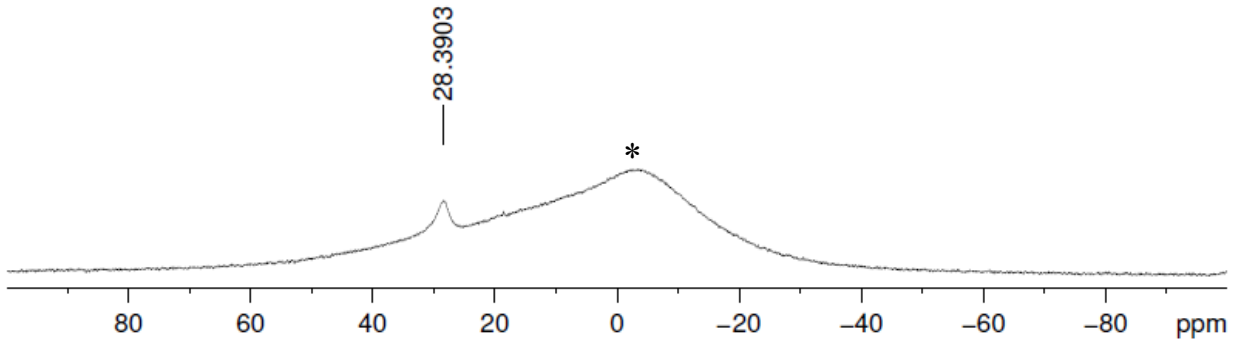


Fig. S3 ^{11}BNMR spectrum of **1** in CD_3OD at 25°C. A broad background peak (*) in the ^{11}BNMR spectrum is assigned to boron nitride used in the NMR probe.

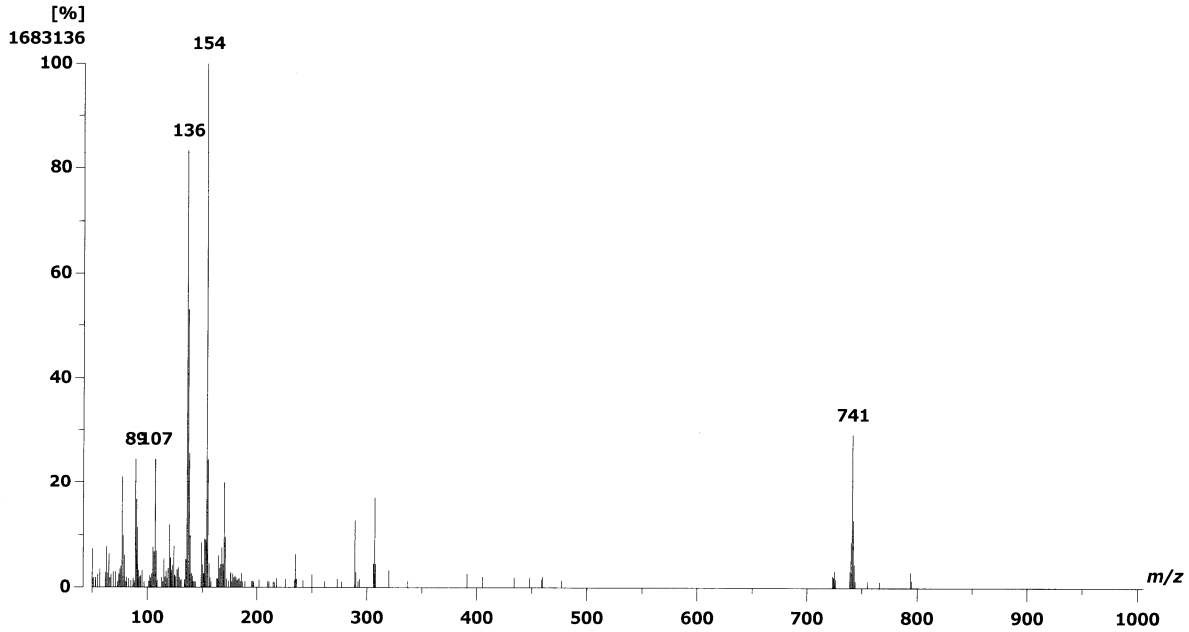


Fig. S4 FAB Mass spectrum of **1**. 3-Nitrobenzyl alcohol was used as a matrix.

2. Fabrication of dansyl-functionalized borax hydrogel

An aqueous solution (0.4 mL) of PVA (M.W. = 146,000 ~ 186,000, 8.0×10^{-1} M*) was added to an aqueous solution (0.1 mL) containing borax (0.47×10^{-1} M) and **1** (6.7×10^{-4} M) in a vial. The resultant mixture was vigorously mixed with a micro spatula to afford homogeneous gel. *The concentration was based on the monomer unit.

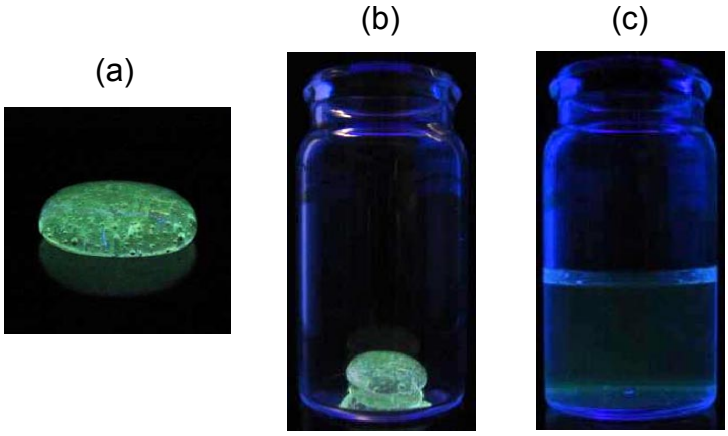


Fig. S5 (a) Photograph of a fluorescent borax hydrogel prepared from PVA, borax and **1**. The hydrogel was immersed in water (5 mL) at room temperature; (b) for 1 min; (c) for 90 min. The borax hydrogel was dissolved in water within 90 min.

3. pH stability test of DBA-PVA system

Fig. S6 The stability of boronate hydrogel (⌀8 mm × 5 mm) against pH. The boronate hydrogels were immersed in aqueous solutions (3 mL) of different pH values (from left to right: pH = 1, 3, 5, 7, 9, and 11) for three months at room temperature.

4. Fabrication of dansyl-functionalized boronate gel film by using 1 and 2 in DMSO.

(a) (b)

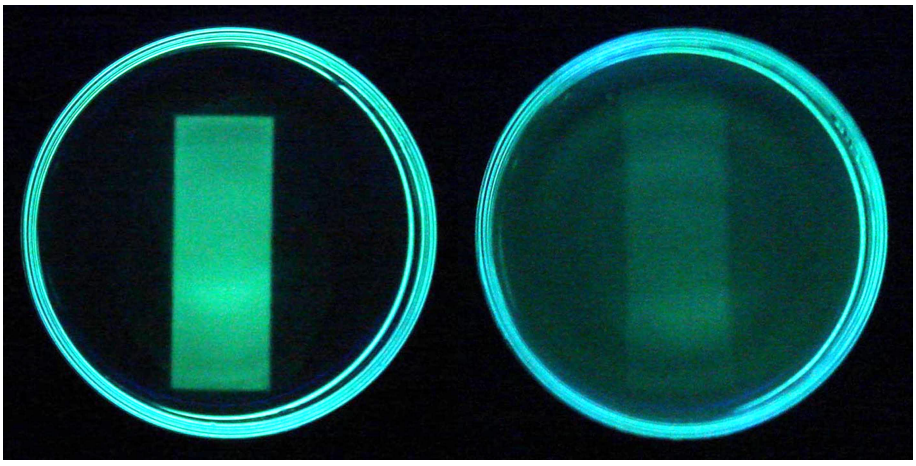
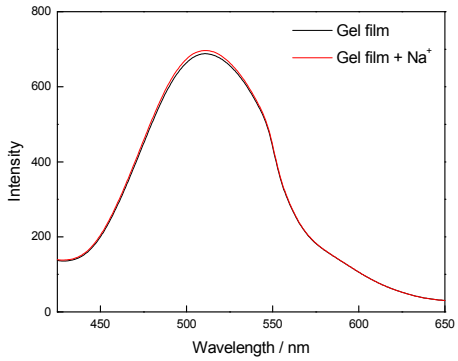
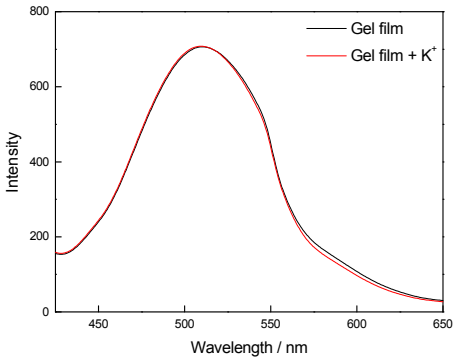
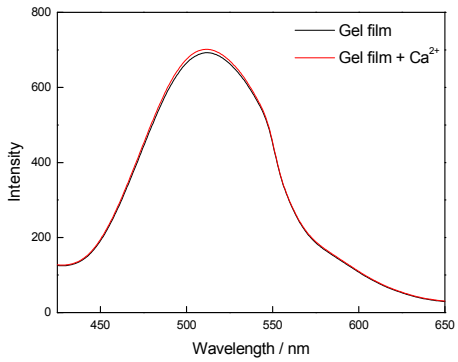


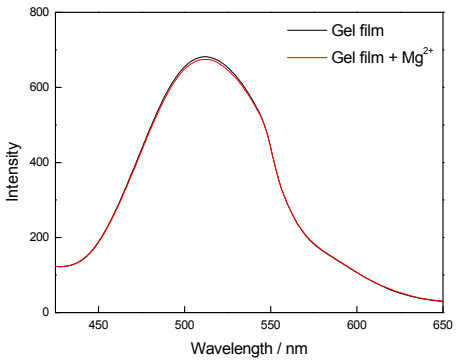
Fig. S7. The boronate gel films incorporating phenylboronic acid-free dansyldiethylenetriamine **2** under irradiation at 365 nm: (a) The gel film was immersed in DMSO (5 mL); (b) after shaking at 100 rpm for 30 min, the leakage of the fluorogenic material from the film was observed.

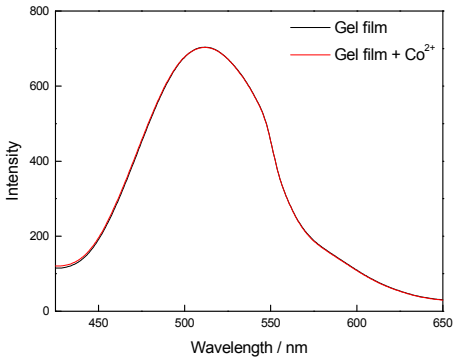
5. Fluorescent spectral change of dansyl-functionalized boronate gel film upon adding varied metal ions

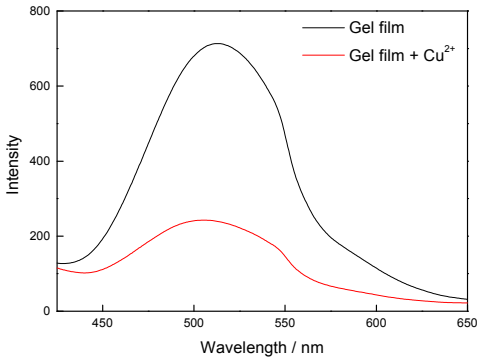


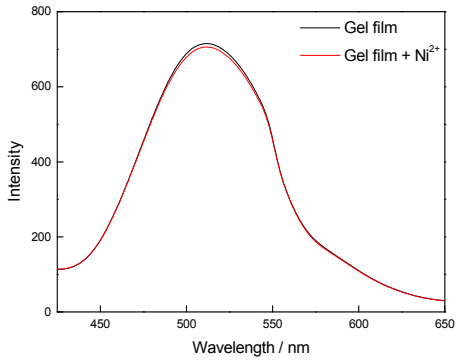


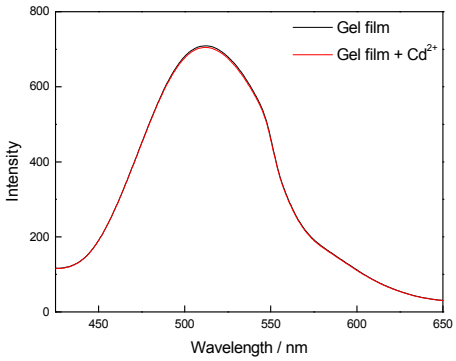












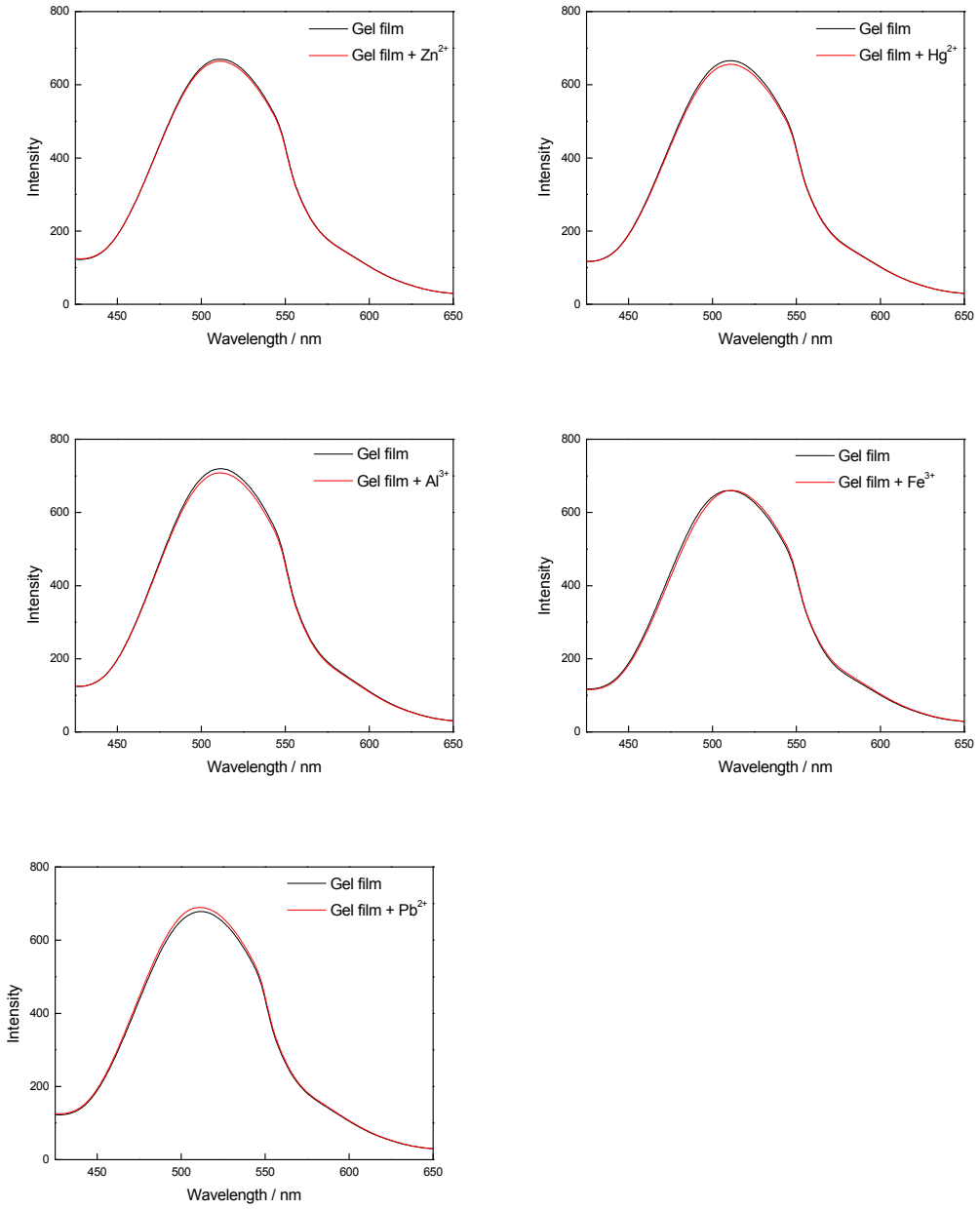
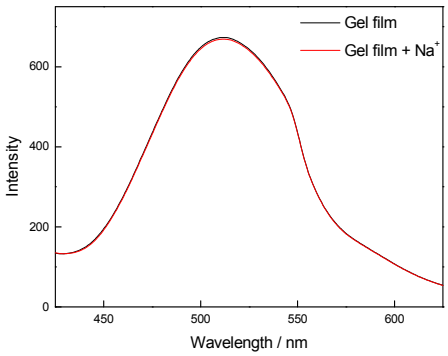
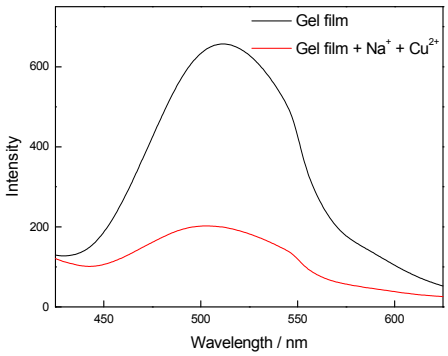
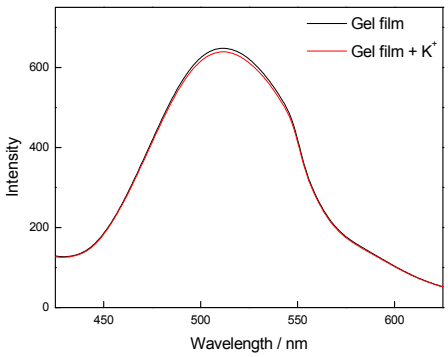


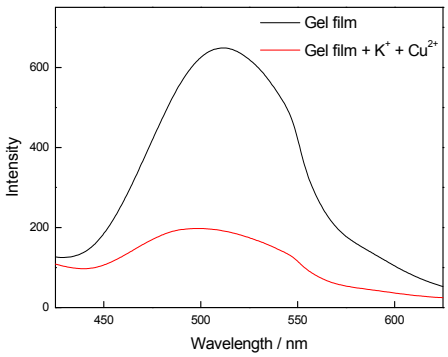
Fig. S8 Fluorescent spectra of dansyl-functionalized boronate gel films in 5 mM HEPES buffer solution (3 mL, pH = 7.0) containing Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, Al^{3+}, Fe^{3+}, and Pb^{2+} (1.25×10^{-5} M). The gel films were immersed in the solution with shaking at 125 rpm for 30 min before the fluorescent measurements: λ_{ex} = 340 nm.

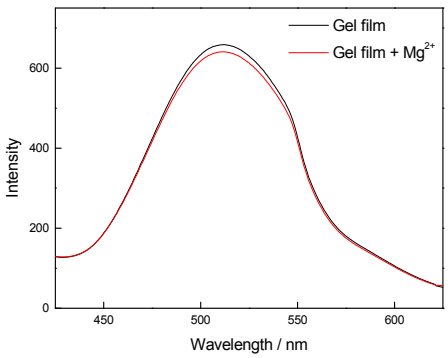
6. Competitive effects of other metal ions to copper ion-induced fluorescent response of dansyl-functionalized boronate gel film

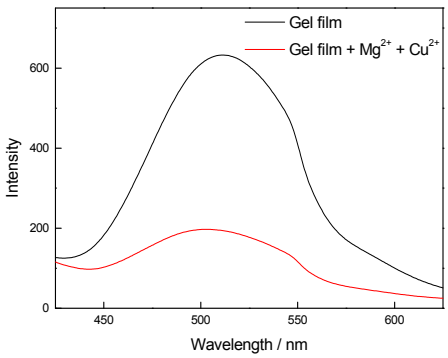


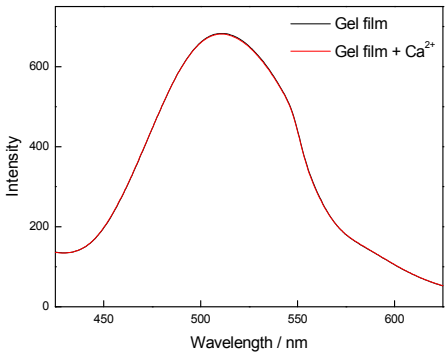


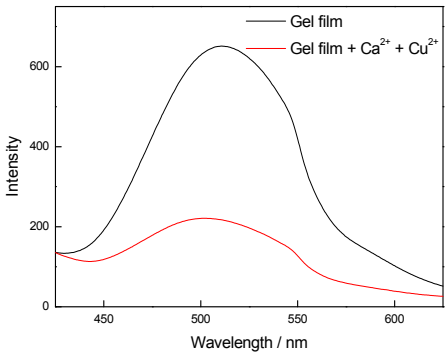


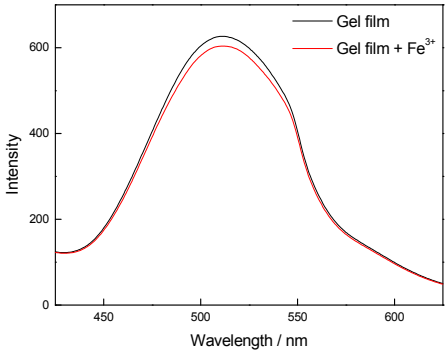


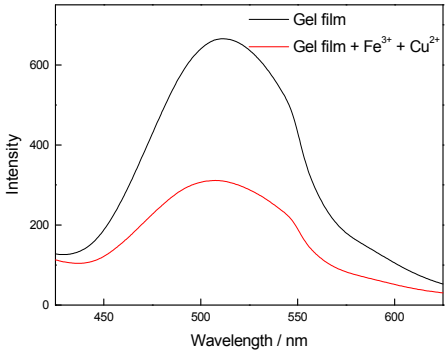


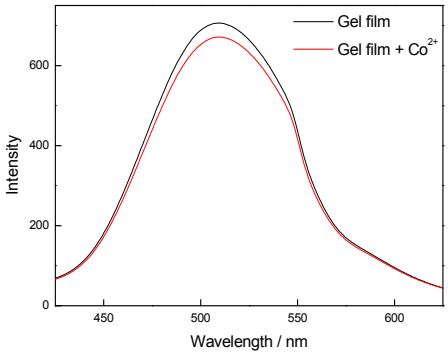


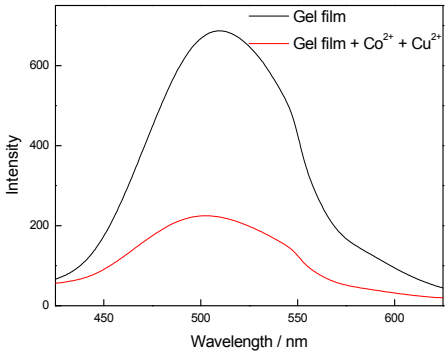


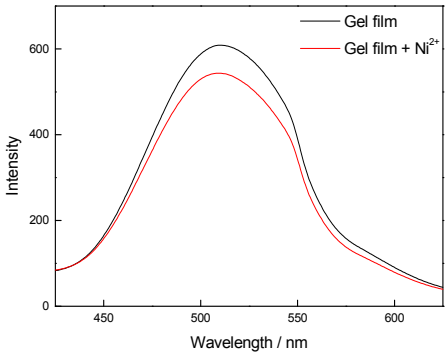


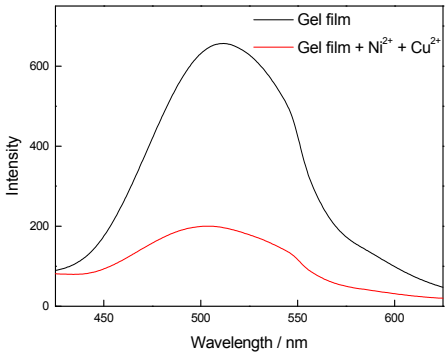


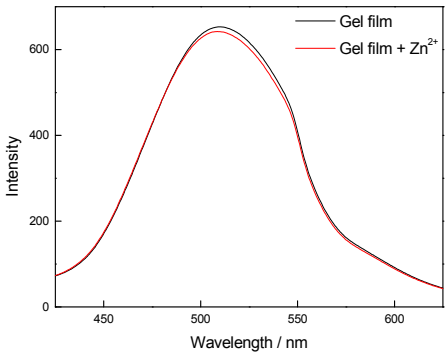


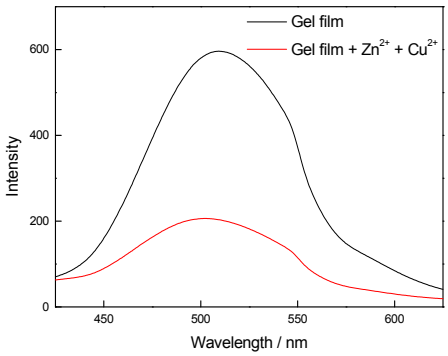












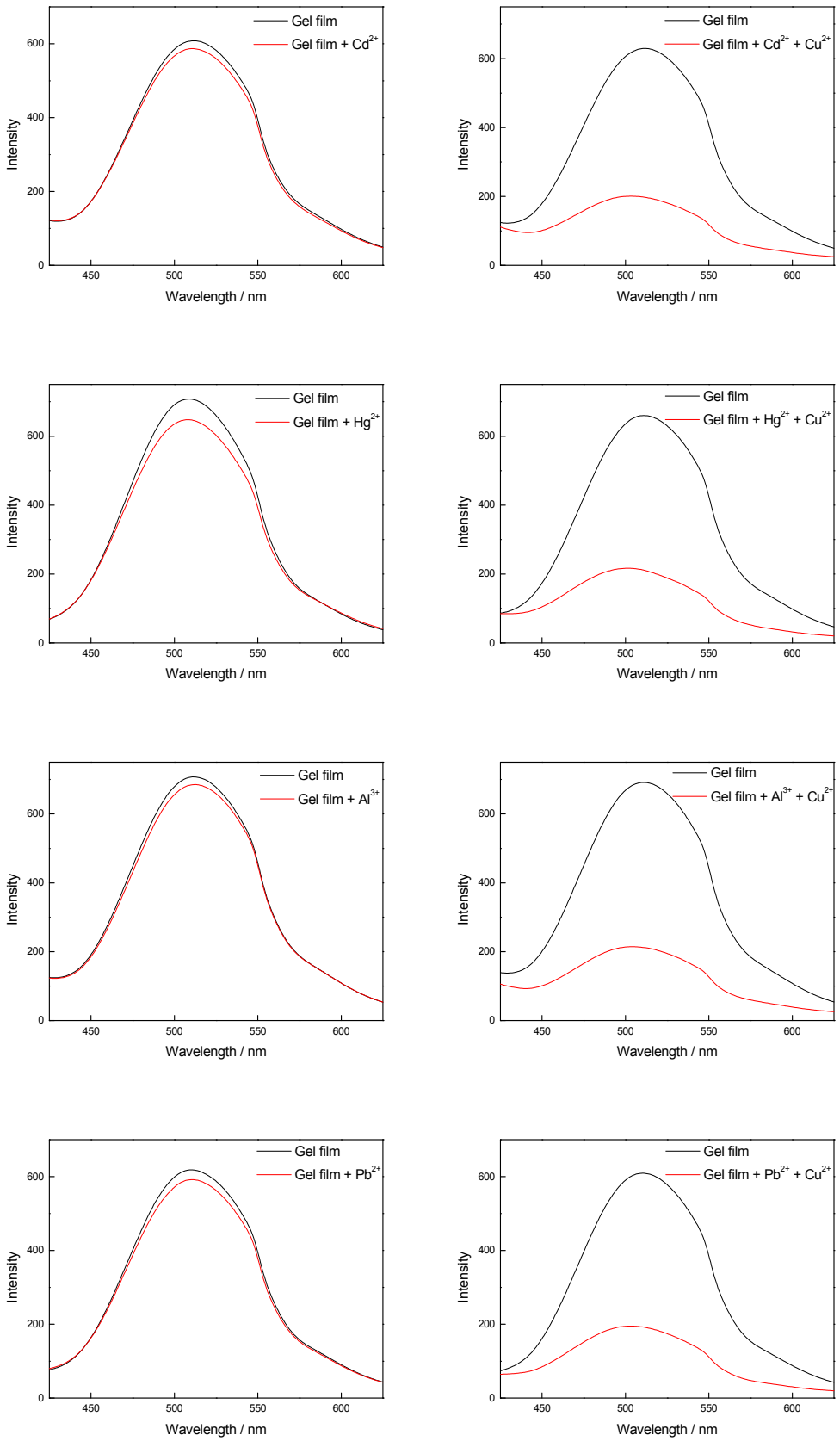


Fig. S9 Fluorescent spectral change of the films upon adding Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, and Pb^{2+} ($[M^{n+}] = 1.25 \times 10^{-4}$ M, left), and the fluorescent response to Cu^{2+} ($[Cu^{2+}] = 1.25 \times 10^{-5}$ M) against the competitive metal ions. The gels were immersed in 5 mM HEPES buffer solution (3 mL, pH = 7.0) with shaking for 30 min at 125 rpm before the fluorescent measurements. Conditions: λ_{ex} = 340 nm.