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)

![NMR spectra](image)

**Fig. S1** $^1$H NMR spectrum of 1 in CD$_3$OD at 25°C.
Fig. S2 $^{13}$C NMR spectrum of 1 in CD$_3$OD at 25°C.

Fig. S3 $^{11}$BNMR spectrum of 1 in CD$_3$OD 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 (ф8 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.

**Fig. S7.** The boronate gel films incorporating phenylboronic acid-free dansyl diethylenetriamine 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

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**Fig. S8** Fluorescent spectra of dansyl-functionalized boronate gel films in 5 mM HEPES buffer solution (3 mL, pH = 7.0) containing Na⁺, K⁺, Mg²⁺, Ca²⁺, Co²⁺, Cu²⁺, Ni²⁺, Cd²⁺, Zn²⁺, Hg²⁺, Al³⁺, Fe³⁺, and Pb²⁺ (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<sub>ex</sub> = 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 × 10\(^{-4}\) M, left), and the fluorescent response to Cu\(^{2+}\) ([Cu\(^{2+}\)] = 1.25 × 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: \(\lambda_{ex} = 340\) nm.