Supporting Information

A "turn-on" ESIPT fluorescence probe of 2-(Aminocarbonyl)phenylboronic acid for selective detection of Cu(II)

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Contents

1 EXPERIMENTAL

1.1 Materials and Methods

2-(aminocarbonyl)phenylboronic acid, Et_3N, $Cu(OAc)_2•H_2O$, EtOH, ACN, DMSO, DMF, KCl, NaCl, $CaCl_2$, $MgCl_2•6H_2O$, $Sr(NO_3)_3$, $AgNO_3$, $ZnCl_2$, $MnCl_2•4H_2O$, $CoCl_2•6H_2O$, $Pd(OAc)_2$, $HgCl_2$, $FeCl_3$, $CrCl_3$, $AlCl_3$, $Pr(NO_3)_3•6H_2O$, Ceric ammonium nitrate were purchased from Shanghai Aladdin Bio-Chem Technology Co, LTD and used as received. The testing solvents were prepared with deionized water. Ganjiang river water, rainwater, tap water were collected by water sampler and pretreated according to literatures[S1, S2].

1.2 General Instrumentation

Emission spectra were performed on a Fluorescence spectrometer (F-4600). Error limits were estimated: λ (±1 nm); τ (±10%); φ (±10%). The solvents were distilled from standard drying agents. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by recrystallization. ^{1}HNMR (400 MHz) and ^{13}CNMR (100 MHz) spectra were recorded on Bruker Avance AV400 spectrometer (Bruker, Billerica, MA, USA) unless otherwise noted. The chemical shifts (δ) were quoted in parts per million from tetramethylsilane for ^{1}H and DMSO-*d6* for ^{13}C spectroscopy. The pH values of real water samples were recorded by B6337-02 Benchtop pH/Conductivity Meters.

1.3 Synthesis of Salicylamide

2-(aminocarbonyl)phenylboronic acid (0.5 mmol), Et_3N (0.75 mmol) and Cu(II) (0.5 mmol) were added into a round bottom flask, and then solvent DMF/H_2O (v/v = 9:1) was added. The mixture was stirred at rt for 2.5 h. Then the mixture was poured into

deionized water and extracted with ethyl acetate. The organic phase was collected and washed with brine, dried over Na_2SO_4, and concentrated by rotary evaporation. The crude product was recrystallization in EtOH to provide the corresponding product salicylamide. Yield 74%. The ^1H NMR and ^{13}C NMR spectroscopy of salicylamide shown as Figure S1 and S2. ^1H NMR (400 MHz, DMSO-*d6*) δ 13.07 (s, 1H), 8.19 (d, *J* = 202.7 Hz, 2H), 7.87 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.44 – 7.39 (m, 1H), 6.90 – 6.85 (m, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*) δ 172.59, 161.58, 134.57, 128.58, 118.83, 117.88, 114.80.

The ^1H NMR spectrum exhibits the typical signals for salicylamide. The multiple peaks range from 6.85 to 6.90 ppm corresponding to the two aromatic hydrogens at the ortho- and para-position of -OH group. The multiple peaks range from 7.39 to 7.44 ppm represent of the aromatic hydrogen at the para- position of the amide group. The dd peaks at 7.87 ppm was the signal of the aromatic hydrogen at the ortho- position of the amide group. The chemical shift of NH_2 on the amide group have a peak splitting of 7.94 and 8.44 ppm, and the chemical shift of -OH proton shifted down field at 13.07 ppm. The ^{13}C NMR spectrum exhibits 7 peaks, which fully agree with the proposed structure for salicyamide.

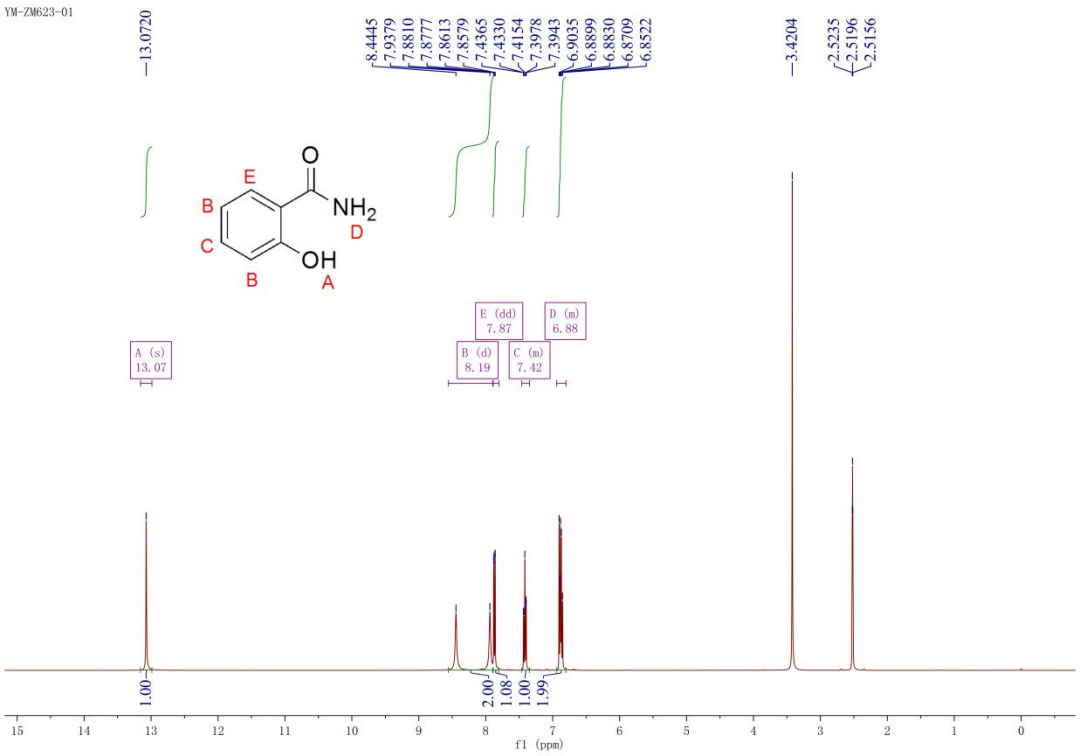


Figure S1. ^{1}H NMR spectrum (400 MHz, DMSO-*d6*) of Salicylamide

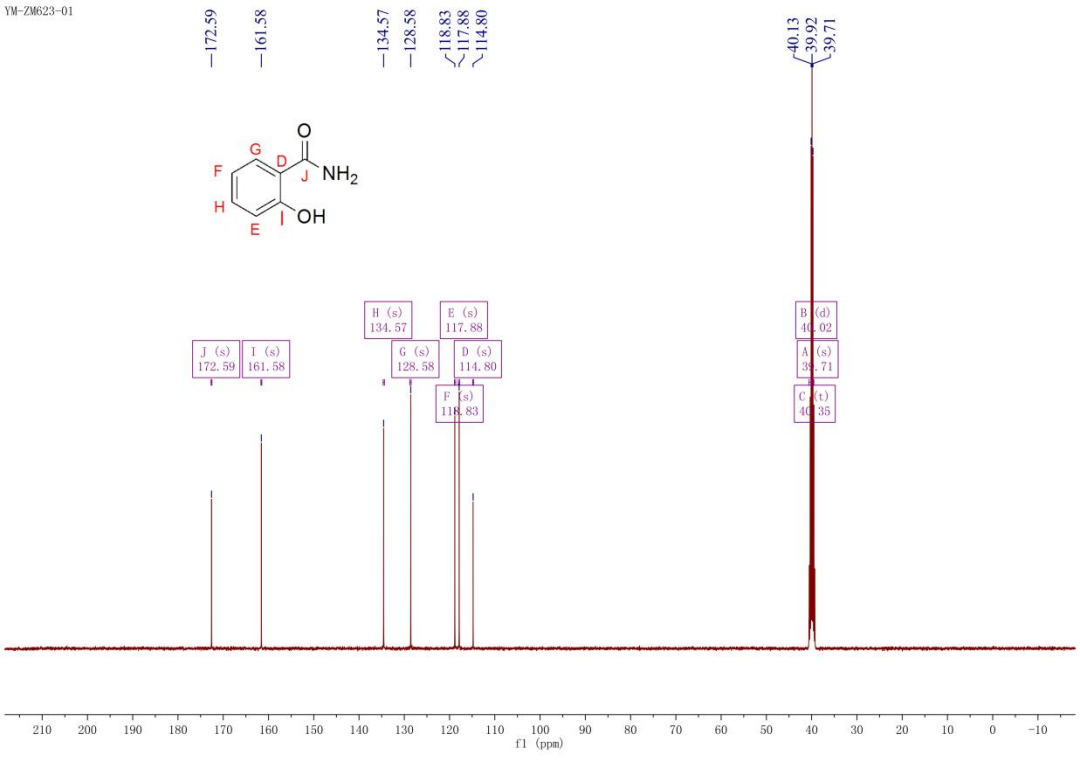


Figure S2. ^{13}C NMR spectrum (400 MHz, DMSO-*d6*) of Salicylamide

1.4 Detection of Cu(II) in different solvents

The stock solutions of 2-(aminocarbonyl)phenylboronic acid (5 mM), Et_3N (5 mM) were prepared in EtOH, DMSO, DMF, or ACN solvents. and the stock solution of Cu(II) (5 mM) was prepared in deionized water. 2-(aminocarbonyl)phenylboronic acid (100 μM) was mixed with Et_3N (50 μM) and Cu(II) (50 μM) in according solvents, and then the mixture was incubated at room temperature for 2.5 h. Emission spectra were measured in the range of 400 nm to 700 nm with an excitation wavelength at 365 nm, and the slit width is 10 nm/20 nm.

1.5 Detection of Cu(II) with different concentration of Et_3N

The stock solutions of 2-(aminocarbonyl)phenylboronic acid (5 mM), Et_3N (5 mM) were prepared in DMF, and the stock solution of Cu(II) (5 mM) was prepared in deionized water. 2-(aminocarbonyl)phenylboronic acid (100 μM), Cu(II) (50 μM) and Et_3N (0−210 μM) were added into DMF solution, and then the mixture was incubated at room temperature for 2.5 h. Emission spectra were measured in the range of 400 nm to 700 nm with an excitation wavelength at 365 nm, and the slit width is 10 nm/20 nm. The detection result was shown as Fig. S3a, and can be found that the fluorescence intensity was proportional to the concentration of Et_3N (0−210 μM), indicating that the fluorescence enhancement is related to the salicylamide, which generated via Cu(II) catalyzed oxidative hyroxylation of 2-(aminocarbonyl)phenylboronic acid under alkaline condition. Fig. S3b displayed the variation trend between fluorescent intensity at 410 nm with the concentration of Et_3N. It can be observed that the fluorescent intensity increased with the increasing Et_3N

concentrations range from 0 μM to 150 μM. When the concentration of triethylamine exceeded 150 μM, the fluorescence intensity tended to be stable. Hence, The optimal concentration of triethylamine was chosen as 150 μM, which enhanced fluorescent intensity upon to 13 times.

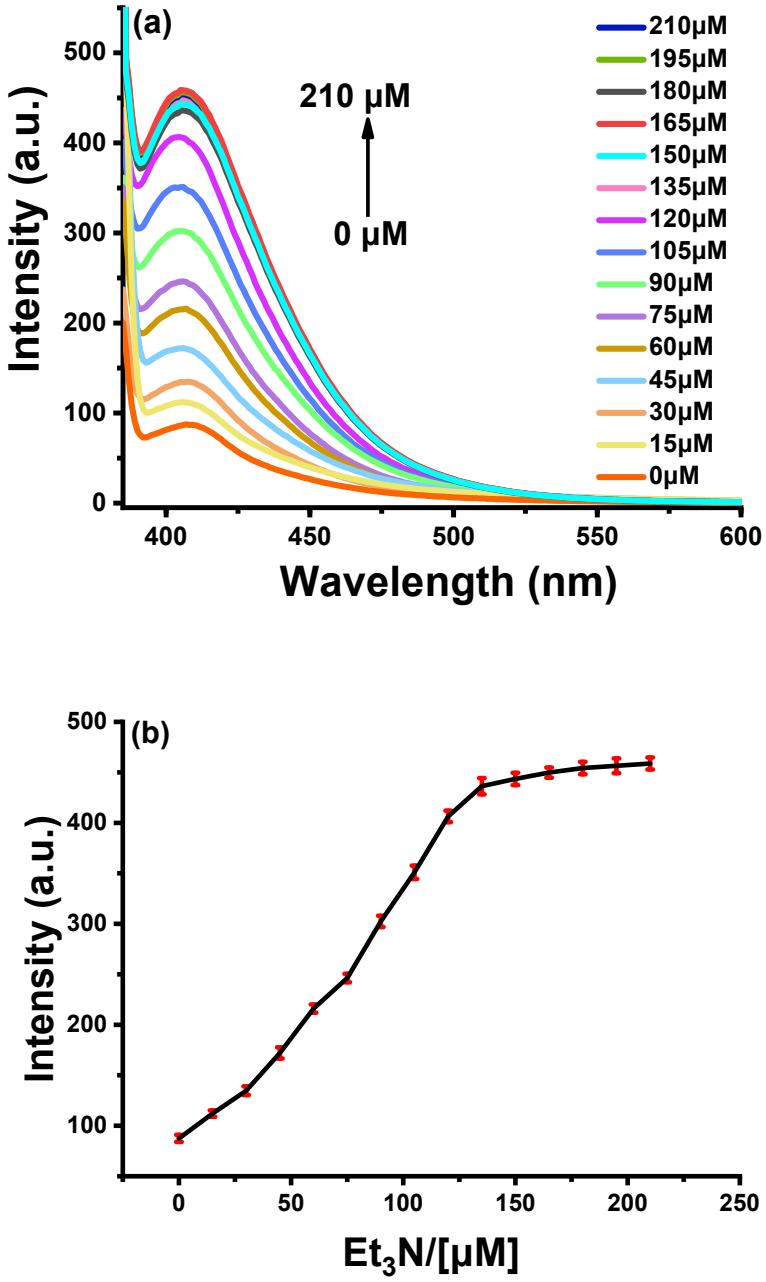


Figure S3. (a) Fluorescence enhancement of 2-(aminocarbonyl)phenylboronic acid(100 μM), Cu(II) (50 μM) with different concentration of Et_3N (0−210 μM) in DMF; (b) The change trend curve of fluorescence intensities at 410 nm with the concentration of Et_3N (0-210 μM).

1.6 Detection of Cu(II) in various percentages of water in DMF

The stock solutions of 2-(aminocarbonyl)phenylboronic acid (5 mM), Et_3N (5 mM)

were prepared in DMF, and the stock solution of Cu(II) (5 mM) was prepared in deionized water. Various amount of those stock solutions were added into dilutes with H_2O/DMF ratio range from (10:0) to (0:10), diluting to the testing solution consist of 2-(aminocarbonyl)phenylboronic acid (100 μM), Et_3N (150 μM) and Cu(II) (50 μM). Then the mixture was incubated at room temperature for 2.5 h. Emission spectra were measured in the range of 400 nm to 700 nm with an excitation wavelength at 365 nm, and the slit width is 10 nm/20 nm. It can be seen in Fig. S4 that the fluorescence intensity decreased when elevating H_2O content in solvent, which may be due to the poor solubility of salicylamide in aqueous solution. The highest fluorescent enhancement was achieved with the diluting solution as pure DMF. Considering that the stock solution of Cu(II) was prepared in deionized water, the testing solution would containing smidgen of water.

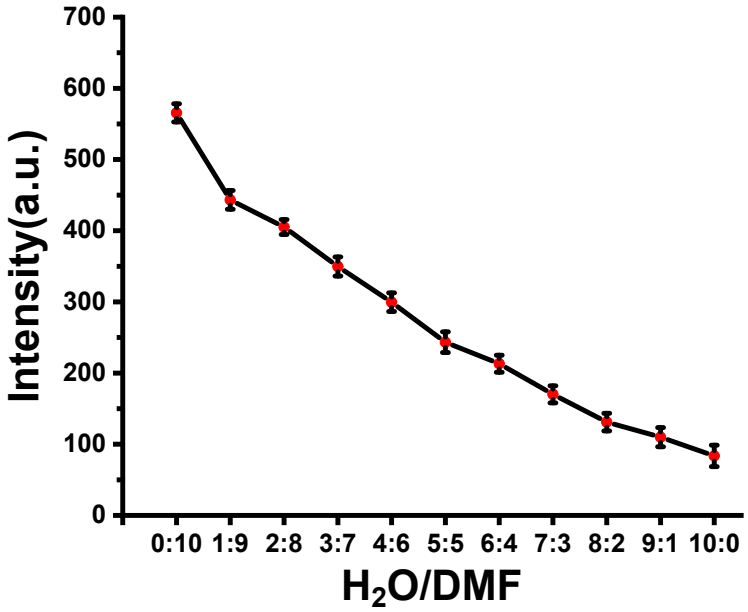


Figure S4. Fluorescence intensities at 410 nm variation of 2-Aminocarbonylphenyl boronic acid (100 μM), triethylamine (150 μM) with 50 μM of Cu(II) in different ratios of H_2O/DMF.

1.7 Detection of Cu(II) in different incubation time

The stock solutions of 2-(aminocarbonyl)phenylboronic acid (5 mM), Et_3N (5 mM)

were prepared in DMF, and the stock solution of Cu(II) (5 mM) was prepared in deionized water. Various amount of those stock solutions were added into DMF, diluting to the testing solution consist of 2-(aminocarbonyl)phenylboronic acid (100 μM), Et_3N (150 μM) and Cu(II) (50 μM). Then the mixture was incubated at room temperature for different time. Under the same conditions, a detection system without Cu(II) was used as the control group. Emission spectra were measured in the range of 400 nm to 700 nm with an excitation wavelength at 365 nm, and the slit width is 10 nm/20 nm.

1.8 Emission titration experiments

The 2-(aminocarbonyl)phenylboronic acid and Et_3N was added into DMF to a final concentration of 100 μM and 150 μM respectively. A various concentrations of Cu(II) (0−96 μM) were then added to DMF containing 2-(aminocarbonyl)phenylboronic acid (100 μM) and Et_3N (150 μM) in a cuvette. Then emission spectra were measured in the range of 400 nm to 700 nm with an excitation wavelength at 365 nm, and the slit width is 10 nm/20 nm.

1.9 Detection of Cu(II) with interference substances

5 mM of various common metal ions were prepared in deionized water as stock solutions. Various metal ion interferers (2 mM K^+ and Na^+, 1 mM Ca^{2+} and Mg^{2+}, 50 μM Sr^{2+}, Ag^+, Zn^{2+}, Mn^{2+}, Co^{2+}, Pd^{2+}, Hg^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Pr^{3+}, Ce^{4+}), instead of Cu^{2+}, were added to DMF solution containing 2-(aminocarbonyl)phenylboronic acid (100 μM) and Et_3N (150 μM). Then 50 μM Cu^{2+} was mixed with this solution to explore the anti-interference capacity of the probe, and the mixture was incubated at room temperature for 2.5 h. Emission spectra were measured in the range of 400 nm to 700 nm with an excitation wavelength at 365 nm, and the slit width is 10 nm/20 nm.

1.10 Preparation of water samples

Ganjiang River water was collected from the Gangjiang river, tap water was collected from chemistry laboratory, and rainwater was collected from Ganzhou. Cu(II) was spiked into various water samples to obtain sample stock solutions with 5 mM of Cu(II).

1.11 Detection of Cu(II) in real water samples

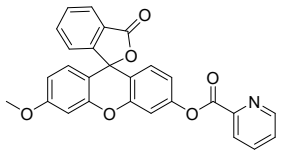
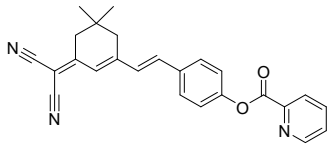
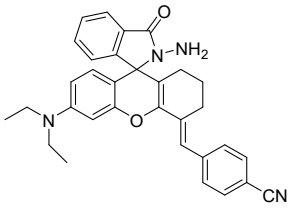
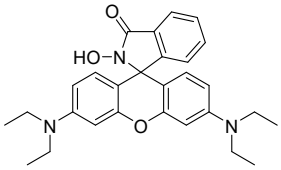
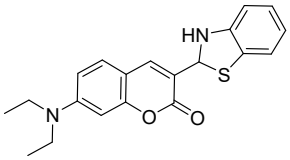
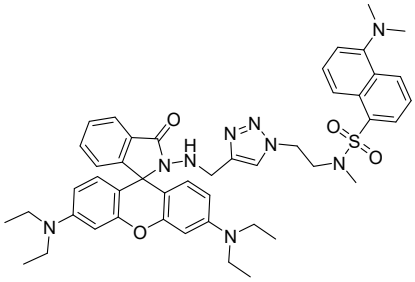
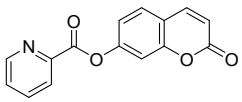
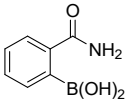
Real water samples were added to a sensing system containing 2-(aminocarbonyl)phenylboronic acid (100 μM) and Et_3N (150 μM), resulting a final solution with 20 μM of Cu(II) in DMF solution. Then the mixture solution was incubated at room temperature for 2.5 h. Emission spectra were measured in the range of 400 nm to 700 nm with an excitation wavelength at 365 nm, and the slit width is 10 nm/20 nm.

2. COMPARISON OF THE COMPOSITE FLUORESCENT PROBE WITH OTHER REPORTED PORBES.

The sensitivity data of several fluorescent probes for the detection of Cu(II) were compared with the proposed probe as shown in table S1. It can be seen that the proposed fluorescent probe possesses the lower detection limit, the wider linear range and higher sensitivity compared with the reported probe. In addition, the easily available 2-(aminocarbonyl)phenylboronic acid and Et_3N make the composite probe an inexpensive and easily operated assay for the detection of Cu(II).

Table S1 Comparison of the proposed method for Cu(II) detection with other previously reported fluorescent probe.

Entry	Probe	Ex/Em (nm)	Reaction time (min)	Linear range (μM)	LOD (nM)	Ref.

1		460/514	1	0-1 μM	55	S3
2		426/590	5	0.5-10 μM	0.2	S4
3		530/663	1440	1-50μM	1800	S5
4		510/575	120	1-20 μM	33	S6
5		457/509	5	0.5-4 μM	58	S7
6		420/540, 568	30	10-50 μM	120	S8
7		325/454	5	0.1-0.9 μM	35	S9
8		**365/410**	**150**	**0-22 μM**	**68**	**This work**

3. REFERENCE

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