

Supplementary Material

A Novel Ratiometric Fluorescence Sensor for Zn²⁺ Detection

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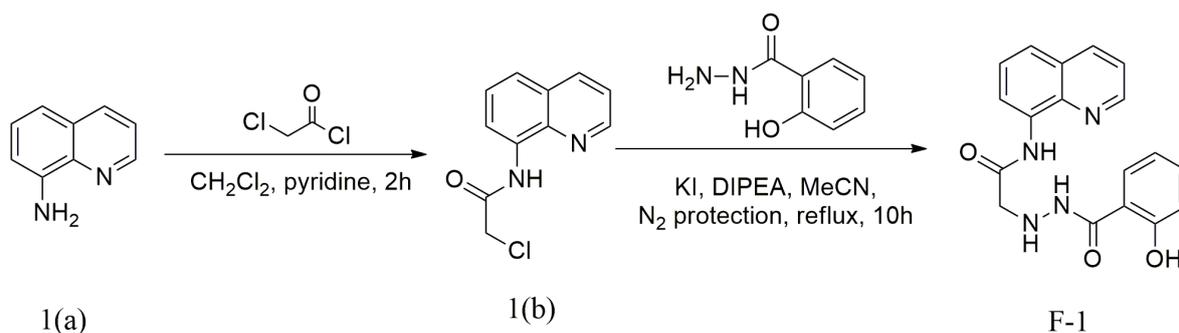
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1 Materials and general methods

8-Aminoquinoline purchased from TCI was recrystallized from ethanol. Chloroacetyl chloride was purchased from Aladdin. Salicylhydrazide and *N,N*-diisopropylethylamine (DIPEA) was purchased from Cantotech, and used as received. Dichloromethane, methanol (MeOH) and acetonitrile (MeCN) were purchased from Guangdong Guanghua Sci-Tech Co.Ltd., and distilled under reduced pressure. Tris-HCl buffer solutions of different pH were prepared using proper amount of Tris and HCl (all of analytical grade) under adjustment by a pH meter. The precursor 2-chloro-*N*-(quinolin-8-yl)acetamide (**1b**) was prepared according to the reported procedure, which was prepared from 8-aminoquinoline (**1a**) and 2-chloroacetyl chloride in dichloromethane.

¹H NMR(400 MHz) and ¹³C NMR(101 MHz) spectra were recorded on a Bruker Ultrashield TM 400 PLUS spectrometer. FT-IR spectra (4000-500 cm⁻¹) in KBr were recorded on a Bruker VERTEX 70V spectrometer. Mass spectrum (MS) was obtained with a Waters Q-TOF premier Mass Spectrometer. UV-Vis spectroscopy measurements were acquired on a SCINCO S-4100 UV/Vis spectrophotometer. Fluorescence spectra were recorded using a Jobin Yvon FluoroLog-3-TCSPC spectrofluorometer.

2. Synthesis and Reactions



Scheme S1

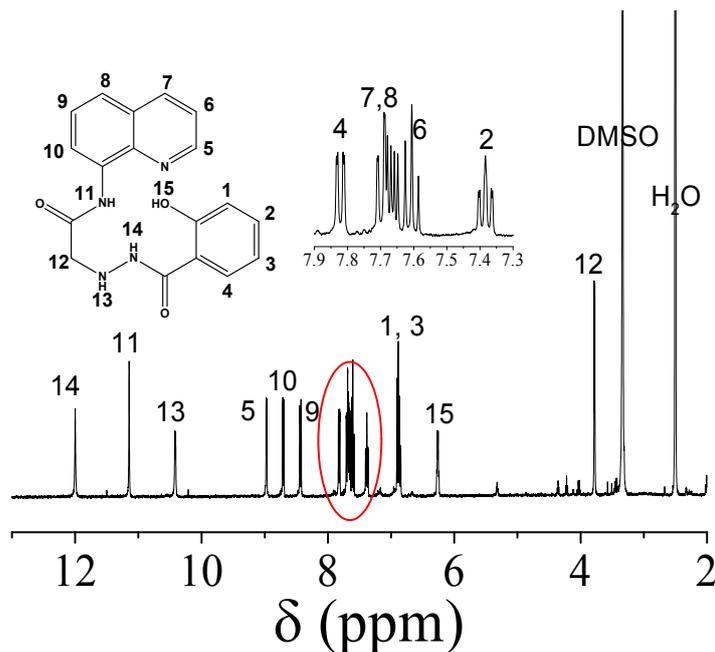
2-(2-(2-hydroxybenzoyl)hydrazinyl)-*N*-(quinolin-8-yl)acetamide (**F-1**) was prepared as follows(Scheme 1): compound 1(b) (110 mg, 0.5 mmol), salicylhydrazide (152 mg, 1 mmol) and KI (25mg, 0.15 mmol) were dissolved in anhydrous MeCN (20 mL) with 1.0 mmol of DIPEA under nitrogen atmosphere. The yellow solution was stirred for 10 h under reflux; then the solvent was removed by rotary evaporation and the residue was directly purified by flash column chromatography (silica gel, petroleum ether/ethyl

acetate/Et₃N = 1/1/0.01, v/v) to provide **F-1** (140 mg, yield 83.5%) as the yellow solid.

3 General spectroscopic procedures.

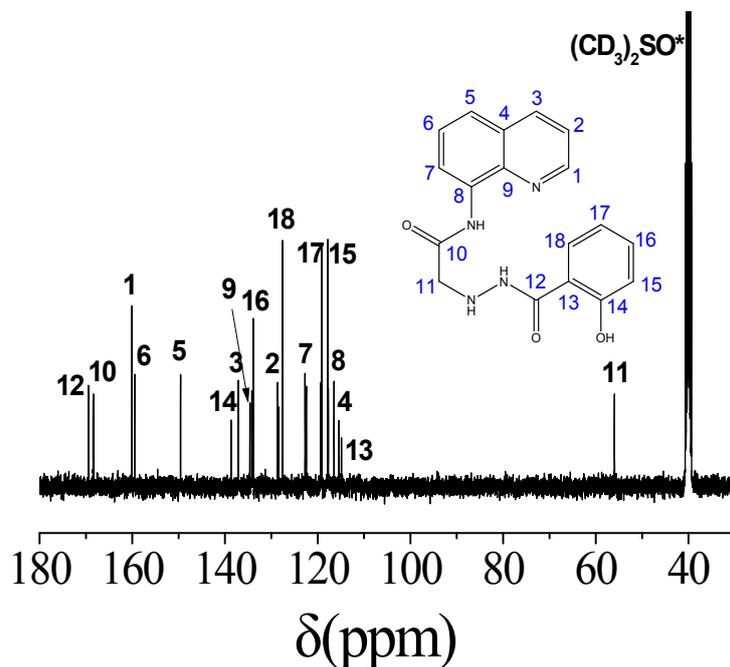
Stock solutions (0.01 M) of chlorinated salts K⁺, Cu²⁺, Fe²⁺, Al³⁺, Fe³⁺, Cr³⁺, Hg²⁺, Pb²⁺, Cd²⁺ and Zn²⁺ were first prepared with 10 mM Tris-HCl buffer solution (pH 7.0). Stock solution was prepared in methanol. Test solutions were prepared by placing calculation amount of the **F-1** stock solution into a test tube, adding an appropriate aliquot of each metal, and then diluting the solution to 3.0 mL with methanol and buffer solution. All fluorescence spectra were recorded 10 min after the addition of determinand at 25 °C with the excitation wavelength set at 340 nm (excitation/emission slit widths: 5 nm).

Figure S1. ¹H NMR spectrum of **F-1** in (CD₃)₂SO



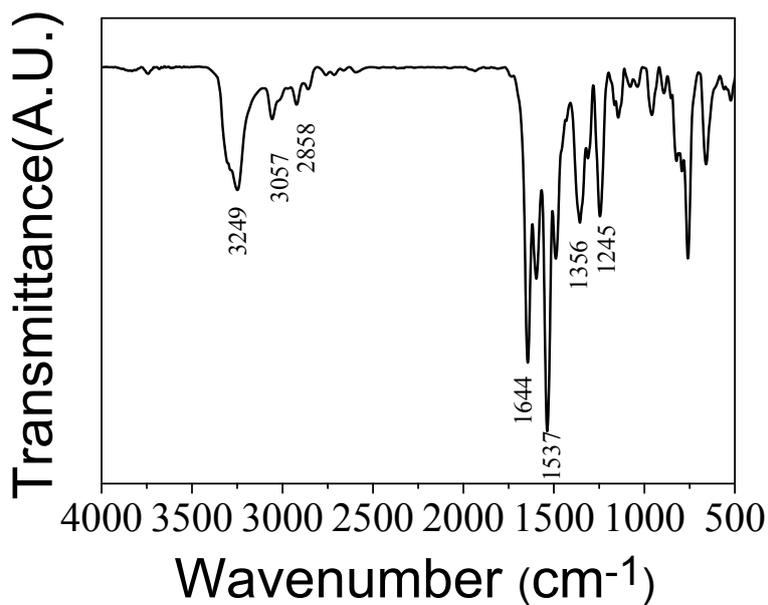
¹H NMR (400 MHz, DMSO) δ 12.00 (s, 1H), 11.15 (s, 1H), 10.42 (d, J = 5.3 Hz, 1H), 8.97 (dd, J = 4.2, 1.6 Hz, 1H), 8.73 – 8.68 (m, 1H), 8.43 (dd, J = 8.3, 1.6 Hz, 1H), 7.82 (dd, J = 8.0, 1.5 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.61 (t, J = 7.9 Hz, 1H), 7.42 – 7.35 (m, 1H), 6.88 (dd, J = 16.0, 7.9 Hz, 2H), 6.26 (d, J = 4.9 Hz, 1H), 3.78 (d, J = 4.5 Hz, 2H).

Figure S2. ^{13}C NMR spectrum of **F-1** in $(\text{CD}_3)_2\text{SO}$



^{13}C NMR (101 MHz, DMSO) δ 169.45 (C12, s), 168.39 (C10, d, $J = 8.7$ Hz), 160.12 (C1, s), 159.49 (C6, s), 149.57 (C5, s), 138.66 (C14, s), 137.08 (C3, s), 134.62 (C9, s), 134.04 (C16, d, $J = 28.9$ Hz), 128.51 (C2, d, $J = 22.9$ Hz), 127.56 (C18, d, $J = 5.5$ Hz), 122.58 (C7, d, $J = 27.2$ Hz), 119.23 (C17, d, $J = 18.7$ Hz), 117.75 (C15, d, $J = 9.4$ Hz), 116.46 (C8, s), 115.40 (C4, s), 114.87 (C13, s), 55.98 (C11, s).

Figure S3. FT-IR spectrum of **F-1**



FT-IR (KBr): 1245 cm^{-1} (Ph—N); 1356 cm^{-1} (Ph—O); 1537 cm^{-1} (N—H bending); 1644 cm^{-1} (C=O); 2858 cm^{-1} , 3057 cm^{-1} (C—H); 3249 cm^{-1} (O—H).

Figure S4. HR-MS spectrum of F-1

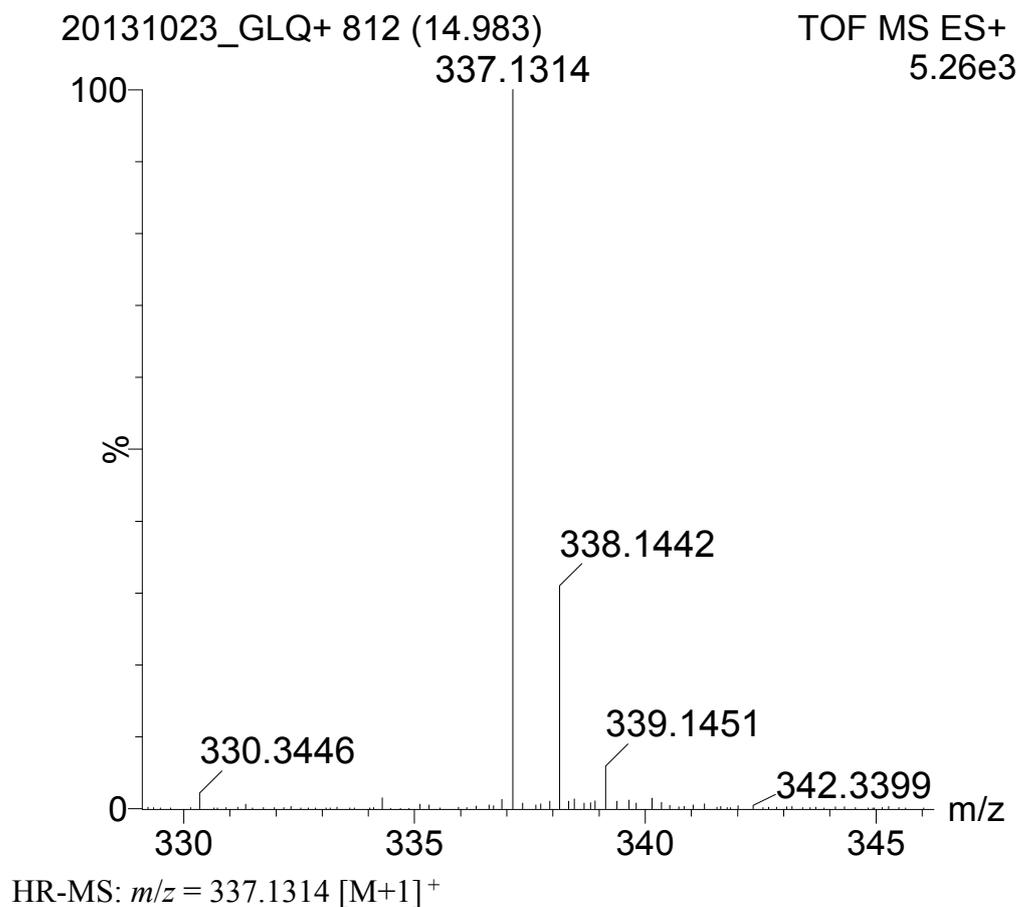
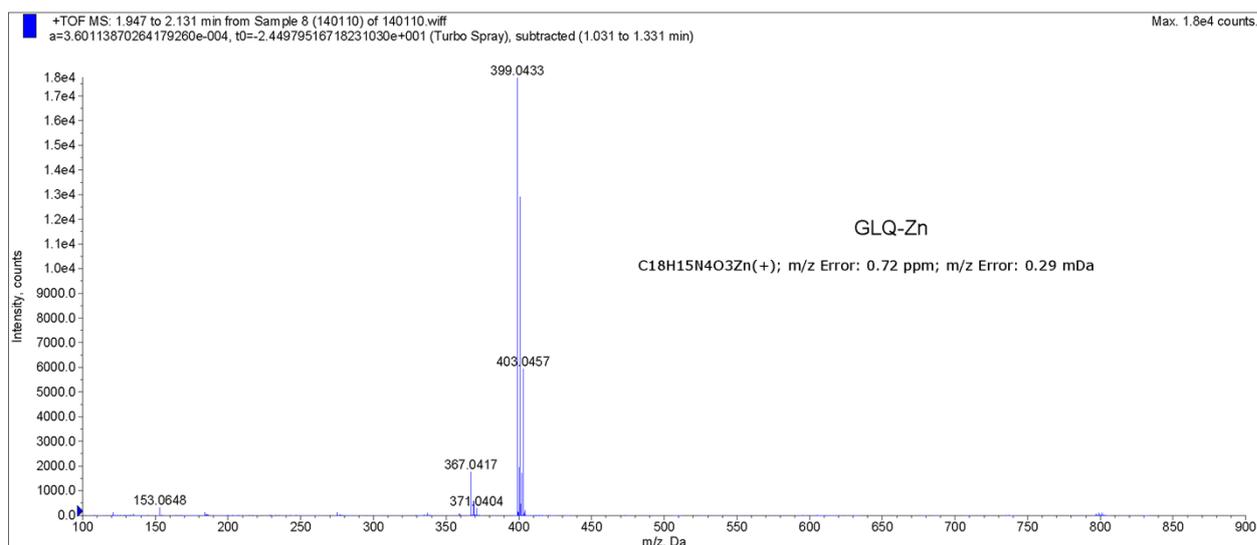


Figure S5. HR-MS spectrum of F-1+Zn²⁺-H



HR-MS: $m/z = 399.0433 [F-1+Zn^{2+}-H]$

Figure S6. The limit of Fe^{2+} and Hg^{2+} that can be tolerated in an error-free detection of Zn^{2+} with F-1 (10 μM). Competitive Fe^{2+} and Hg^{2+} ions with different concentration were first added into the detection solution and then 1 equiv. Zn^{2+} ion 20 minutes later, respectively.

