A novel turn-on fluorescent probe for Hg\textsuperscript{2+} in water based on 8-hydroxyquinoline

1. Reagent and apparatus

8-hydroxyquinoline (98%), allyl bromide (98%), methyl iodide (98%), 5-hydroxyquinoline (99%), Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O, ZnSO\textsubscript{4}·7H\textsubscript{2}O, Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, CoCl\textsubscript{2}·6H\textsubscript{2}O, NiSO\textsubscript{4}·6H\textsubscript{2}O, CuCl\textsubscript{2}·2H\textsubscript{2}O, AgNO\textsubscript{3}, CdCl\textsubscript{2}·2.5H\textsubscript{2}O, HgCl\textsubscript{2}, and Pb(NO\textsubscript{3})\textsubscript{2} were purchased from Aladdin Co., Shanghai, China. All chemical reagents and solvents used were purchased from commercial suppliers and used without further purification. Deionized water was used throughout the fluorescence determination.

\textsuperscript{1}H NMR and \textsuperscript{13}C NMR were recorded on a Bruker AV–300 NMR using trimethylsilane as an internal standard. Fluorescence spectra were recorded on a F380 spectrofluorometer (Tianjing Gangdong Technology Co. Ltd, China) with 5 nm slit for both excitation and emission. The excitation and emission wavelength were 370 and 495 nm, respectively. High Performance Liquid Chromatography-Mass spectra were performed on a Bruker Esquire 2000 HCT LC/MS system.

2. Synthesis of AHQB, 1-methyl-8-hydroxy quinolinium Iodide (MHQI), and 1-allyl-5-hydroxy quinolinium bromide (A5HQB)

The synthetic route of AHQB, MHQI, and A5HQB is shown in Scheme 1.
8-Hydroxyquinoline (2.90 g, 20 mmol) and acetone (15.0 mL) were placed in a 100 mL flask. After heated to 50 °C under stirring, a catalytic amount of KI was introduced, allyl bromide (3.63 g, 30 mmol) in 5.0 mL of acetone was then added dropwise within 5 min. The resultant mixture was refluxed for 24 h, yielding pale yellow precipitate. The mixture was cooled to room temperature and filtered, and the solid was washed with ethyl acetate and then dried to constant weight under vacuum at 40 °C, 2.85 g of AHQB as a pale yellow powder was obtained. Yield: 53.5%. \(^1\)H NMR (300 MHz, \(^6\)D-DMSO) \(\delta\) (ppm): 12.01 (s, 1H), 9.45 (d, 1H, J=6.0), 9.29 (d, 1H, J=6.0), 8.21 (m, 1H, J=6.0-15.0), 7.95 (m, 2H, J=6.0-30.0), 7.67 (t, 1H, J=9.0), 6.38 (m, 1H, J=6.0-27.0), 6.03 (d, 2H, J=6.0), 5.40 (d, 1H, J=6.0), 5.19 (d, 1H, J=15.0). \(^{13}\)C NMR (75 MHz, \(^6\)D-DMSO) \(\delta\) (ppm): 151.49,
8-Hydroxyquinoline (0.72 g, 5 mmol) and acetone (5.0 mL) were placed in a 50 mL flask. After heated to 50 °C under stirring, methyl iodide (1.06 g, 7.5 mmol) in 5.0 mL of acetone was added dropwise within 5 min, the resultant mixture was refluxed for 24 h, forming pale yellow precipitate. The mixture was cooled to room temperature and filtered, and the solid was washed with ethyl acetate and then dried to constant weight under vacuum at 40 °C, 0.72 g of MHQI as a pale yellow powder was obtained. Yield: 50.3%. \(^1\)H NMR (300 MHz, \(d_6\)-DMSO) \(\delta\) (ppm): 11.84 (s, 1H), 9.37 (d, 1H, \(J=6.0\)), 9.21 (d, 1H, \(J=9.0\)), 8.13 (m, 2H, \(J=3.0-12.0\)), 7.92 (m, 1H, \(J=6.0-21.0\)), 7.62 (m, 1H, \(J=3.0-9.0\)), 4.92 (s, 3H). MS(m/z) cal.: 286.98; found: 287.5. M.p.: 136.8-138.2 °C.

5-Hydroxyquinoline (100 mg, 6.9 mmol) and acetone (10.0 mL) were placed in a 50 mL flask. After heated to 50 °C under stirring, a catalytic amount of KI was introduced, then allyl bromide (125 mg, 1.0 mmol) in 3.0 mL of acetone was added dropwise within 5 min, the resultant mixture was refluxed for 24h, yielding orange precipitate. The mixture was cooled to room temperature and filtered, and the solid was washed with ethyl acetate and then dried to constant weight under vacuum at 40 °C, 0.11 g of A5HQB as an orange powder was obtained. \(^1\)H NMR (300 MHz, \(d_6\)-DMSO) \(\delta\) (ppm): 12.16 (s, 1H), 9.63 (d, 1H, \(J=6.0\)), 9.43 (d, 1H, \(J=9.0\)), 8.15 (m, 2H, \(J=3.0-12.0\)), 7.95 (d, 1H, \(J=9.0\)), 7.47 (d, 1H, \(J=9.0\)), 6.30 (m, 1H, \(J=6.0-27.0\)), 5.76 (d, 2H, \(J=6.0\)), 5.33 (m, 2H, \(J=9.0-39.0\)). \(^{13}\)C NMR (75 MHz, \(d_6\)-DMSO) \(\delta\) (ppm):
3. Preparation of solutions of AHQB, metal ions and anions

A stock solution of AHQB (1.0×10^{-3} mol·L^{-1}) was prepared by dissolving 2.7 mg of AHQB in 10.0 mL of deionized water. Solutions of various metal ions (Ca^{2+}, Zn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}; 1.0×10^{-3} mol·L^{-1}) were prepared by dissolving 0.01 mmol of the corresponding inorganic salts in 10.0 mL of deionized water. Solutions of various anions (F^{-}, Cl^{-}, Br^{-}, I^{-}, AcO^{-}, CN^{-}, H_{2}PO_{4}^{-}, and HSO_{4}^{-}; 1.0×10^{-3} mol·L^{-1}) were prepared by dissolving the corresponding tetra–butylammonium salts in deionized water.

4. General procedure for ions response

About 60 μL of AHQB solution and 300 μL of metal ion (or anion) solution were placed in a 3.0 mL cuvette, deionized water was then added to a total volume of 3.0 mL. All samples were prepared at room temperature, shaken for 10 s and rested for 2 h before fluorescence determination.

5. Titration of Hg^{2+}

Titration experiments were carried out at room temperature. Approximately 60 μL of AHQB solution and different volumes of Hg^{2+} solution were placed in a 3.0 mL cuvette. Deionized water was added to this mixture to a total volume of 3.0 mL. Characterization was performed by fluorospectrophotometer.
6. Anti-jamming investigation

Metal-Ion Competition Studies: Approximately 60 μL of AHQB solution, 300 μL of various metal ions, and 60 μL of Hg\textsuperscript{2+} solution were placed in a 3.0 mL cuvette. Deionized water was added to a total volume of 3.0 mL. Characterization was performed by fluorospectrophotometer.

Anion Competition Studies: Approximately 60 μL of AHQB solution, 300 μL of anion solution, and 60 μL of Hg\textsuperscript{2+} solution were placed in a 3.0 mL cuvette, deionized water was added to a total volume of 3.0 mL. Characterization was performed by fluorospectrophotometer.