Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

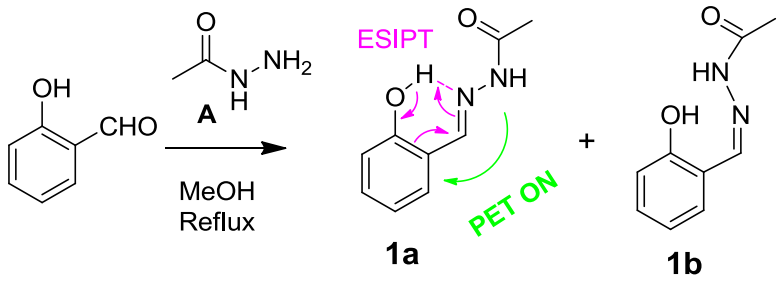
for

A Simple Sensitive ESIPT On-Off Fluorescent Sensor for Selective Detection of Al^{3+} in Water

Junfeng Wang,[a] Yi Pang[a,b]*

[a] Department of Chemistry & [b] Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325 U.S.A; E-mail: yp5@Uakron.edu

Synthesis of Dye 1



Scheme S1. Synthesis of Dye **1**

Acethydrazide **A** (150 mg, 2.03 mmol) and 2-hydroxybenzaldehyde **B** (245 mg, 2.01 mmol) were dissolved in MeOH (5.0 mL), and the mixture was heated to reflux for 2 hours. The resulting mixture was cooled down and the precipitate was collected by simple filtration to afford dye **1** in over 90% yield as needle-like crystals. The dye **1** could exist in the rotamers **1a** and **1b**.

Isomer **1a**: ^{1}H NMR (300 MHz, DMSO-d_6): 11.58 (1H, s), 11.18 (1H, s), 8.33 (1H, s, –CH=N–), 7.48 (1H, d, J = 7.5 Hz), 7.27 (1H, t, J = 7.5 Hz), 6.90 (2H, m), 1.97 (3H, s); ^{13}C NMR (75 MHz, DMSO-d_6): 165.4, 157.3, 146.4, 131.1, 129.5, 119.4, 119.2, 116.3, 21.3. HRMS Cal. $C_9H_{11}N_2O_2$ 179.0821: found M+H$^+$ 179.1028; M+Na$^+$ $C_9H_{10}N_2O_2Na$ Cal. 201.0640, found 201.0802.

^{1}H NMR (300 MHz, CD_3OD): 8.31 (1H, s), 7.43 (1H, d, J = 7.8 Hz), 7.34 (1H, t, J = 7.2 Hz), 6.97 (2H, m), 2.13 (3H, s).

Isomer **1b:** ^{1}H NMR (300 MHz, DMSO-d_6): 11.20 (1H, s), 11.10 (1H, s), 8.26 (1H, s, –CH=N–), 7.61 (1H, d, J = 7.8 Hz), 7.23 (1H, t, J = 7.8 Hz), 6.84 (2H, m), 2.17 (3H, s);

^{13}C NMR (75 MHz, DMSO-d_6): 171.4, 156.3, 140.9, 130.8, 126.8, 119.9, 118.5, 116.1, 20.3.

^{1}H NMR (300 MHz, CD_3OD): 8.22 (1H, s), 7.47 (1H, d, J = 8.1 Hz), 7.34 (1H, t, J = 8.1 Hz), 6.94 (2H, m), 2.34 (3H, s).

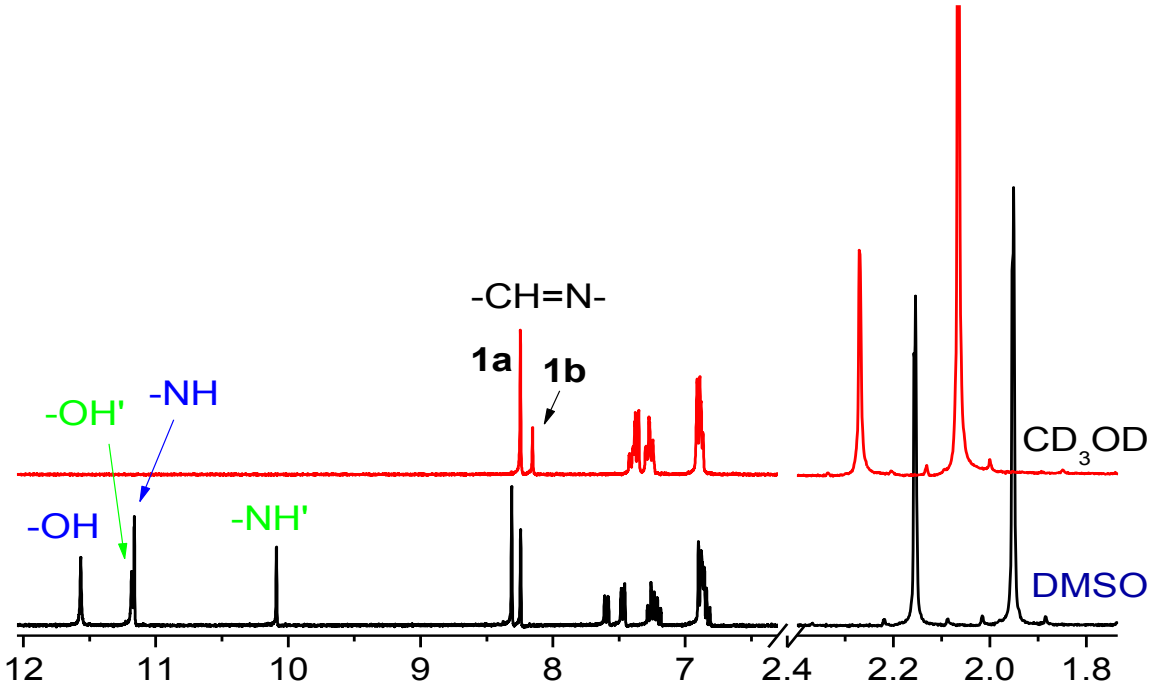


Figure S1. ^{1}H NMR spectra of dye **1** in deuterated Methanol and DMSO. The isomer ratio of **1a:1b** is dependent on the solvent.

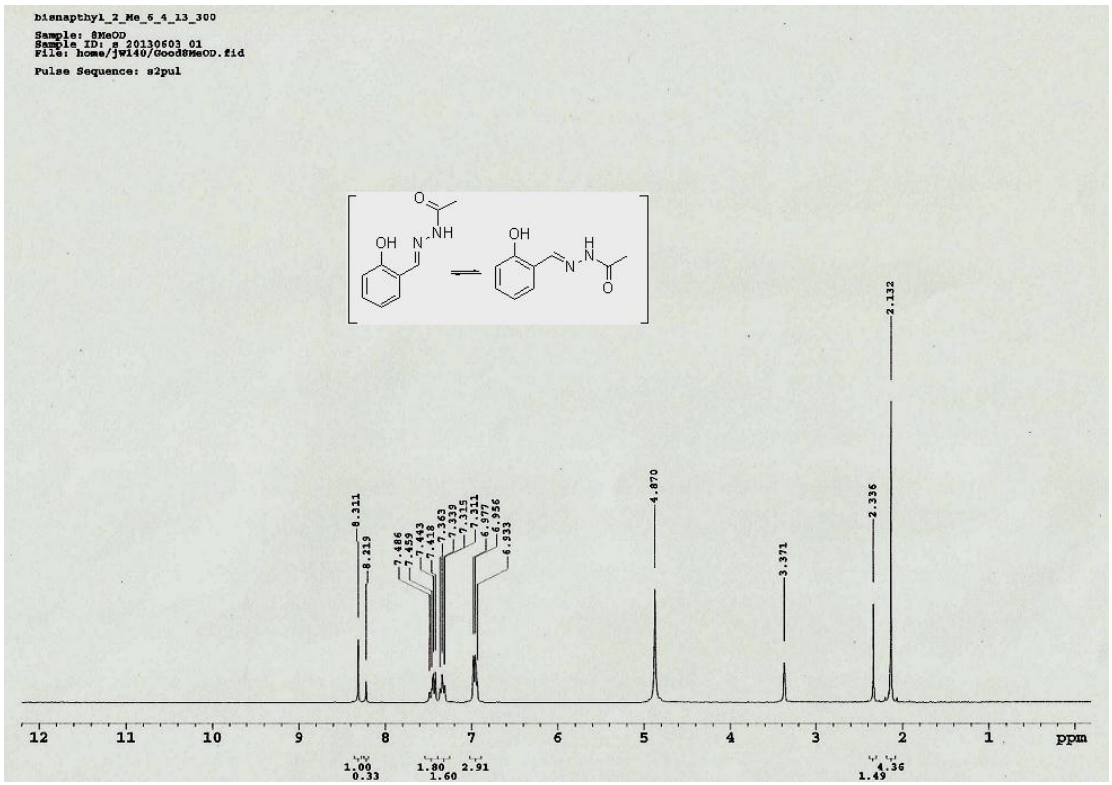


Figure S2. ^{1}H NMR of dye **1** in CD_3OD

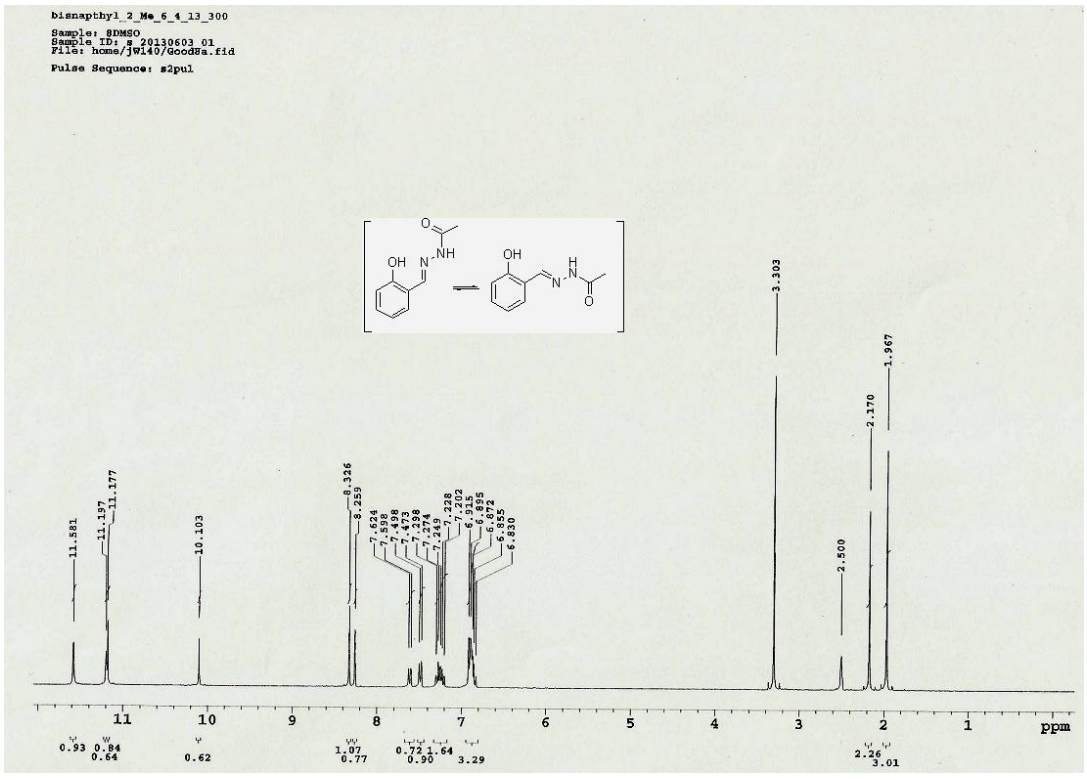


Figure S3. ^{1}H NMR of dye **1** in DMSO-d_6

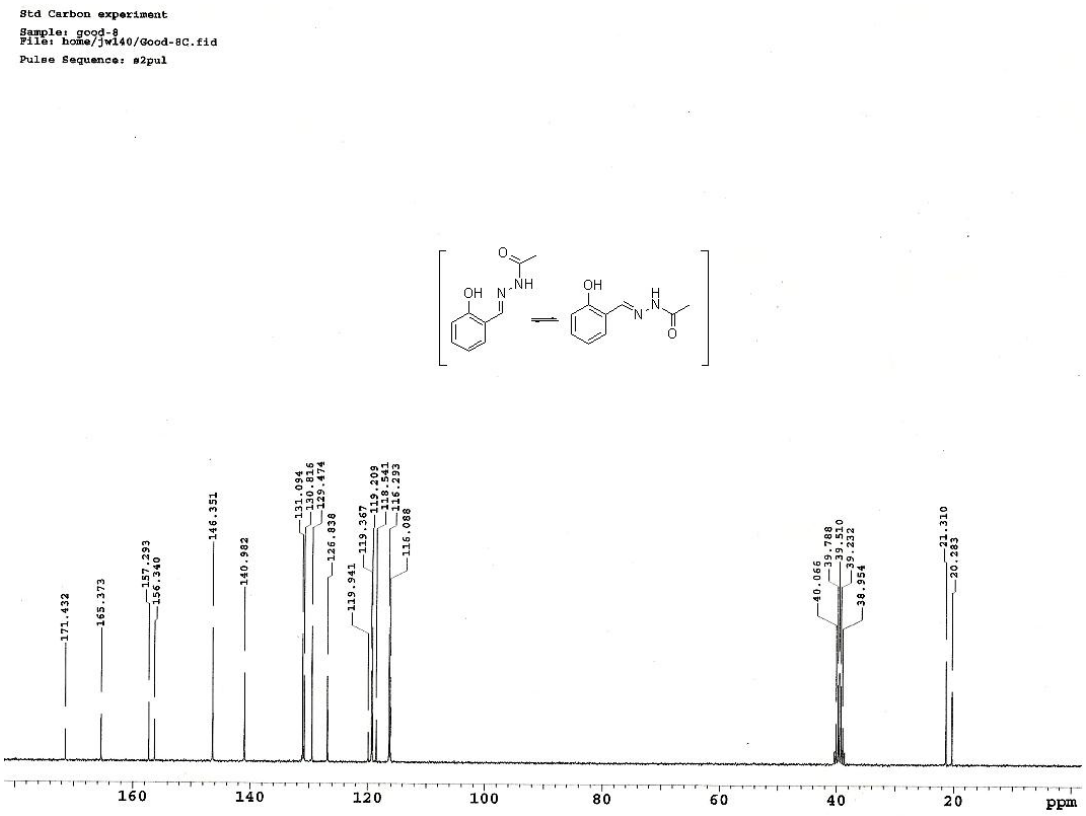
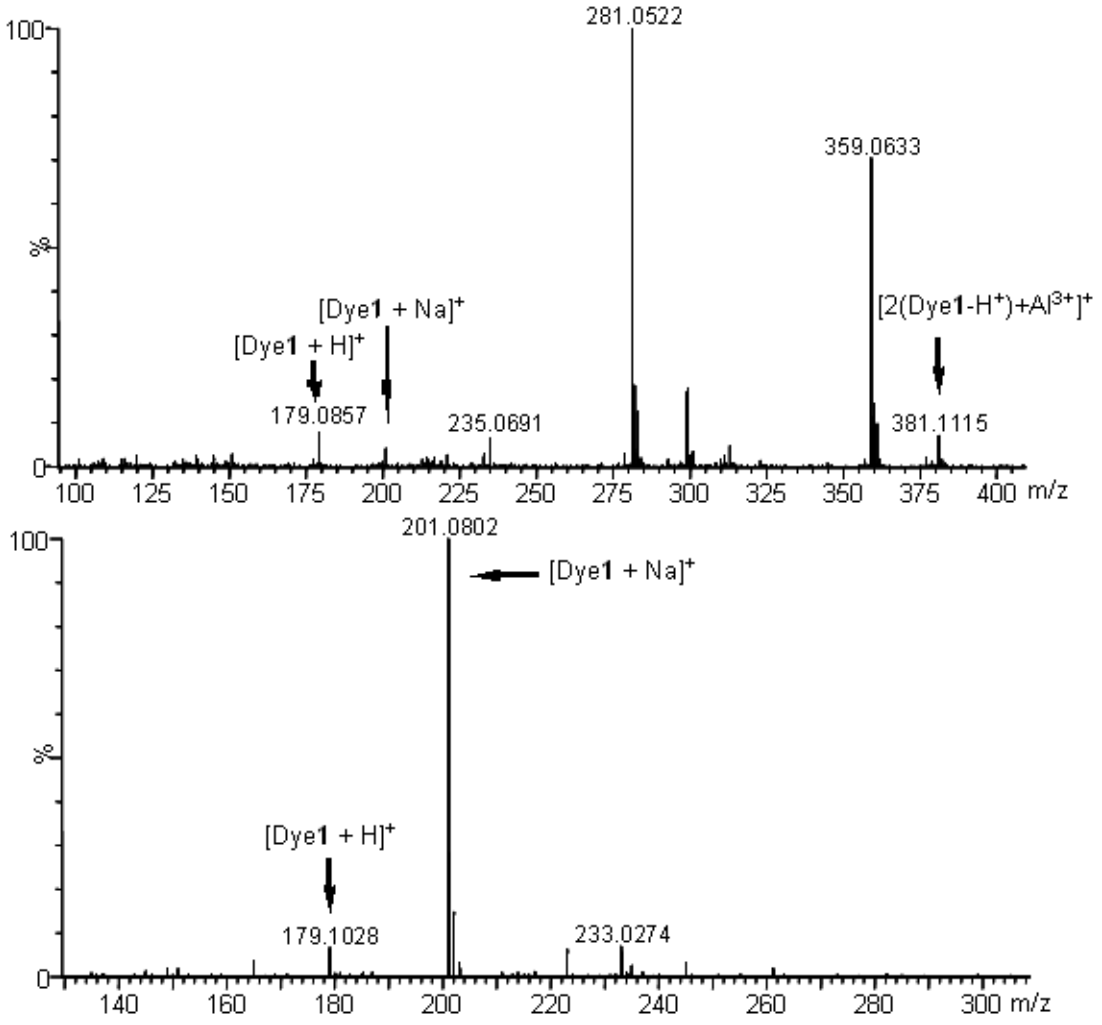


Figure S4. ^{13}C NMR of dye **1** in DMSO-d_6

(a)



(b)

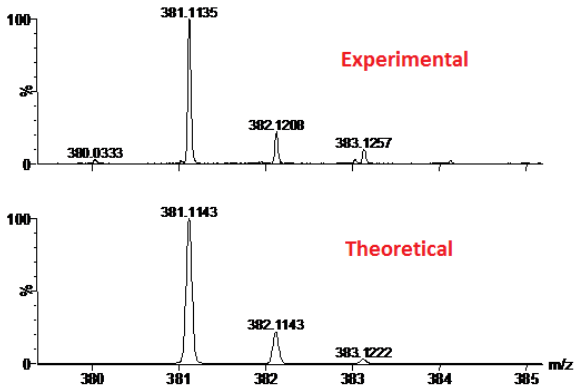


Figure S5. (a) HRMS of dye **1** and "dye **1** + Al^{3+}. (b) Experimental mass spectrum of the complex "dye **1**+Al^{3+}" matches the calculated pattern.

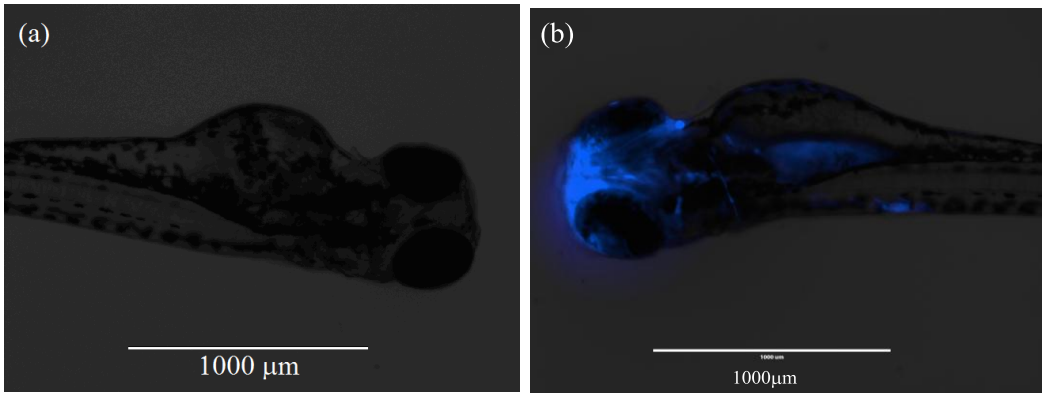


Figure S6a: Fluorescent images of Al^{3+} in Zebrafish at 96 hours post fertilization (hpf). (a) zebrafish exposed to dye **1** only in the fish tank at the concentration of 10 µM for 2 hours; (b) zebrafish exposed to 10 µM dye **1** and Al^{3+} for 2 hours.

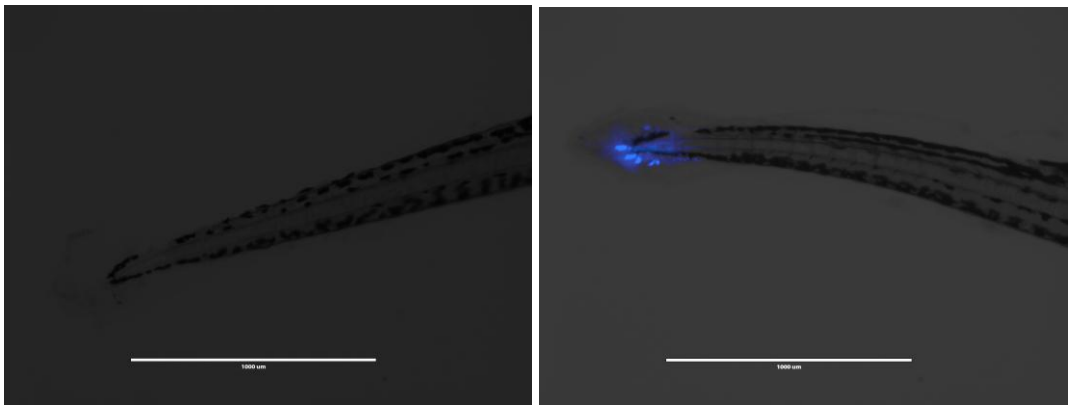


Figure S6b: Fluorescent images of Al^{3+} in Zebrafish at 96 hours post fertilization (hpf). (left) fish exposed to dye **1** only in the fish tank at the concentration of 10 µM for 2 hours; (right) fish exposed to 10 µM dye **1** and Al^{3+} for 2 hours. The scale bar represents 1000µm.

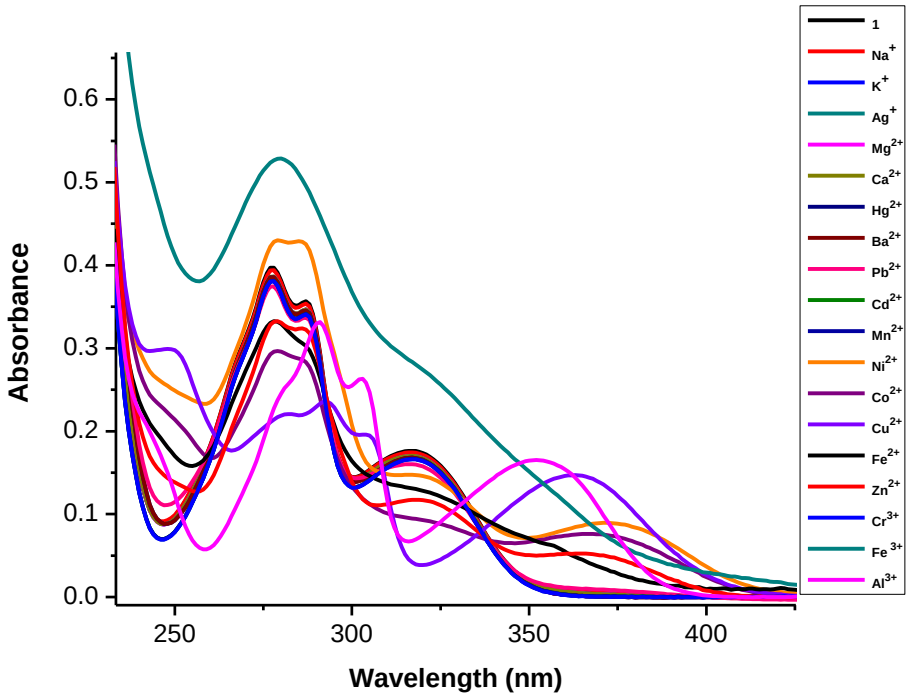


Figure S7. UV-vis spectra of **1** (20 μM) with various metal ions (5.0 equiv.) in pure water: Na^{+}, K^{+}, Ag^{+}, Mg^{2+}, Ca^{2+}, Hg^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Zn^{2+}, Cr^{3+}, Fe^{3+}, Al^{3+}.

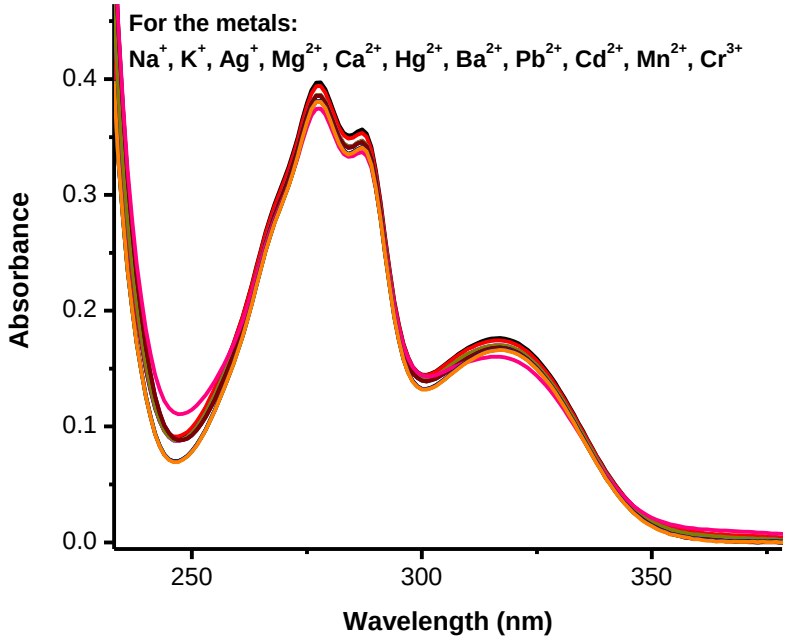


Figure S8. UV-vis spectra of **1** (20 μM) with various metal ions (5.0 equiv.) in pure water: Na^{+}, K^{+}, Ag^{+}, Mg^{2+}, Ca^{2+}, Hg^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}.

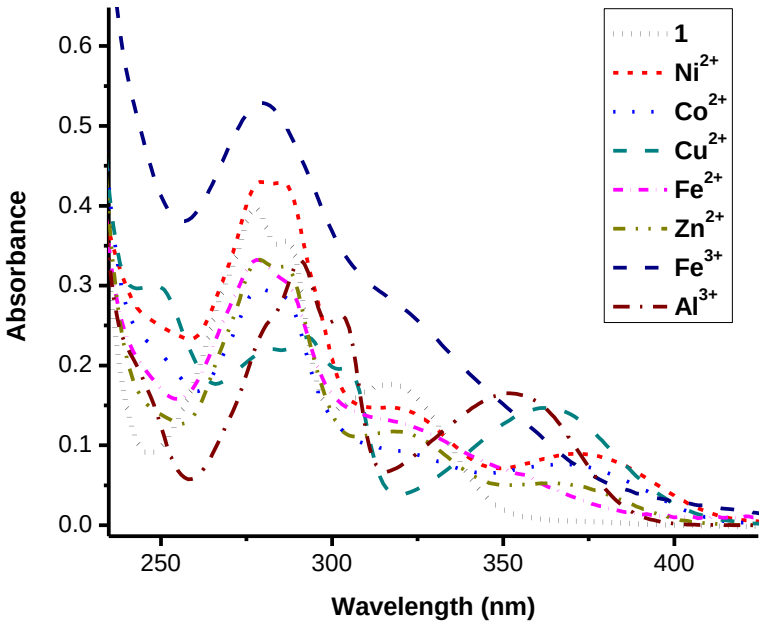


Figure S9. UV-vis spectra of **1** (20 μM) with various metal ions (5.0 equiv.) in pure water: Ni^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}.

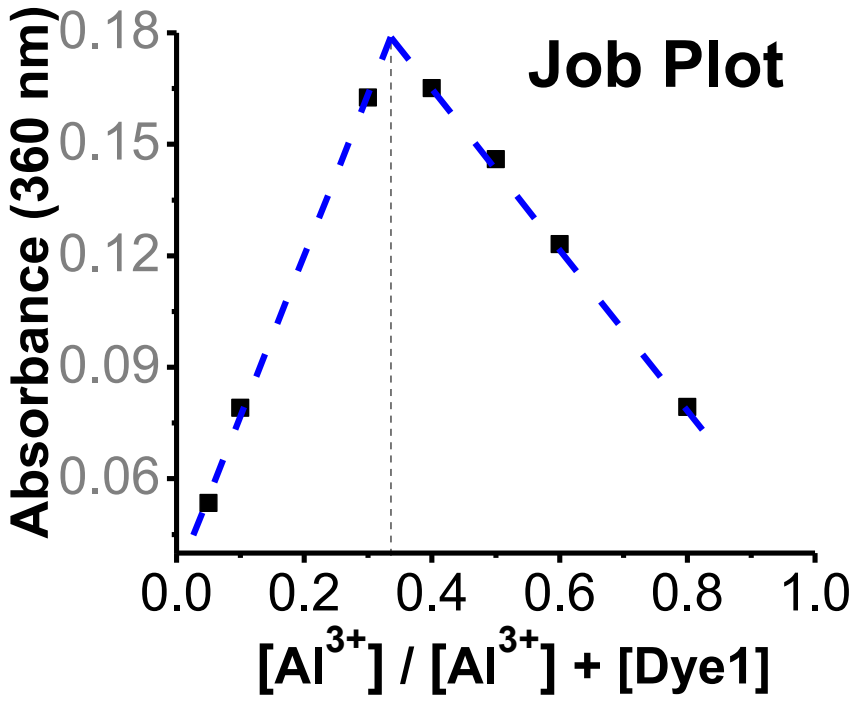


Figure S10. The Job's plot examined between dye **1** and Al^{3+}.

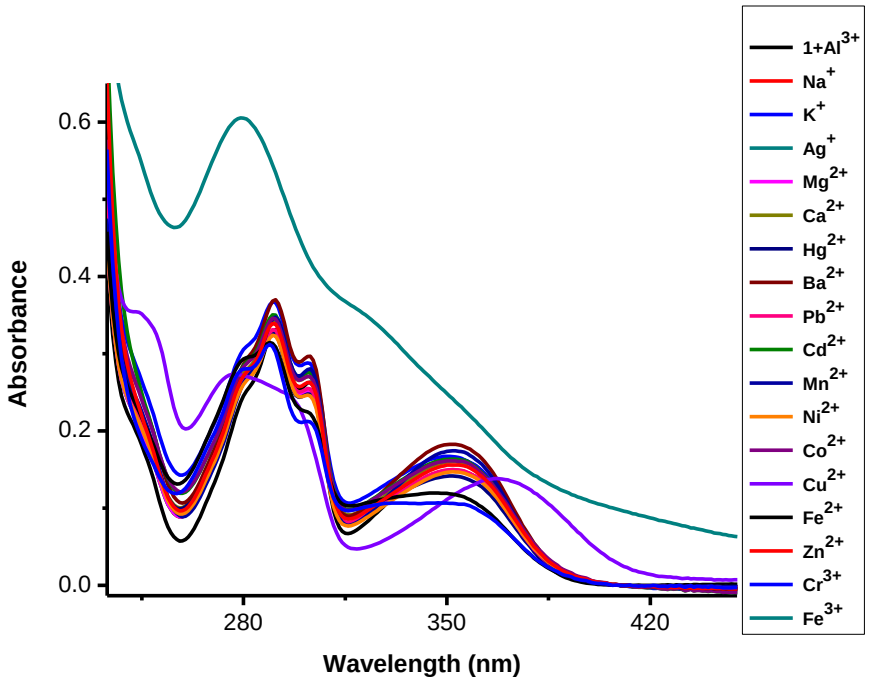


Figure S11. UV-vis spectra of **1** (20.0 μM) in complete water in the presence of 5.0 equiv. of Al^{3+} and the other metal ion(s): K^{+}, Na^{+}, Ag^{+}, Mg^{2+}, Ca^{2+}, Hg^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Zn^{2+}, Cr^{3+}, Fe^{3+}.

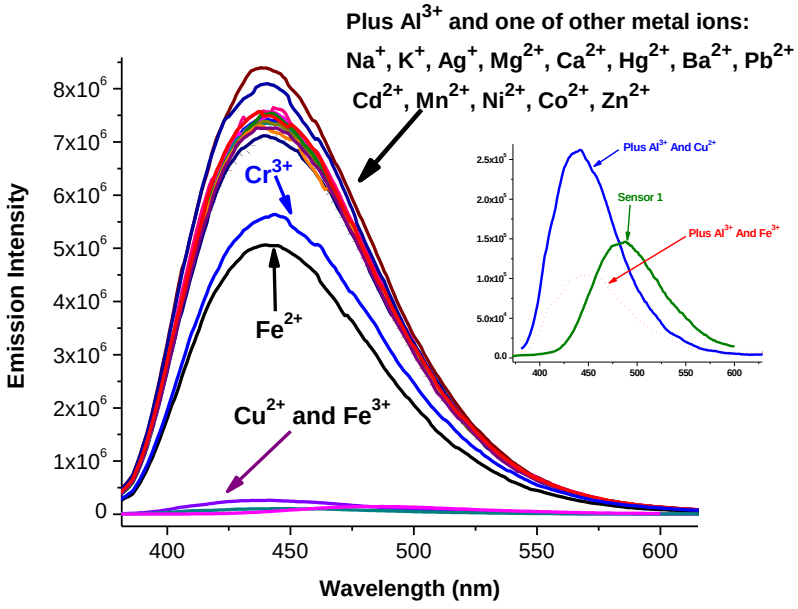


Figure S12. Fluorescence spectra of **1** (20.0 μM) in complete water in the presence of 5.0 equiv. of Al^{3+} and the other metal ion(s): K^{+}, Na^{+}, Ag^{+}, Mg^{2+}, Ca^{2+}, Hg^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Zn^{2+}, Cr^{3+}, Fe^{3+}.

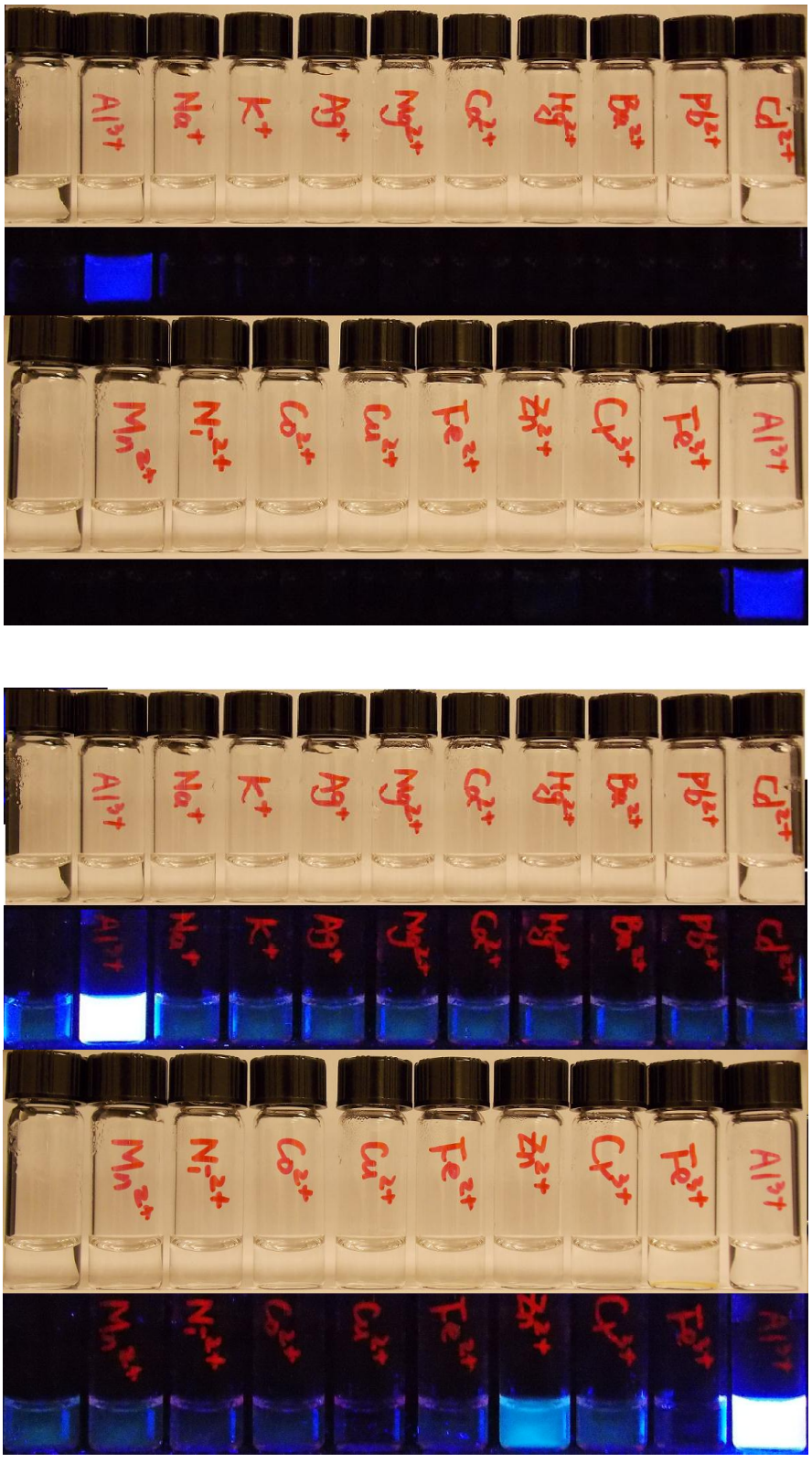


Figure S13. Fluorescent images of **1** (20.0 μM) in complete water in the presence of 5.0 equiv. of different metal ion.

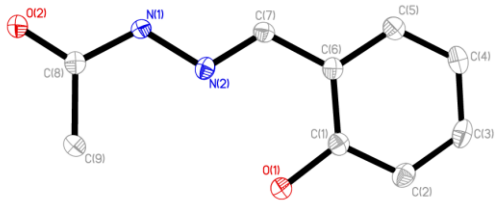


Figure S14. Crystal structure of **1a**, where hydrogen atoms are omitted for clarity.

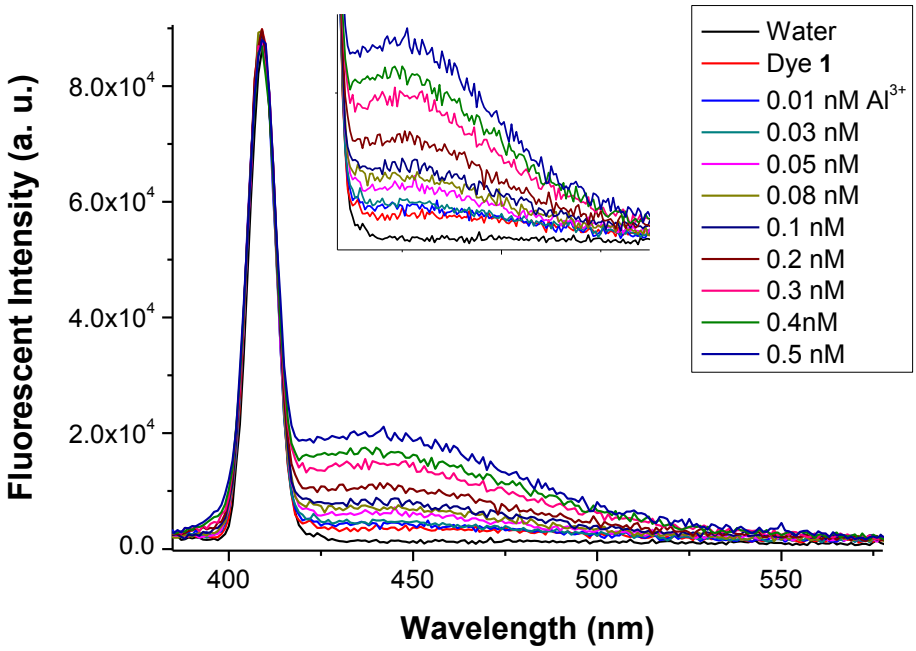


Figure S15. Fluorescent intensity of Dye **1** (120 nM) upon addition of different concentration of Al^{3+}. The sharp signal at ~410 nm was from the scattering of water. The inset at the top shows the enlarged region for 415-525 nm.