

A Turn-on and Reversible Schiff base Fluorescence Sensor for Al³⁺ ion

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Supplementary Data

2-(2-nitrophenoxy)ethanol (1)

To a solution of 2-nitrophenol (3.02 g, 21.7 mmol) in ethylene glycol (30 mL) was added K₂CO₃ (2.99 g, 21.6 mmol). The reaction mixture was refluxing for 10 h and extracted by CH₂Cl₂ and water. The organic layer was then dried over MgSO₄, filtered, and concentrated. The resulting residue was purified by silica column chromatography (Hexanes/EtOAc 10:1) to give **1** (2.78 g, 70%) as a brown oil; R_f 0.55 (EtOAc/ Hexane = 1 : 1); ¹H NMR (300 MHz, CDCl₃) δ: 7.61 (dd, *J* = 1.8, 8.1 Hz, 1H), 7.36 (td, m, 1H), 6.93 (dd, *J* = 8.1 Hz, 1H), 6.85 (td, *J* = 0.6, 7.8 Hz, 1H), 4.031 (t, *J* = 4.5, 4.6 Hz, 2H), 3.777 (t, *J* = 4.5, 4.6 Hz, 2H), 3.423 (s, 1H) ; ¹³C NMR (75MHz, MeOD) δ: 155.9, 139.2, 134.3, 125.2, 120.3, 114.7, 70.9, 60.2

(E)-2-(((2-(2-hydroxyethoxy)phenyl)imino)methyl)phenol (2)

A mixture of **8** (2.00 g, 11.0 mmol) and 10% Pd-C (0.14 g) in methanol (20 mL) was stirred under H₂ atmosphere (balloon pressure) for 12 h when the starting material was completely consumed. The reaction mixture was filtered and the filtrate was concentrated to get the crude amine product. The crude amine product was added to a solution of 2-hydroxybenzaldehyde (1.37 g, 11.2 mmol) in dry EtOH. The reaction mixture was stirred at the room temperature for 4 h and the EtOH was removed. The resulting residue was purified by silica column chromatography

(Hexanes/EtOAc 10:1) to give **2** (1.98 g, 66%) as a yellow solid; m.p = 94°C; R_f 0.43

(EtOAc/ Hexane = 1 : 1); ¹H NMR (300 MHz, MeOD) δ: 8.72 (s, 1H), 7.35 (dd, *J* =

1.5, 4.5 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.14 (td, *J* = 1.5, 7.4 Hz, 1H), 6.98 (d, *J* = 8.0

Hz, 1H), 6.95 (td, *J* = 1.2, 7.0 Hz, 1H), 6.79 – 6.73 (m, 2H), 4.50 (s, 1H), 4.01 (t, *J* =

4.8 Hz, 2H), 3.82 (t, *J* = 4.8 Hz, 2H); ¹³C NMR (75 MHz, MeOD) δ: 164.4, 163.1,

153.7, 137.5, 134.7, 133.8, 129.4, 122.8, 120.8, 120.5, 119.8, 118.7, 114.9, 71.7, 61.9;

HRMS (ED): Calcd for C₁₅H₁₆NO₃ (M+H), m/z 258.1130; found m/z 258.1135.

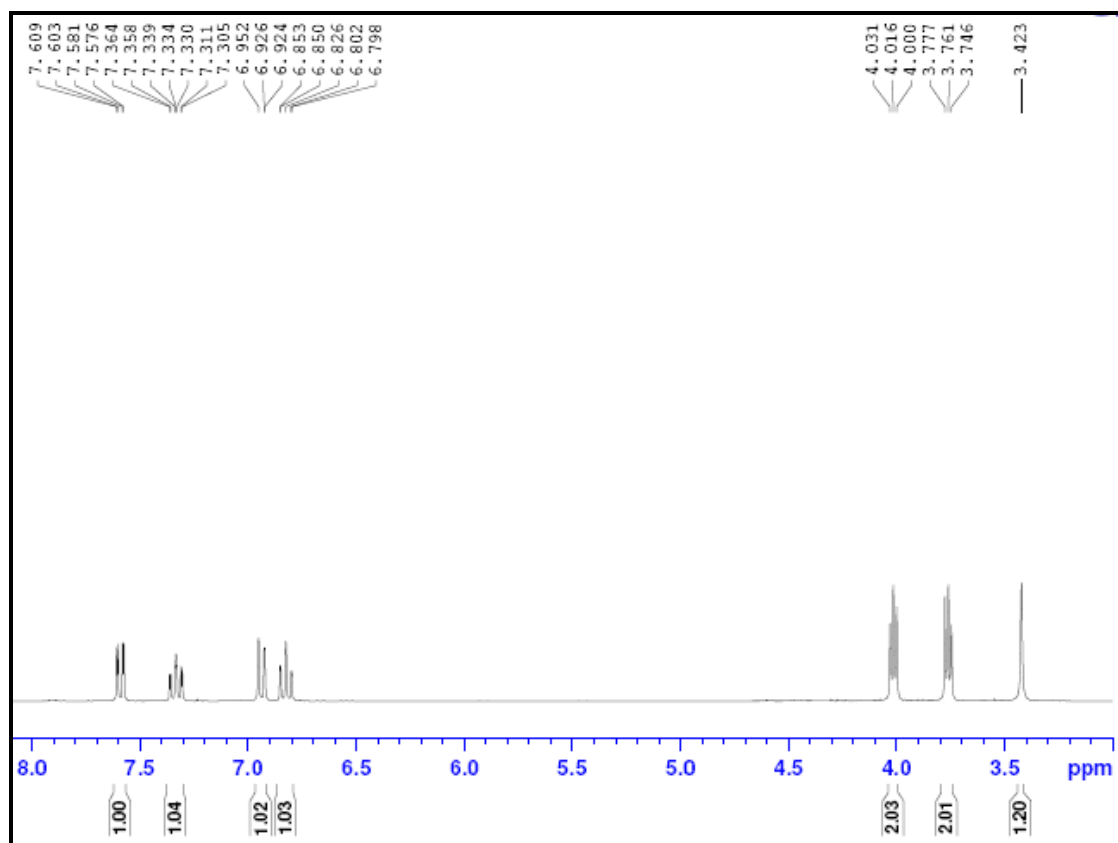


Fig. S1 ¹H NMR Spectra of **1**.

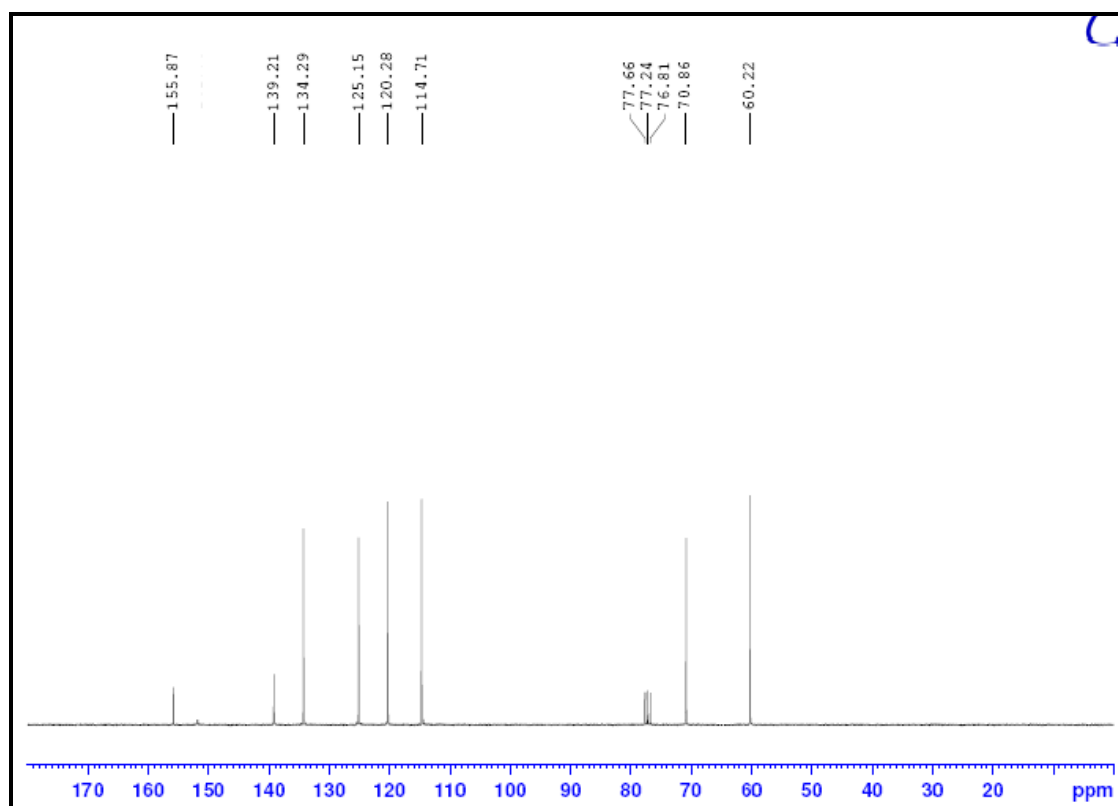


Fig. S2 ¹³C NMR Spectra of **1**.

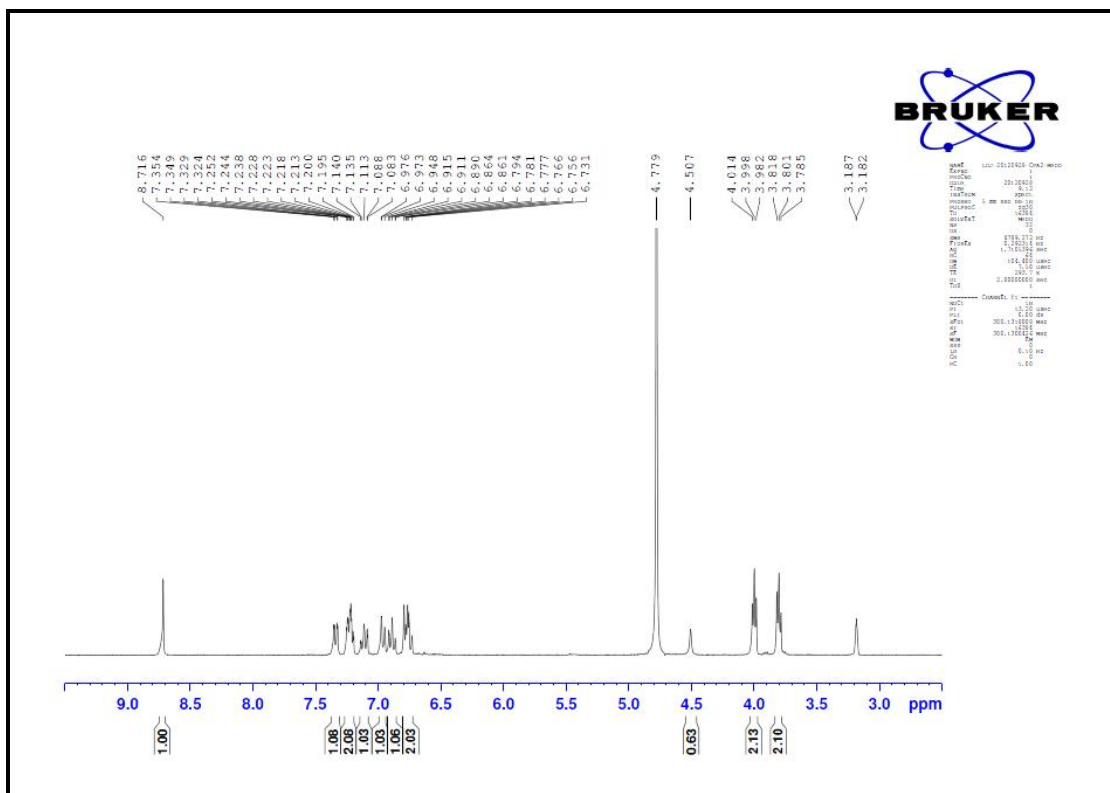


Fig. S3 ¹H NMR Spectra of 2.

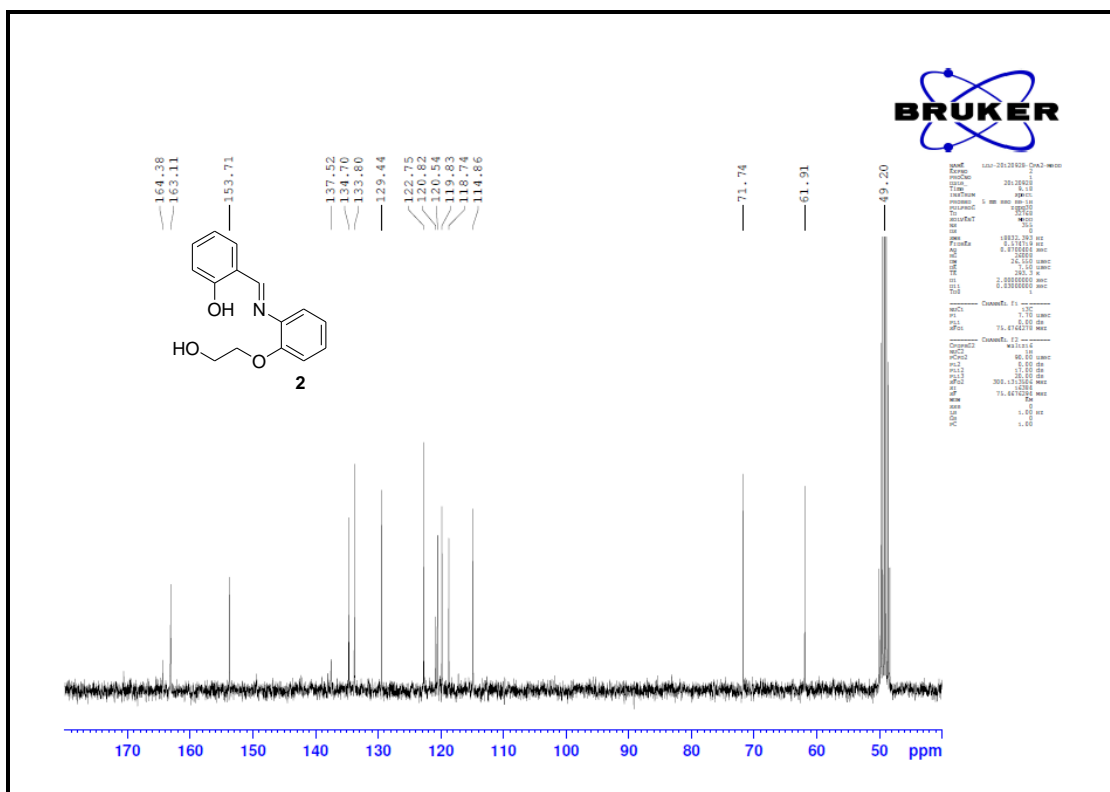


Fig. S4. ¹³C NMR Spectra of 2.

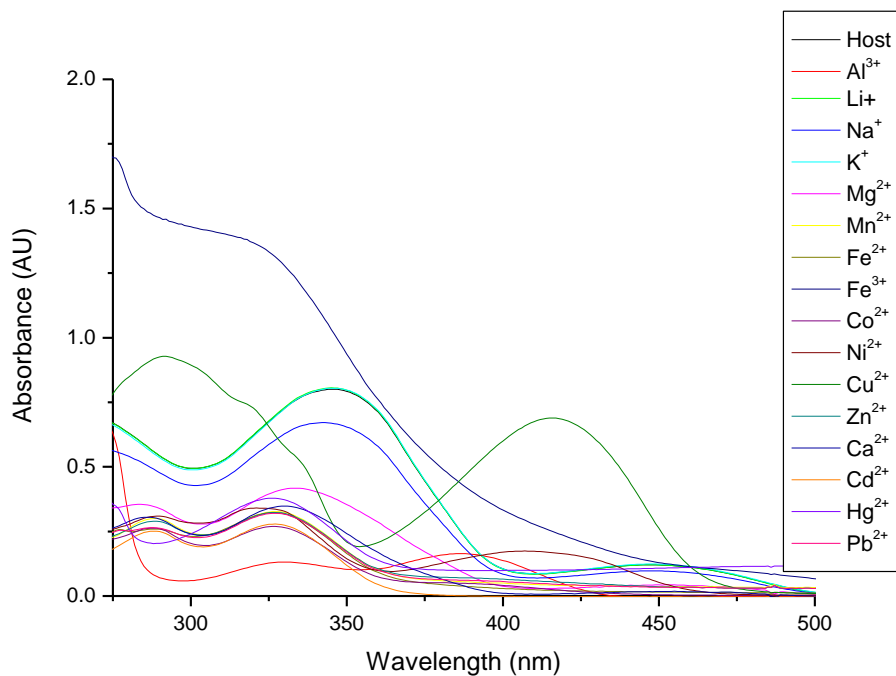


Fig. S5 UV/vis spectra of **1** (80 μM) recorded in EtOH-H₂O (95:5 v/v) after addition of 10 equiv of various metal ions.

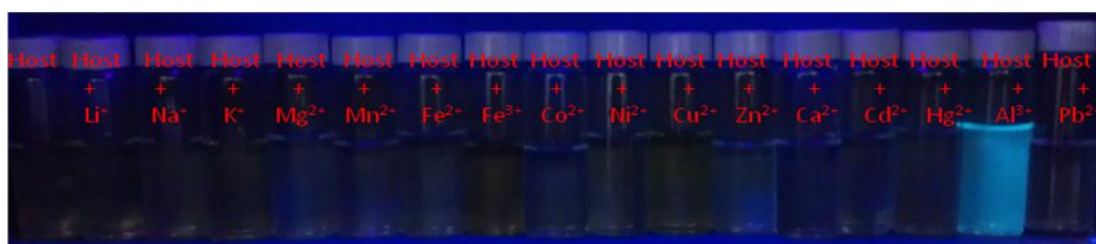


Fig. S6 Fluorescence changes excited by UV lamp ($\lambda_{\text{ex.}} = 346 \text{ nm}$) of receptor **2** upon addition of 10 equiv of various metal cations in EtOH-H₂O (95:5 v/v).

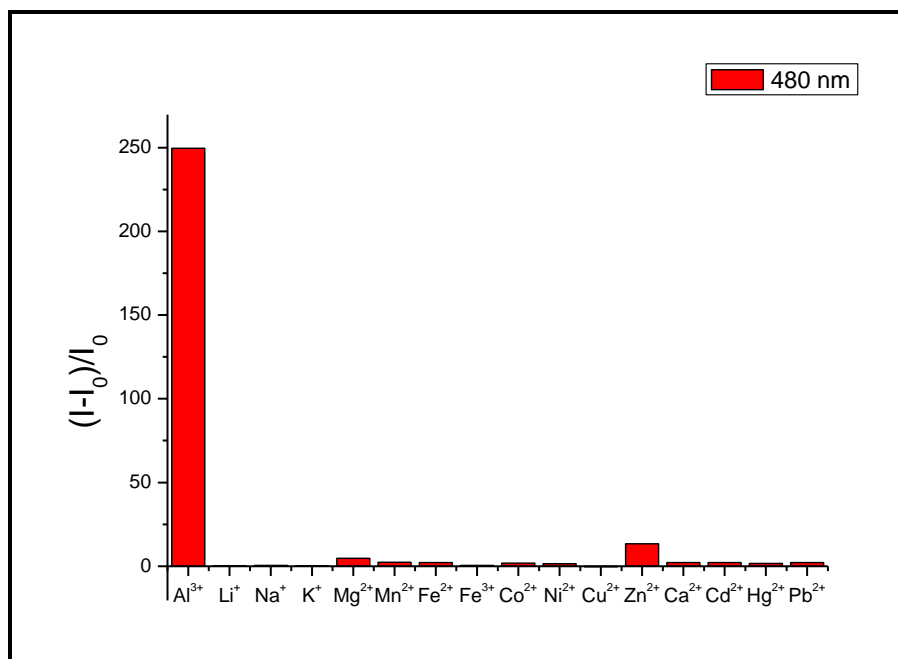


Fig. S7 Variation of the fluorescence intensity at 480 nm ($\lambda_{ex.} = 346$ nm) of receptor **2** (80 μ M) in the presence of 10.0 equiv of various metal ions in EtOH-H₂O (95:5 v/v).

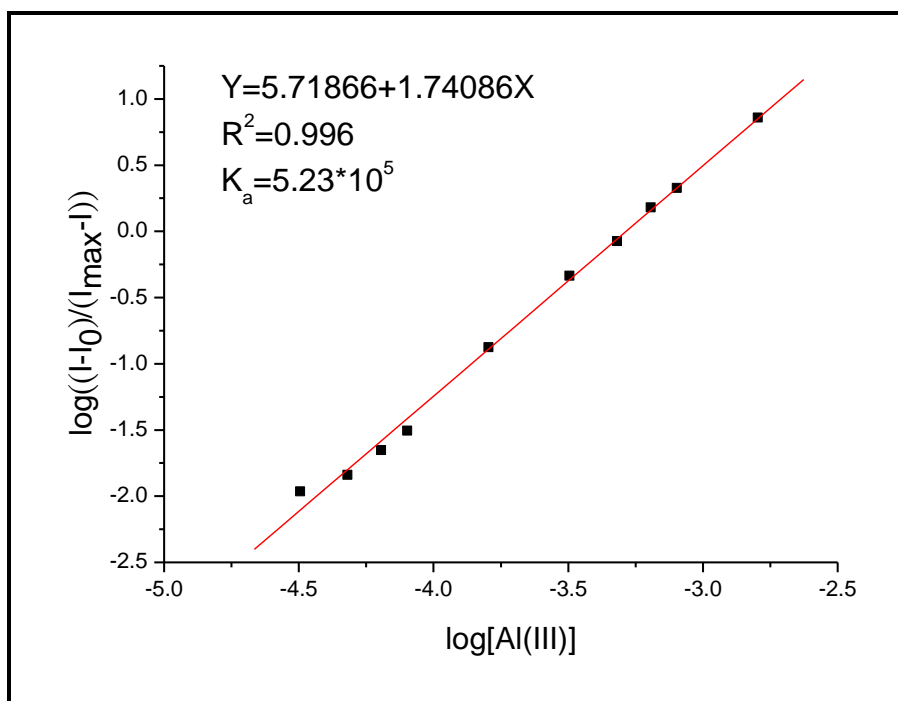


Fig. S8 Hill plot

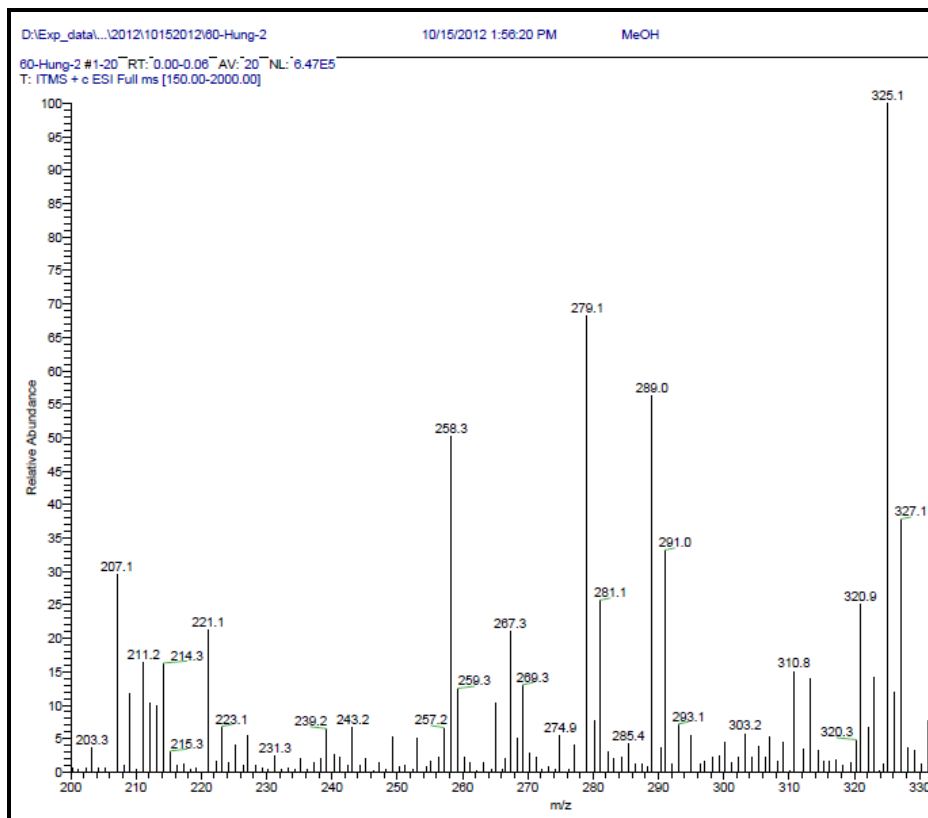


Fig. S9 ESI Mass spectrum for [receptor 2-Al³⁺+H₂O+ Na⁺] complex

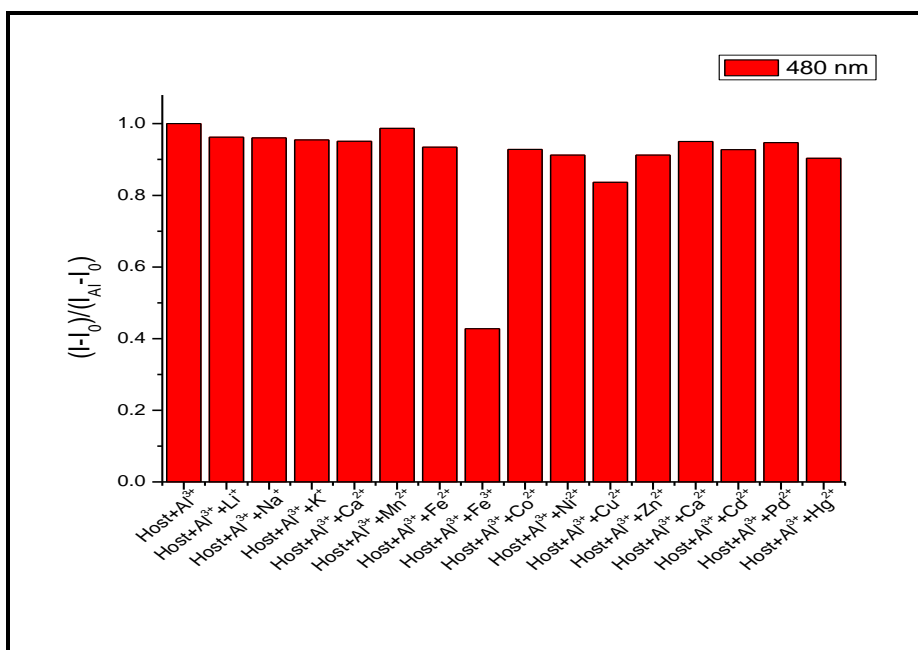


Figure S10. Competition experiment of receptor **2** towards Al³⁺ in the presence of 10 equiv of other cations. [2] = 80 μM, [Al³⁺] = 800 μM, and [Xⁿ⁺] = 800 μM in EtOH-H₂O (95:5 v/v). λ_{ex} = 346 nm.

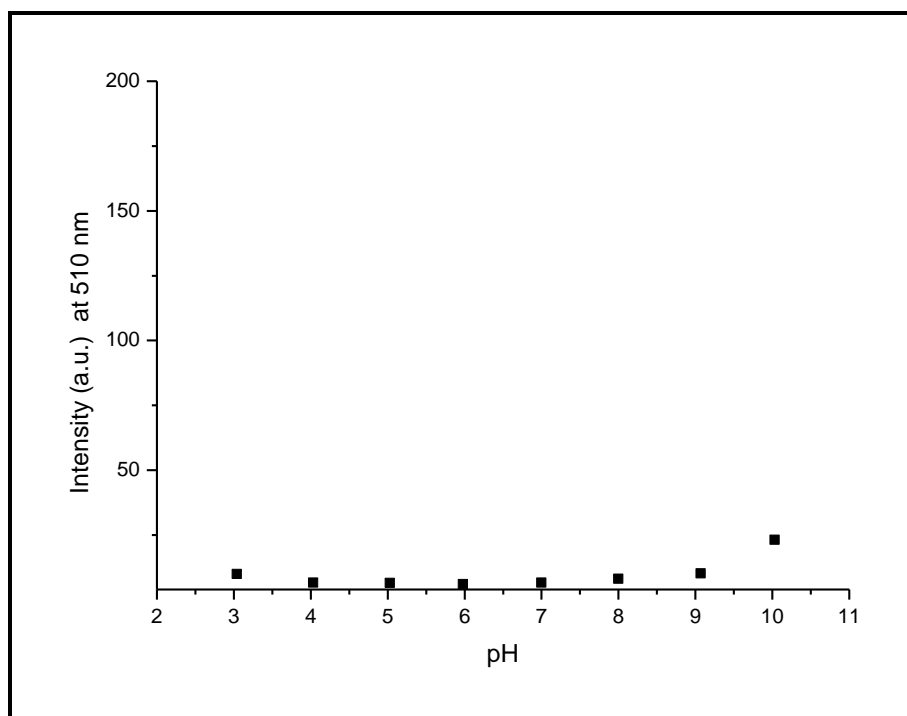


Fig. S11 Variation of fluorescence spectra of receptor **2** in EtOH-H₂O (95:5 v/v) as a function of pH at 510 nm; $\lambda_{\text{ex}}=346$ nm

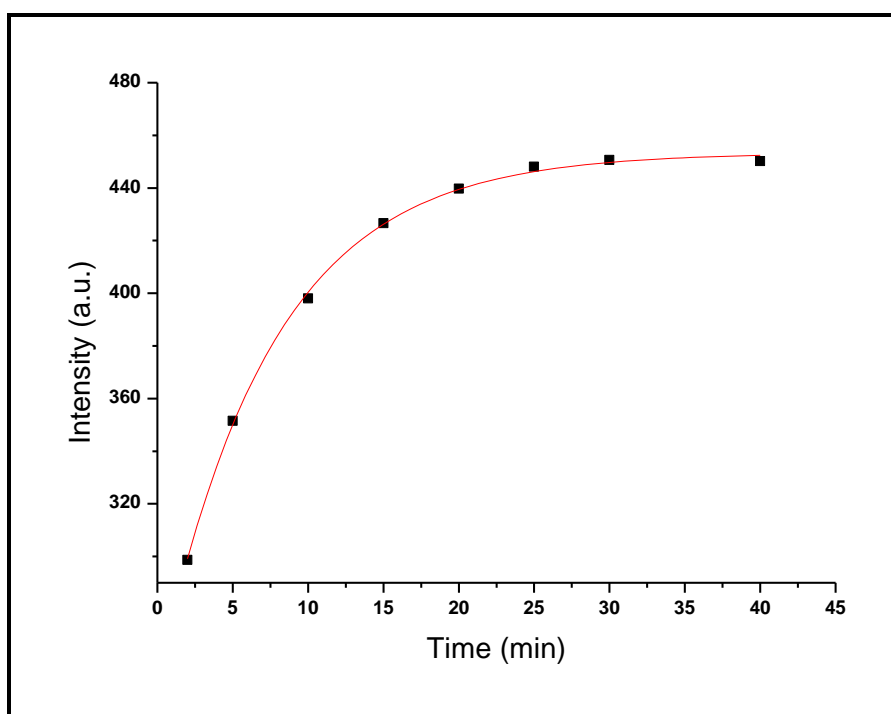


Fig. S12 Time evolution of receptor **2** in EtOH-H₂O (95:5 v/v) in the presence of 10 equiv of Al³⁺ ion.