# Supporting Information for:

# A Novel ppb-Level Sensitive and Highly Selective Europium-Based Diketone Luminescent Sensor for the Quantitative Detection of Aluminum Ions in Water Samples

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Crystal Structure

Single crystal X-ray data for the investigated compound was collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and dual Mo and Cu microfocus sealed X-ray source as well as a low-temperature Oxford Cryostream 800 liquid nitrogen cooling system at 100(2) K. Data collection strategy was calculated within CrysAlisPro (1.171.40.12b; Rigaku Oxford Diffraction, 2018) to ensure desired data redundancy and percent completeness. Unit cell determination, initial indexing, data collection, frame integration, Lorentz-polarization corrections and final cell parameter calculations were carried out using CrysAlisPro. An absorption correction was performed using the SCALE3 ABSPACK scaling algorithm embedded within CrysAlisPro. The structure was solved using ShelXT[1], all non-hydrogen atoms were refined anisotropically using ShelXL[2] and space group was unambiguously verified by PLATON[3]. All hydrogen atoms were attached via the riding model at calculated positions. Olex2[4] was used for the preparation of the published materials.

| **Empirical Formula** | $C_{42}H_{36}EuF_9N_2O_6S_3$ |
|---|---|
| **Formula Weight** | 1083.87 |
| **Temperature (K)** | 219.9(3) |
| **Crystal System** | Orthorhombic |
| **Space group** | $P2_12_12_1$ |
| **a (Å)** | 11.83190(10) |
| **b (Å)** | 14.77490(10) |
| **c (Å)** | 26.3973(3) |
| **α (°)** | 90 |
| **β (°)** | 90 |
| **γ (°)** | 90 |
| **Volume ($Å^3$)** | 4614.65(6) |
| **Z** | 4 |
| **Density calculated (g/mL)** | 1.560 |
| **Absorption coefficient ($mm^{-1}$)** | 11.733 |
| **θmax (°)** | 80.273 |
| **Reflections Collected** | 36297 |
| **Independent Reflections** | 9870 |
| **Absorption Correction** | spherical harmonics |
| **Goodness-of-Fit on $F^2$** | 1.028 |
| **Final R Indices [I>2sigma(I)]** | R1 = 0.0368, wR2 = 0.0938 |
| **R Indices (all data)** | R1 = 0.0396, wR2 = 0.0953 |
| **Largest Diff. Peak and Hole** | 0.799 and -0.547 e.$Å^{-3}$ |

**Table S1**: Crystal structure data for the $Eu(tta)_3$([4,4'-$(t\text{-}bu)_2$-2,2'-bpy)] complex.

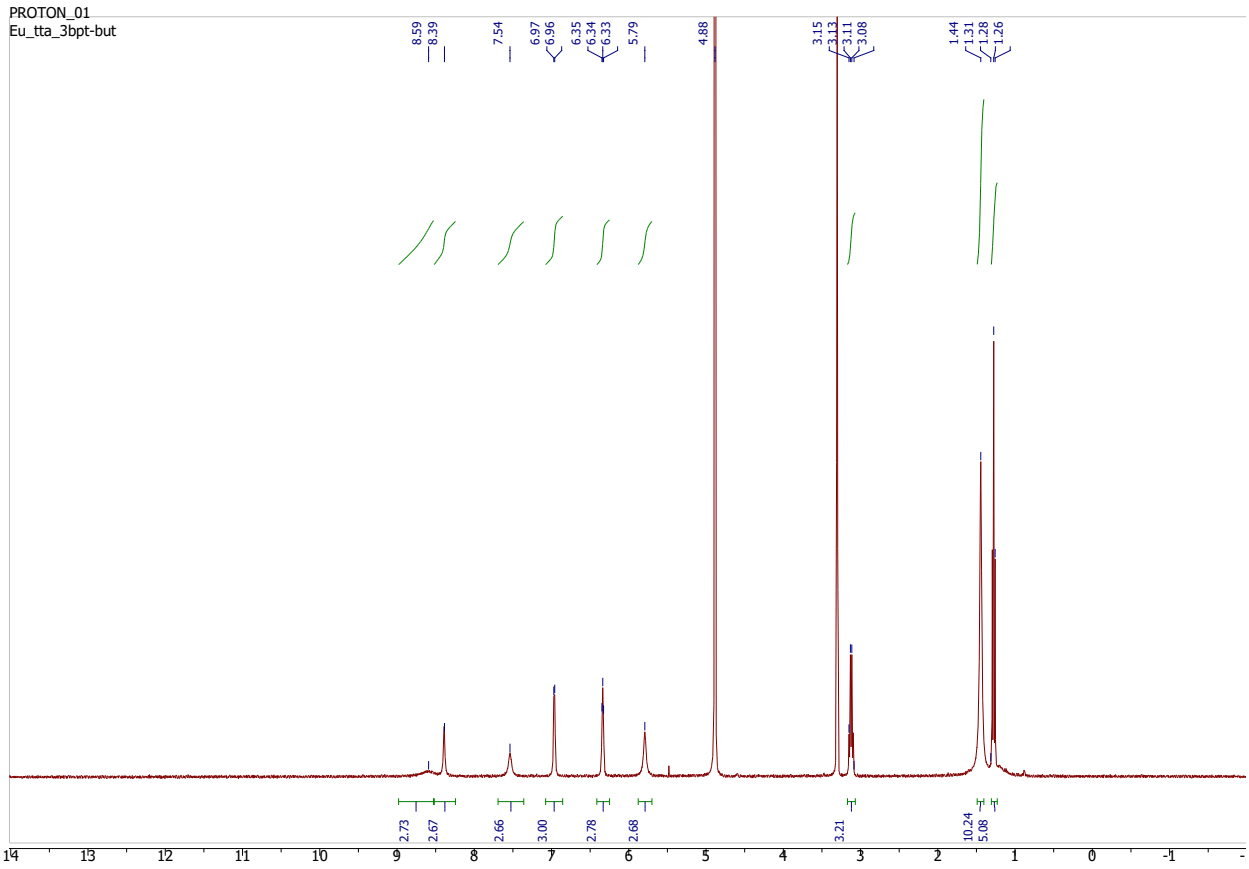



Figure S1: $^{1}H$ NMR spectrum of $Eu(tta)_3([4,4'\text{-}(t\text{-}bu)_2\text{-}2,2'\text{-}bpy)]$ (complex **1**).

$^{1}H$ NMR (500MHz, $CD_3OH$, 25 °C), δ (ppm) = 8.59 (s, 3H, Protons attach to aromatic ring in thenoyltrifluoroacetone ligand), 8.39 (s, 3H, Protons attach to aromatic ring in thenoyltrifluoroacetone ligand), 7.54 (s, 3H, Protons attach to aromatic ring in thenoyltrifluoroacetone ligand), 6.96 {d, 3H, J = 5 Hz, Protons attach to aromatic ring in 4,4'-(t-bu)$_2$-2,2'-bpy ligand}, 6.34 {t, 3H, J = 5 Hz, Protons attach to aromatic ring in 4,4'-(t-bu)$_2$-2,2'-bpy ligand}, 5.79 (s, 3H, protons place between diketone group in thenoyltrifluoroacetone ligand), 3.12 {q, 3H, J = 15 Hz, protons from tertiary butyl group in 4,4'-(t-bu)$_2$-2,2'-bpy ligand}, 1.44 {s, 10 H, protons from tertiary butyl group in 4,4'-(t-bu)$_2$-2,2'-bpy ligand}, 1.28 {t, 5H, J = 15 Hz, protons from tertiary butyl group in 4,4'-(t-bu)$_2$-2,2'-bpy ligand}, 4.88 (water), 3.31 ($CD_3OH$, solvent).

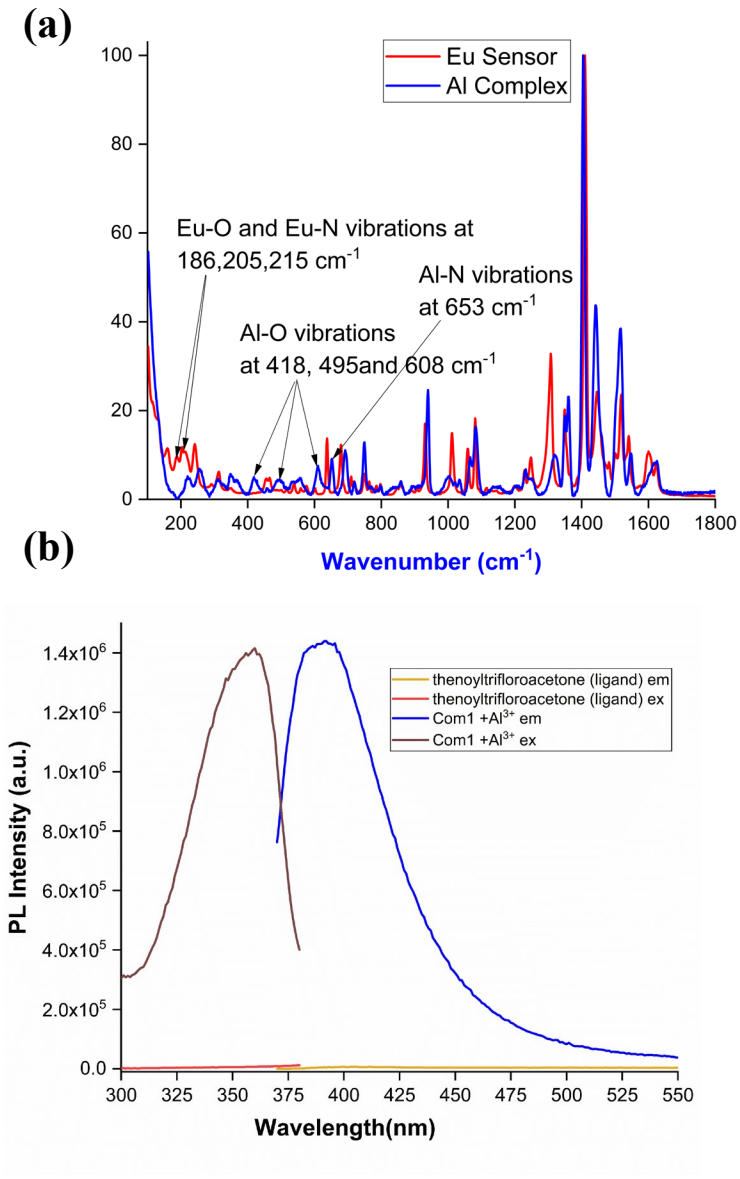
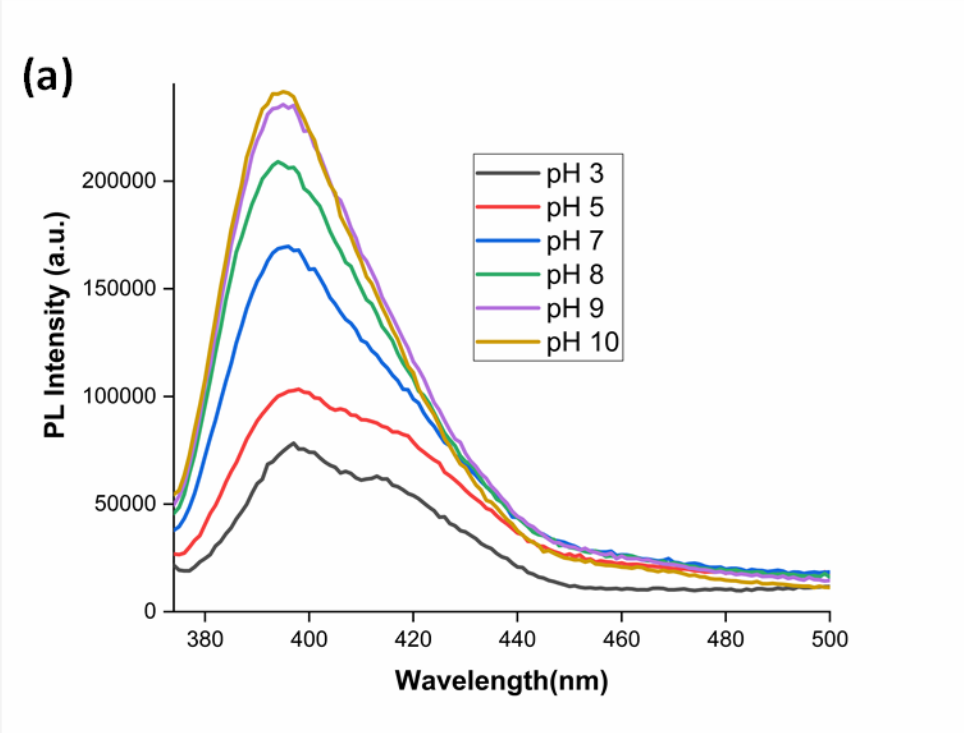
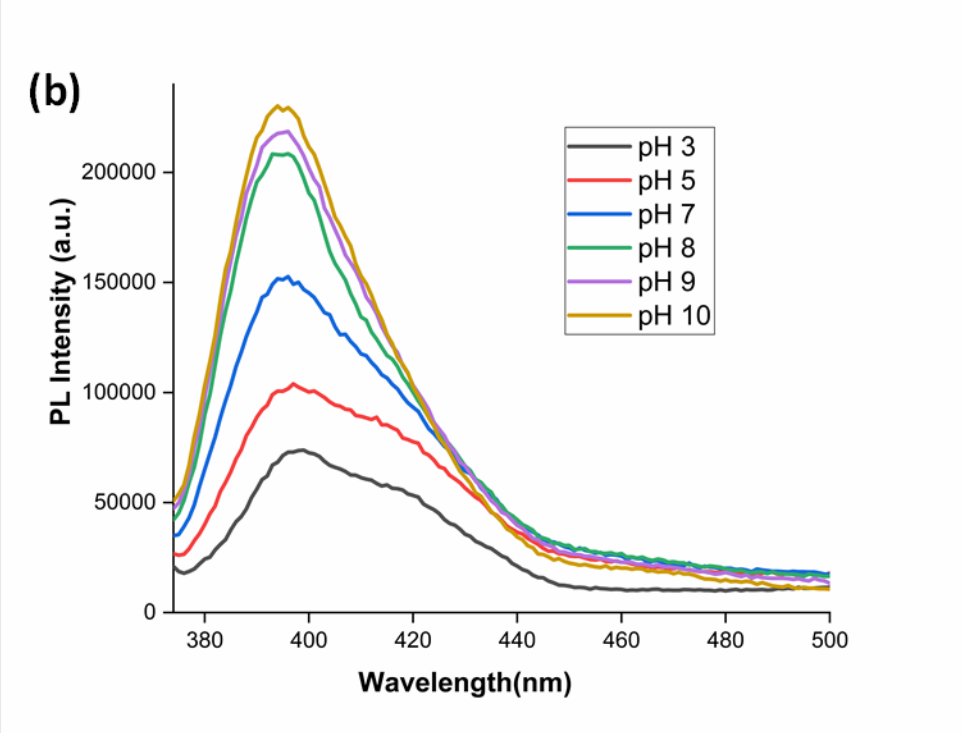



Figure S2: (a)Raman spectra of complex **1** with and without $Al^{3+}$ ions (normalized scattering intensity). (b) The emission spectrum of thenoyltrifluoroacetone (tta) and the Complex1+ $Al^{3+}$.


(a)
PL Intensity (a.u.)
0
50000
100000
150000
200000
380
400
420
440
460
480
500
Wavelength(nm)
pH 3
pH 5
pH 7
pH 8
pH 9
pH 10


(b)
PL Intensity (a.u.)
0
50000
100000
150000
200000
380
400
420
440
460
480
500
Wavelength(nm)
pH 3
pH 5
pH 7
pH 8
pH 9
pH 10

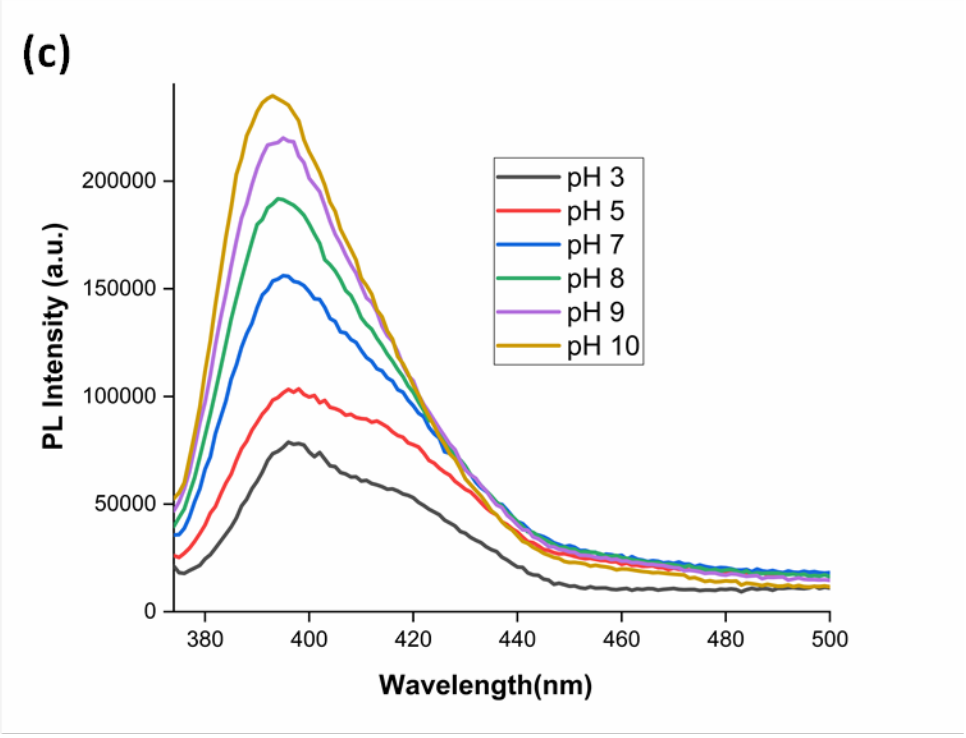



Figure S3: Effect of pH towards $Al^{3+}$ sensing in methanol (excitation at 364 nm; emission at 398 nm). (a) Trial 01. (b) Trial 02. (c) Trial 03.

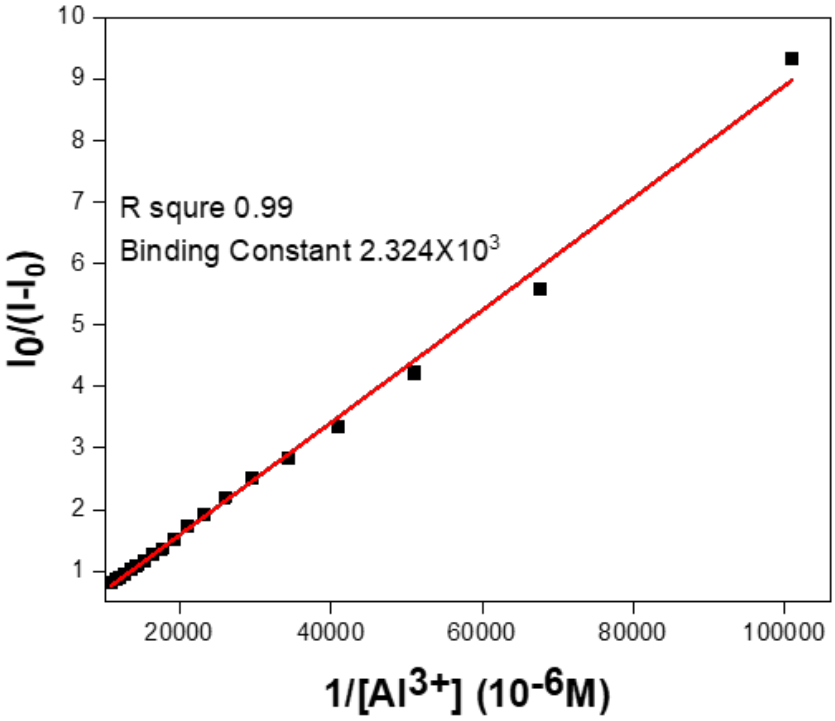


Figure S4: Determination of binding constant for $Al^{3+}$ sensing in methanol. The Equation used for the calculation is $I_0/(I-I_o) = I_0/(K_a(I-I_o)[Al^{3+}]^{1/2}) + I_0/(I-I_o)$ . Ka (binding constant) was solved by Intercept/slop of the graph.[5,6]

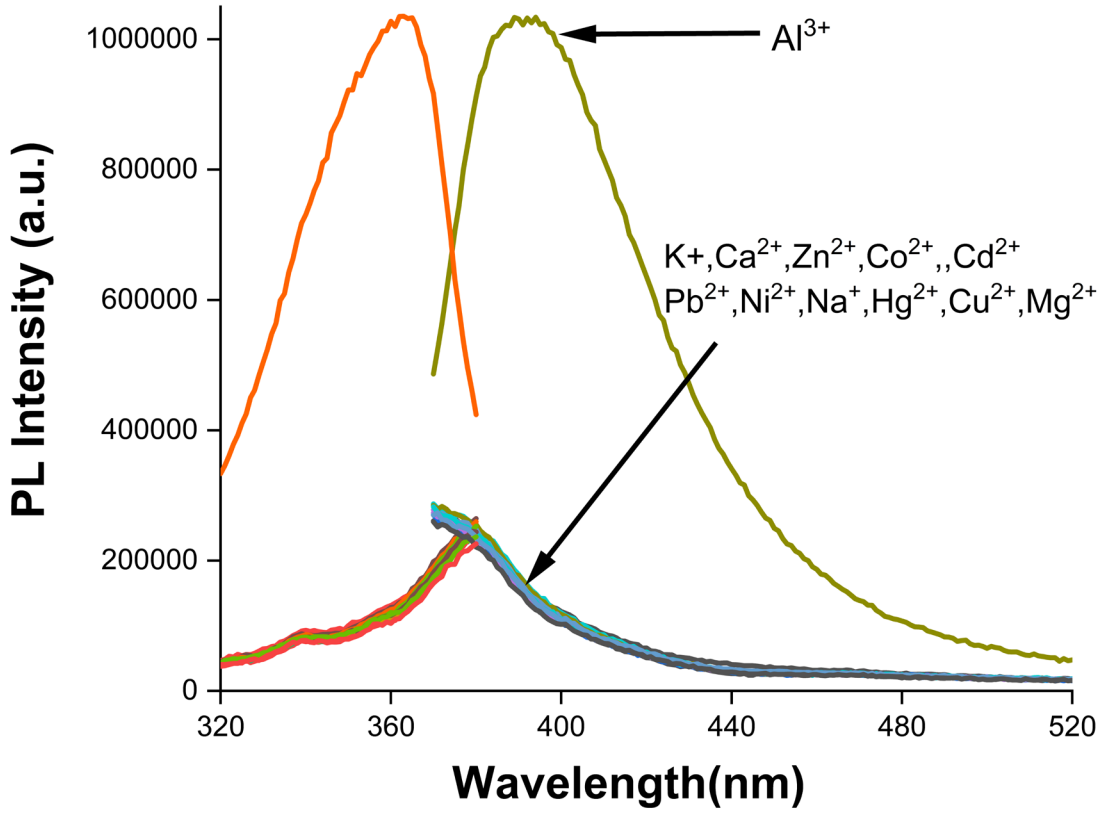



Figure S5: Selectivity study of complex **1** for aluminum in methanol (excitation at 364 nm; emission at 398 nm).

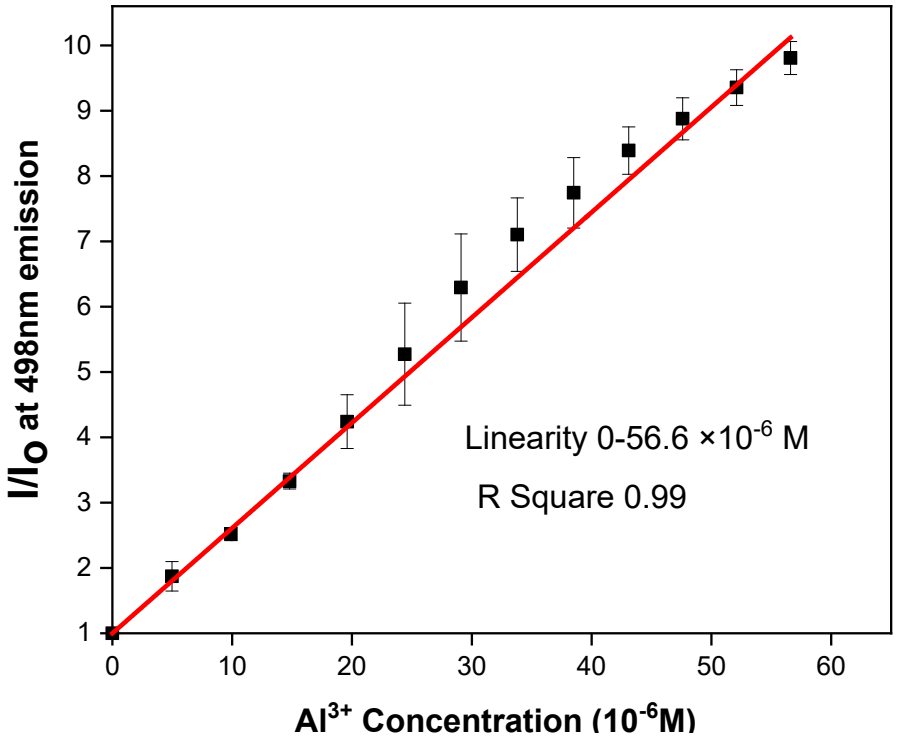



Figure S6: Linear relationship with $Al^{3+}$ concentration in methanol.

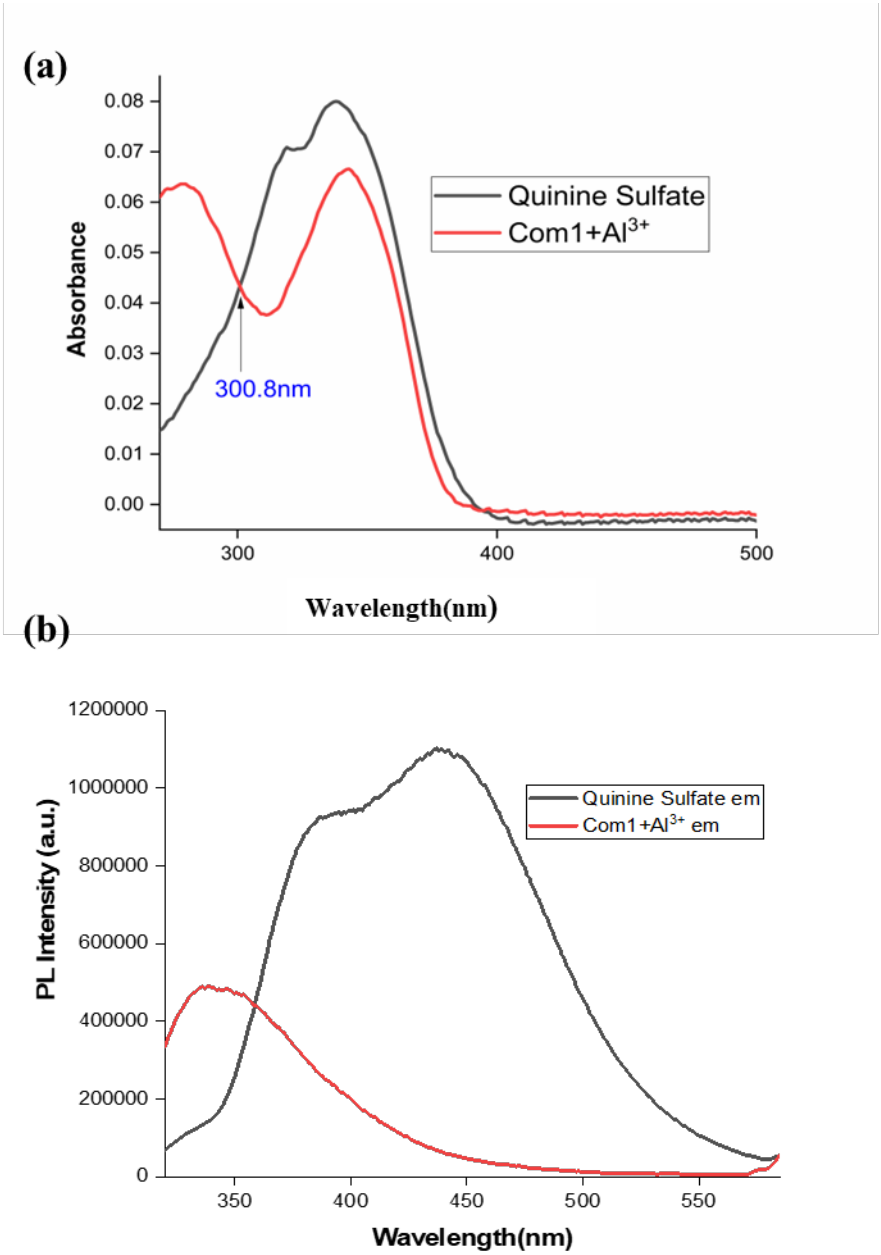



Figure S7: Relative quantum yield study (a) Absorption spectra of the Quinine sulfate and the Complex 1+$Al^{3+}$ solution. (b) Emission spectra of the Quinine sulfate and the Complex 1+$Al^{3+}$ solution at 301nm excitation.

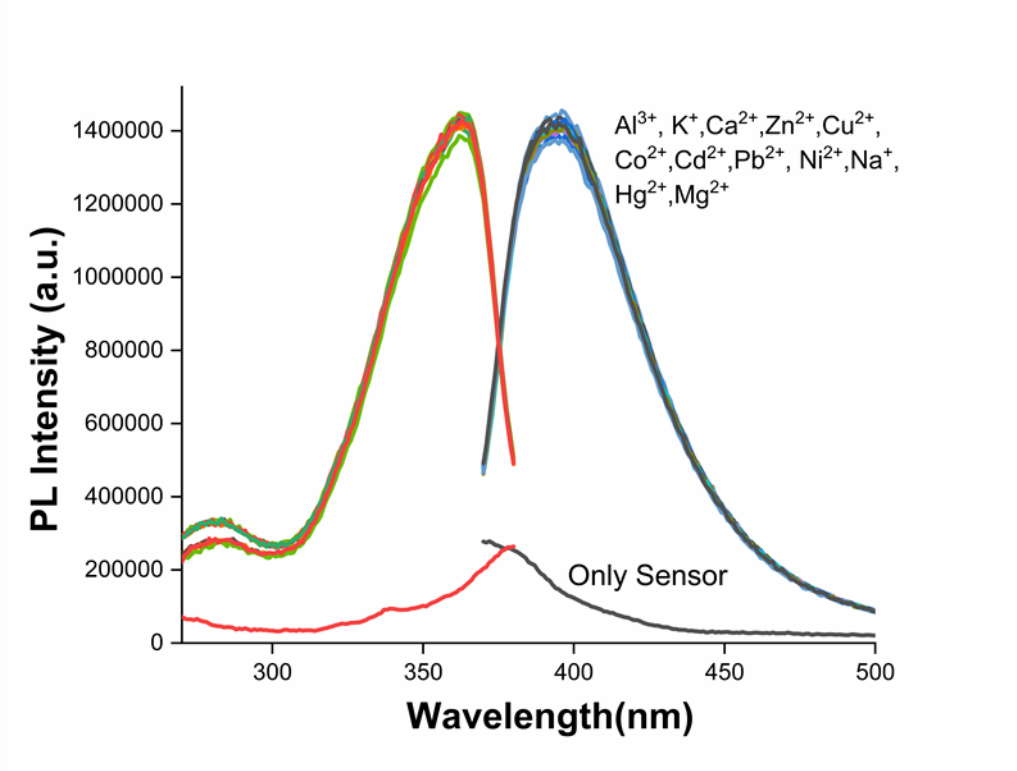



Figure S8: Interference study with 12 metals in methanol (excitation at 364 nm; emission at 398 nm).

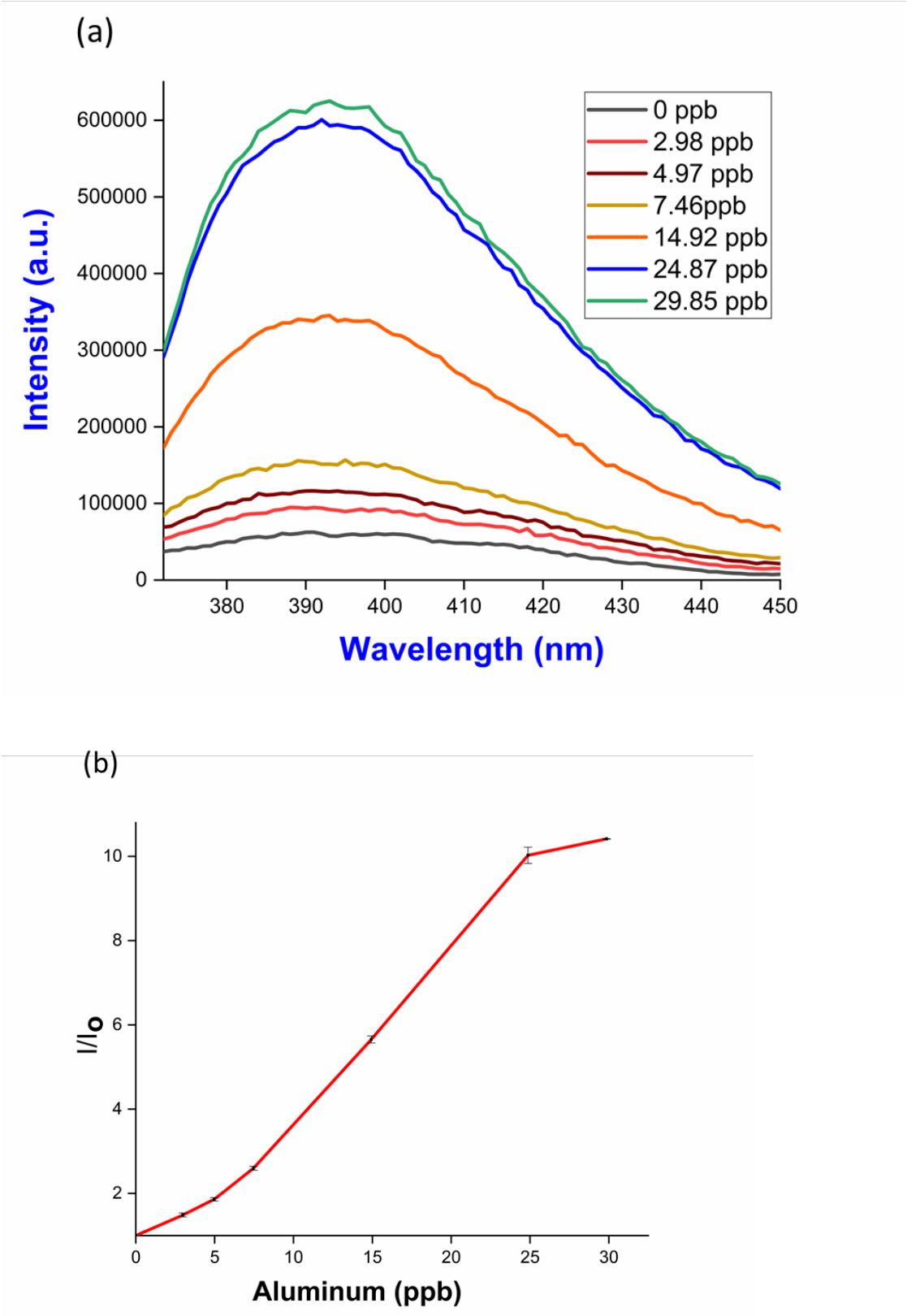



Figure S9: (a) Aluminum ion titration in the methanol-water mixture (200:1v/v). (b) Calibration curve in the methanol-water mixture (200:1v/v) (excitation at 364 nm; emission at 398 nm).

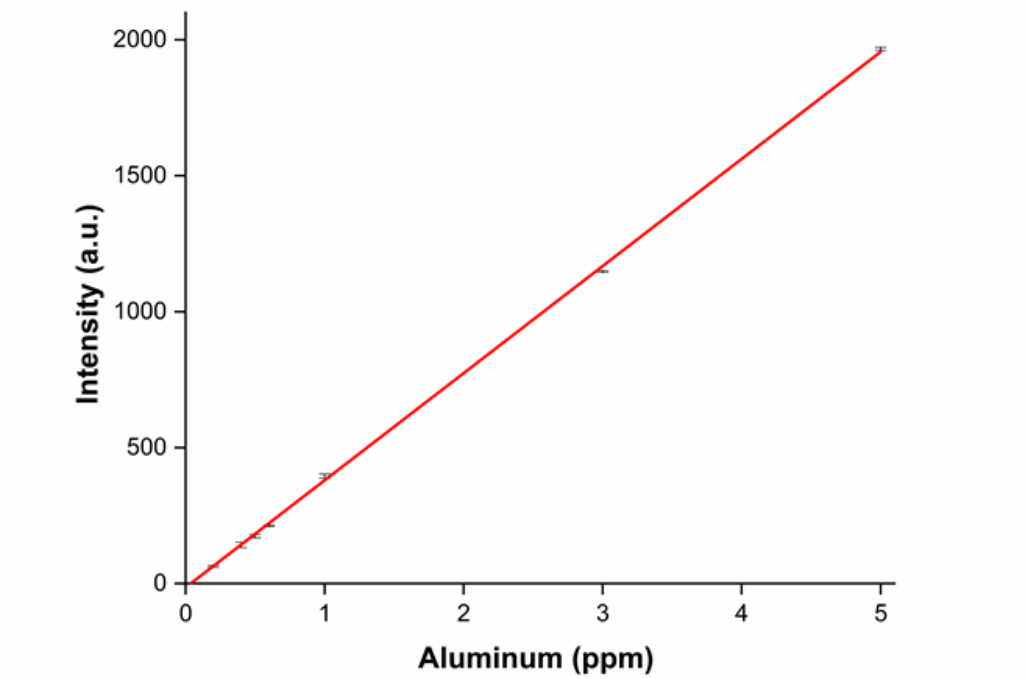



Figure S10: Standard curve for $Al^{3+}$ ions from ICP-OES in Millipore water.

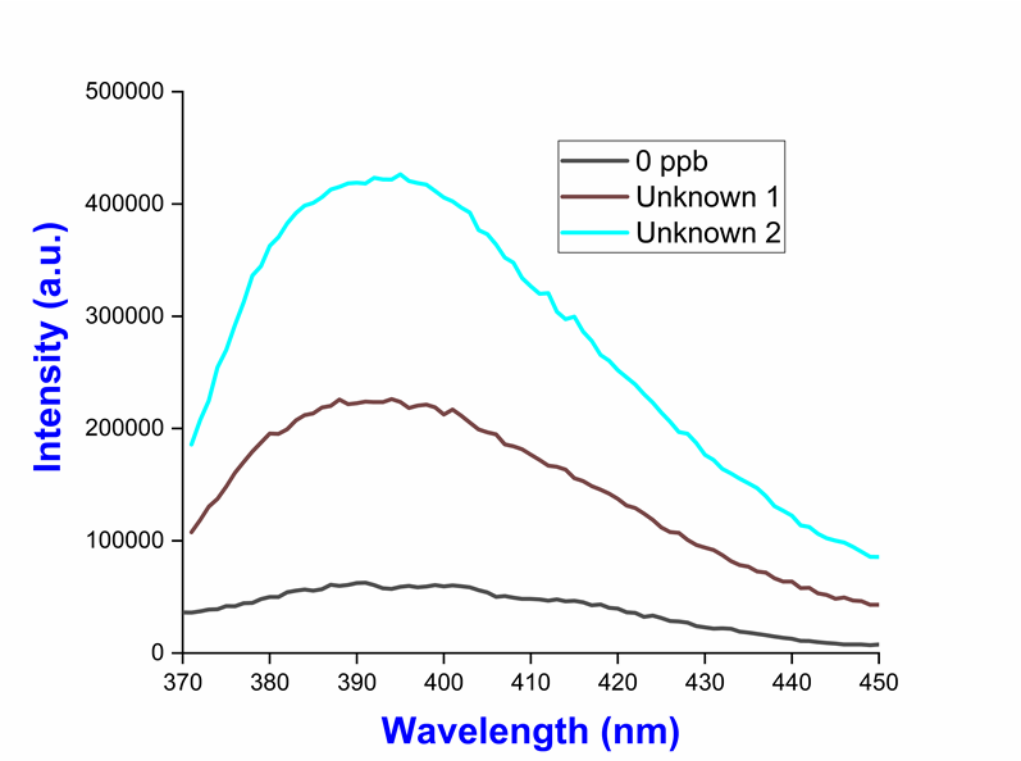



Figure S11: Luminescence spectra of Unknown Sample-1 and Unknown Sample-2 in methanol-water mixture (200:1 v/v) (excitation at 364 nm; emission at 398 nm).

**Supplementary References**


1. Sheldrick, G. M. (2015). "SHELXT--Integrated space-group and Crystal structure determination", *Acta Cryst. A71*, 3-8.

2. Sheldrick, G. M. (2015) "Crystal structure refinement with SHELXL", *Acta Cryst., C71*, 3-8

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4. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst., 42*, 339-341.

5. Song, Huimin, *et al.* (2021) "A novel fluorescent sensor for $Al^{3+}$ and $Zn^{2+}$ based on a new europium complex with a 1, 10-phenanthroline ligand." *Journal of Rare Earths, 39*: 460-468.

6. Yadav, Pranjalee, *et al.* (2021) "Development of a reversible chromogenic sensor for $Cu^{2+}$ in aqueous ethanol." *Materials Letters, 295*, 129869.