

Imine containing benzophenone scaffold as efficient chemical device to detect selectively Al³⁺

Sougata Sinha,^a Rik Rani Koner,^a Sunil Kumar,^a Jomon Mathew,^b Monisha P.V.,^a Imran Kazi,^a Subrata Ghosh^{a,*}

^a*School of Basic Sciences, Indian Institute of Technology Mandi, Mandi-175001, H.P, India*

^b*Schulich Faculty of Chemistry and the Lise Meitner Minerva Center for Computational Quantum Chemistry, Technion-Israel Institute of Technology, Haifa, Israel*

*Corresponding author: Tel. +91-1905-237926; Fax: +91-1905-237924

E-mail address: subrata@iitmandi.ac.in

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General Experimental:

All chemicals required for synthesis were purchased from Sigma-Aldrich, Merck and S. D. Fine Chemicals, and used without further purification. The solvents were distilled prior to use. Spectroscopic grade solvents were used for the spectral studies. Nitrate salts of all the metal ions or cations were used (Hg^{2+} was used as perchlorate salt, Fe^{2+} as sulphate salt and Sn^{2+} as chloride salt). For measurement in water medium Tris-HCl buffer (pH 7) was used. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance III 600 MHz spectrometer and Bruker Avance 300 MHz spectrometer in $\text{DMSO-}d_6$ and CDCl_3 . FT-IR and mass spectra were recorded on a Perkin Elmer Spectrum 2 spectrophotometer and Q-TOF micromass spectrometer respectively. Absorption and fluorescence spectra were recorded on a Shimadzu UV-2450 and Cary Eclipse spectrophotometers respectively. All the spectral studies were performed at 25 °C. The excitation wavelength for fluorescence measurements was 334 nm ($\lambda_{\text{ex}}=334$ nm) and 1 cm quartz cell was used with 5 slit width for both excitation and emission. All measurements were carried out within few seconds of the addition of metal ions.

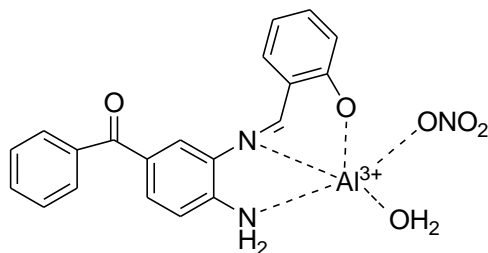
A general procedure for the synthesis of compound 1

3,4-Diaminobenzophenone (0.424 g, 2 mmol) was dissolved under stirring condition in ethanol (10 mL) at room temperature. To this solution, salicylaldehyde (0.366 g, 3 mmol) was added slowly and the reaction whole mixture was left stirring at room temperature. After 30 minutes bright yellow precipitate was observed. The reaction mixture was left stirring for one more hour. The solid was filtered, washed with ethanol several times and dried under vacuum. The product was characterized by common spectroscopic tools and the data were in well agreement with the reported data.¹

Yield: 78% (495 mg), Yellow solid, Melting point: 134-135 °C, FT-IR (KBr, ν in cm^{-1}): 997, 1076, 1121, 1150, 1178, 1263, 1274, 1286, 1325, 1365, 1399, 1433, 1456, 1490, 1507, 1558, 1569, 1580, 1609, 1620, 1648, 2663, 3054, 3207, 3343, 3467; $^1\text{H-NMR}$ (600 MHz, $\text{DMSO-}d_6$) δ 6.13 (s, 2H), 6.81 (s, 1H), 6.949 (t, 2H, $J = 7.8$ Hz), 7.39 (t, 1H, $J = 7.8$ Hz), 7.46 (d, 1H, $J = 8.4$ Hz), 7.49-7.52 (m, 3H), 7.57-7.59 (m, 1H), 7.66 (d, 2H, $J = 6.6$ Hz), 7.74 (d, 1H, $J=7.8$), 8.88 (s, 1H), 12.25 (brs, 1H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 114.36, 117.55, 119.7, 119.9, 121.23, 128.13, 128.61, 129.94, 132.08, 133.04, 133.98, 135.14, 139.04, 145.72, 161.15, 163.98, 195.50.

Synthesis of 1- Al^{3+} complex

A 5 mL methanolic solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.089 g, 0.2378 mmol) was added drop wise to a magnetically stirred solution (5 mL) of **1** (0.075 g, 0.2378 mmol) in methanol. The color of the ligand solution was changed from light yellow to orange upon addition $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. After two hours of stirring at room temperature, the color of the reaction mixture was further changed to deep brown. The stirring was continued for two more hours. Then the solution was dried using rotary evaporator which yielded a deep brown 1- Al complex. The possible structures of the complex (as shown below) are on the basis of Job's plot, mass spectral studies, FT-IR and ^1H NMR studies.



Binding constant calculation:

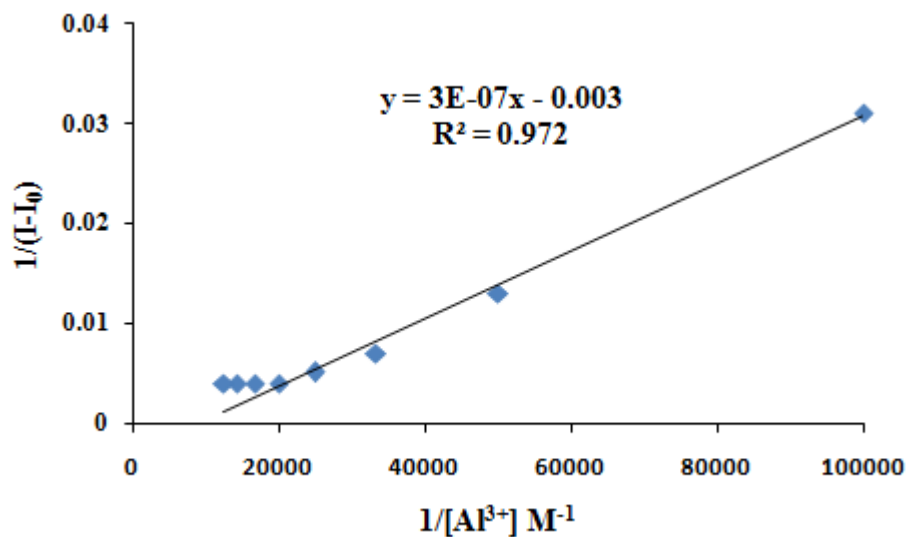


Figure S1: Binding constant calculation from spectrometric titration of **1** with Al^{3+} in methanol using Benesi-Hildebrand equation.²

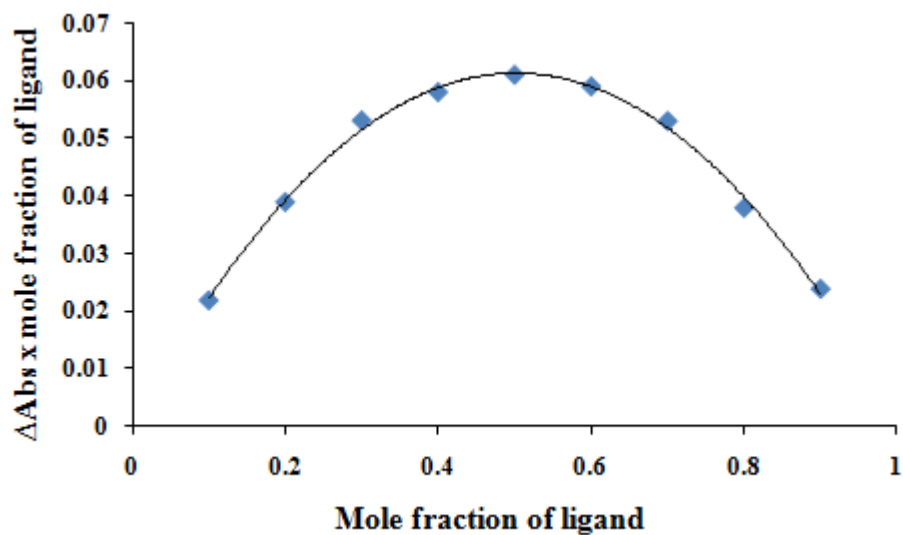


Figure S2: Job's plot³ for **1**- Ga^{3+} complex in methanol.

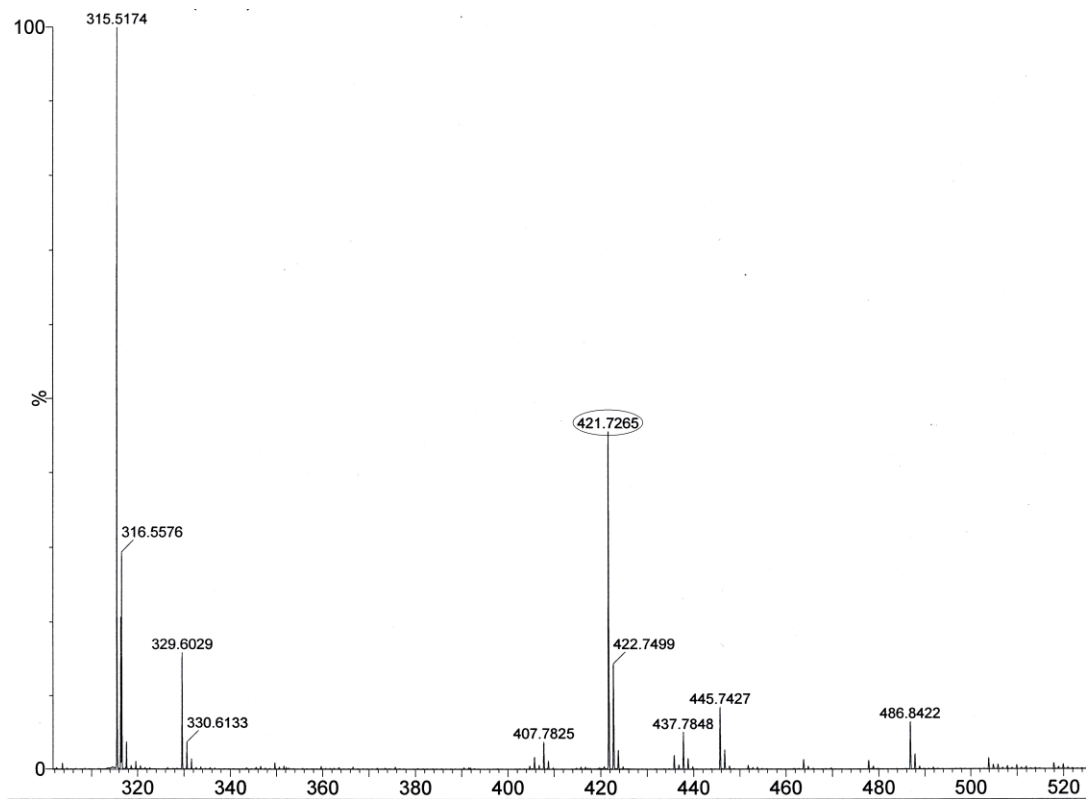


Figure S3: ESI- mass spectra of 1-Al^{3+} complex in MeOH

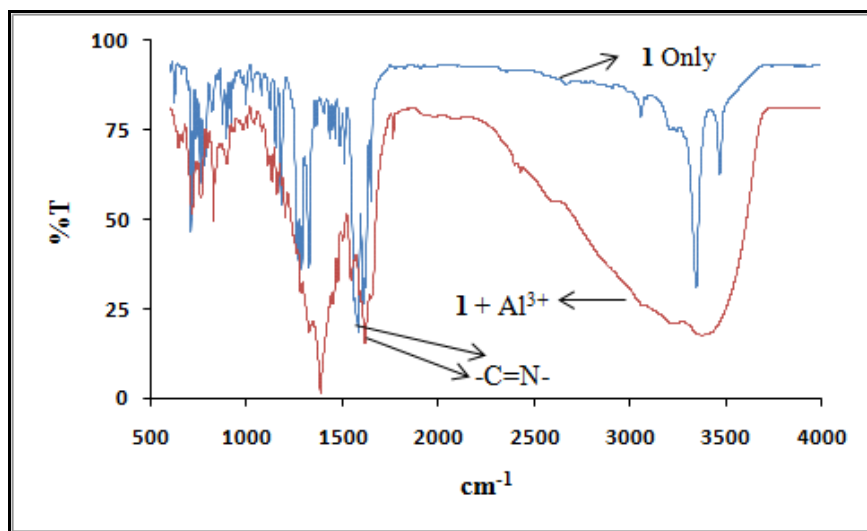


Figure S4: FT-IR spectra of compound **1** and 1-Al^{3+} complex.

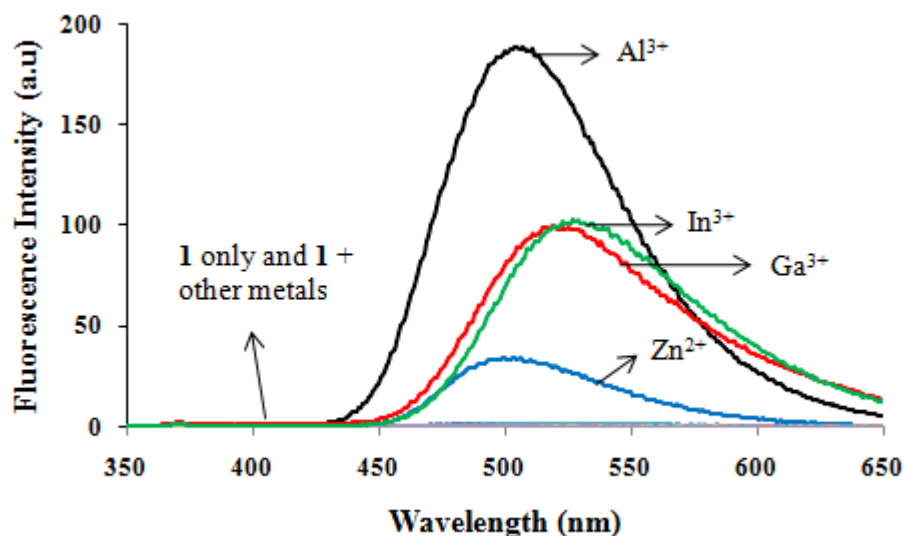


Figure S5: Fluorescence spectra of compound **1** (1×10^{-5} M), and **1** in the presence of 13×10^{-5} M of 24 different metal ions ($\lambda_{\text{ex}} = 334$ nm, Temperature: 25 °C) in ethanol.

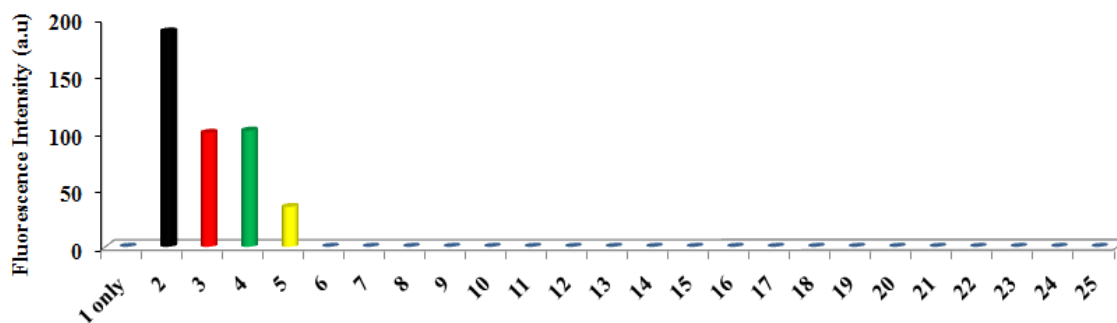


Figure S6: Emission spectra of compound **1** (1×10^{-5} M), and **1** in the presence of 13×10^{-5} M of 24 different metal ions as bar graphs.

2=Compound **1** + Al^{3+} , 3= Compound **1** + Ga^{3+} , 4= Compound **1** + In^{3+} , 5= Compound **1** + Zn^{2+} , 6= Compound **1** + Li^{+} , 7= Compound **1** + Na^{+} , 8= Compound **1** + K^{+} , 9= Compound **1** + NH_4^{+} , 10= Compound **1** + Ca^{2+} , 11= Compound **1** + Ba^{2+} , 12= Compound **1** + Mg^{2+} , 13= Compound **1** + Mn^{2+} , 14= Compound **1** + Ag^{+} , 15= Compound **1** + Sr^{2+} , 16= Compound **1** +

Cd^{2+} , 17= Compound **1** + Hg^{2+} , 18= Compound **1** + Ni^{2+} , 19= Compound **1** + Co^{2+} , 20= Compound **1** + Fe^{2+} , 21= Compound **1** + Pb^{2+} , 22= Compound **1** + Cu^{2+} , 23= Compound **1** + Fe^{3+} , 24= Compound **1** + Cr^{3+} , 25= Compound **1** + Sn^{2+}

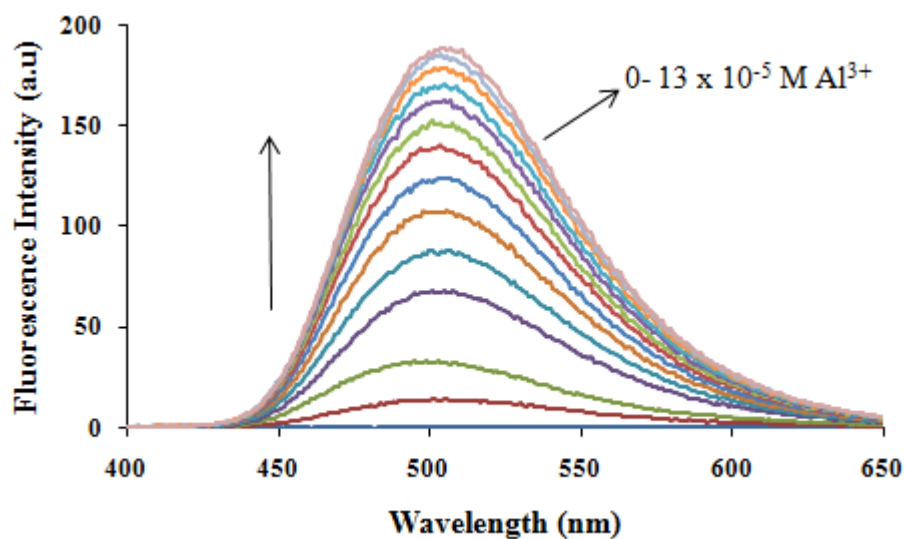


Figure S7: Fluorescence titration spectra of compound **1** (1×10^{-5} M) in the presence of 0- 13×10^{-5} M Al^{3+} in ethanol.

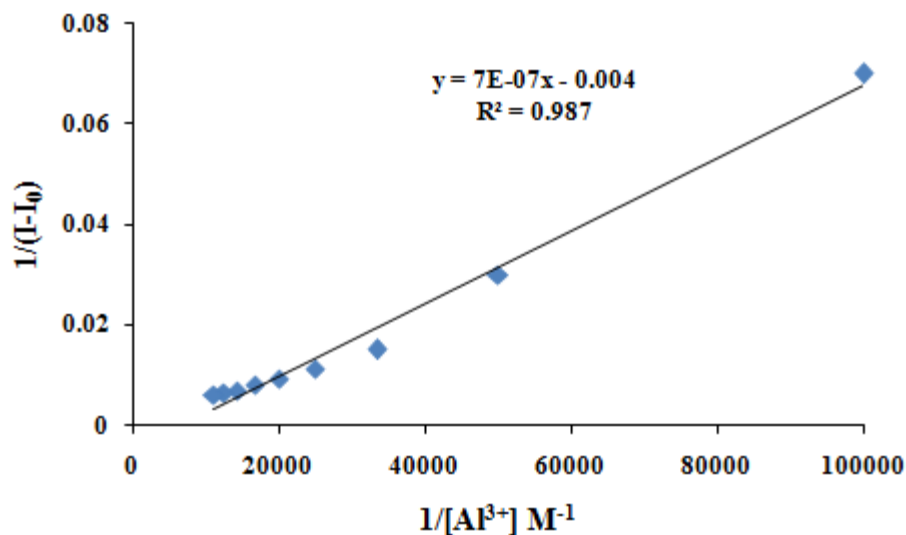


Figure S8: Binding constant calculation from spectrometric titration of **1** with Al^{3+} in ethanol using Benesi-Hildebrand equation².

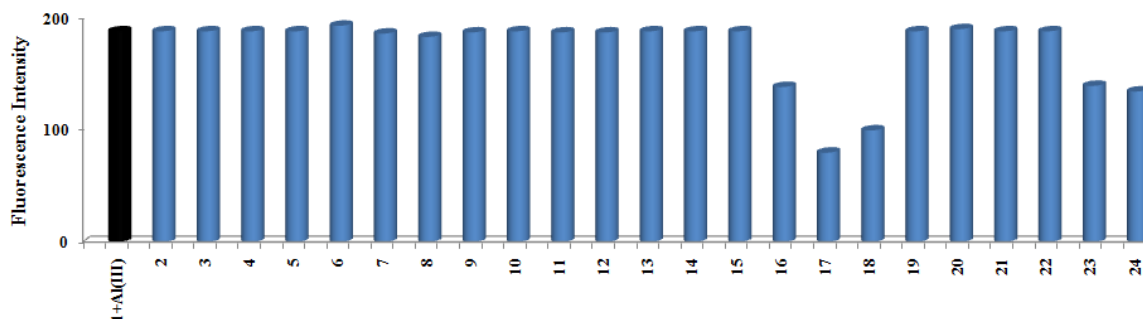


Figure S9: Fluorescence response of compound **1** (1×10^{-5} M) towards Al^{3+} (13×10^{-5} M) in the presence of excess amount (150 μ M) of 23 different competing cations (listed as follows) in ethanol.

(2) $Li^{+} + Al^{3+}$ (3) $Na^{+} + Al^{3+}$ (4) $K^{+} + Al^{3+}$ (5) $Ba^{2+} + Al^{3+}$ (6) $Ca^{2+} + Al^{3+}$ (7) $Mg^{2+} + Al^{3+}$ (8) $Ag^{+} + Al^{3+}$ (9) $Mn^{2+} + Al^{3+}$ (10) $Sn^{2+} + Al^{3+}$ (11) $NH_4^{+} + Al^{3+}$ (12) $Sr^{2+} + Al^{3+}$ (13) $Pb^{2+} + Al^{3+}$ (14) $Co^{2+} + Al^{3+}$ (15) $Ni^{2+} + Al^{3+}$ (16) $Cu^{2+} + Al^{3+}$ (17) $Fe^{3+} + Al^{3+}$ (18) $Fe^{2+} + Al^{3+}$ (19) $Hg^{2+} + Al^{3+}$ (20) $Zn^{2+} + Al^{3+}$ (21) $Cd^{2+} + Al^{3+}$ (22) $Cr^{2+} + Al^{3+}$ (23) $Ga^{3+} + Al^{3+}$ (24) $In^{3+} + Al^{3+}$

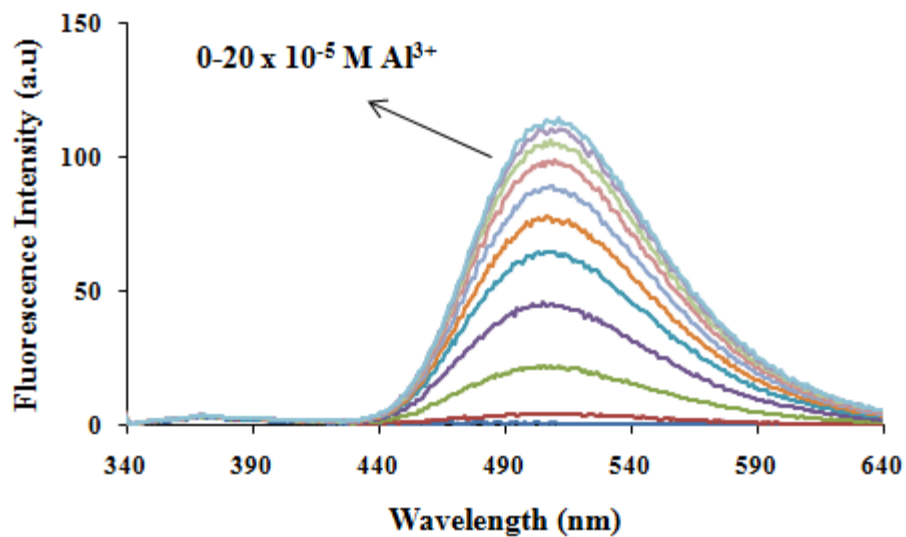


Figure S10: Fluorescence titration spectra of compound **1** (1×10^{-5} M) in the presence of 0 - 20×10^{-5} M Al^{3+} in MeOH- H_2O (99:1).

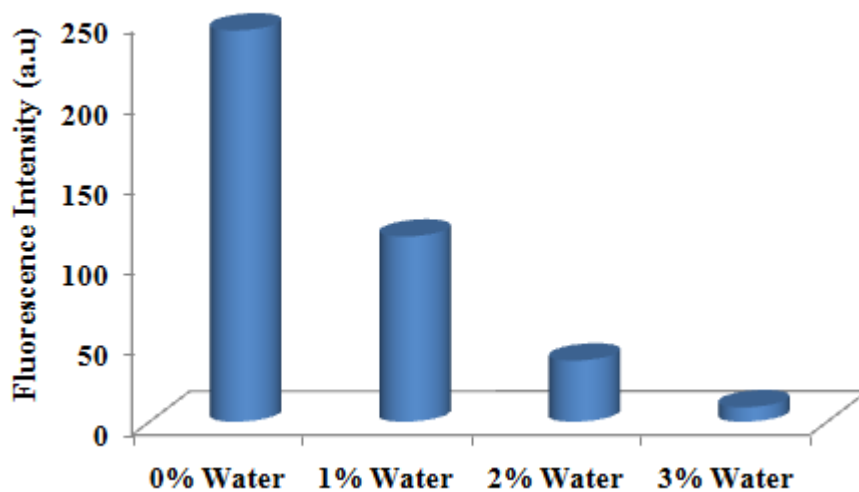


Figure S11: Changes in fluorescence intensity with different percentage of water.

¹H NMR spectra

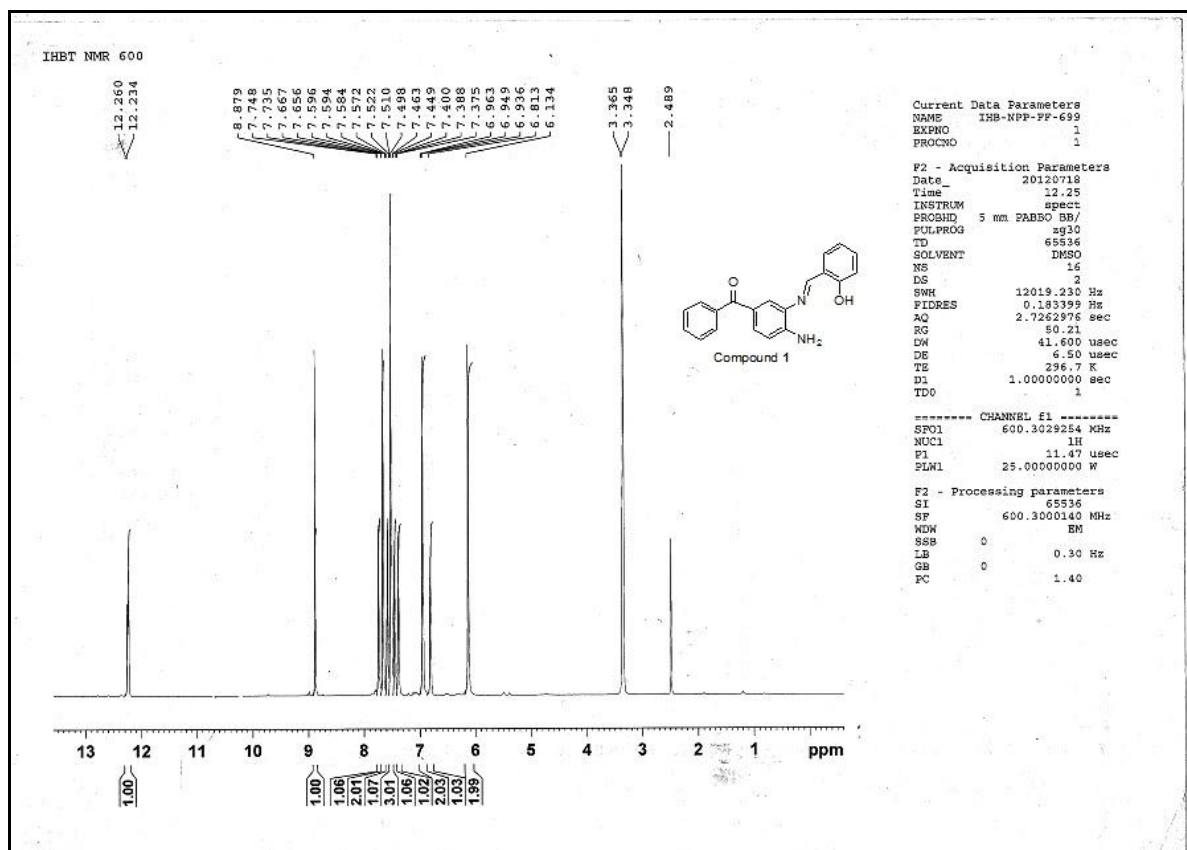


Figure S12: ¹H NMR spectra of compound 1.

¹³C NMR spectra

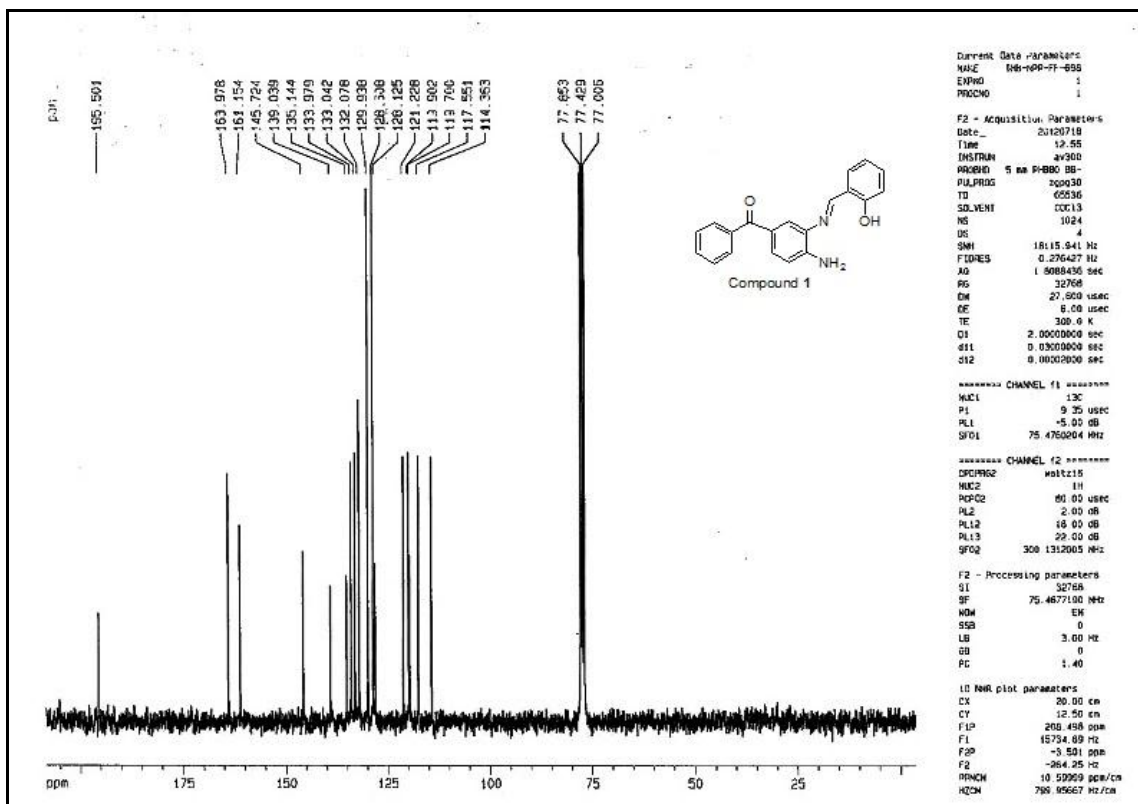


Figure S13: ¹³C NMR spectra of compound 1.

References:

1. M. Asadi, M. S. Khah, *J. Iran. Chem. Soc.*, 2010, **7**, 875-882.
2. H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.
3. P. Job, *Ann. Chim. Applicata*, 1928, **9**, 113–203.