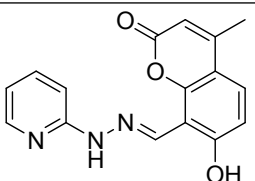
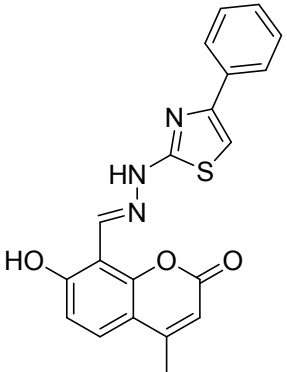
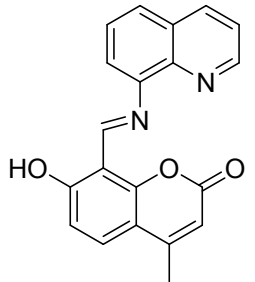
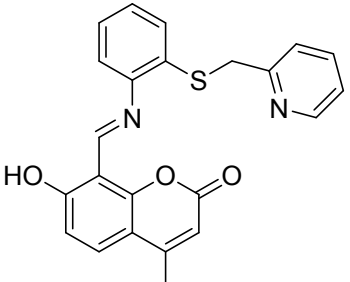


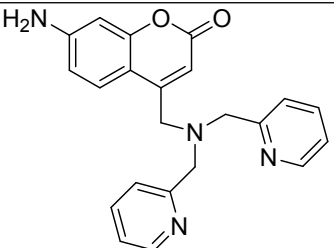
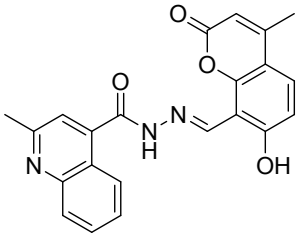
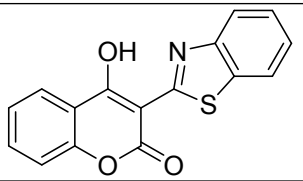
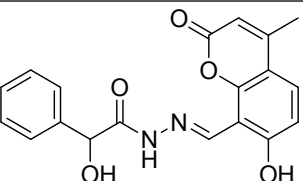
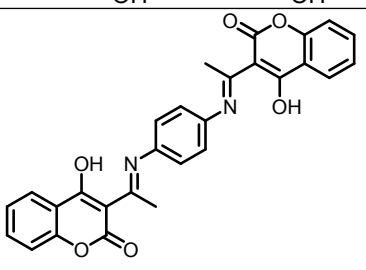
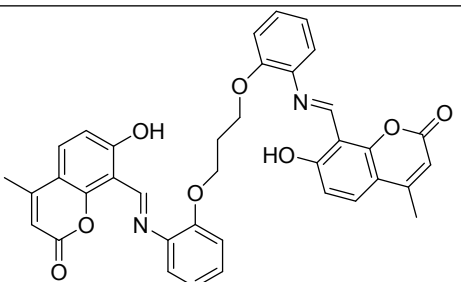
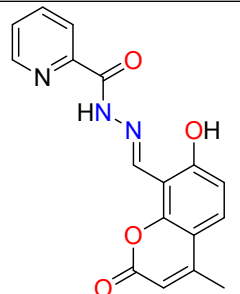
Supplementary material

Designing of Coumarinyl-Picolinoyl hydrazide Schiff base for the fluorescence turn-on-off sequential sensing of Al³⁺ and nitroaromatics, and electronic device fabrication

Rakesh Purkait, Arka Dey, Sunanda Dey, Partha Pratim Ray* and Chittaranjan Sinha*

Table S1

Sl no	Probe	AIE	Sensing ion, solvent, LOD	Electrical conductivity	Ref.
1		No	Mg ²⁺ , Ethanol, 105 nM	No	31
2		No	Zn ²⁺ (72 nM) and AcO ⁻ (94 nM) in DMSO/H ₂ O (v/v = 3:7)	No	32
3		No	Zn ²⁺ , THF, 100 nM	No	33
4		No	Zn ²⁺ , MeOH/H ₂ O(v/v, 3:1), 78 nM	No	34

5		No	Zn ²⁺ (26 nM) and ClO ⁻ (2 μM) in 10 mM HEPES	No	35
6		No	Al ³⁺ , Ethanol, 820 nM	No	36
7		No	Zn ²⁺ , CH ₃ CN/H ₂ O (95:5, v/v), 35 nM	No	37
8		No	Ca ²⁺ , DMF/HEPES buffer 1:1(v/v), 33.3 μM	No	38
9		No	Zn ²⁺ (19 nM) and Cu ²⁺ (1.87 nM) in CH ₃ CN : H ₂ O (1 : 1, v/v,)	No	39
10		No	Zn ²⁺ , CH ₃ CN:H ₂ O 9 : 1(v/v), 11 nM	No	40
11		Yes	Al ³⁺ , Water, 6.99 nM	Yes	This work

Materials and methods

Picolinic acid and hydrazine hydrate were purchased from High media and Merck respectively. All other organic chemicals and inorganic salts were obtained from commercial suppliers Merck and used without further purification. Aqueous solutions were prepared using Milli-Q water (Millipore). Elemental analyses were performed using a Perkin-Elmer USA elemental analyzer. UV-vis spectra were recorded on Perkin Elmer Lambda 25 spectrophotometer and fluorescence spectra were obtained using a Perkin Elmer spectrofluorimeter model LS55, Luminescence lifetime measurements were carried out by using time-correlated single photon counting set up from Horiba Jobin-Yvon; FT-IR spectra (KBr disk, 4000-400 cm^{-1}) from a Perkin Elmer LX-1 FTIR spectrophotometer. NMR spectra were obtained on a Bruker (AC) 300 MHz FT-NMR spectrometer using TMS as an internal standard. ESI mass spectra were recorded from a Water HRMS model XEVO-G2QTOF#YCA351 spectrometer. All of the measurements were conducted at room temperature. To calculate band gap we have use the tauc's equation,

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

Where α , E_g , h , ν is the absorption coefficient, optical band gap, Planck's constant and frequency of light. A is a constant which is considered as 1 for ideal case. By extrapolating the linear region of the plot $(\alpha h\nu)^2$ vs. $h\nu$ (Figure 1) to $\alpha = 0$ absorption and using the above equation, the direct optical band gap of our synthesized compound has been evaluated as 2.78 eV. The dielectric study of our synthesized compound has been performed by the impedance spectrum which has been evaluated as a function of frequency and recorded at room temperature by the computer controlled Agilent make precision 4294A LCR meter at the frequency range 40 Hz to 11 MHz. In this regard we have calculated the capacitance (C), impedance (Z) and phase angle (θ) of the sample.

Preparation of probe, H-CPh

Picolinohydrazide was prepared from Picolinic acid as per report and also 7-hydroxy-4-methyl-2-oxo-2H-chromene-8-carbaldehyde was synthesized from 7-hydroxy-4-methyl-coumarin following reported method. The condensation of Picolinohydrazide (137 mg, 1.0 mmol) was dissolved in 7 ml MeOH and 7 ml MeOH solution of 7-hydroxy-4-methyl-2-oxo-2H-chromene-8-carbaldehyde (804 mg, 1.0 mmol) was added to amine solution drop by drop. Then the mixture was stirred for 5 hr to get a pale greenish yellow precipitate of (E)-N'-((7-hydroxy-4-methyl-2-oxo-2H-chromen-8-yl)methylene)picolinohydrazide (**H-CPh**). The Collected precipitate of **H-CPh** was dried in open air. Yield: 88%. M.P. >200 °C (**Scheme 1**). Microanalytical data: C₂₀H₁₃N₃O₃ calcd (found): C, 63.16(63.05); H, 4.05(4.13); N, 13.00(12.85) %. ¹H NMR (300 MHz, DMSO-d₆): 12.95 (s, 1H, NH), 12.93 (s, 1H, -OH), 9.41 (s, 1H, imine-H), 8.74 (d, 1H, 4.5 Hz), 8.15-8.04 (m, 2H), 7.73-7.67 (m, 2H), 6.97 (d, 1H, 8.7 Hz), 6.25 (s, 1H) 2.40 (s, 3H, -CH₃) (**Fig. S1**); ESI-mass peak for **CPh** at 323.99 (calculated mass of **CPh**, 323.30) (**Fig. S2**); FTIR: ν₃₄₆₁ cm⁻¹(OH), ν₃₂₉₉ cm⁻¹(NH), ν₁₆₈₅ cm⁻¹(C=O), ν₁₆₀₉ cm⁻¹(C=N) (**Fig S3**)

General method for UV-Vis and fluorescence studies

CPh (1.73 mg, 0.001 mmol) was dissolved in DMSO and diluted to prepare 20 μL using 2 ml required solvent. The metals solutions (40 μl) were transferred to solution of **H-CPh**. After mixing both absorption and emission spectra were recorded at room temperature. Fixing excitation slit = 15.0 and emission slit = 5.0, fluorescence experiment had been carried out using excitation wavelength 340 nm for AIEE study and 400 nm for cation sensing study.

CRS-RP-PQ 38 (0.659) Cm (1:56)

TOF MS ES+
8.08e4

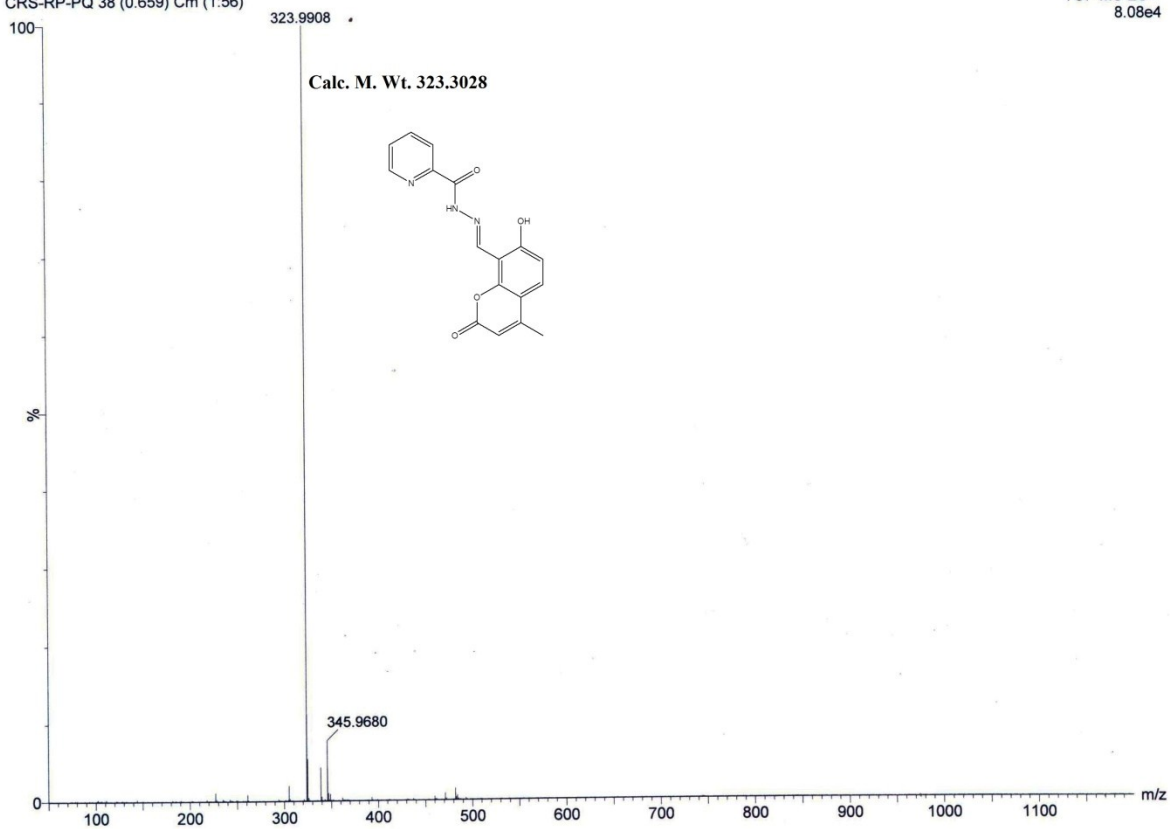


Fig S1 Mass spectra of **H-CPh**

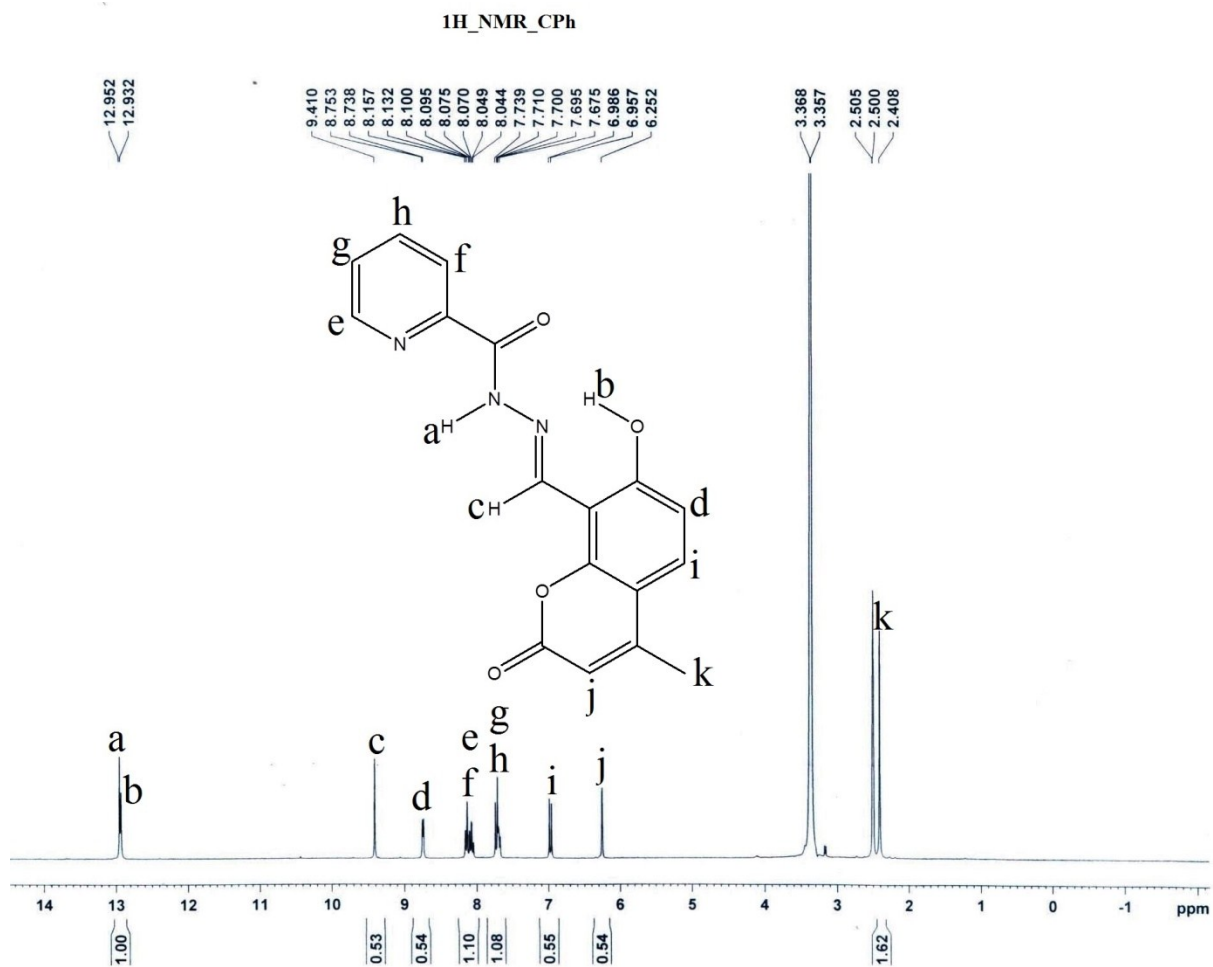


Fig S2 1H NMR of H-CPh in DMSO-d₆

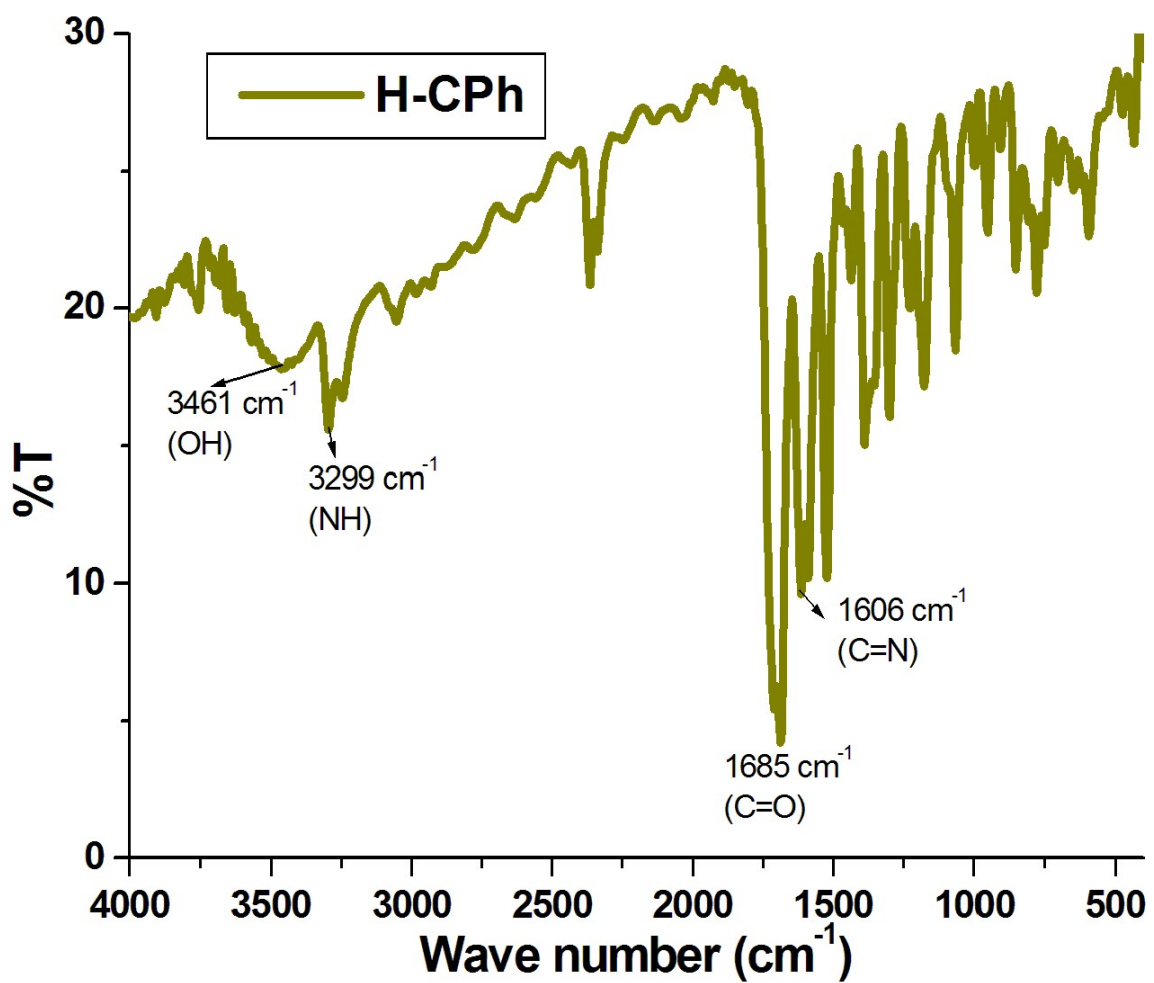


Fig S3 FT-IR spectrum of H-CPh

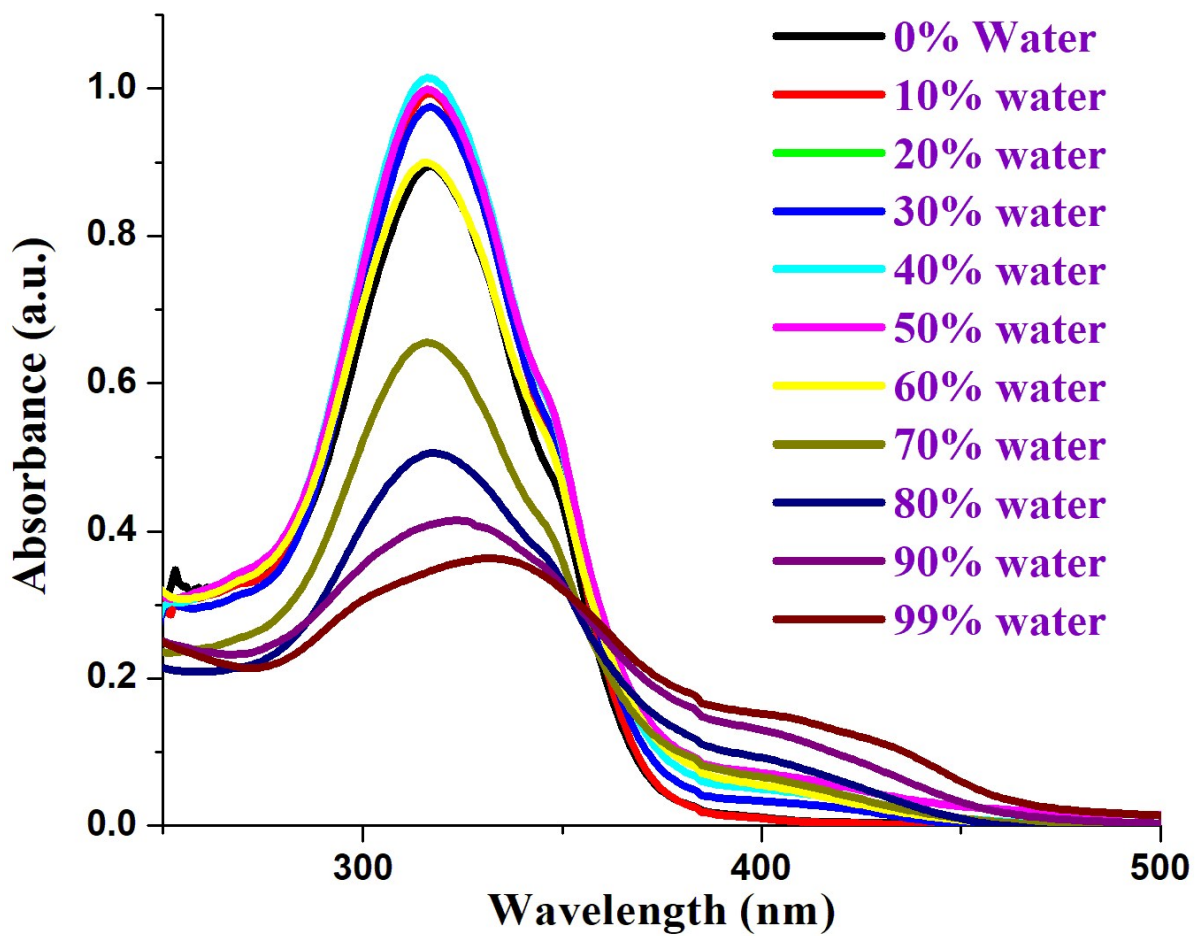


Fig S4 UV-Vis spectra of H-CPh on increasing water percentage in DMSO-water mixture

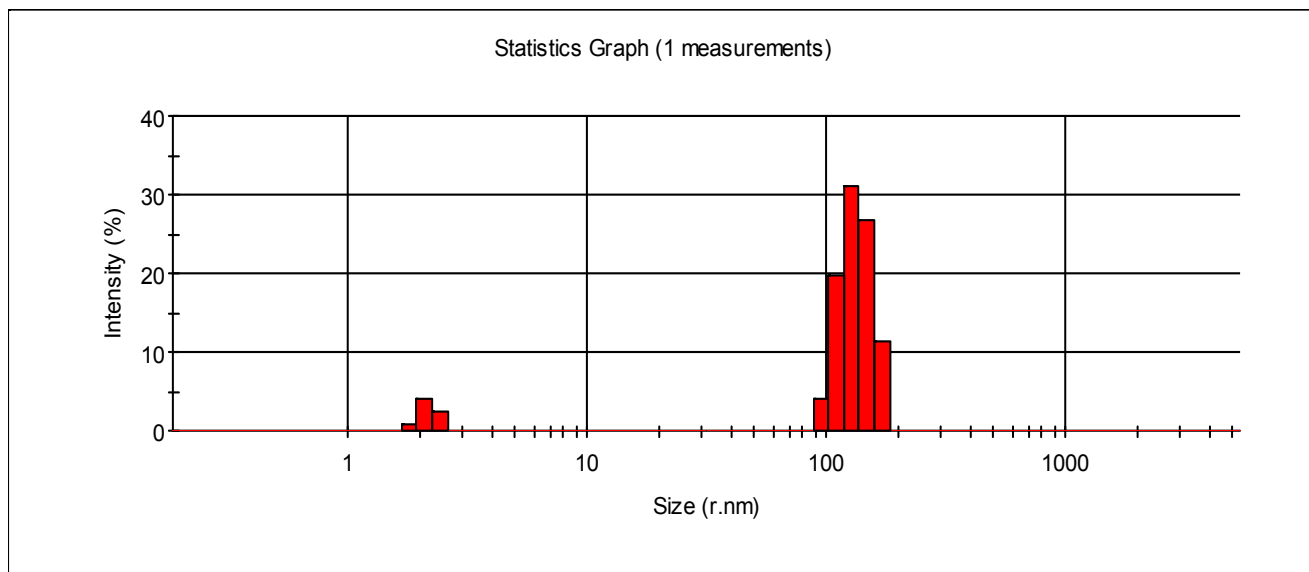


Fig S5 DLS spectra of H-CPh in DMSO

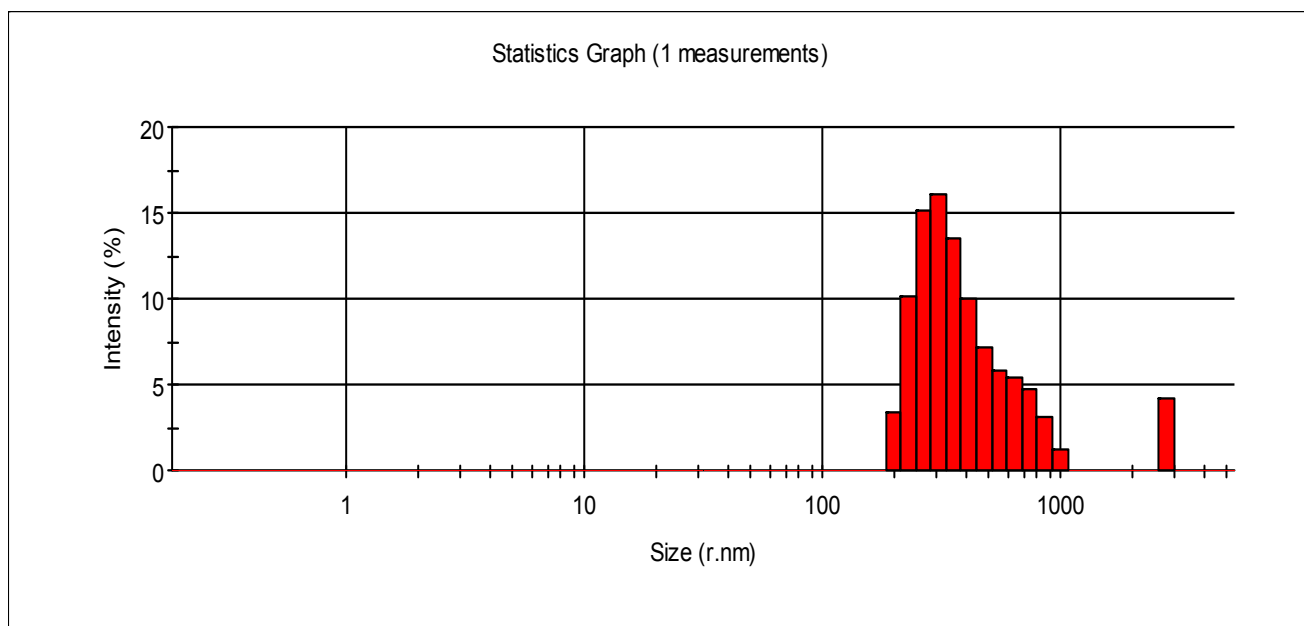


Fig S6 DLS spectra of **H-CPh** in 90% water

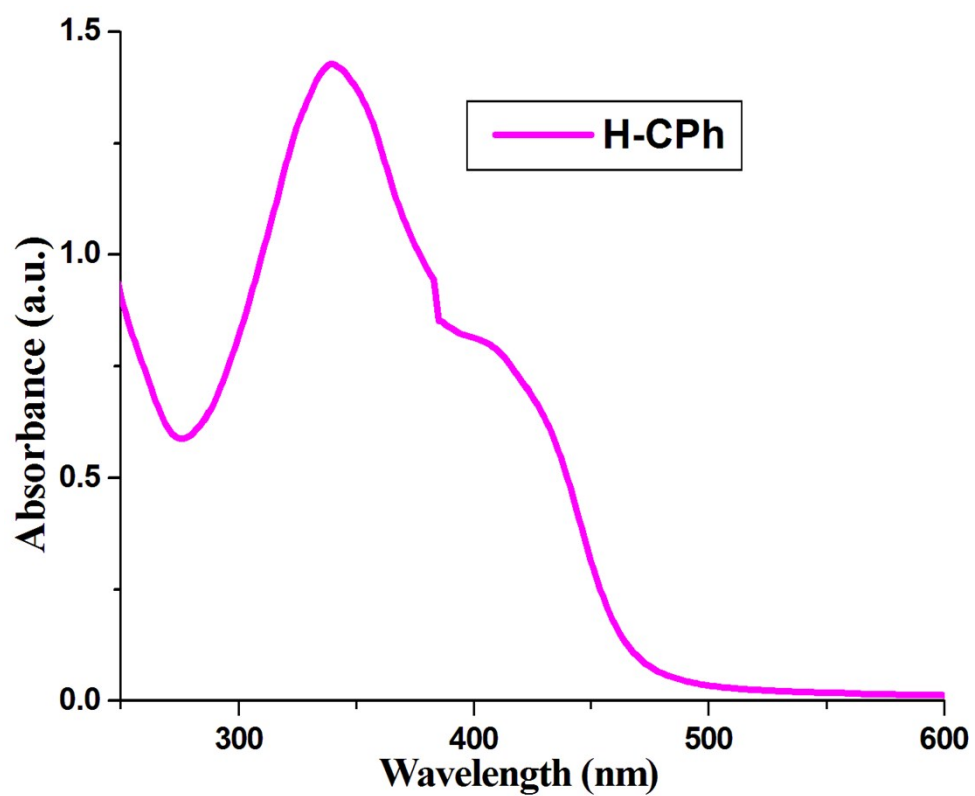


Fig S7 UV-vis spectrum of **H-CPh** in water

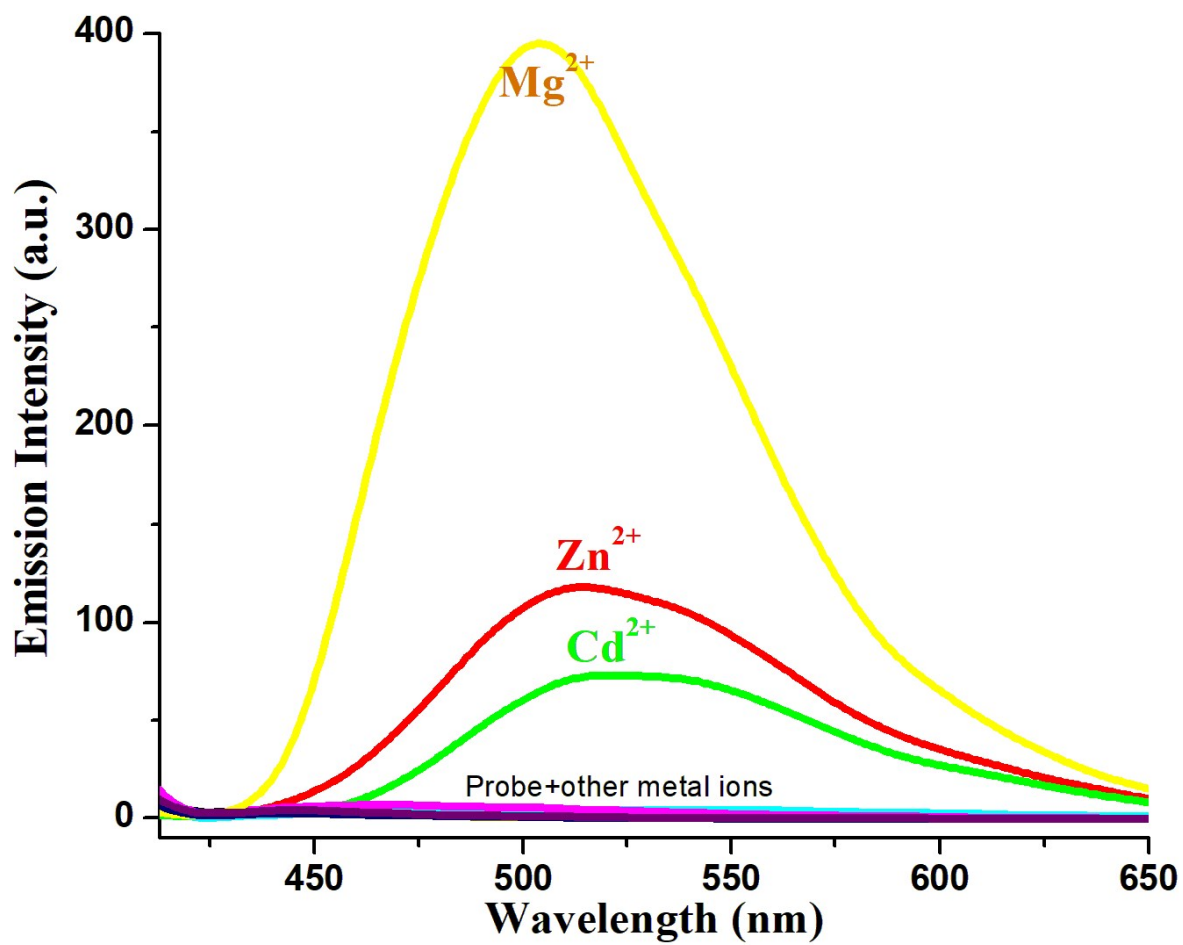


Fig S8 Fluorescence spectra of H-CPh in presence of various cations in DMSO

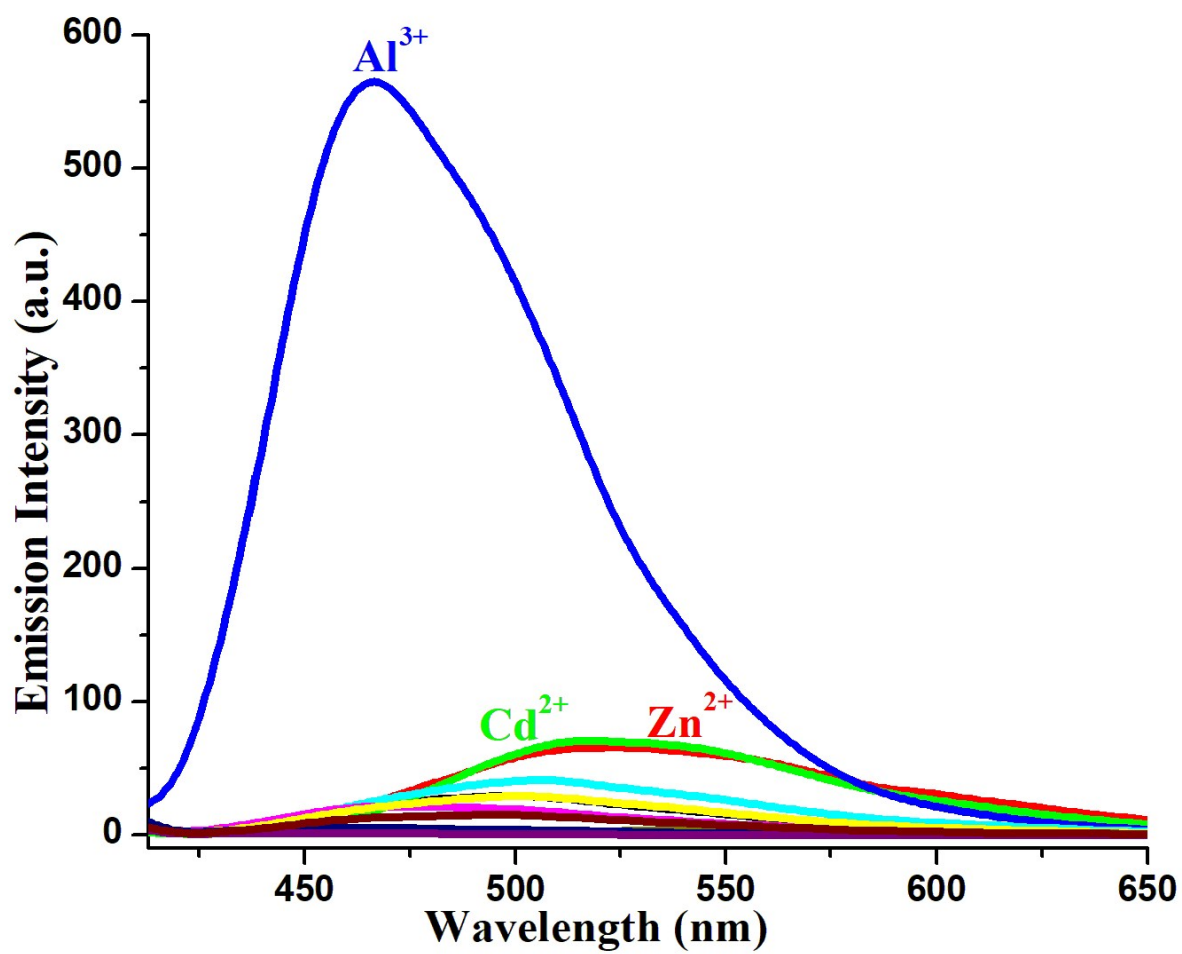


Fig S9 Fluorescence spectra of H-CPh in presence of various cations 3:1 DMSO-water

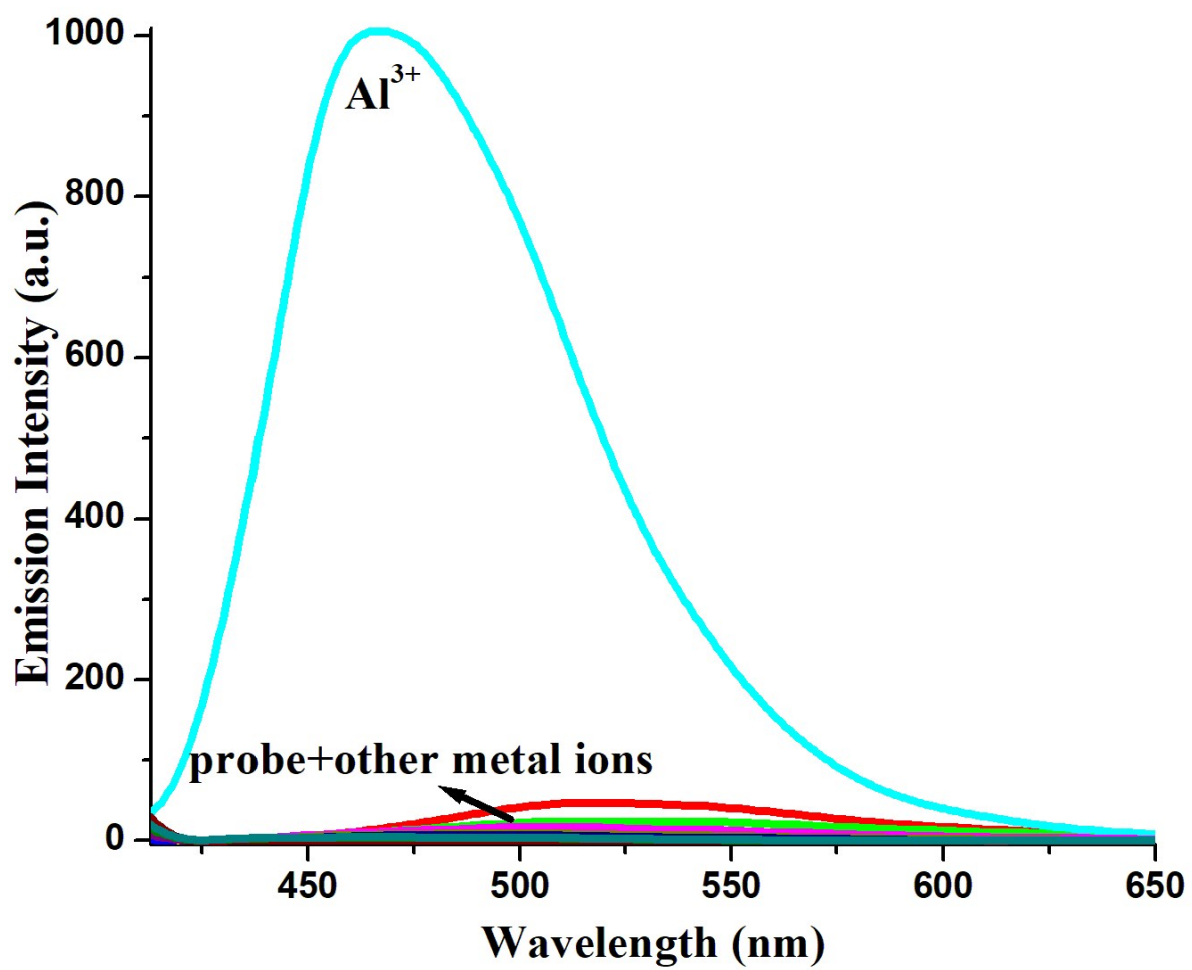


Fig S10 Fluorescence spectra of H-CPh in presence of various cations in 1:1 DMSO-Water

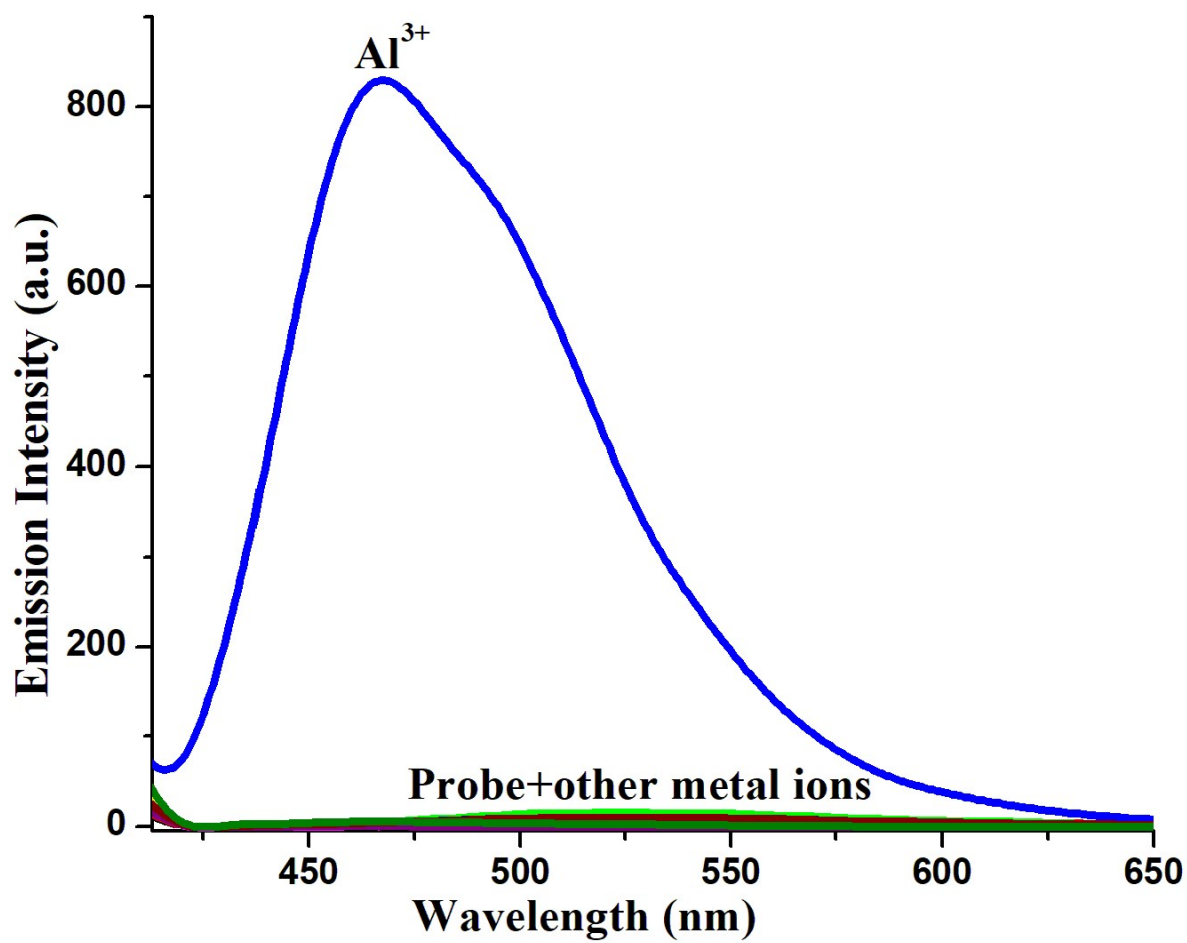


Fig S11 Fluorescence spectra of H-CPh in presence of various cations in 1:3 DMSO-Water

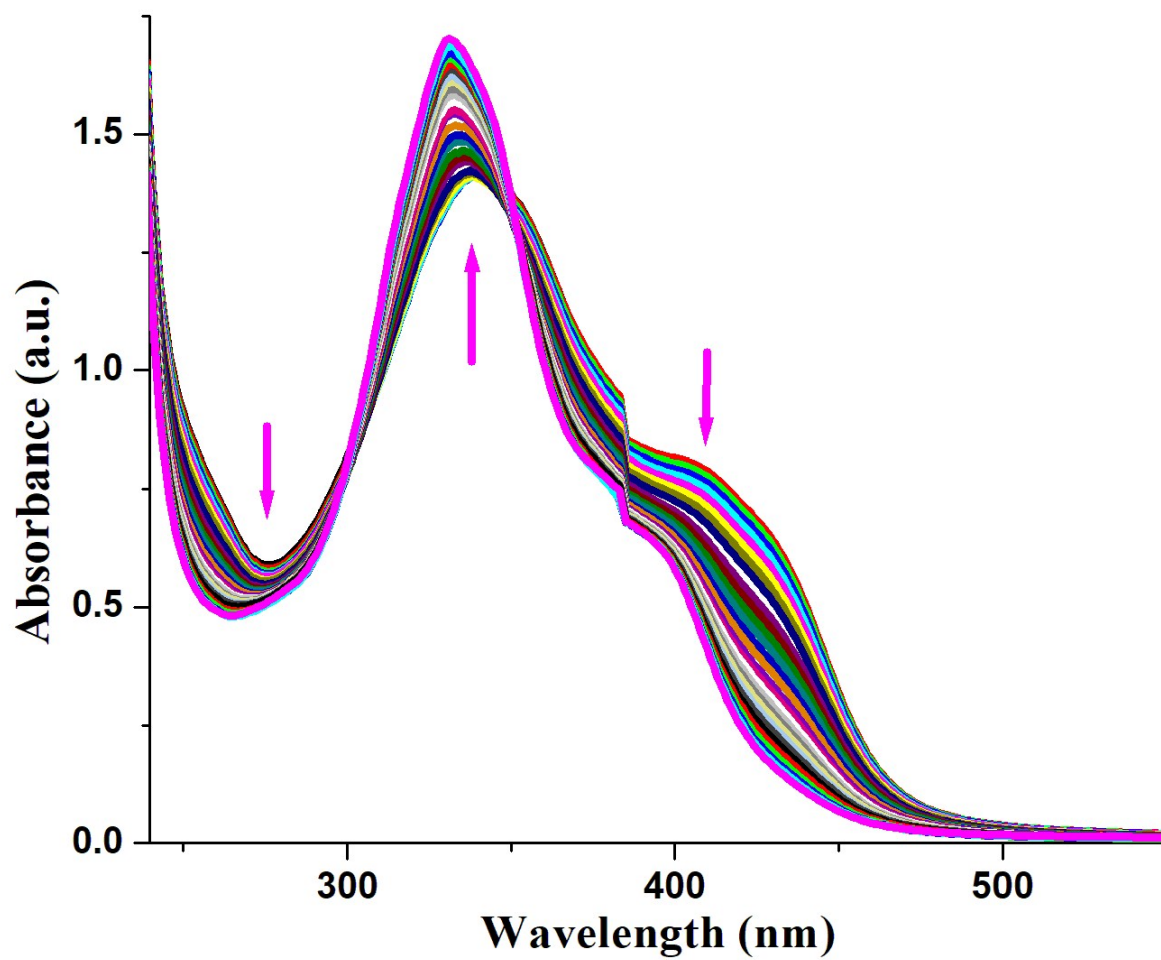


Fig S12 UV-vis spectra of **H-CPh** on incremental addition of Al^{3+} in water (hepes buffer, pH 7.2) medium.

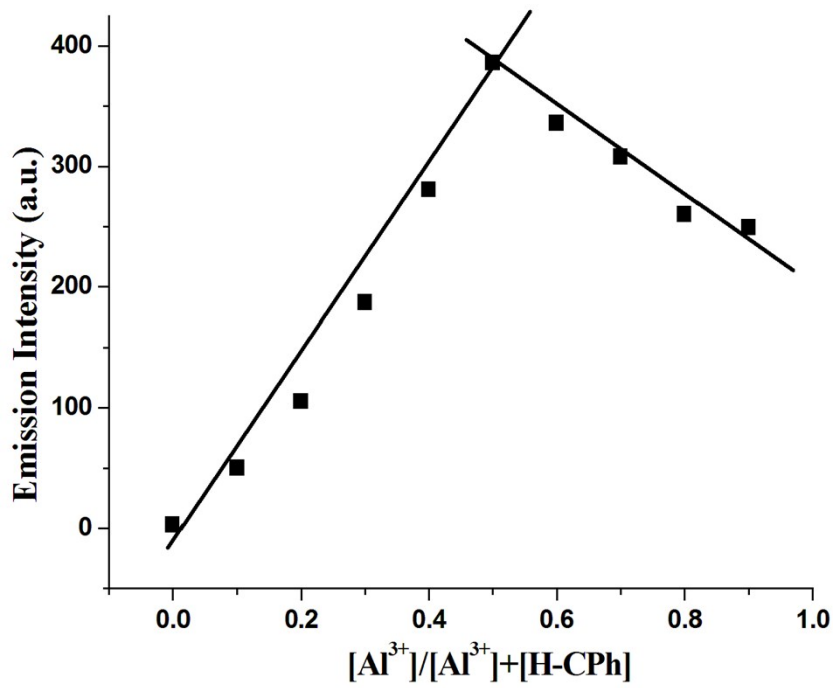


Fig S13 Job'S plot for binding of Al³⁺ with **H-CPh** by fluoremetric method

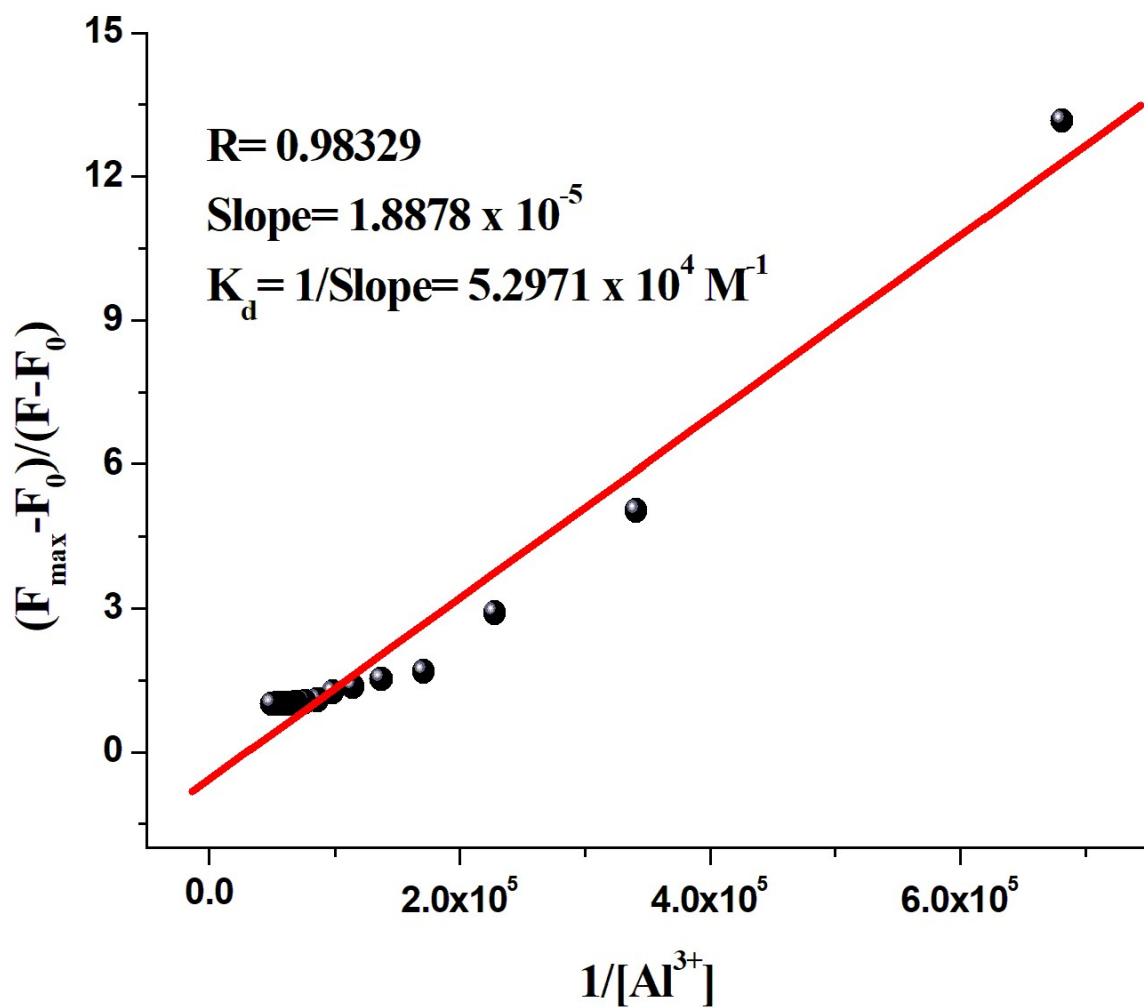


Fig S14 Benesi-Hildebrand plot for determining binding constant of Al^{3+} with **H-CPh**

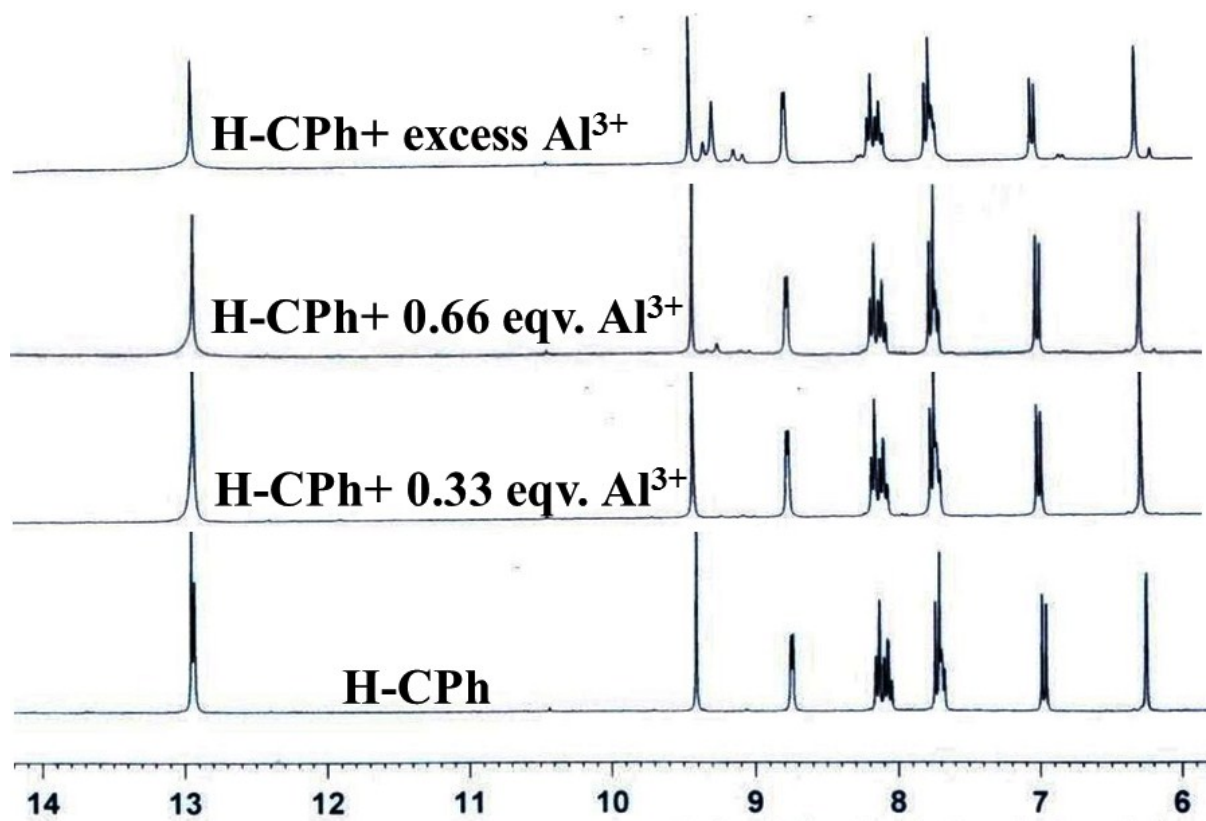


Fig S15 ¹H NMR spectra of **H-CPh** on gradual addition of Al³⁺ in DMSO-d₆

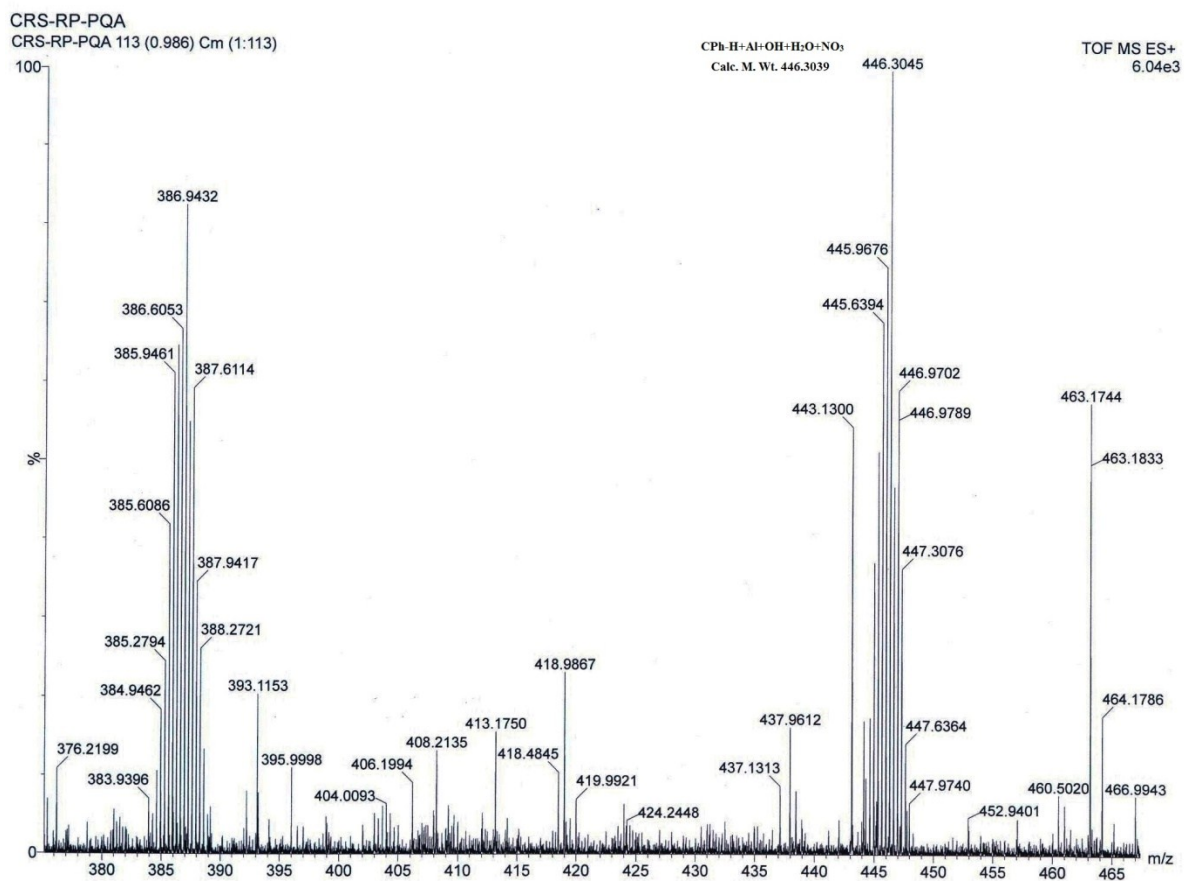


Fig S16 Mass spectrum of Al³⁺ complex

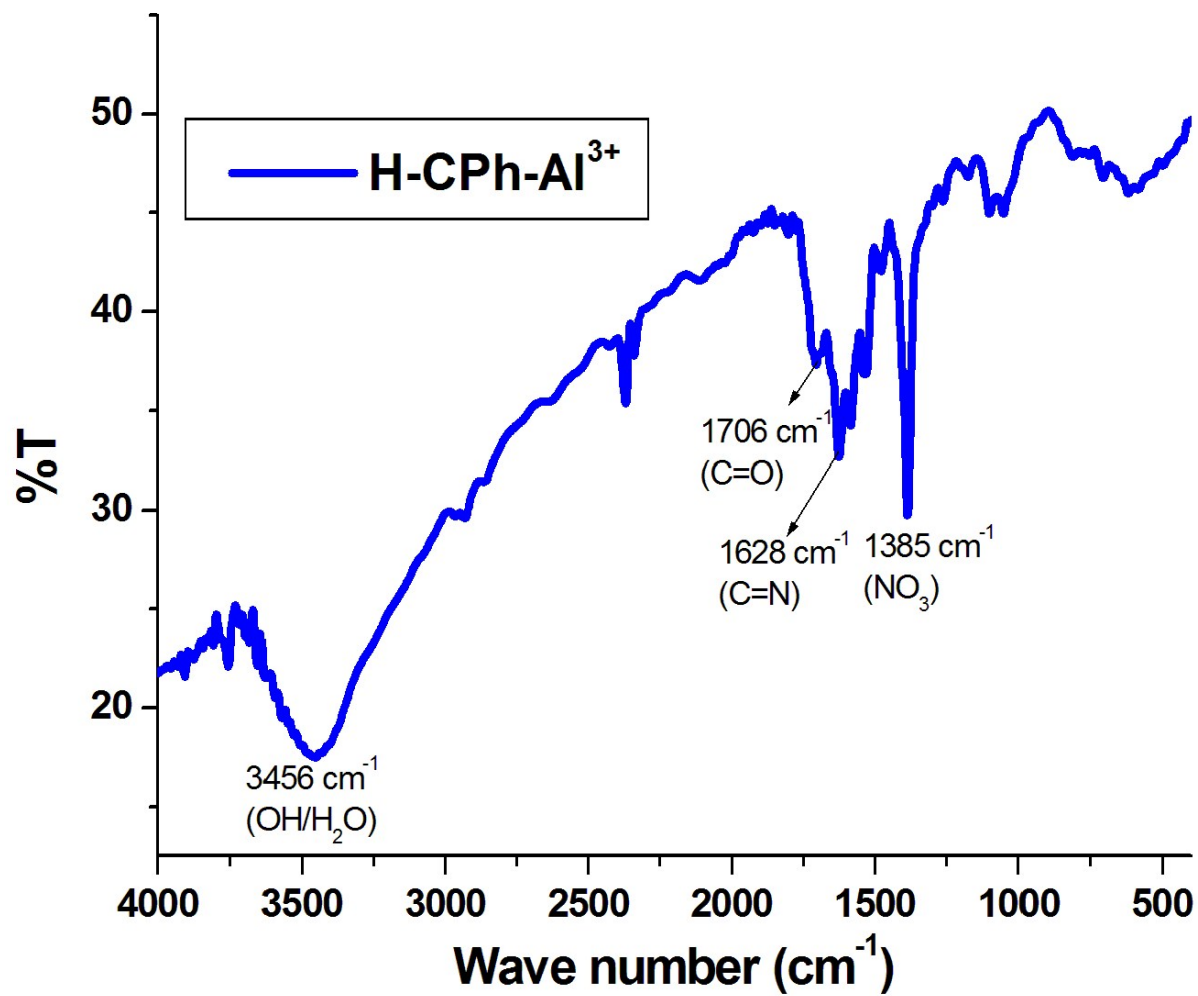


Fig S17 FT-IR spectrum of Al³⁺ complex

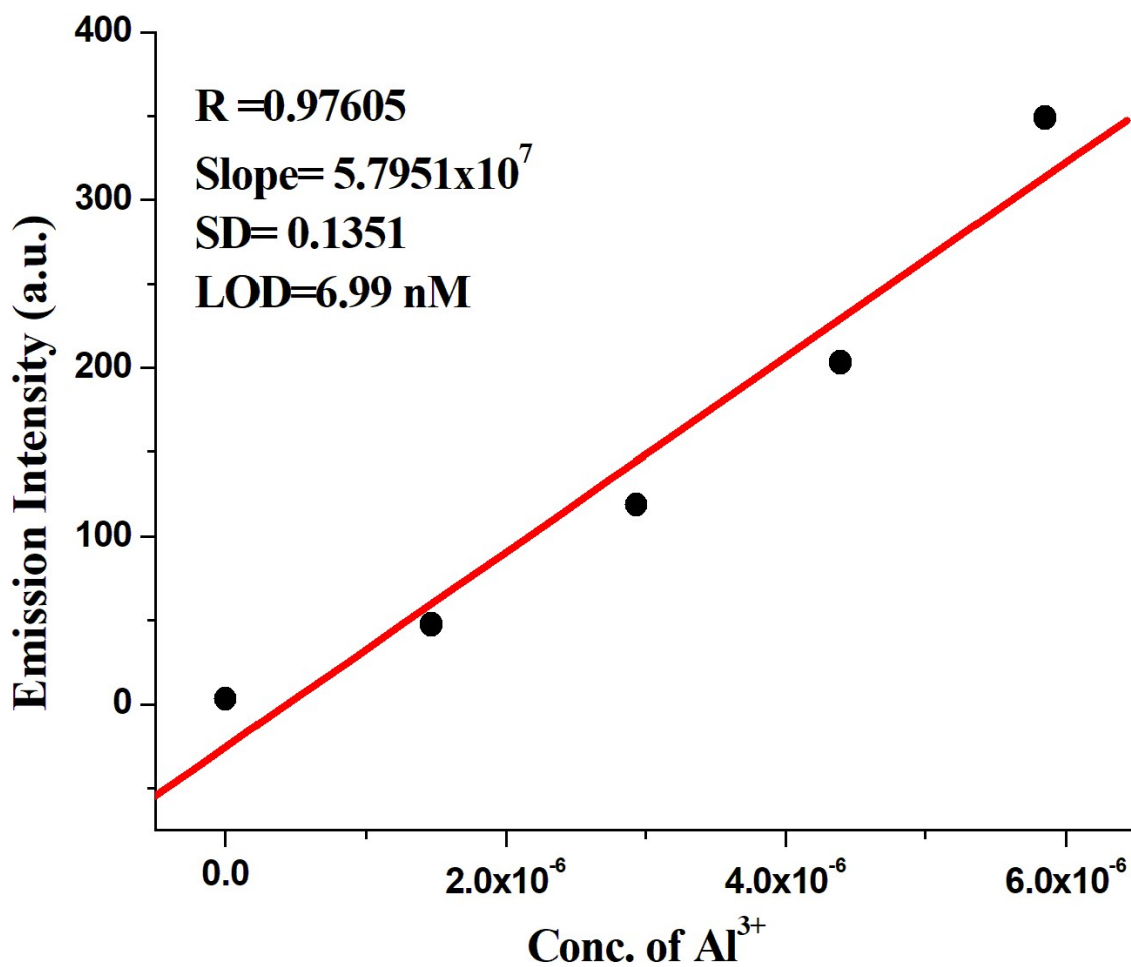


Fig S18 Limit of detection determining plot for Al^{3+}

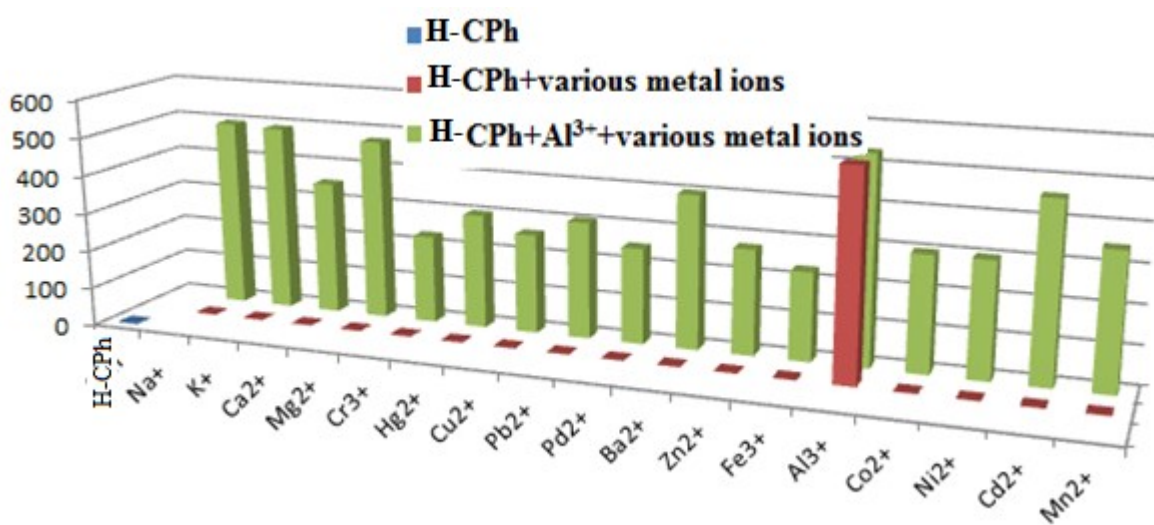


Fig S19 Interfering study on Al^{3+} sensitivity

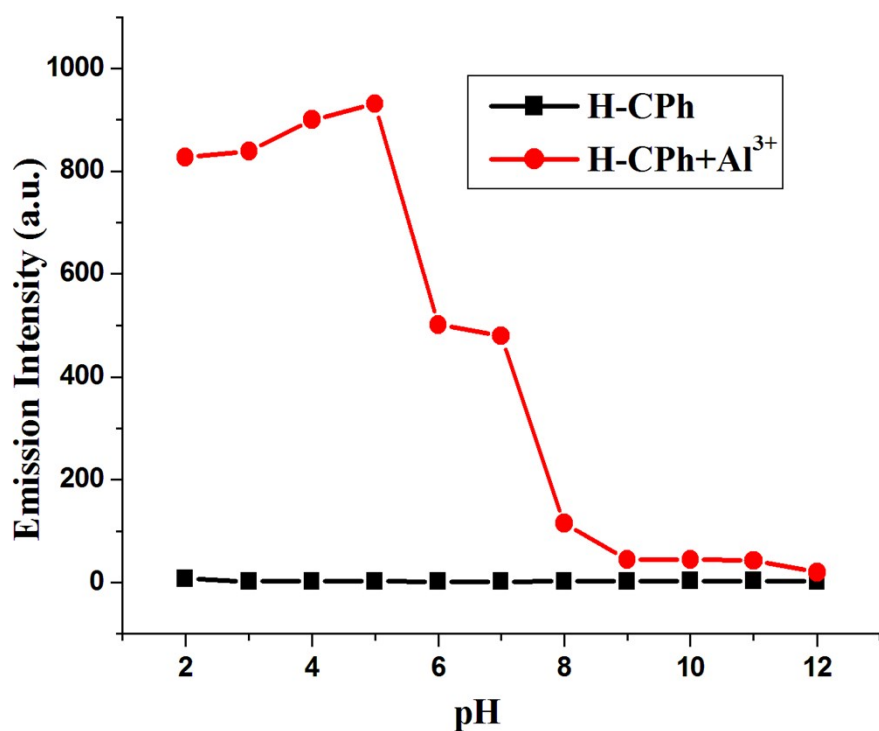


Fig S20 pH dependence fluorescence sensitivity of Al³⁺ by the probe H-CPh

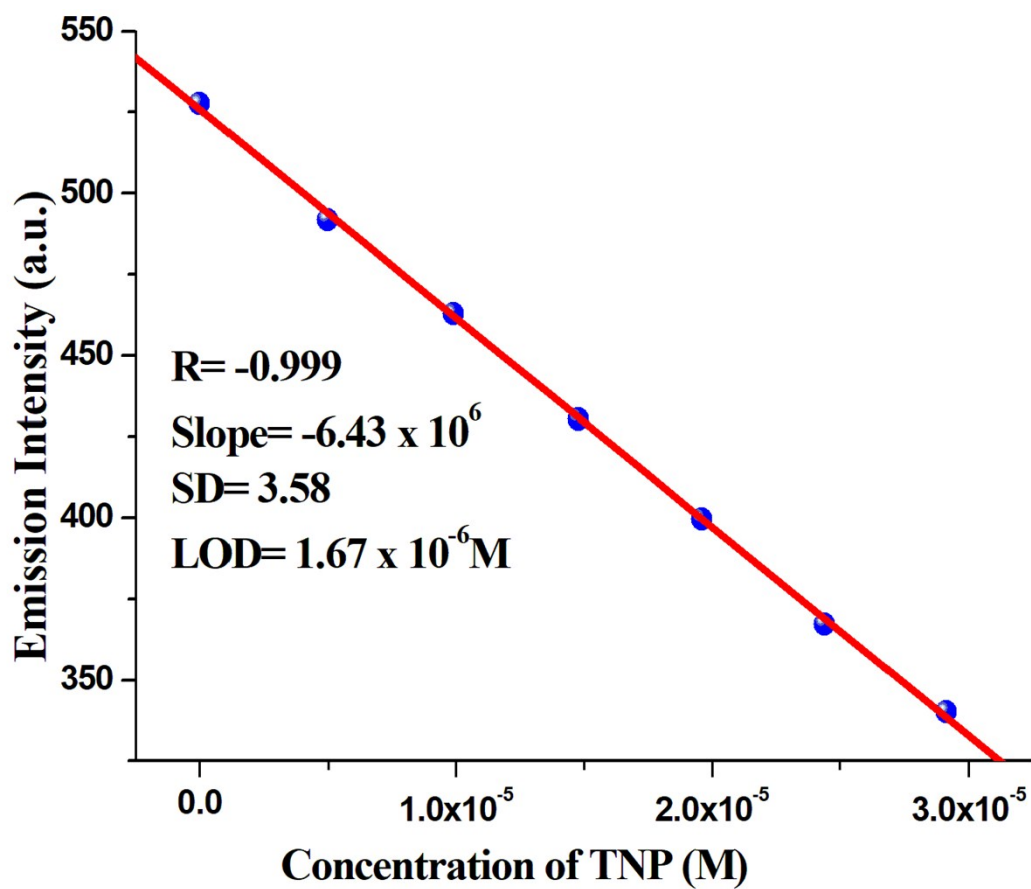


Fig S21 Limit of detection determining plot for TNP

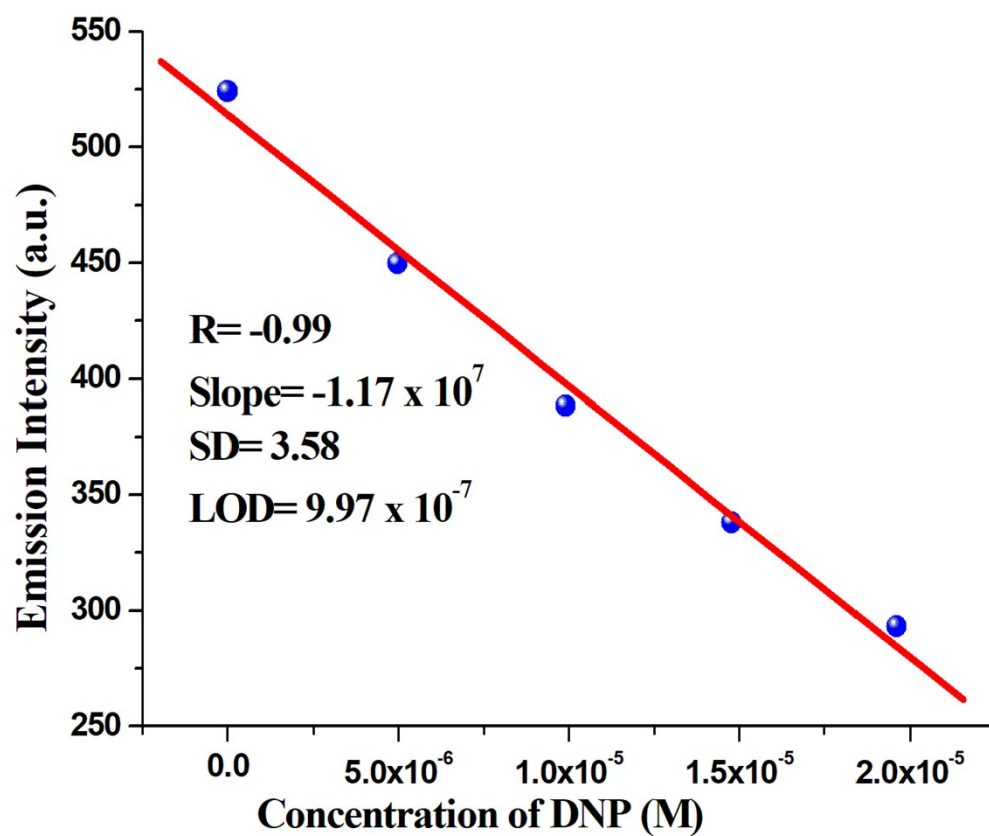


Fig S22 Limit of detection determining plot for DNP

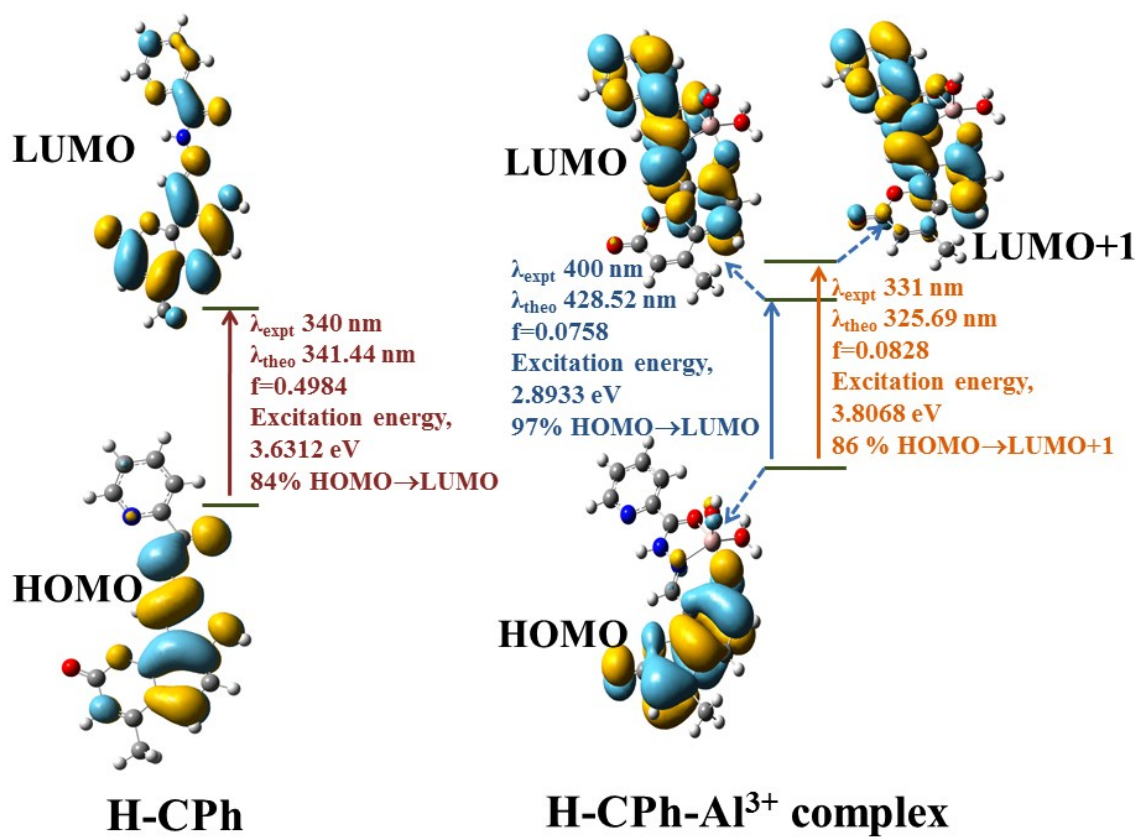


Fig S23 Theoretical electronic transitions of H-CPh and its Al³⁺ complex