Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

A hydrazone based probe for the selective fluorescent detection of Al(III) and Al(III)-probe complex mediated secondary PPi sensing: computational studies, interpretation of molecular logic circuit and memory device and intracellular application

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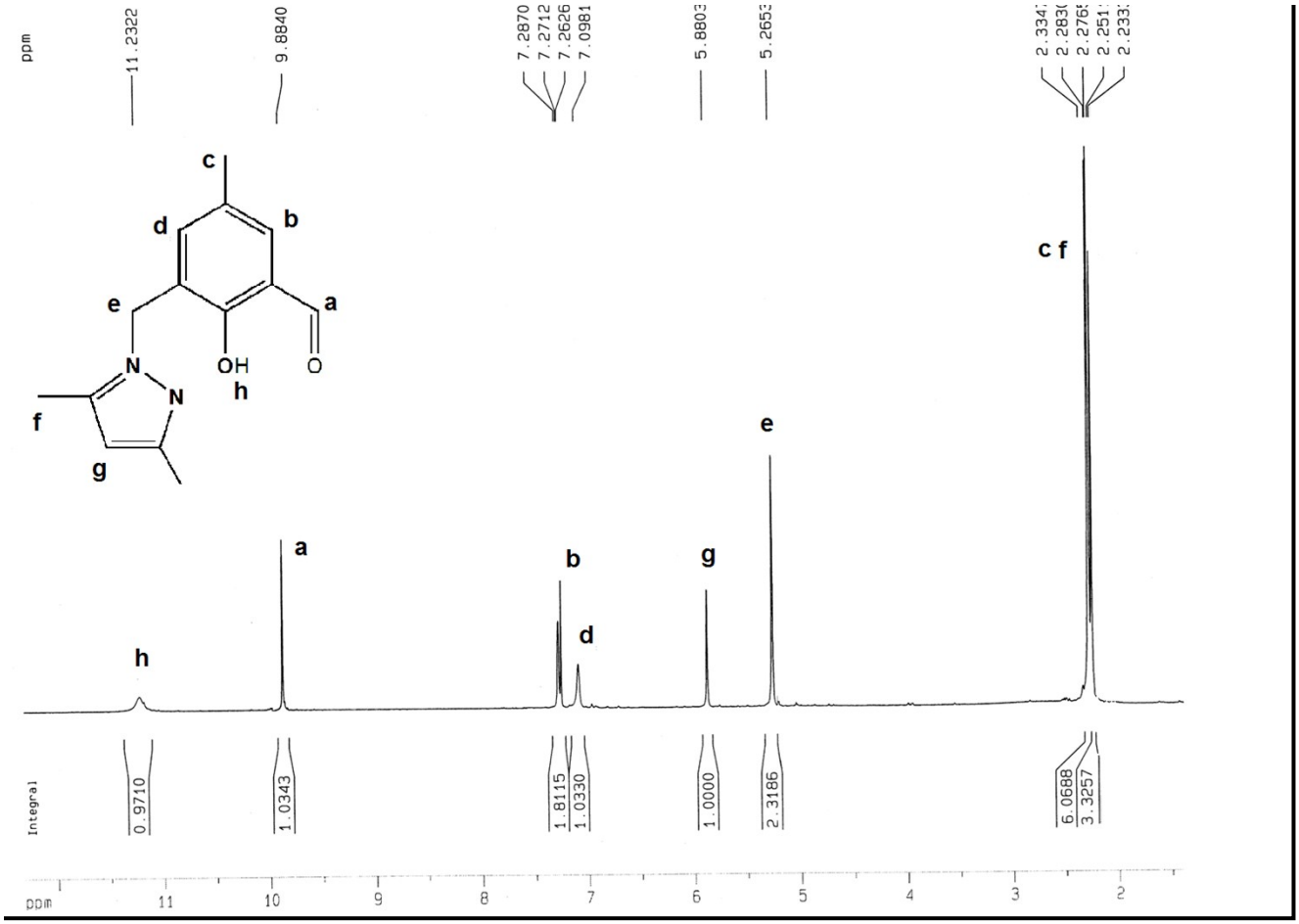


Fig.S1. ^{1}H-NMR spectrum of L^{1} in DMSO-d_6.

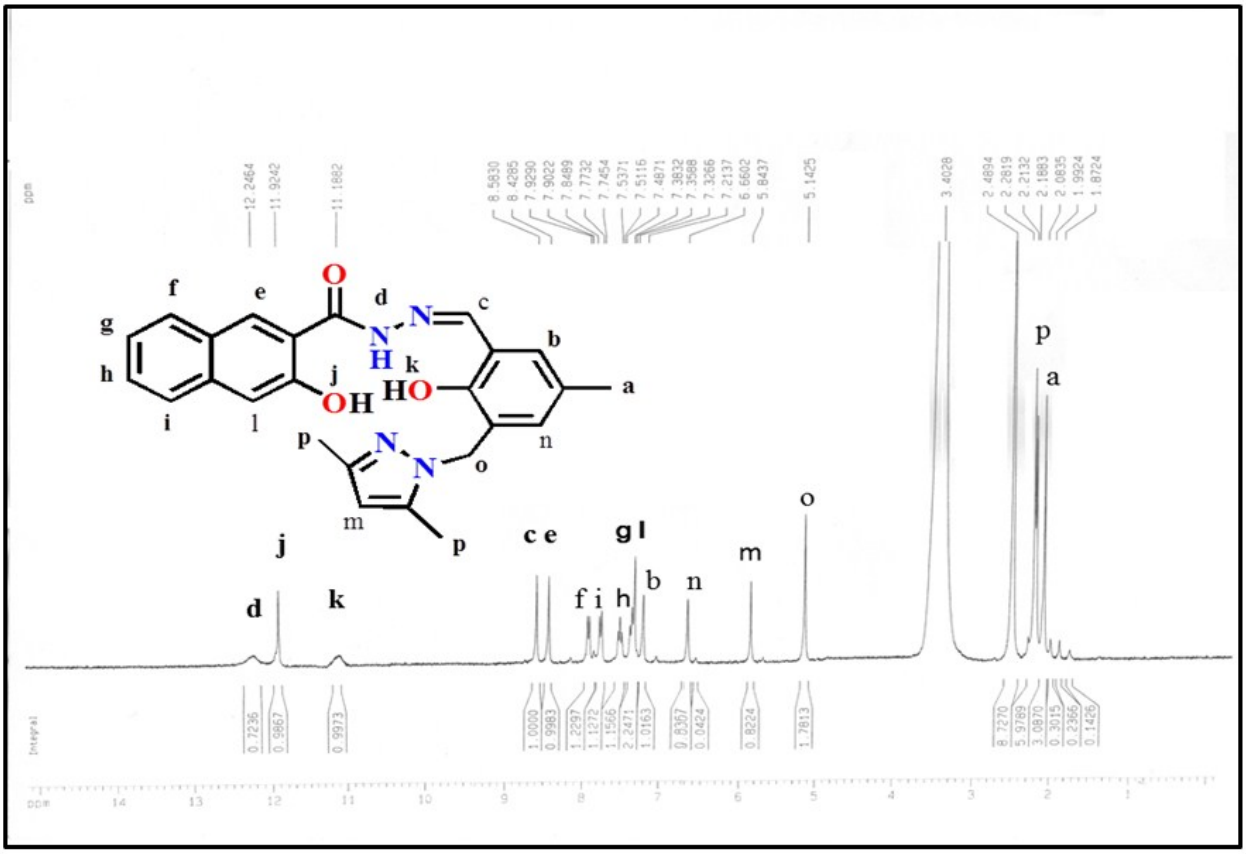


Fig.S2. ^{1}H-NMR spectrum of Nap-hyz-pyz.(H_3L^3)

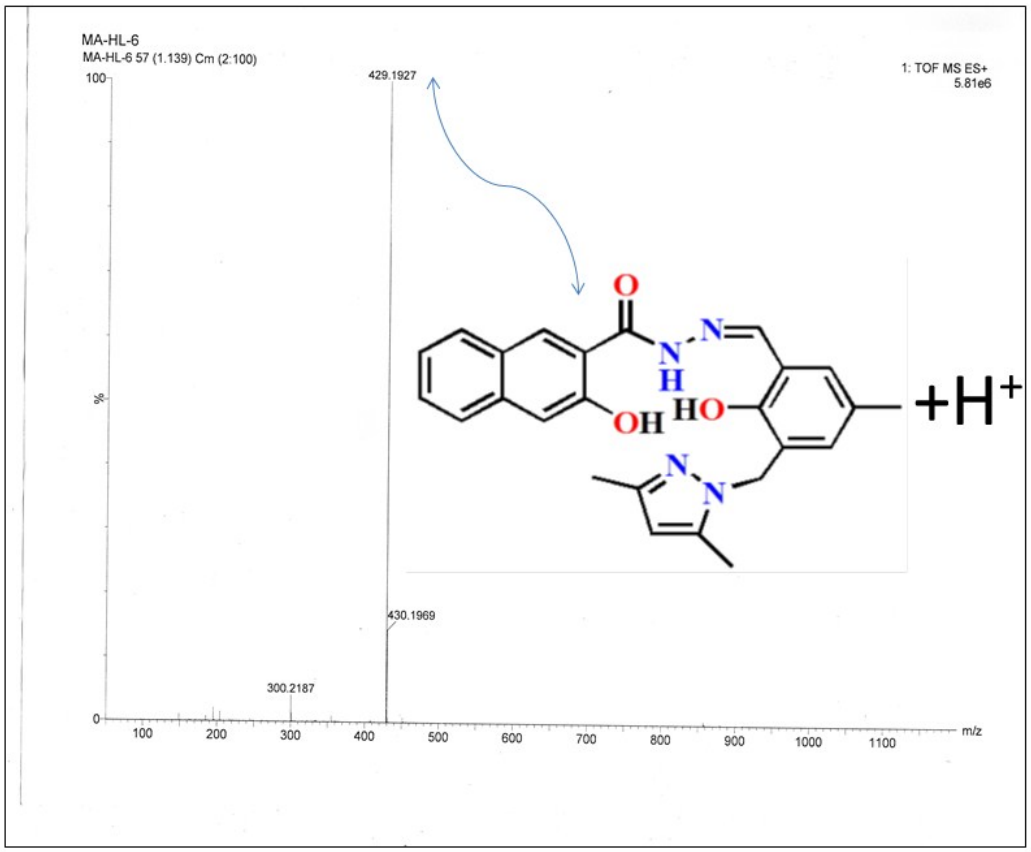


Fig.S3. Mass spectrum of Nap-hyz-pyz in MeOH.

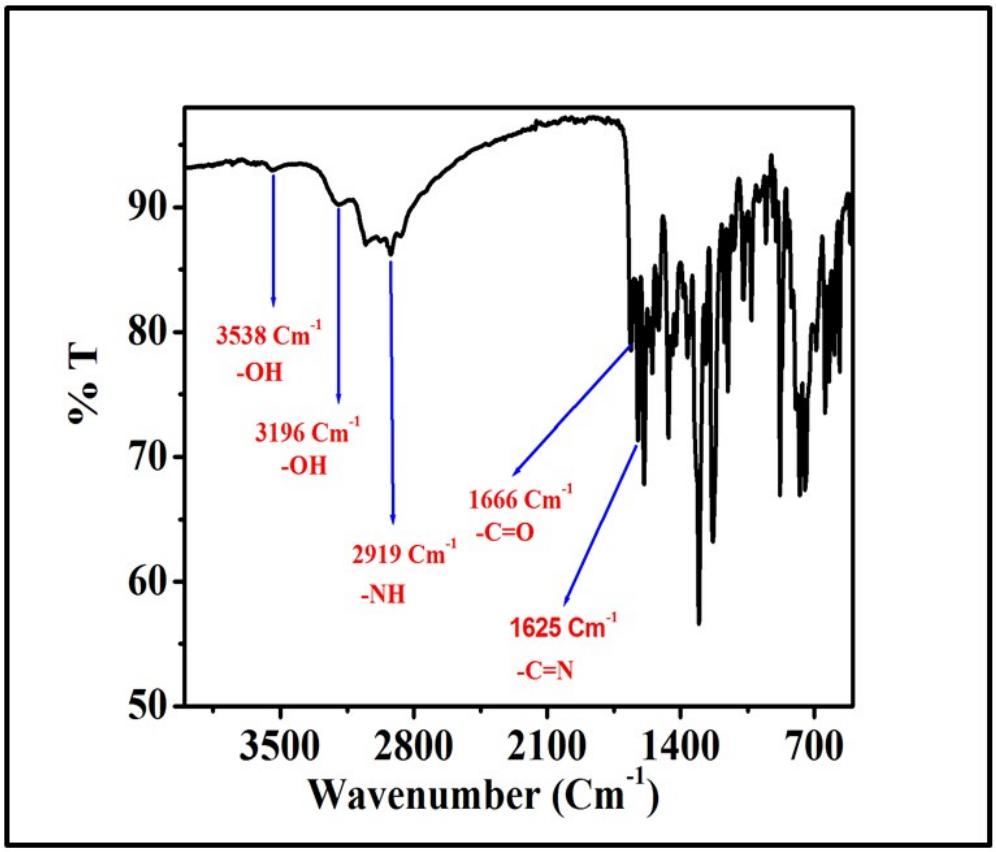


Fig.S4. IR spectrum of ligand Nap-hyz-Pyz.

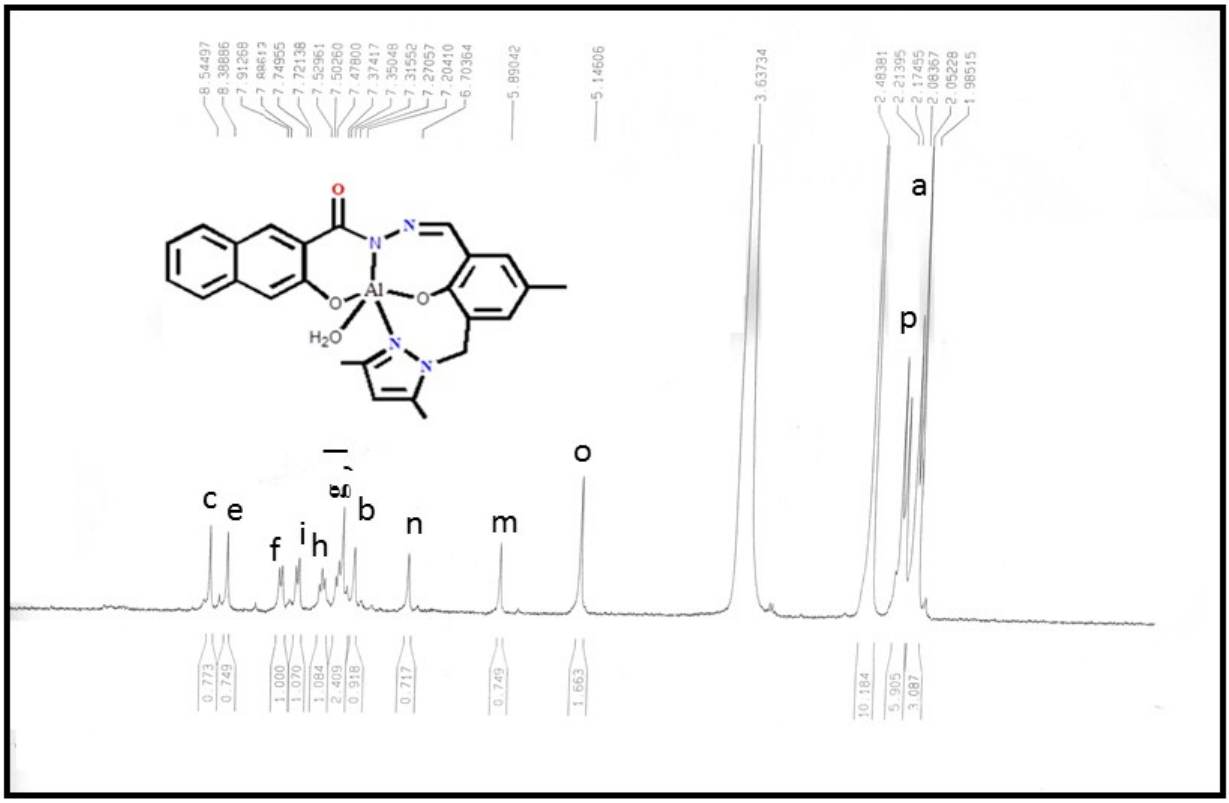


Fig.S5. ^{1}H-NMR spectrum of ^{1}H-NMR spectrum of (Nap-hyz-pyz + Al^{3+}) Complex in DMSO-d_6.

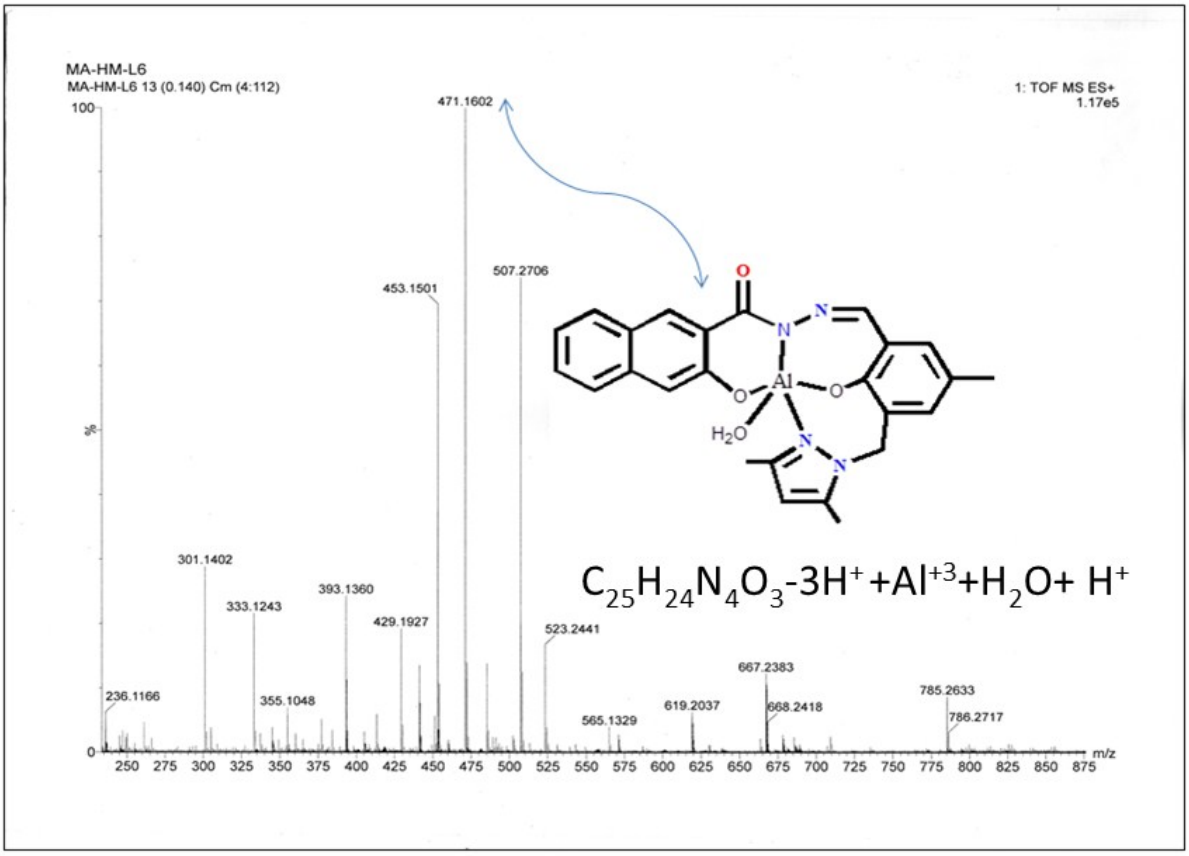


Fig.S6. Mass spectra of [(Nap-hyz-pyz) - 3H$^+$ + Al^{3+} + H_2O + H$^+$]

JOB's Plot

This method is based on the measurement of a series of solutions in which molar concentrations of two reactants vary but their sum remains constant. The fluorescence intensity of each solution was measured at a suitable wavelength and plotted against the mole fraction of one reactant. A maximum in fluorescence intensity appeared at the mole ratio corresponding to the combining ratio of the reactants. The composition of the complex was determined by JOB's method and found to be (1:1) with respect to ligand for Al^{3+}.

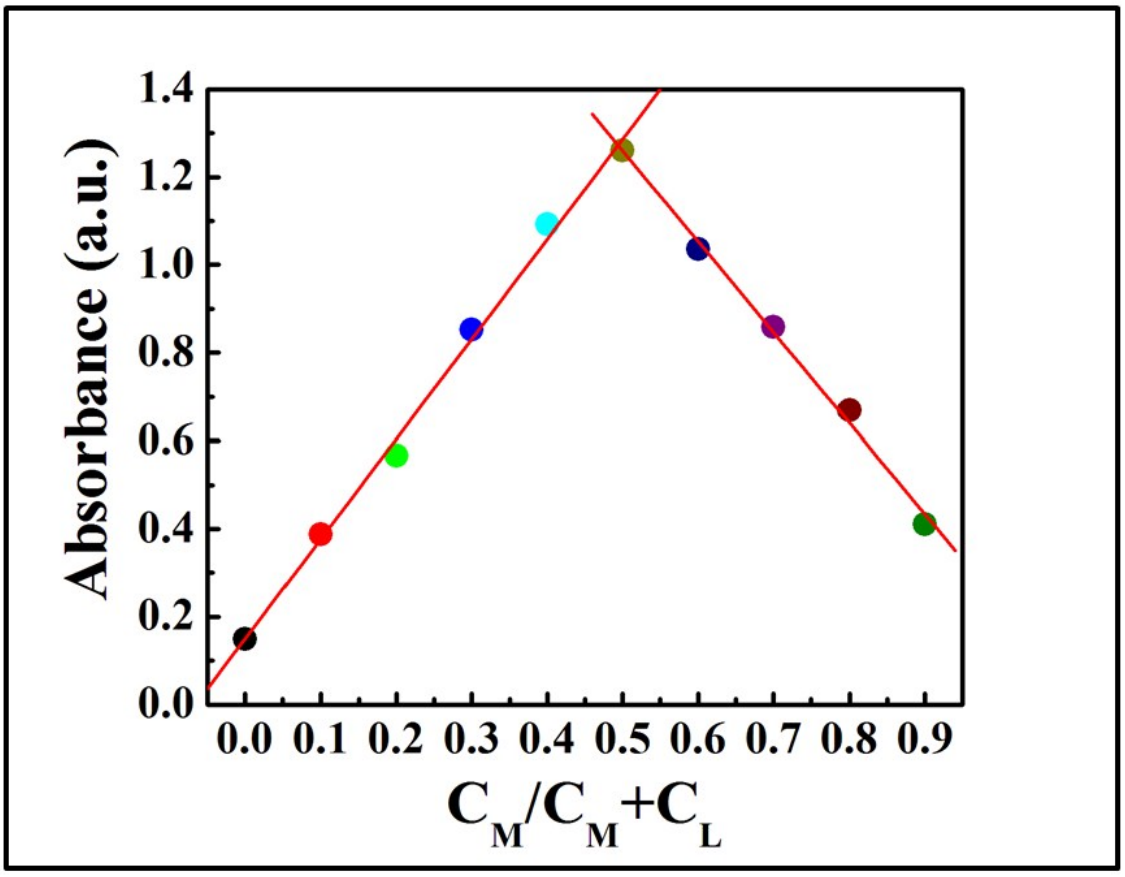


Fig.S7. JOB's plot for Al^{3+}.

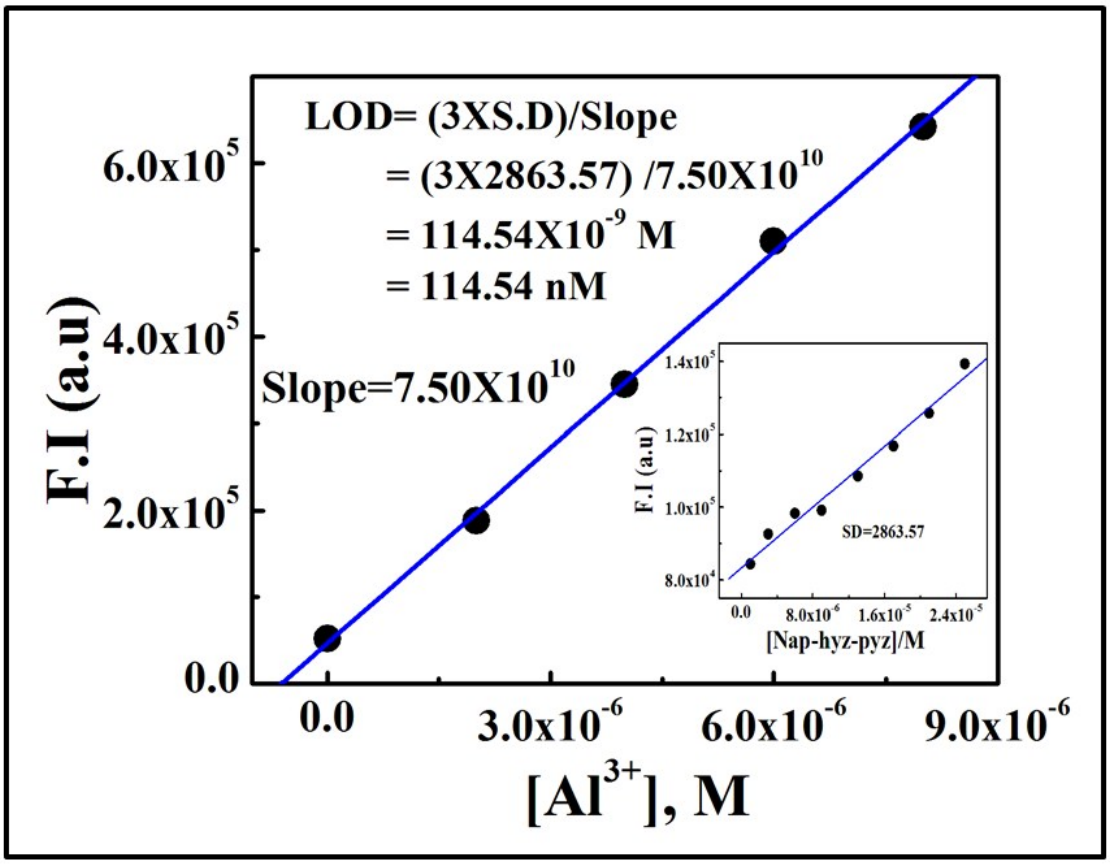


Fig.S8. LOD of Al^{3+}

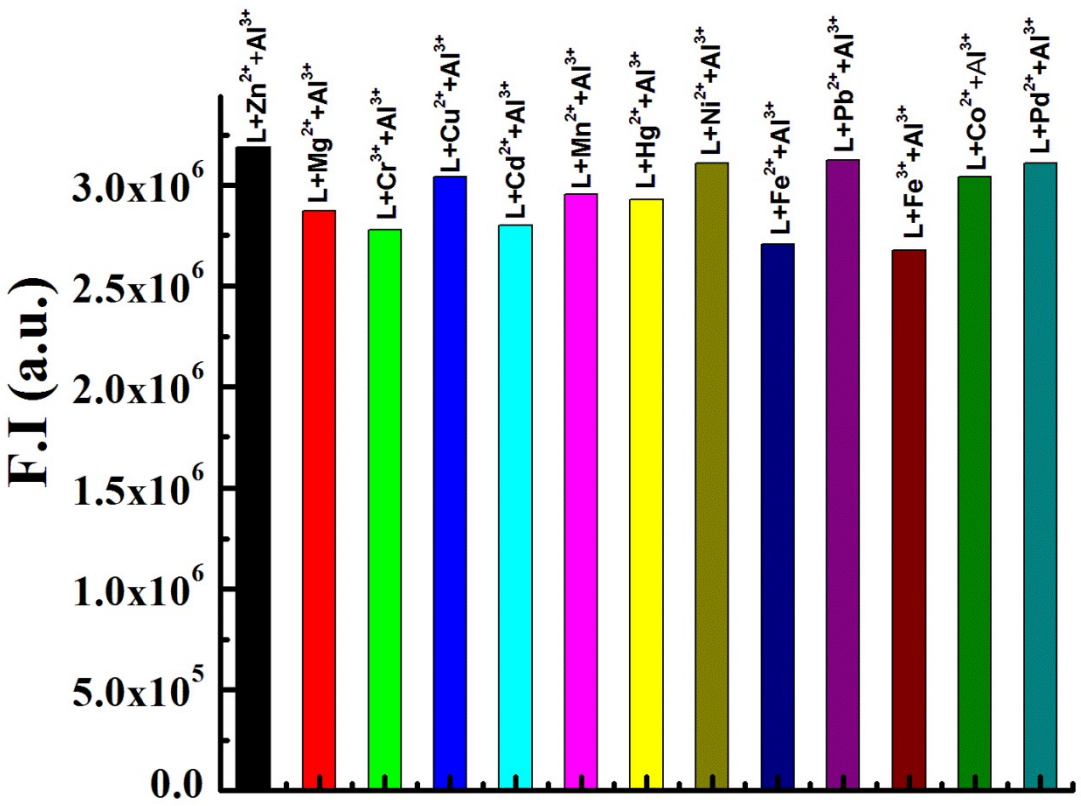


Fig.S9 Selectivity study of Al^{3+} in presence of different cations

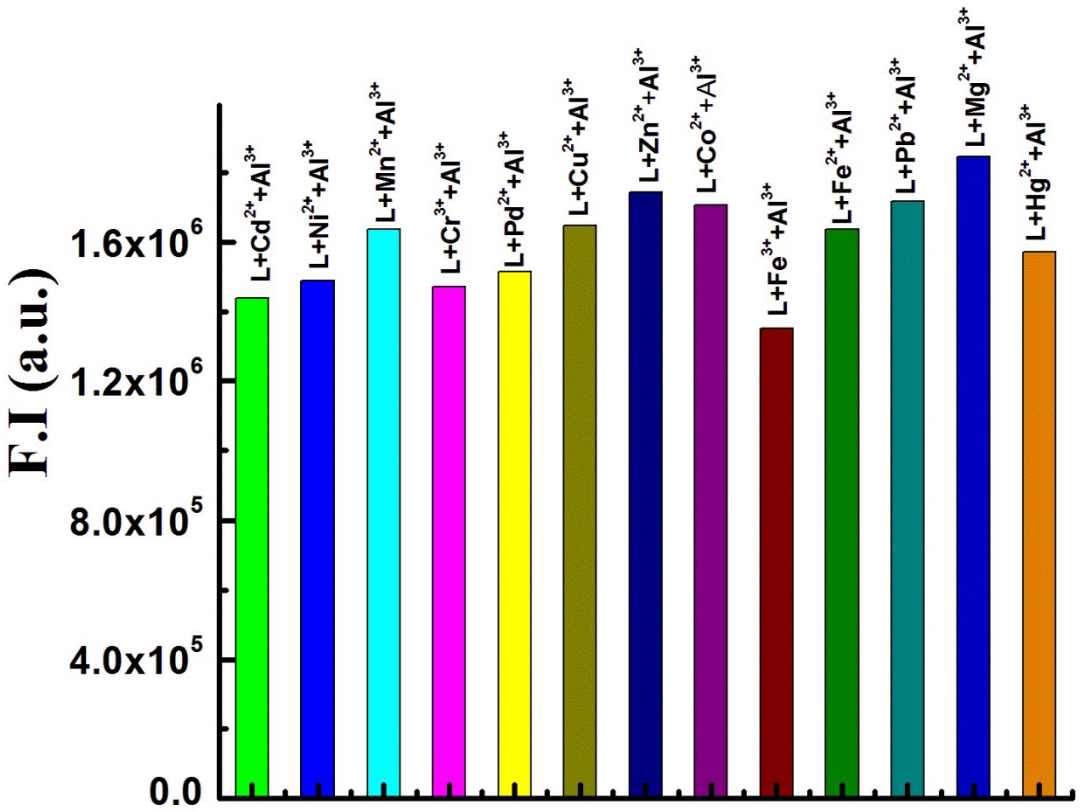


Fig.S10. Selectivity study of Al^{3+} in presence of different cations at pH 5

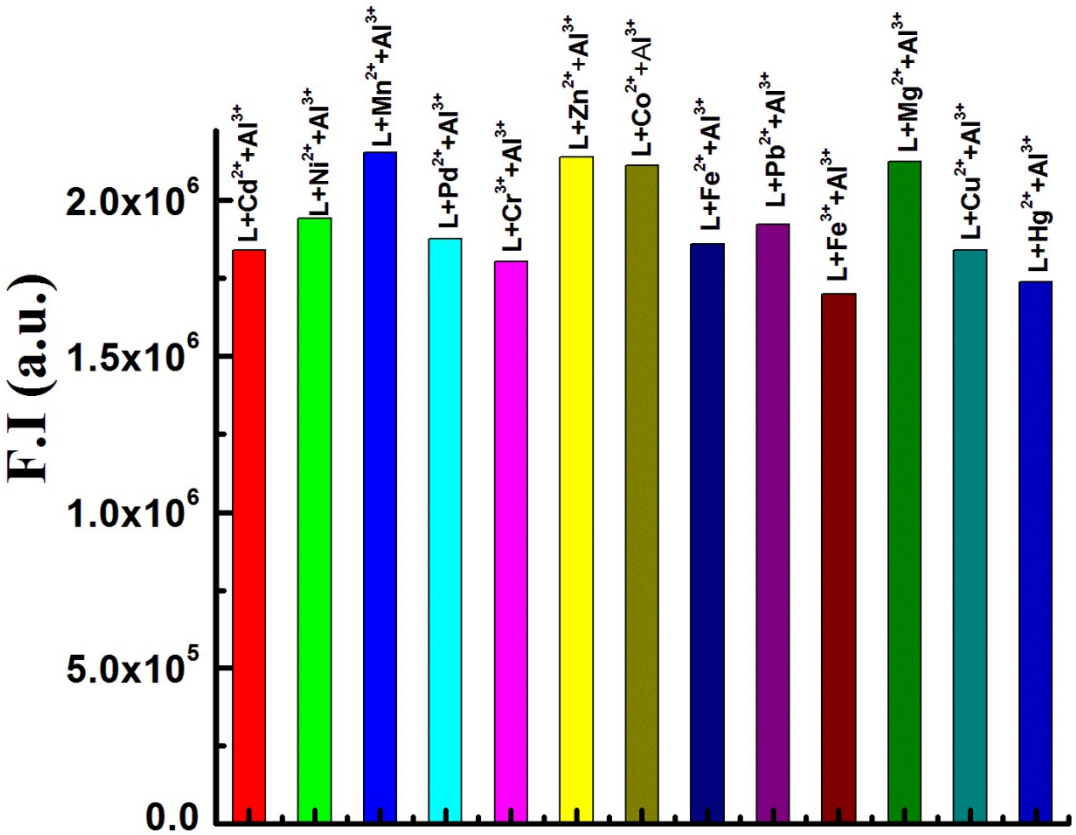


Fig.S11. Selectivity study of Al^{3+} in presence of different cations at pH 8

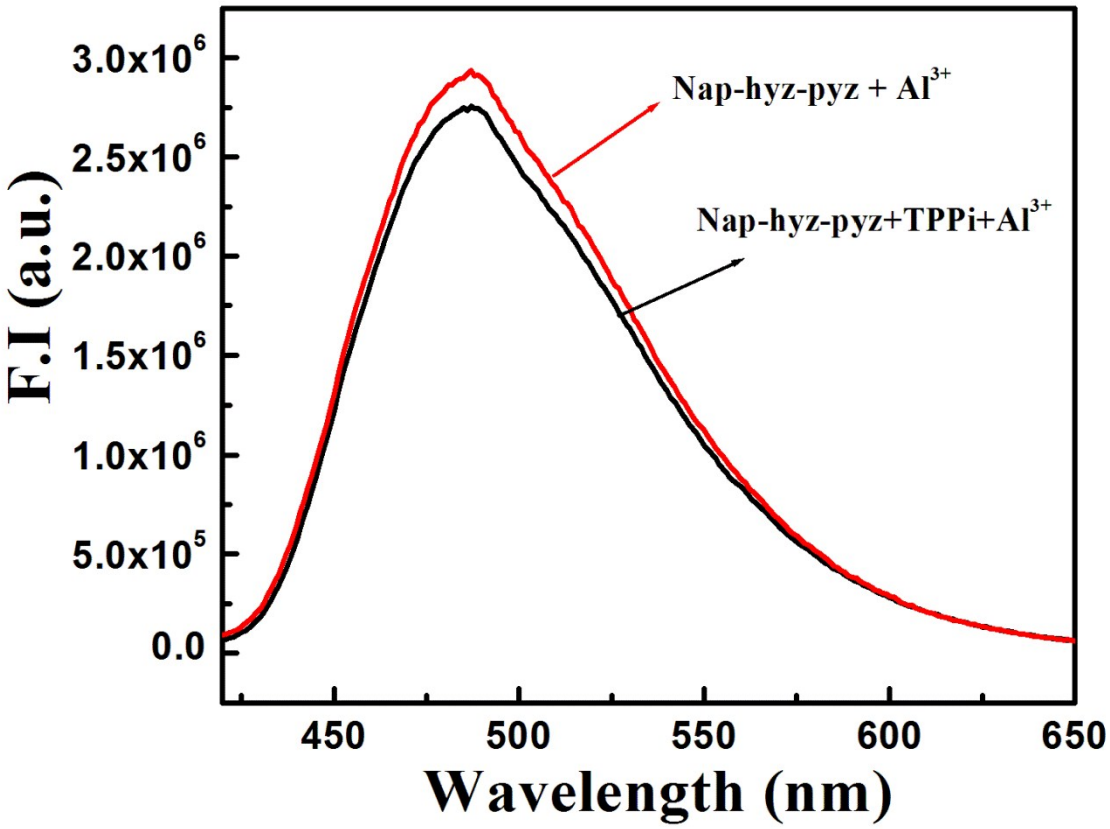


Fig.S12. Selectivity study of Al^{3+} in presence of TPPi

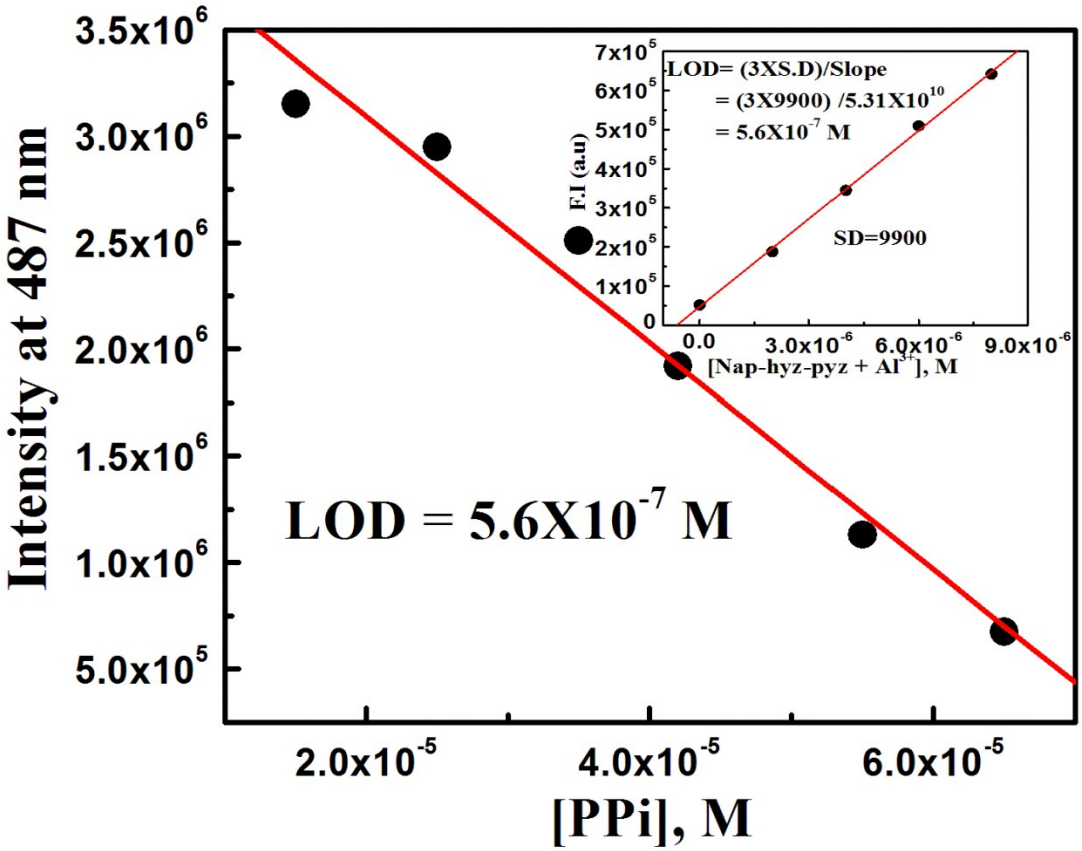


Fig.S13. LOD of PPi

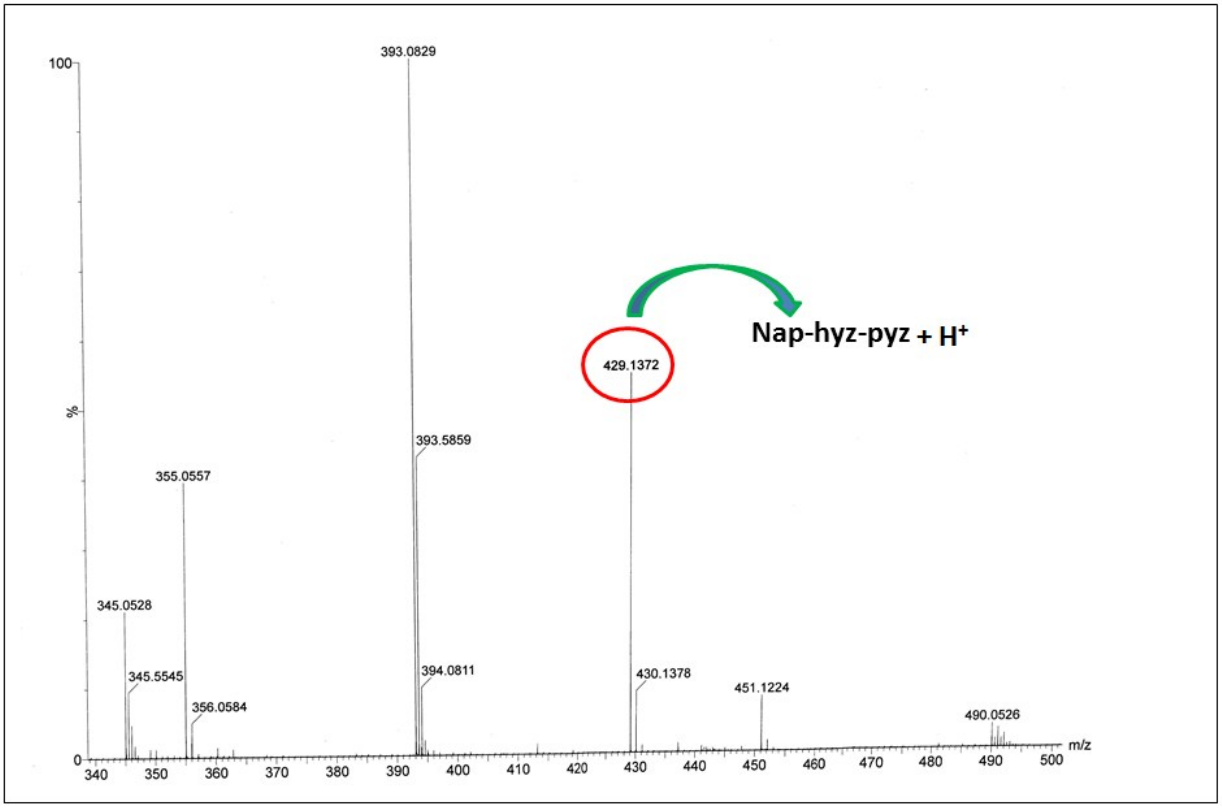


Fig.S14. Mass spectra of Nap-hyz-pyz+Al^{3+} complex after adding PPi

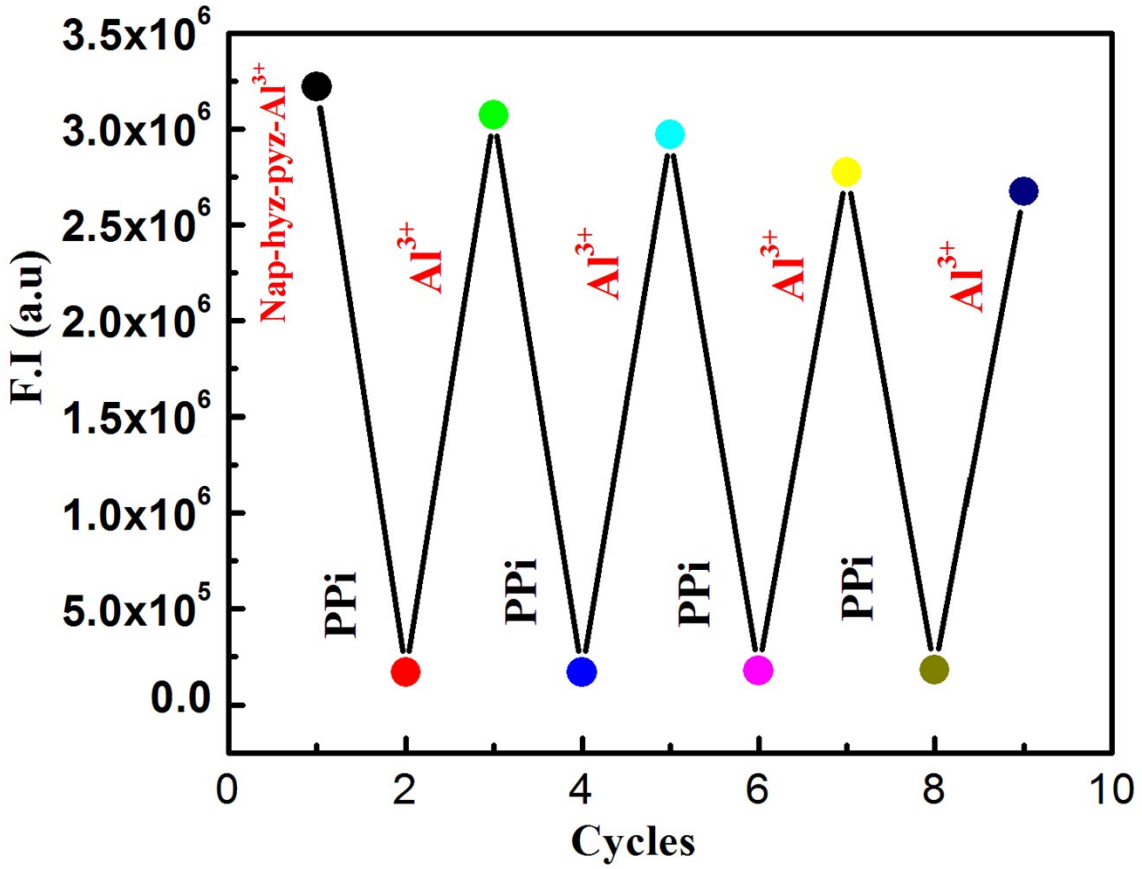


Fig.S15. Cascade fluorescence ON-OFF-ON response of Nap-hyz-pyz with sequential addition of Al^{3+} and PPi.

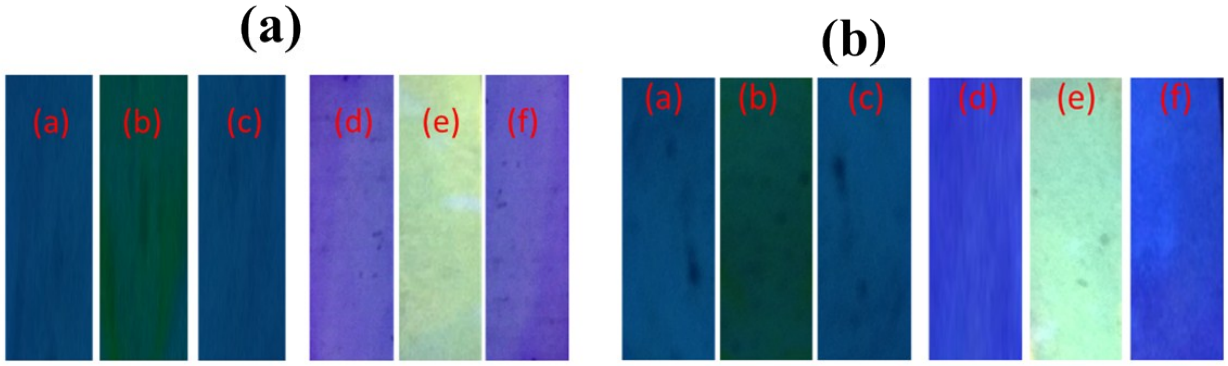


Fig.S16. (a) Color changes on test paper at **pH 5** (a) Nap-hyz-pyz (b) Nap-hyz-pyz + Al^{3+} (c) Nap-hyz-pyz + Al^{3+}+ PPi under day light and (d) Nap-hyz-pyz (e) Nap-hyz-pyz + Al^{3+} (f) Nap-hyz-pyz + Al^{3+}+ PPi under UV light. **(b)** Color changes on test paper at **pH 8** (a) Nap-hyz-pyz (b) Nap-hyz-pyz + Al^{3+} (c) Nap-hyz-pyz + Al^{3+}+ PPi under day light and (d) Nap-hyz-pyz (e) Nap-hyz-pyz + Al^{3+} (f) Nap-hyz-pyz + Al^{3+}+ PPi under UV light.

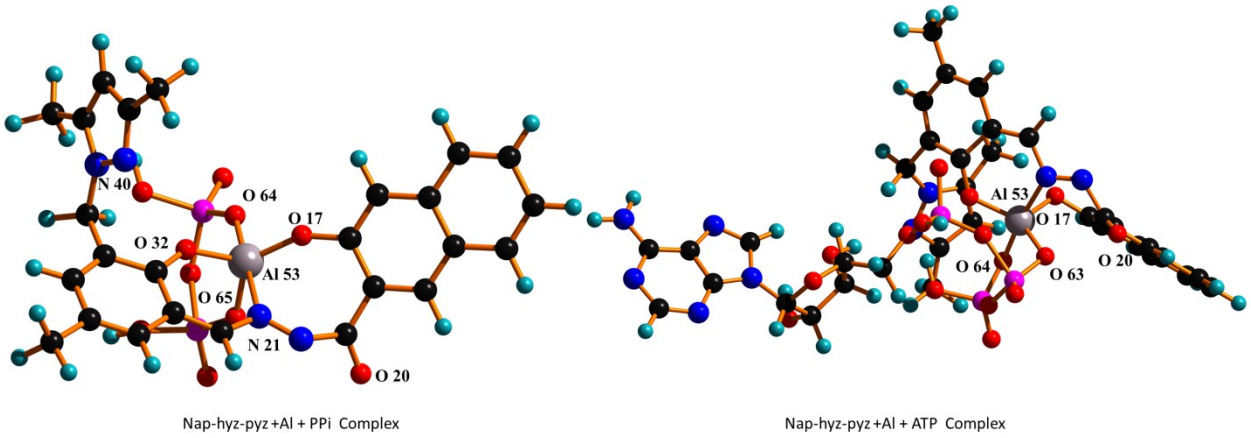


Fig. 17 (a) Optimized geometry of **Nap-hyz-pyz +Al+ PPi** and **Nap-hyz-pyz +Al+ ATP** complex

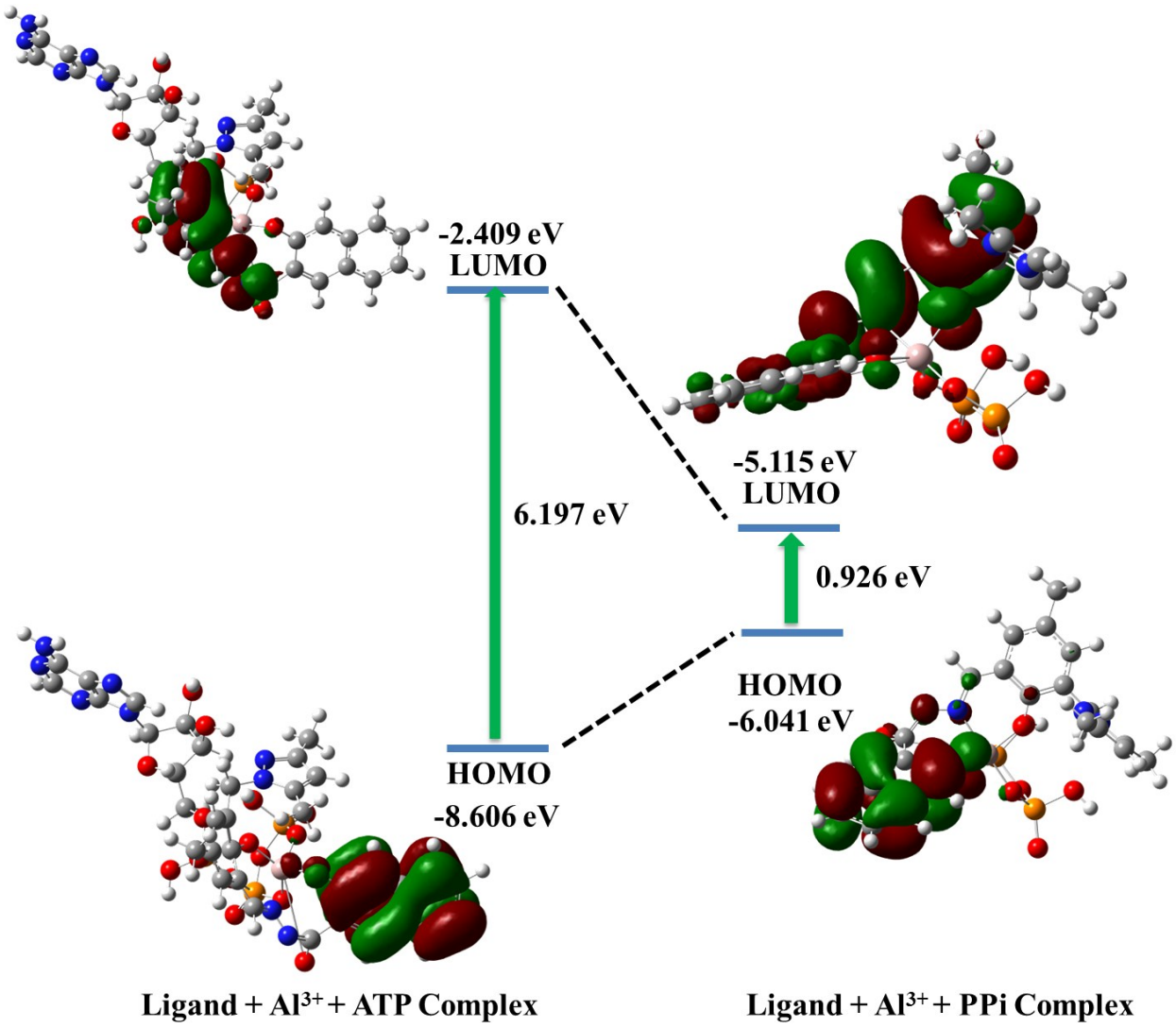


Fig.S17(b). HOMO-LUMO Energy gap of Ligand+Al^{3+} +ATP Complex and Ligand+Al^{3+} +PPi Complex

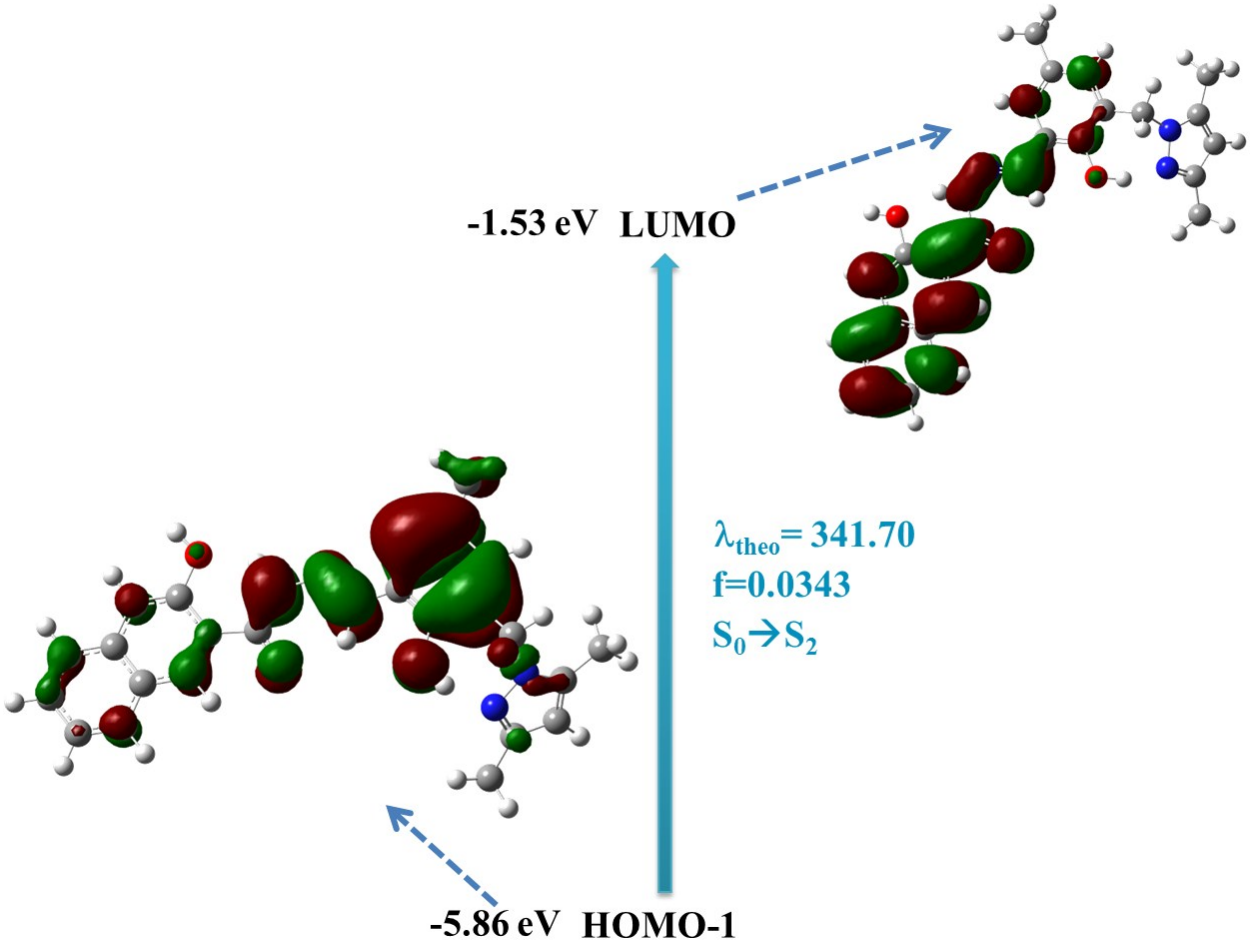


Fig.S18. $S_0 \longrightarrow S_2$ electronic transion of ligand Nap-hyz-pyz

Table S1. Vertical excitation energies and oscillator strengths (f_{cal}) of some low-lying excited singlet states obtained from TDDFT// B3LYP/6-31+G calculations of Nap-hyz-pyz**.**

Electronic transition	Composition	Excitation energy	Oscillator strength (f_{cal})	CI	λ_{exp} (nm)
$S_0 \rightarrow S_2$	HOMO –1→ LUMO	3.6284 eV (347.70 nm)	0.1343	0.68098	350

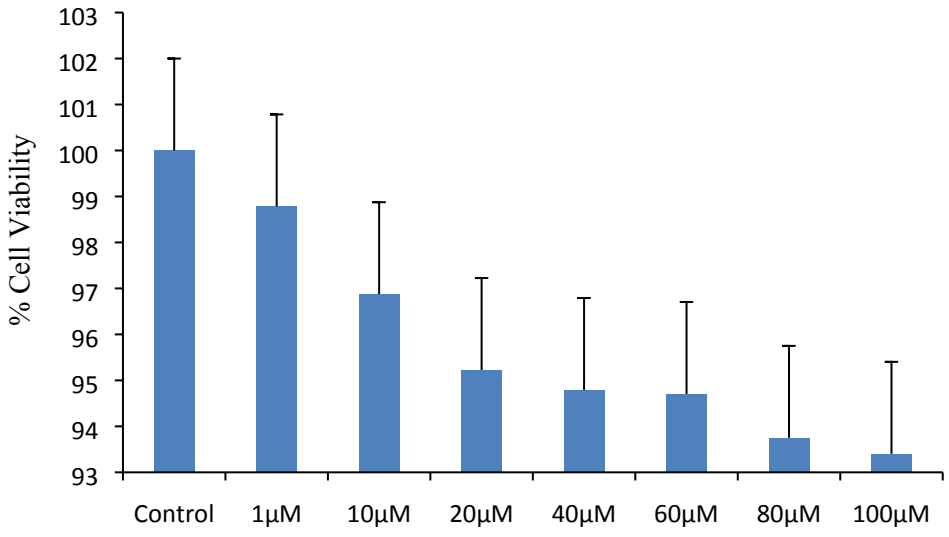


Fig.S19. MTT assay of ligand Nap-hyz-pyz.

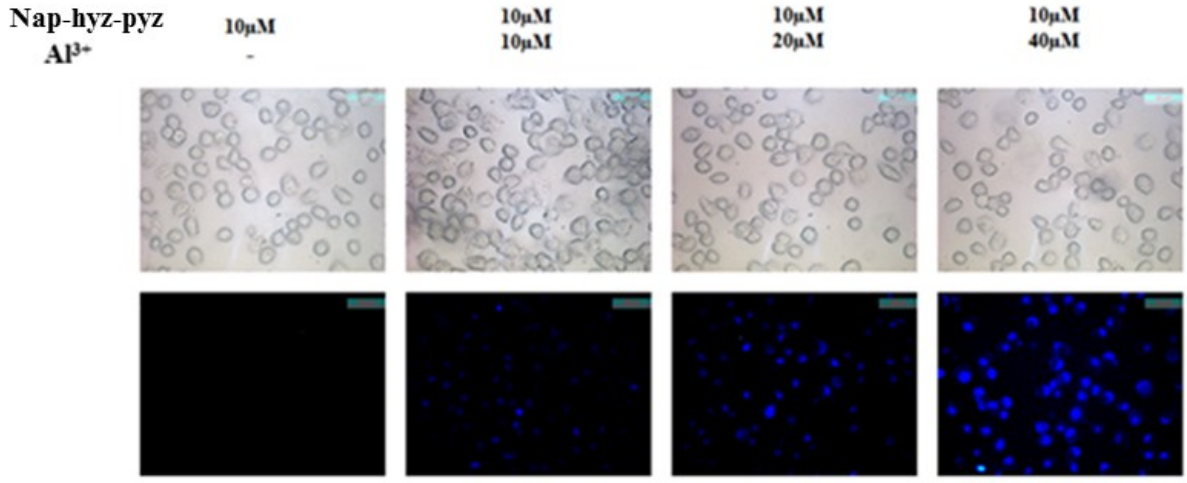


Fig.S20. The fluorescence images of HepG2 cells were capture (40X) after incubation with 10 μM, 20 μM and 40μM of Al^{2+} for 60 min at 37°C, followed by washing thrice with 1X PBS and incubation with 10μM of Nap-hyz-pyz for 60 min at 37 °C.The fluorescence images show absence of signal by the fluorophoreNap-hyz-pyz (10μM) in absence of Al^{3+} ion, while the fluorescence gradually increases, highly at 40 μM of Al^{3+} concentration.

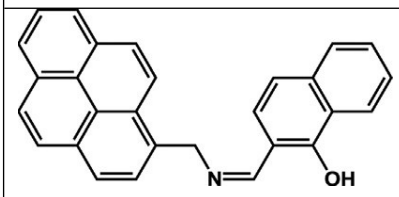
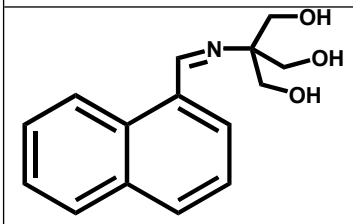
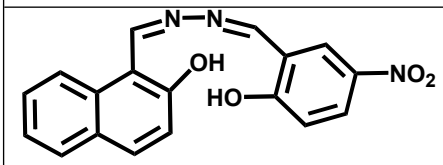
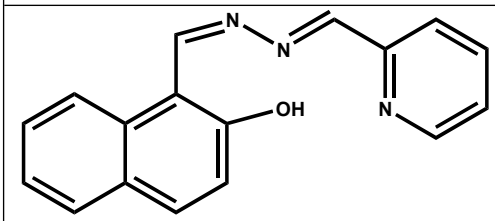
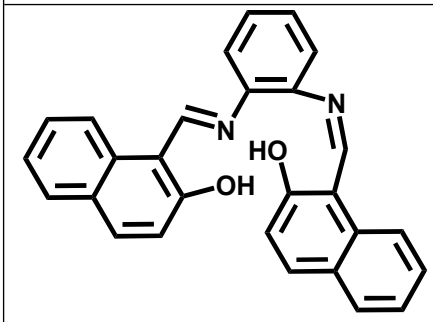
Calculation of Quantum Yield:

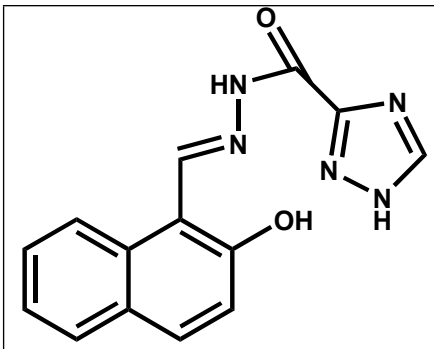
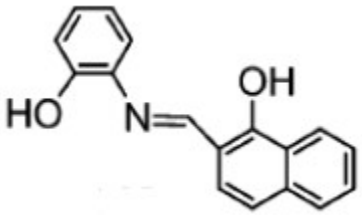
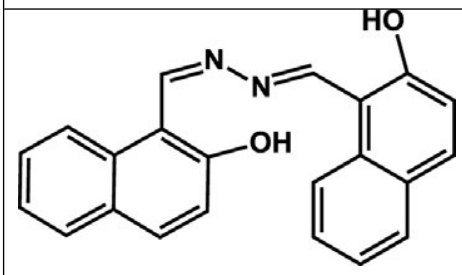
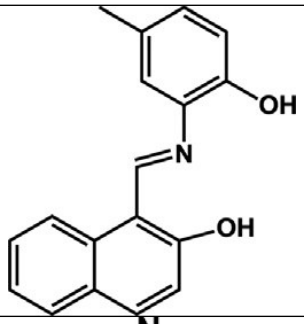
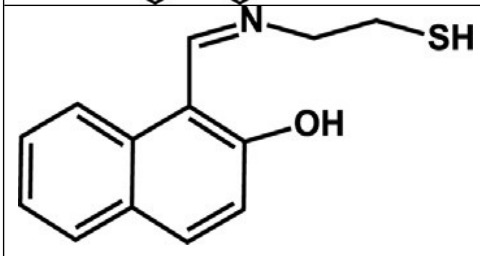
Fluorescence quantum yields (Φ) were estimated by integrating the area under the fluorescence curves using the equation,

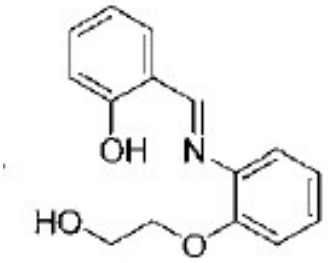
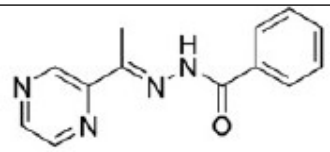
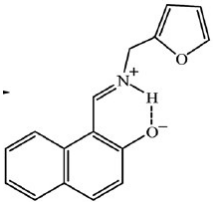
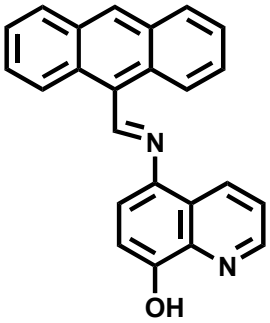
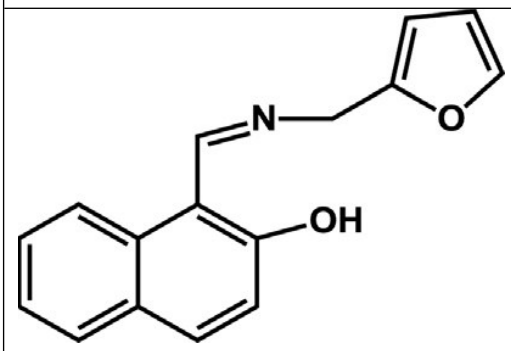
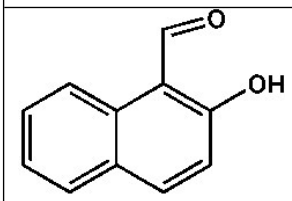
$$\Phi_{sample} = (OD_{std} \times A_{sample})/(OD_{sample} \times A_{std}) \times \Phi_{std}$$

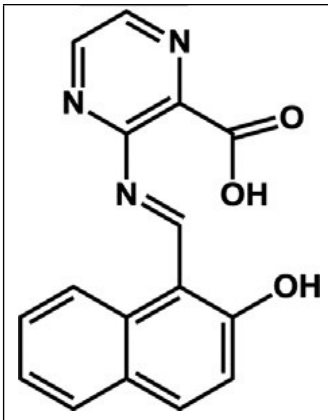
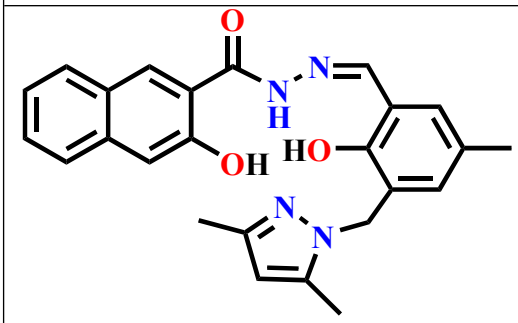
Where A_{sample} and A_{std} are the area under the fluorescence spectral curves and OD_{sample} and OD_{std} are the optical densities of the sample and standard, respectively at the excitation wavelength. Coumarine153 has been used as the standard with Φ_{std} = 0.504 in ethanol for measuring the quantum yields of **Nap-hyz-pyz** and of **Nap-hyz-pyz–Al^{3+}**systems.

Table S2. Comparison of few aspects of some recently published fluorescent chemosensors for Al^{3+} ion

Ligand	K_f/ *M-1*	Solvent	LOD	Biological study	Ref
	1.9×10^4	DMSO/H_2O (2 : 1, v/v)	2.16 μM	Done	**40**
	1.19×10^8	H_2O	0.1 μM	-	**41**
	1.04×10^4	water:methanol (1:9, *v/v*)	4.39 μM	-	**42**
	-	water:methanol (1:9, *v/v*)	2.8 μM	-	**43**
	2.67×10^6	DMF	1 μM	-	**44**

	1.26×10^3	MeCN–H2O (v/v,1/1)	9.82 µM	-	**45**
	2.5×10^3	50 mM Bis–Tris buffer	-	Done	**46**
	5.25×10^4	water:methanol (1:4, *v/v*)	0.12 µM	Done	**47**
	$1.44(\pm 0.07) \times 10^4$	water:methanol (1:9, *v/v*)	-	Done	**48**
	5.89×10^6	DMSO/H_2O (4:6, *v/v*)	1.023 µM	-	**49**

	5.23×10^5	EtOH–H_2O (95 : 5 v/v)	0.89 µM	-	**50**
	1.24×10^7	EtOH	0.1 µM	-	**51**
	0.35×10^5	DMSO/water (1/100)	60µM	Done	**52**
	2.10×10^2	ACN:H_2O (1:9)	1.08 µM	Done	**53**
	0.35×10^5	DMSO/H_2O (1/100, *v/v*)	0.603 µM	Done	**52**
	8.32×10^6	EtOH/H2O (95 : 5, v/v)	3.28 µM	-	**54**

	2.08×10^{6} M^{-2}	EtOH/H2O (9 : 1, v/v)	0.521 µM	-	**55**
	$(3.78 \pm 0.1) \times 10^{4}$	H_2O:MeOH (6:4 V/V)	114.54 nM	Done	**This work**