Supporting Information

A differentially selective chemosensor for ratiometric responses to Zn^{2+} and Al^{3+} in aqueous media with applications for molecular switches

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1. General:

The chemicals and solvents were purchased from Sigma-Aldrich Chemicals Private Limited and were used without further purification. Melting points were determined on a hot-plate melting point apparatus in an open-mouth capillary and were uncorrected. ^{1}H-NMR and ^{13}C NMR spectra were recorded on Brucker 400 MHz instruments respectively. For NMR spectra, d_6-DMSO was used as solvent with TMS as an internal standard. Chemical shifts are expressed in δ □units and ^{1}H–^{1}H coupling constants in Hz. UV-vis titration experiments were performed on a JASCO UV-V530 spectrophotometer and fluorescence experiment was done using PTI fluorescence spectrophotometer with a fluorescence cell of 10 mm path. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer, using KBr discs.

2. Job Plot by fluorescence method:

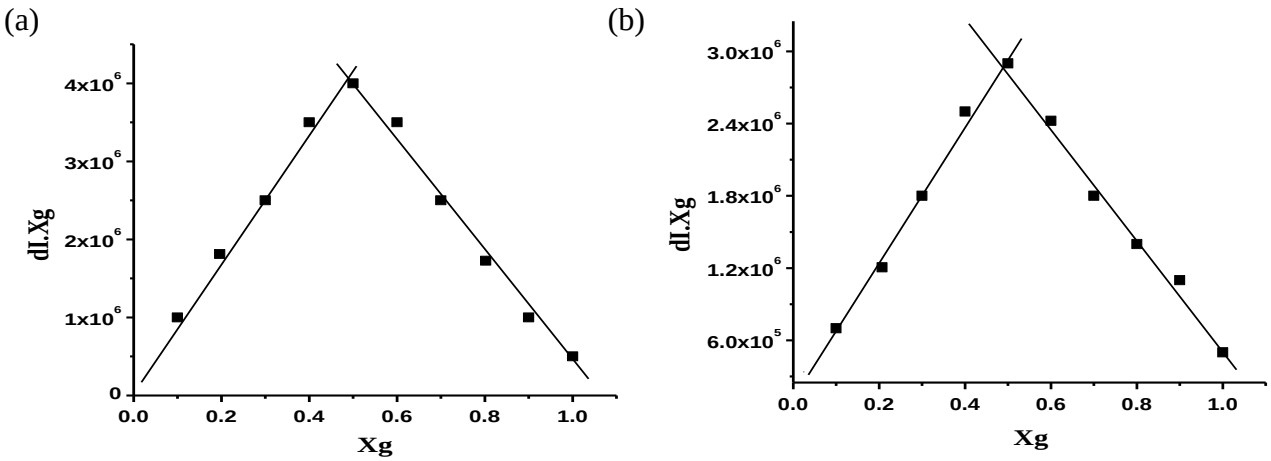


Figure S1: Job plot diagram of receptor i.e. PMN with (a) Al^{3+} and (b) Zn^{2+}.

A series of solutions containing **PMN (**c = 2 x 10^{-5} ML^{-1}**)** , $Al(NO_3)_3 9H_2O$ **(**c = 2 x 10^{-4} ML^{-1}**)** and $ZnCl_2$ **(**c = 2 x 10^{-4} ML^{-1}**)** were prepared such that the sum of the total metal ion and **PMN** volume remained constant (2ml). CH_3CN:H_2O (3:7) is used as solvent at pH 7.1 using HEPES buffer. The mole fraction (**X**) of Al^{3+} and Zn^{2+} were varied from 0.1 to 1.0. The corrected fluorescence was plotted against the molar fraction of the Al^{3+} and Zn^{2+} solutions.

3. Determination of the association constant:

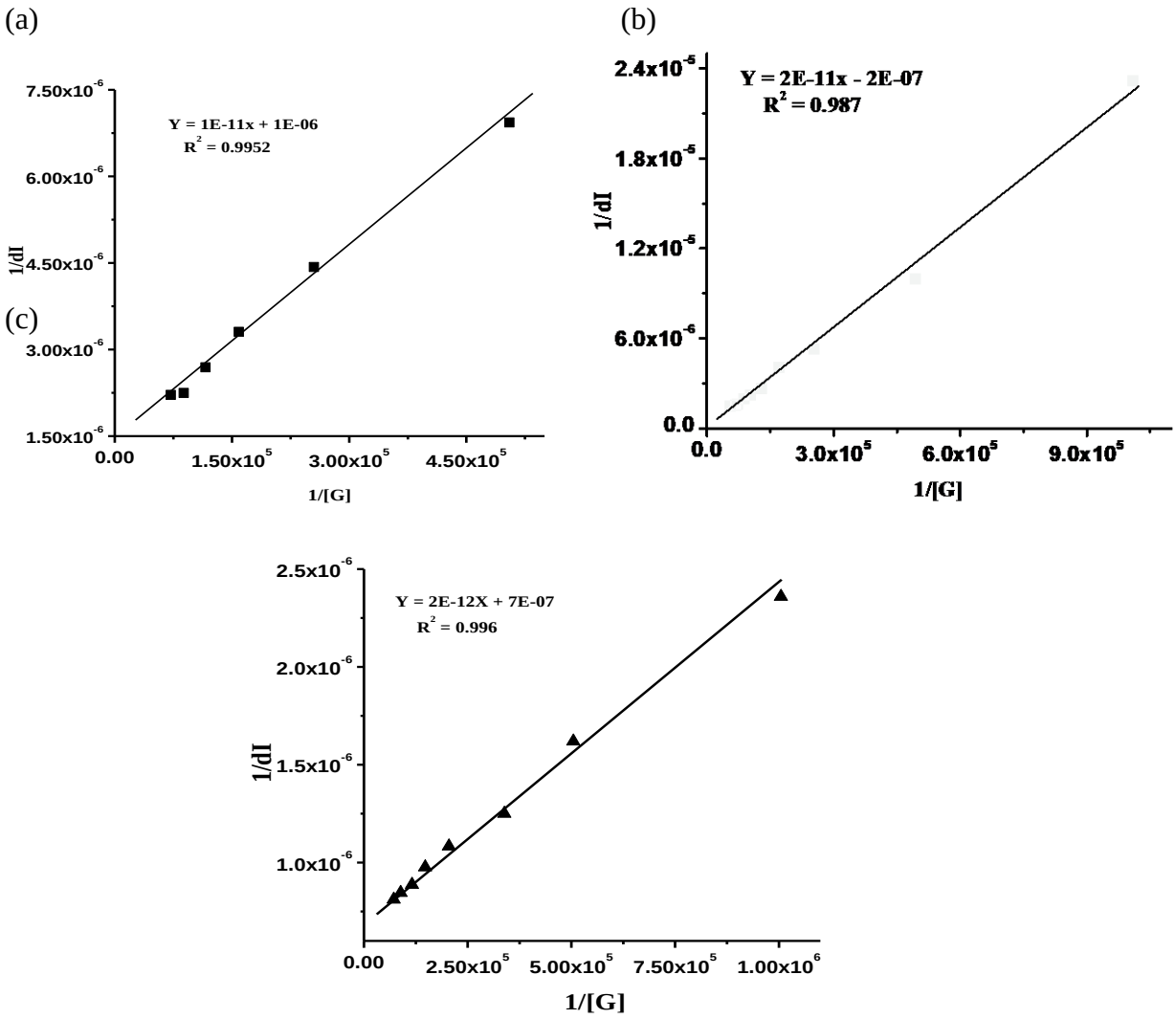


Figure S2: Bensei-Hildebrand plot from fluorescence titration spectral data of receptor PMN with (a) Al^{3+} and (b) Zn^{2+} in CH_3CN : H_2O (3: 7) and (c) Al^{3+} in water

The spectra of these solutions were recorded by means of Fluorescence methods. Binding constant was calculated according to the Benesi-Hildebrand equation. K_a was calculated following the equation stated below.

$$\mathbf{1/(F\text{-}Fo) = 1/\{K(Fmax–Fo)\ [Al^{3+}]_n\} + 1/[Fmax\text{-}Fo]}$$

$$\mathbf{1/(F\text{-}Fo) = 1/\{K(Fmax–Fo)\ [Zn^{2+}]_n\} + 1/[Fmax\text{-}Fo]}$$

Here Fo is the fluorescence of receptor in the absence of guest, F is the fluorescence recorded in the presence of added guest, Fmax is fluorescence in presence of added $[Al^{3+}]$max and $[Zn^{2+}]$max, K is the association constant (M^{-1}). The association constant (K_a) could be determined from the slope of the straight line of the plot of 1/(F-Fo) against $1/[Al^{3+}]_n$ and

$1/[Zn^{2+}]_n$ respectively. The association constant (K_a) as determined by fluorescence titration method for sensor with Al^{3+} is found to be 1 x 10^5 M^{-1} and with Zn^{2+} is found to be 1 x 10^4 M^{-1}

4. Calculation of the detection limit:

(a) (b)

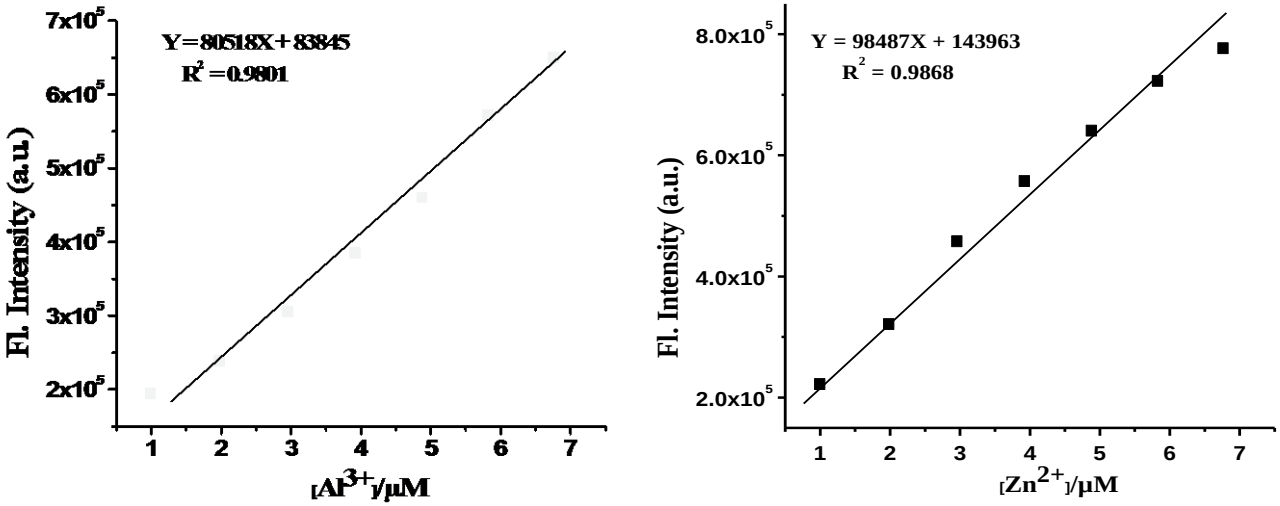


Figure S3: The linear change of fluorescence intensity as a function of (a) $[Al^{3+}]$ at 432 nm and (b) $[Zn^{2+}]$ at 446 nm

The detection limit DL of **PMN** for Al(III) and Zn(II) were determined from the following equation[1]:

DL = K* Sb1/S

Where K = 2 or 3 (we take 3 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

From the graph (a) we get slope = 80518, and Sb1 value is 26100 and from graph (b) we get slope = 98487 and Sb1 value is 96751.68.

Thus using the formula we get the Detection Limit for Al^{3+} is 0.648 μM i.e. PMN can detect Al^{3+} ion in this minimum concentration and Detection Limit for Zn^{2+} 1.96 μM.

5. Competition experiment in water:

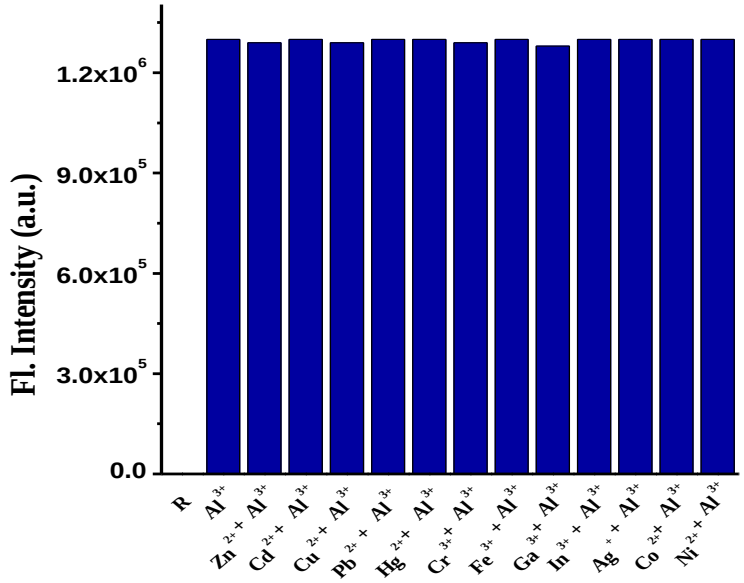
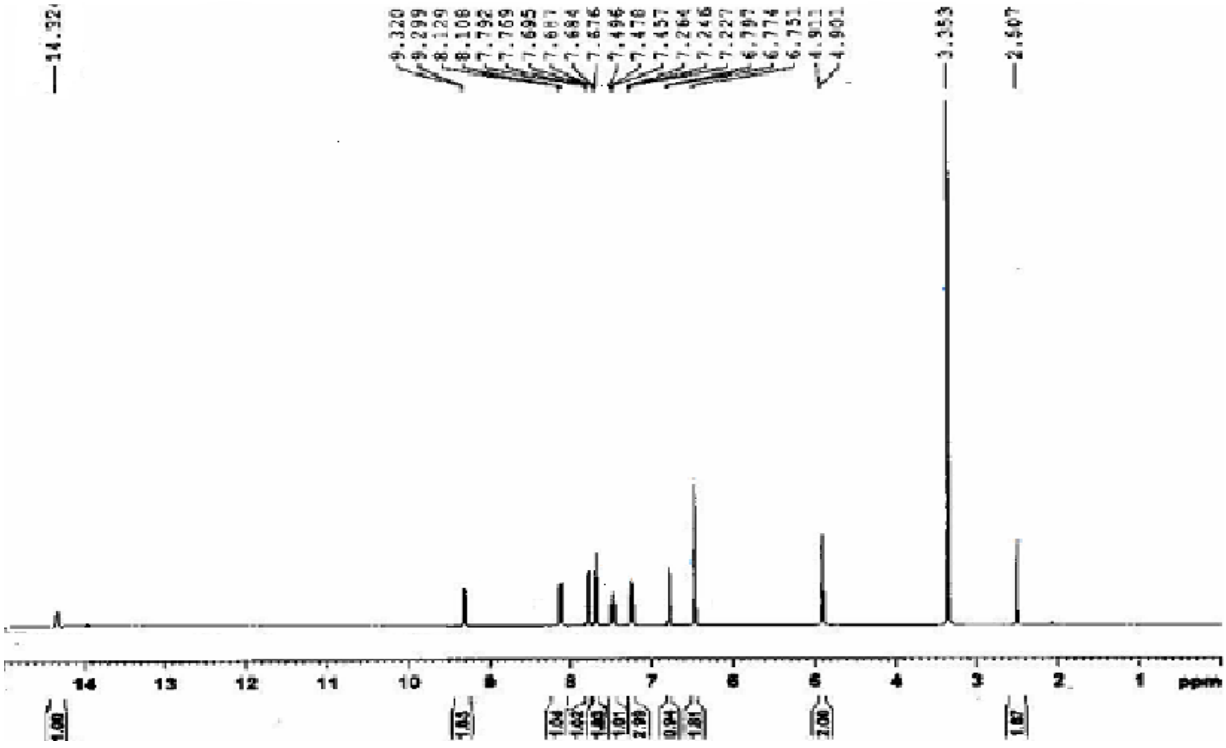


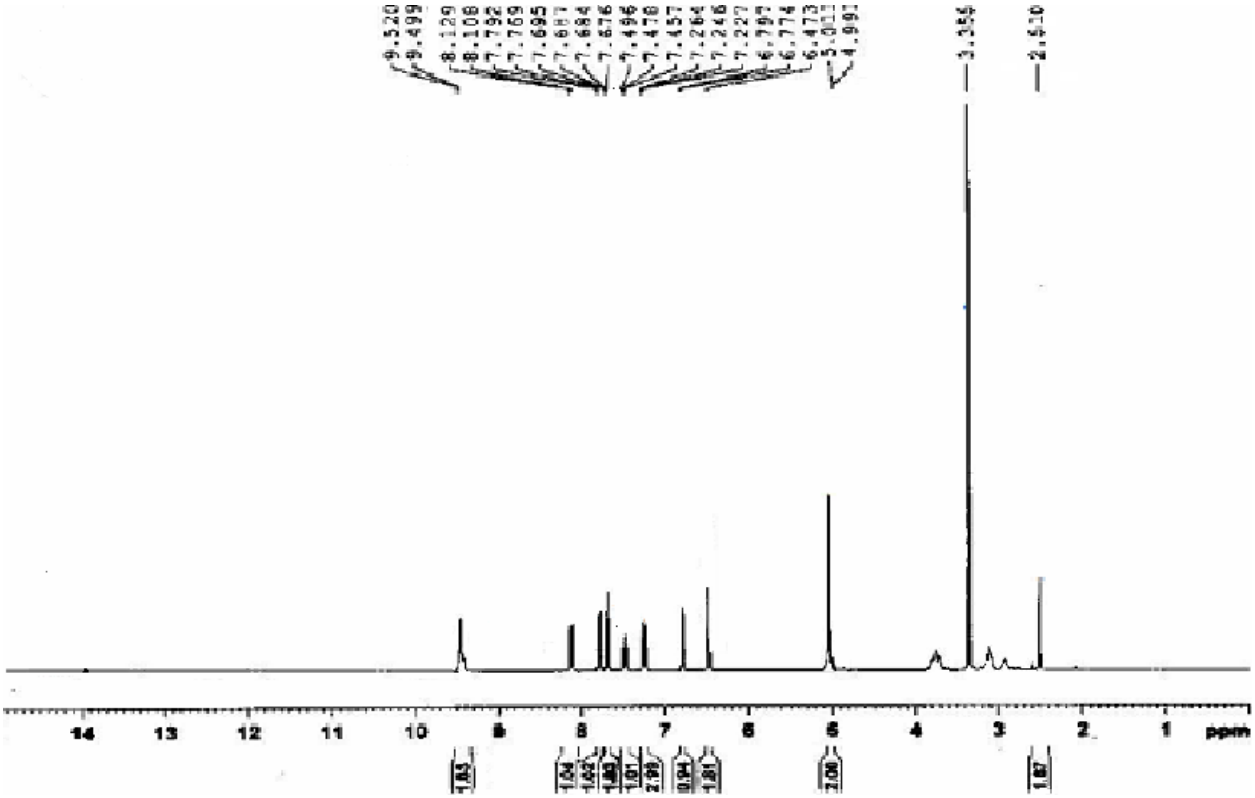
Figure S4: Fluorescence response of probe PMN in presence of Al^{3+} (1 equiv.) additional various metal ions (10 equiv.) in 20 mM HEPES buffer at pH =7.1

6. ^{1}H NMR, ^{13}C NMR and ESI MS spectra of PMN and Al^{3+} and Zn^{2+} complex of PMN :

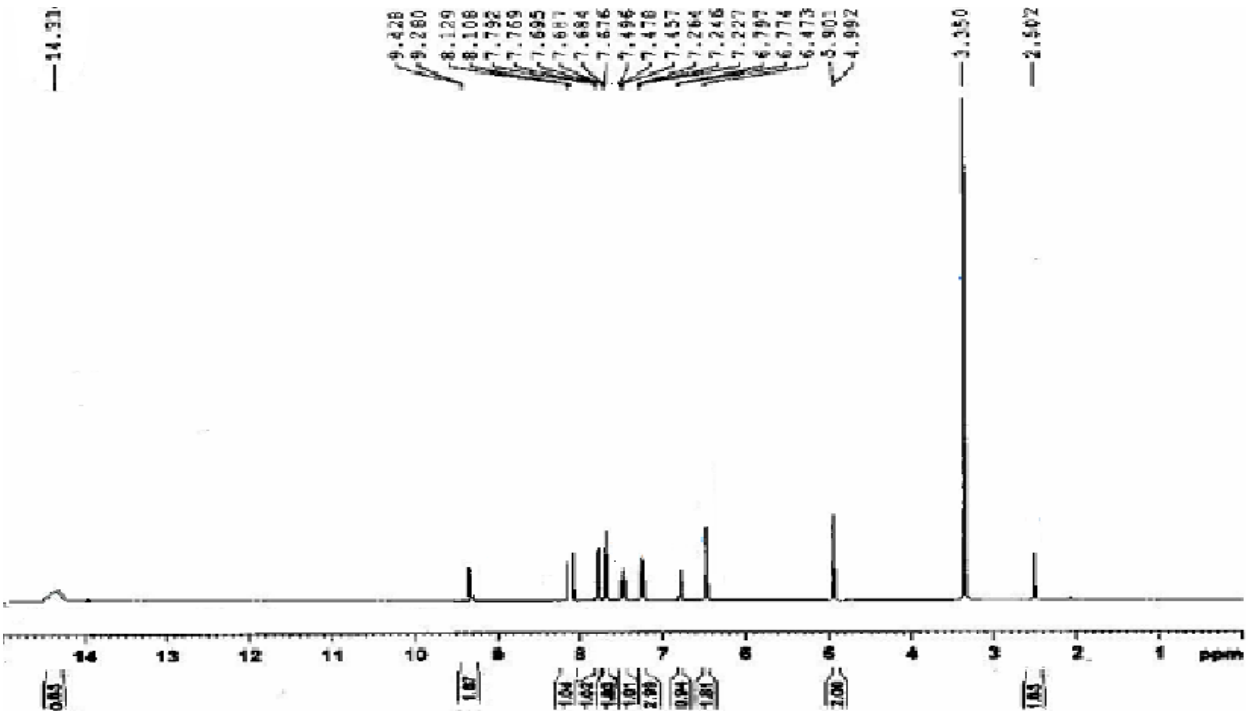
^{1}H NMR spectrum of Receptor i.e. PMN:



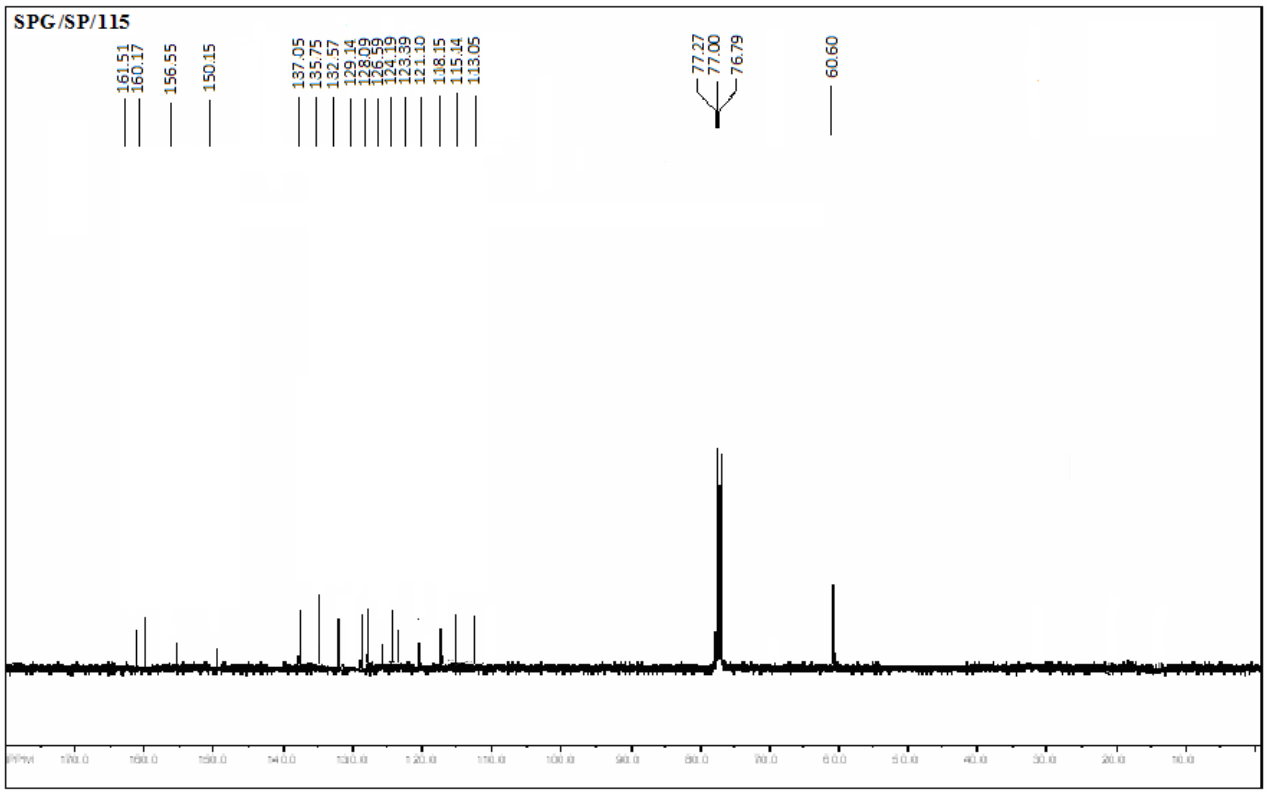
^{1}H NMR spectrum of Receptor i.e. PMN + 1 equiv. Al^{3+} :



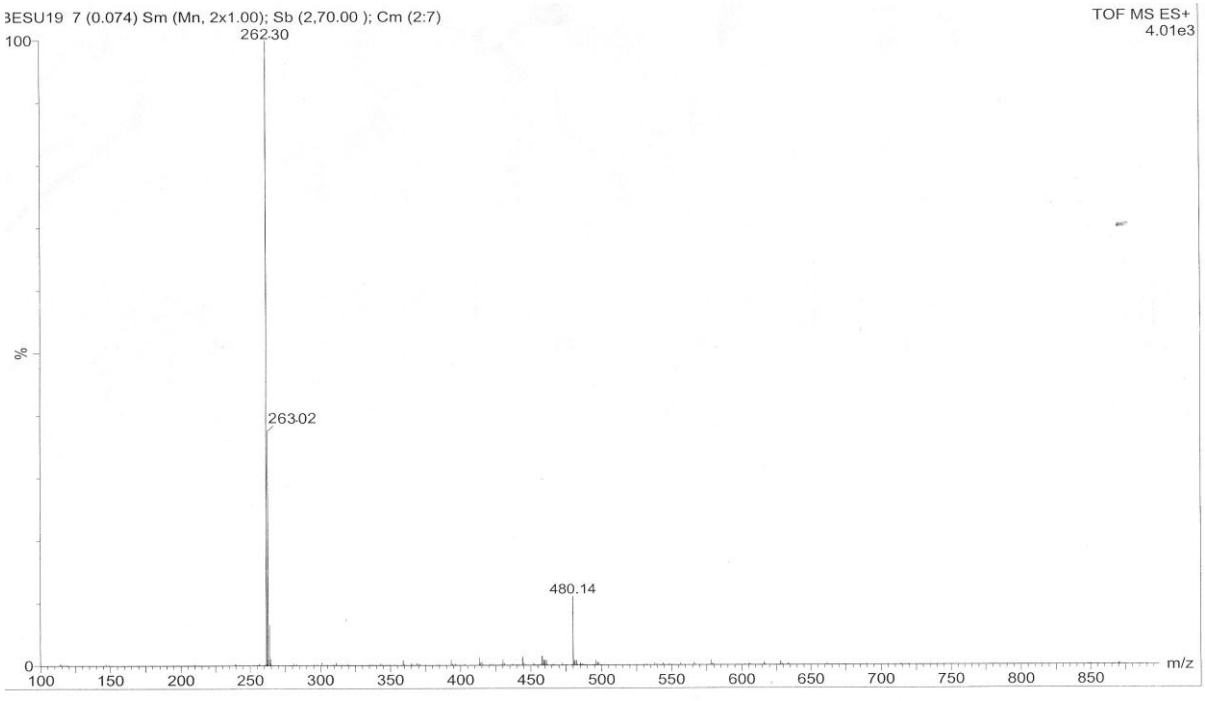
^{1}H NMR spectrum of Receptor i.e. PMN + 1 equiv. Zn^{2+} :



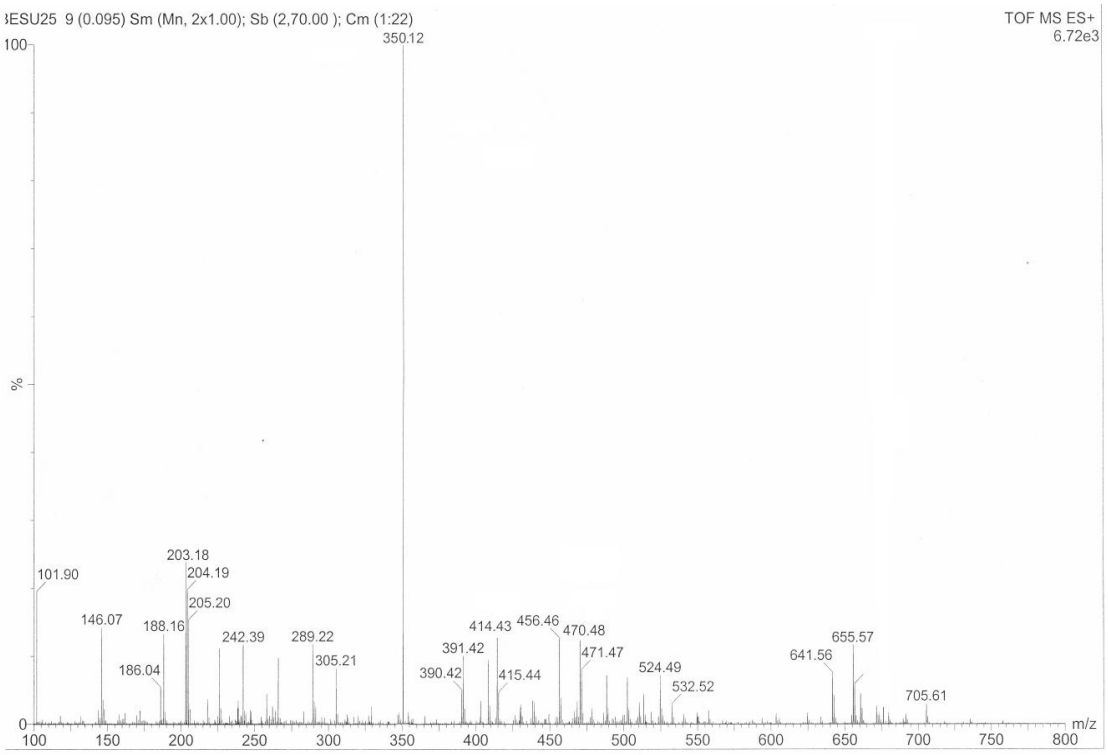
^{13}C NMR spectrum of Receptor:



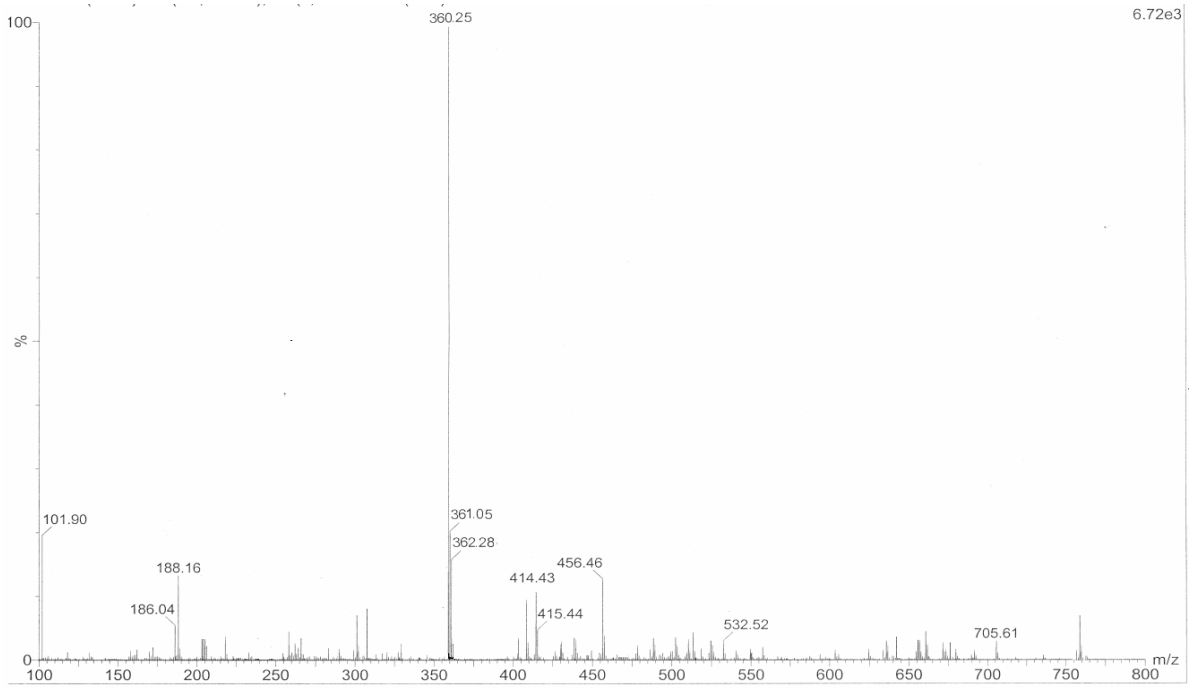
ESI MS Mass Spectra of PMN:



ESI MS Spectra of Al-Complex of Receptor:

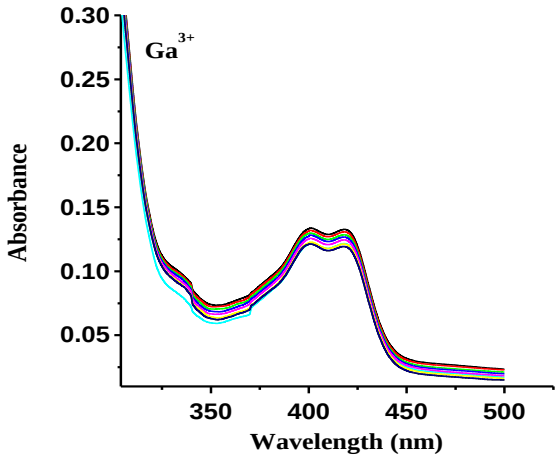


ESI MS Spectra of Zn-Complex of Receptor:

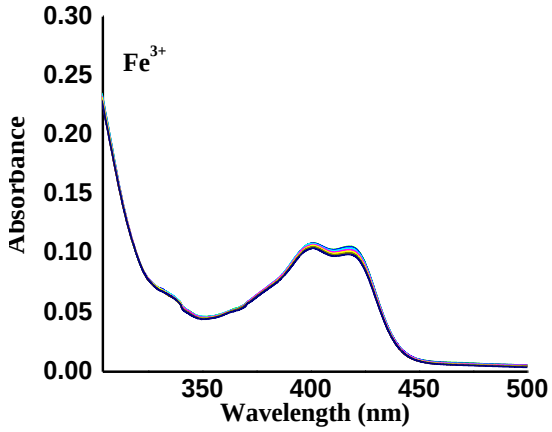


7. UV-vis absorption spectra of PMN with different cations as Ga^{3+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Ag^{+}, Cd^{2+}, In^{3+}, Cr^{3+} in CH_3CN : H_2O (3:7, v/v) (The solutions of metal ions were prepared from $GaCl_3$, $FeCl_3$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $PbCl_2$, $HgCl_2$, $Cu(ClO_4)_2 \cdot 6H_2O$, $AgNO_3$, $Cd(ClO_4)_2 \cdot H_2O$, $Pb(ClO_4)_2$, $InCl_3$ and $CrCl_3.6H_2O$, respectively in CH_3CN-H_2O)

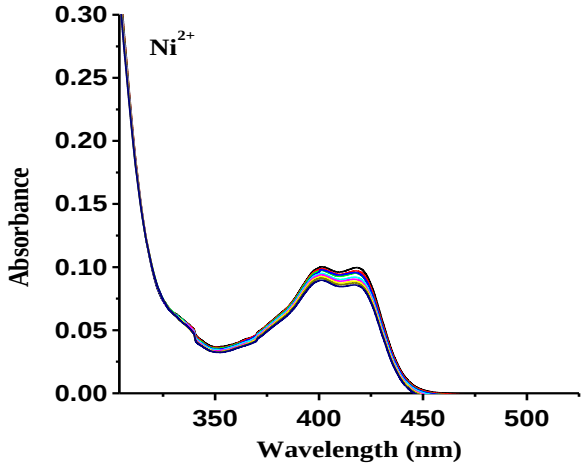
(a)



(b)



(c)



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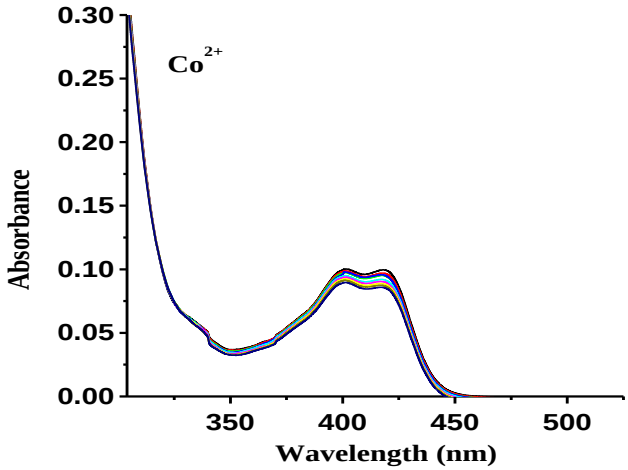

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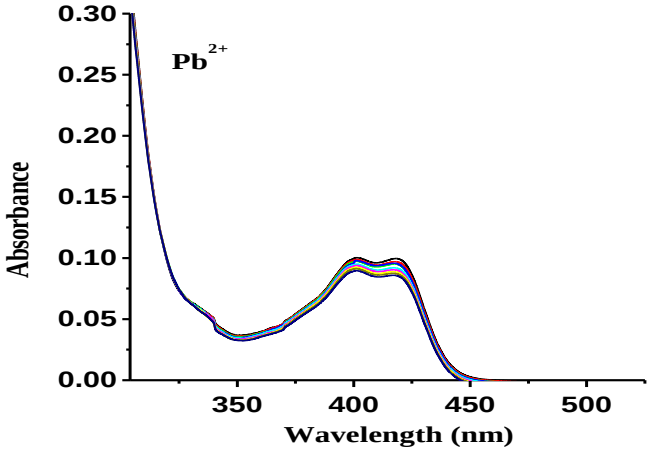

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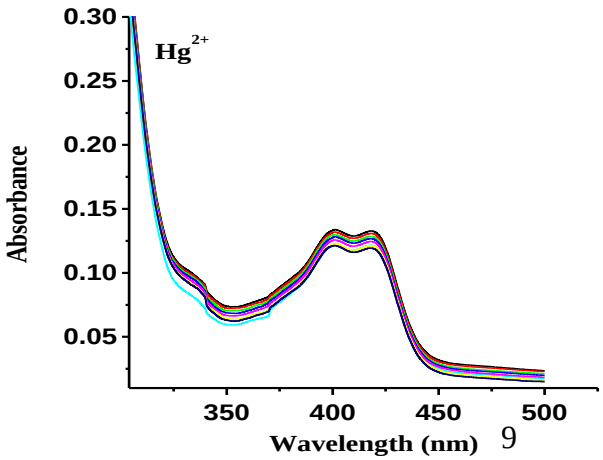

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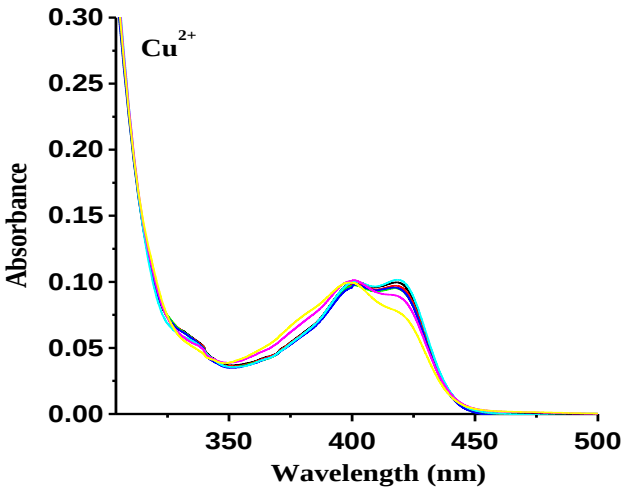

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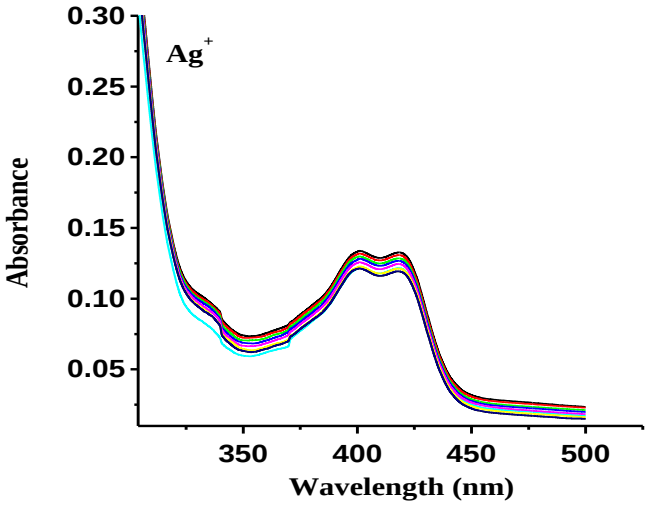
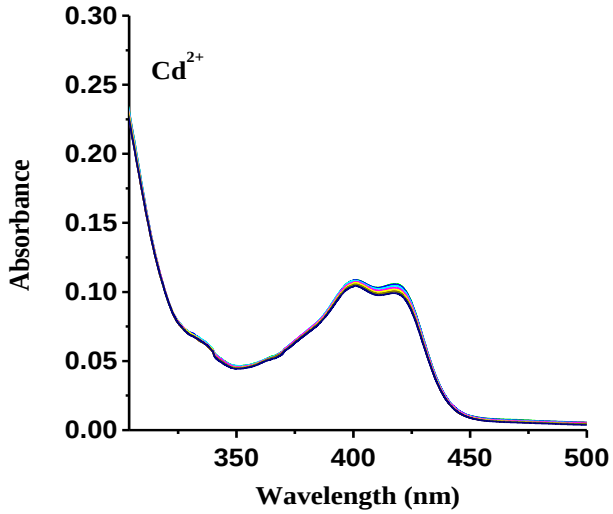
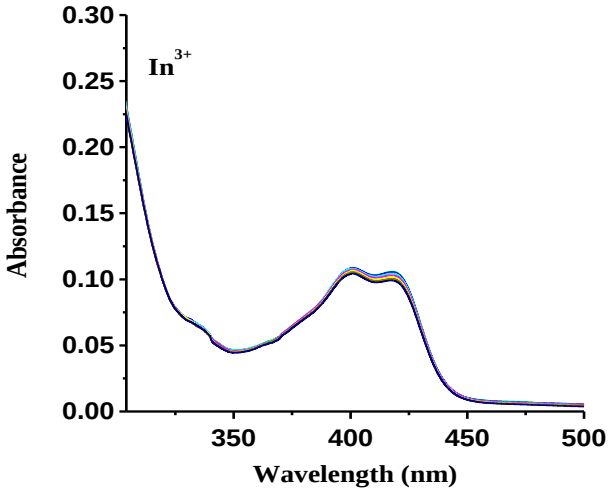


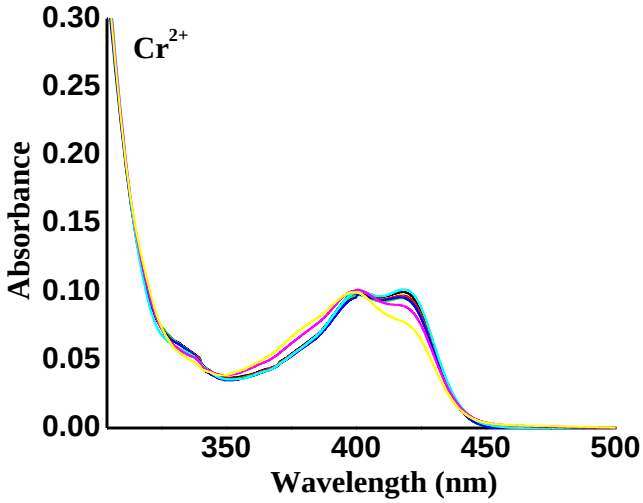
(i)



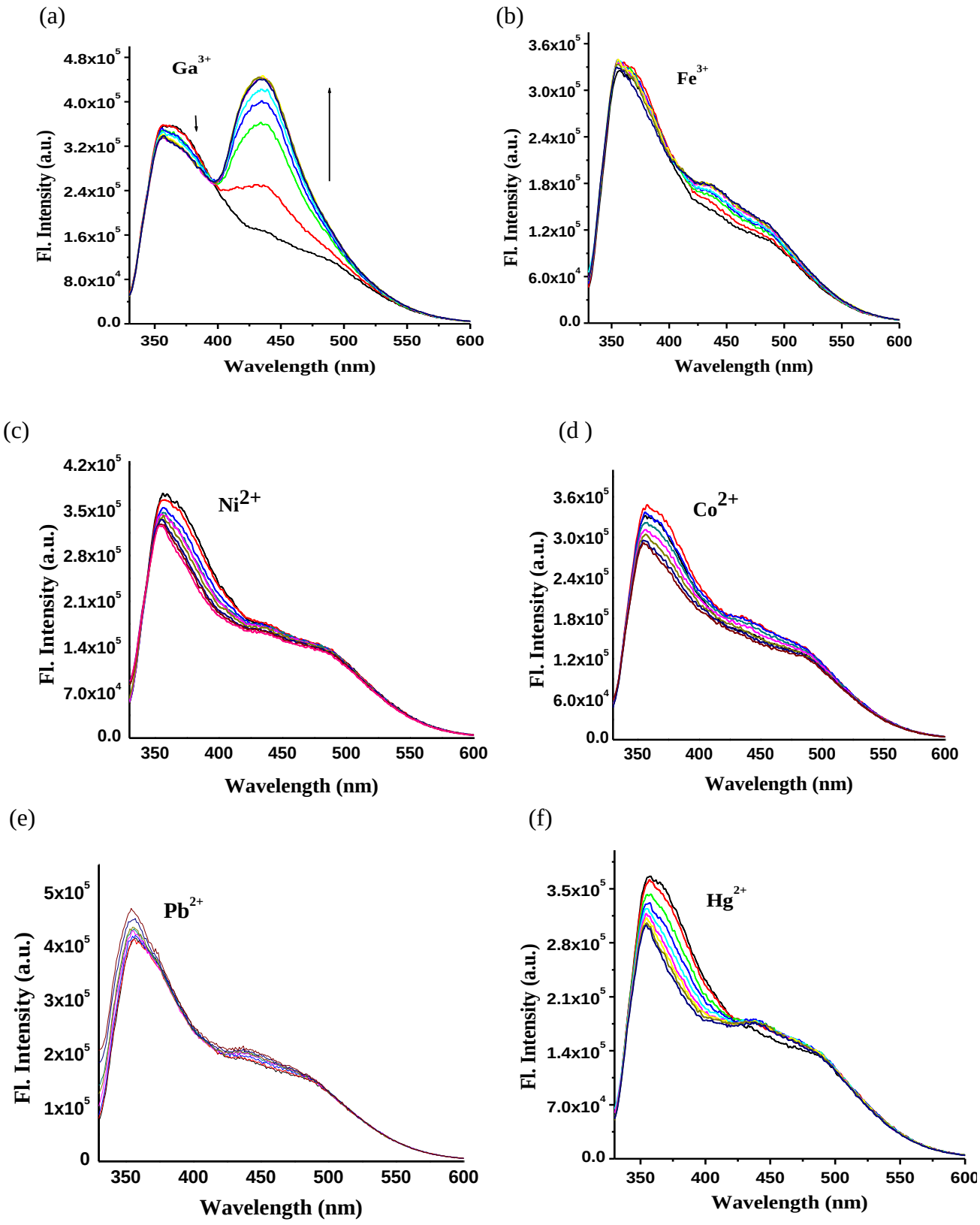
(j)



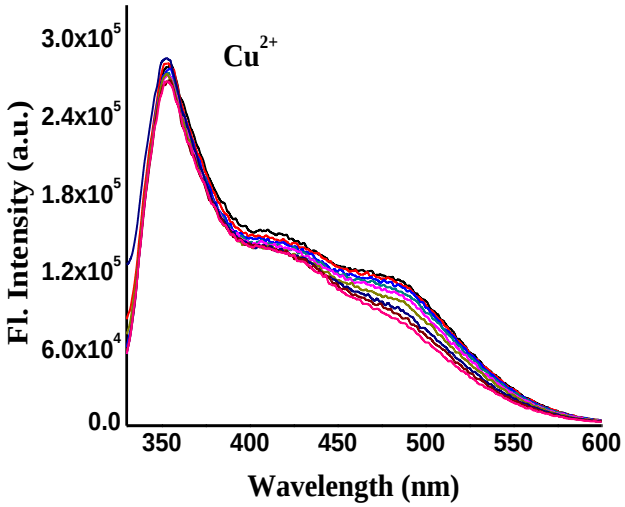
(K)



8. Fluorescence emission spectra of PMN with different cations as Ga^{3+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Ag^{+}, Cd^{2+}, In^{3+}, Cr^{3+} in CH_3CN : H_2O (3:7, v/v) (The solutions of metal ions were prepared from $GaCl_3$, $FeCl_3$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $PbCl_2$, $HgCl_2$, $Cu(ClO_4)_2 \cdot 6H_2O$, $AgNO_3$, $Cd(ClO_4)_2 \cdot H_2O$, $Pb(ClO_4)_2$, $InCl_3$ and $CrCl_3.6H_2O$, respectively in CH_3CN-H_2O)



(g)



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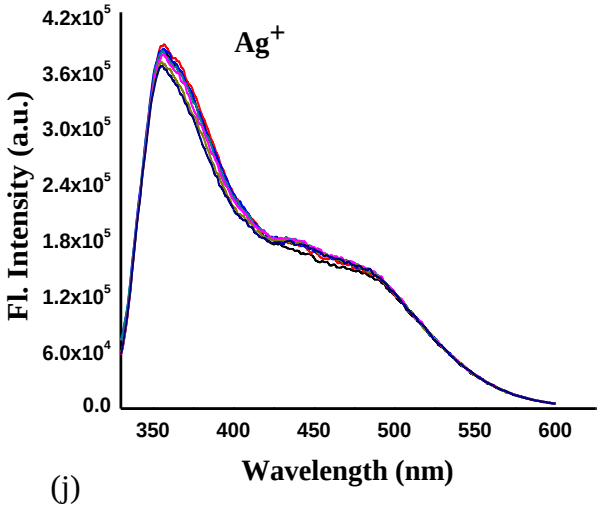

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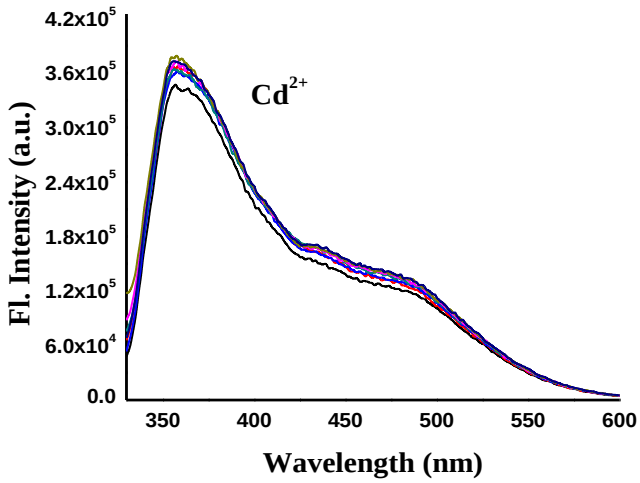

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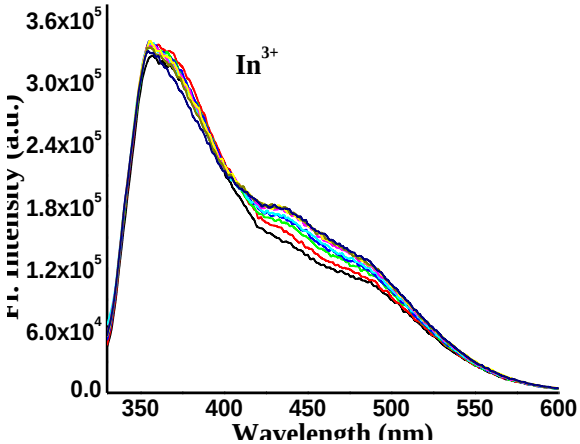

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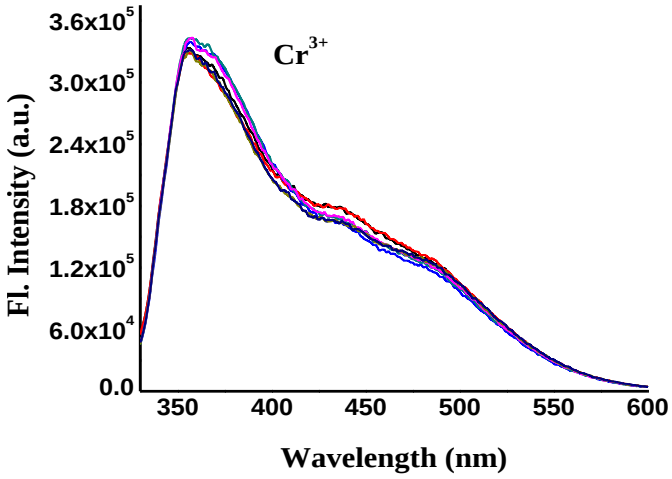
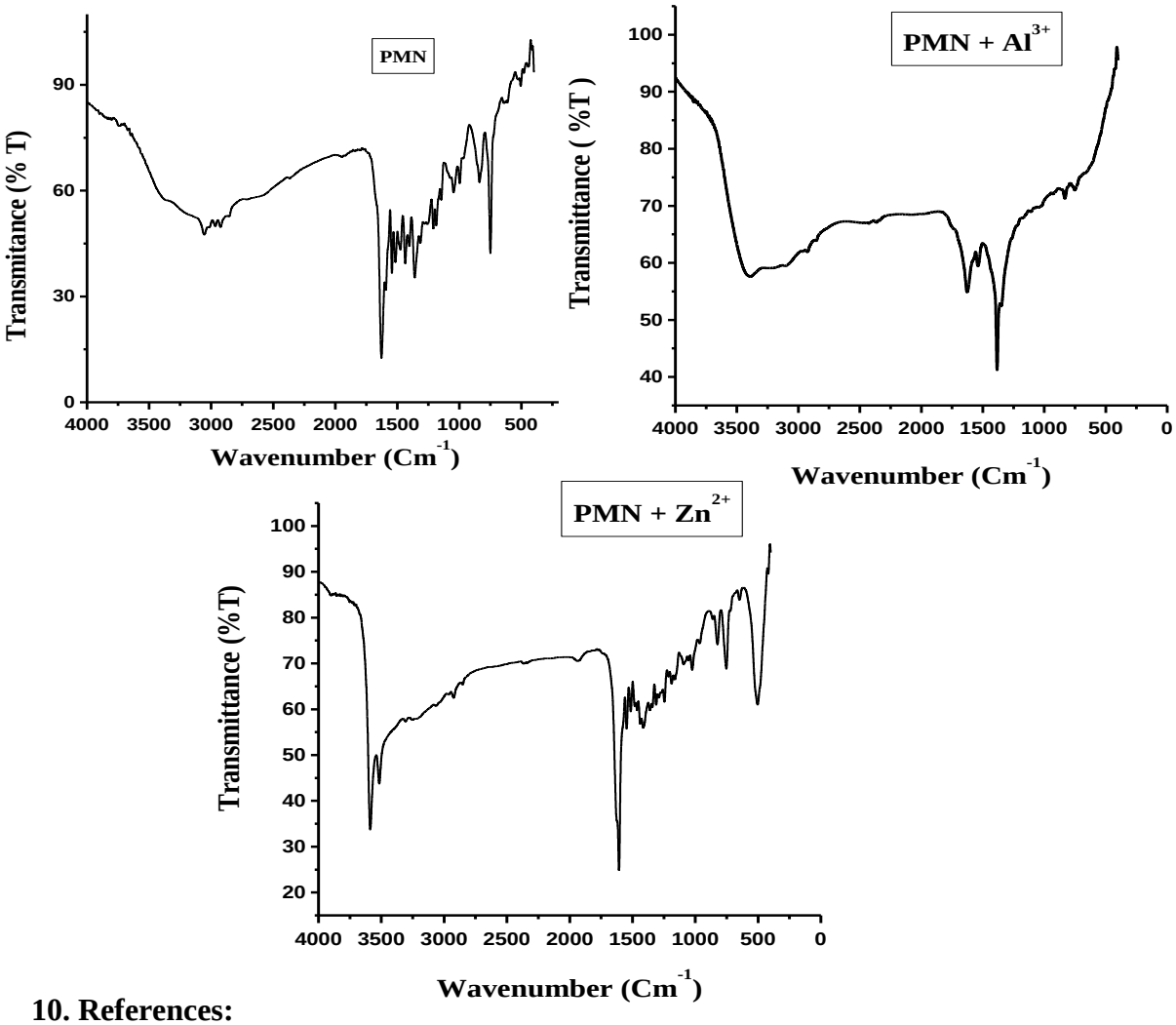


9. FT-IR data of PMN and its complex with Al^{3+} and Zn^{2+} ions :



10. References:

1. M. Zhu, M. Yuan, X. Liu, J. Xu, J. Lv, C. Huang, H. Liu, Y. Li, S. Wang, D. Zhu, *Org. Lett.* 2008**, 10**, 1481-1484