Supporting Information

A differentially selective molecular probe for detection of trivalent ions (Al^{3+}, Cr^{3+} and Fe^{3+}) upon single excitation in mixed aqueous medium

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CONTENTS

1. Calculation of the detection limit:

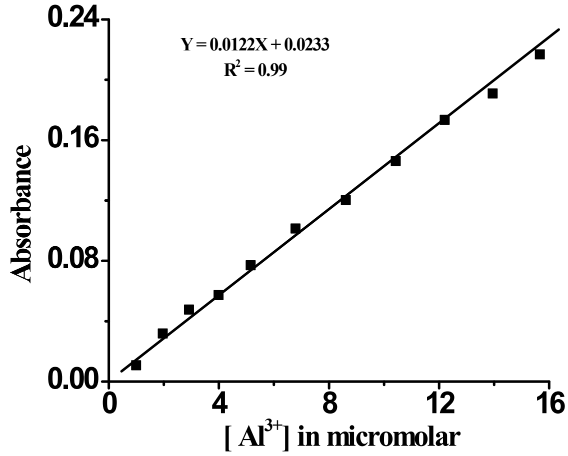


Figure S1: Absorbance change of RDN upon gradual addition of Al^{3+}.

The detection limit DL of **RDN** for Al^{3+} was determined from the following equation[1]:

DL = K* Sb1/S

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

From the graph we get slope = 6.868, and Sb1 value is 0.006129

Thus using the formula we get the Detection Limit = 1.78 nM i.e. RDN can detect Al^{3+} in this minimum concentration.

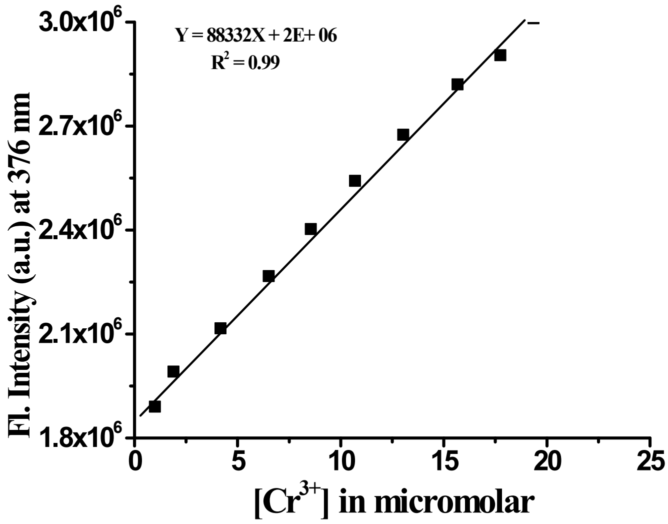


Figure S2: Fluorescence change of RDN upon gradual addition of Cr^{3+}.

From the graph we get slope = 88332, and Sb1 value is 104322

Thus using the formula we get the Detection Limit = 2.36 μM i.e. RDN can detect Cr^{3+} in this minimum concentration.

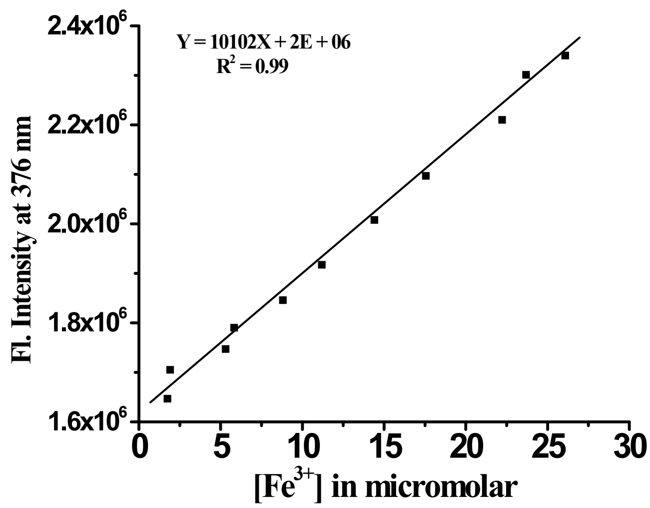


Figure S3: Fluorescence change of RDN upon gradual addition of Fe^{3+}.

From the graph we get slope = 10102, and Sb1 value is 14674.1

Thus using the formula we get the Detection Limit = 2.90 μM i.e. RDN can detect Fe^{3+} in this minimum concentration.

2. pH effect on RDN moiety:

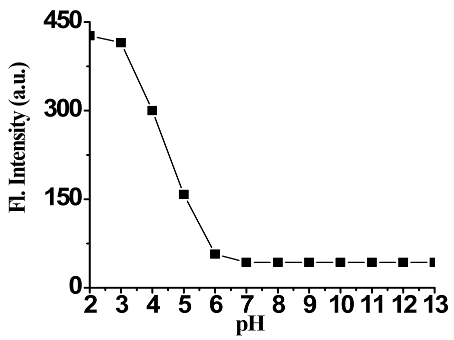
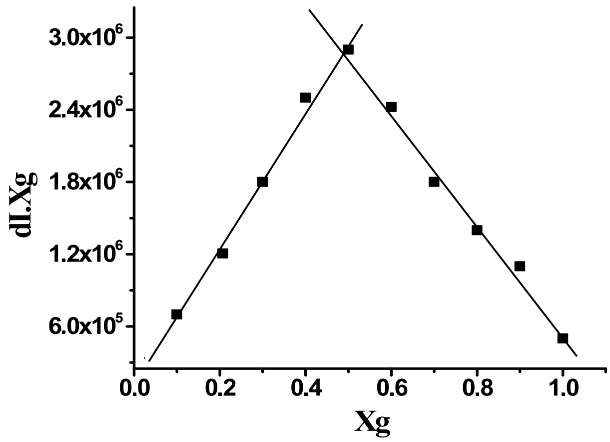


Figure S4: The change of fluorescence intensity of the receptor i.e. RDN (c = $2x10^{-5}$ M) (at 582 nm) with pH.

3. Job Plot by fluorescence method:

(a)



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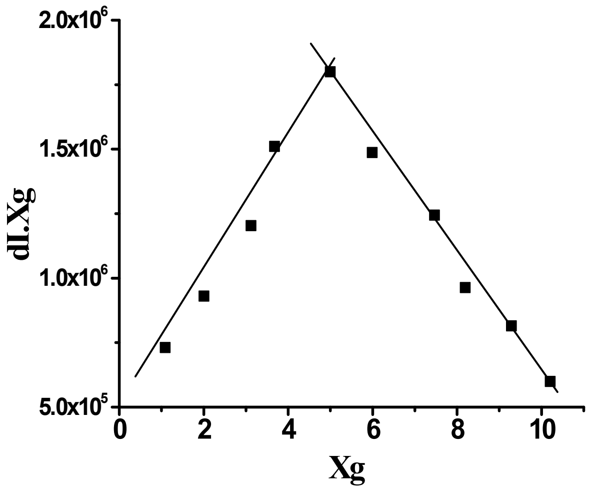

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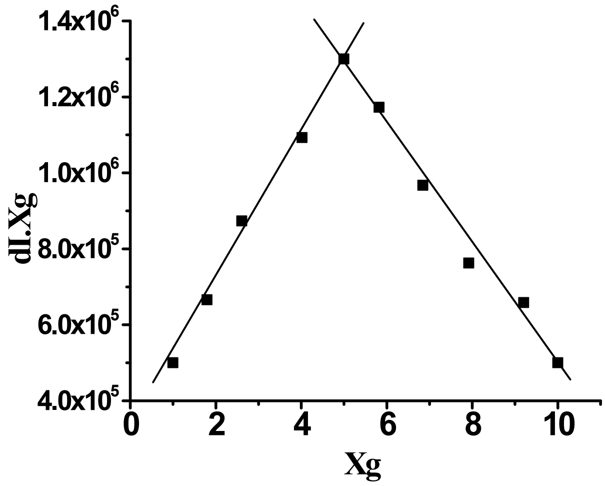
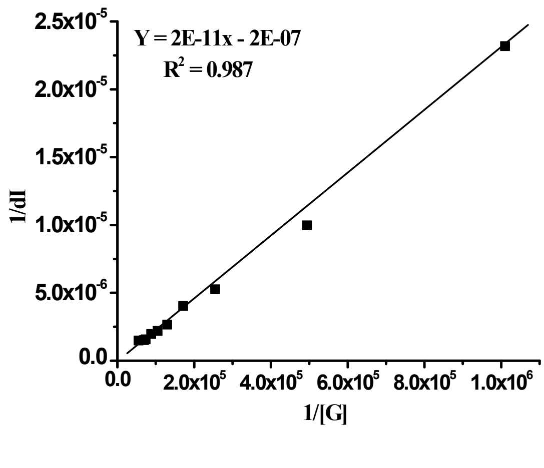


Figure S5: Job plot diagram of receptor i.e. RDN with (a) Al^{3+} (b) Cr^{3+} and (c) Fe^{3+}

4. Determination of the association constant:

(a)



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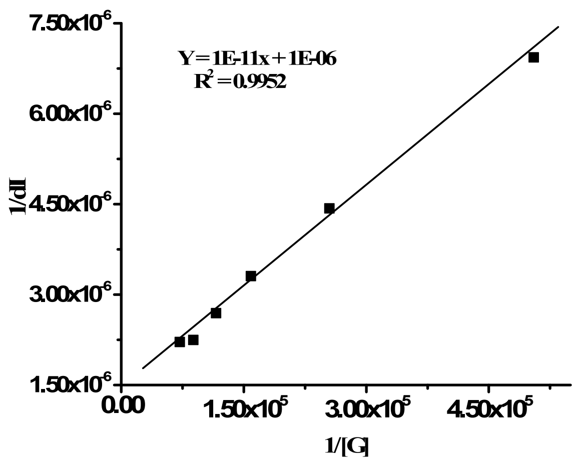

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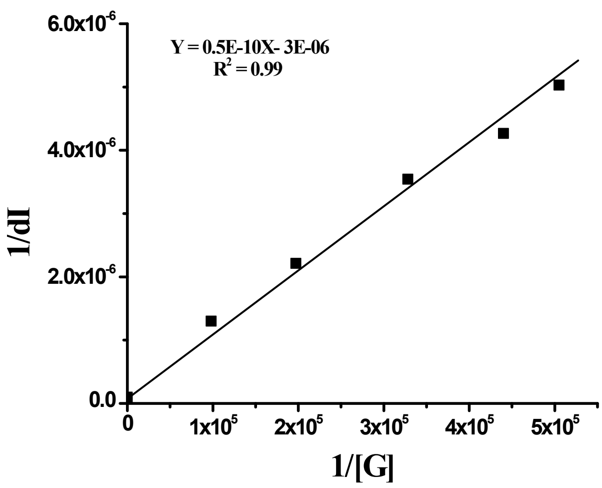


Figure S6: Benesi-Hildebrand plot from fluorescence titration spectral data of receptor RDN with (a) Al^{3+} (b) Cr^{3+} and (c) Fe^{3+}

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.

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

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

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

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, $[Cr^{3+}]$max and $[Fe^{3+}]$max respectively. 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 $1/[Al^{3+}]_n$, $1/[Cr^{3+}]_n$ and $1/[Fe^{3+}]_n$ respectively. The association constant (K_a) as determined by fluorescence titration method for sensor with Al^{3+} , Cr^{3+} and Fe^{3+} are found to be $1 \times 10^4\ M^{-1}$, $2.6\ X\ 10^2\ M^{-1}$ and $1.2\ X\ 10^2\ M^{-1}$ respectively.

5. Competition bar diagram:

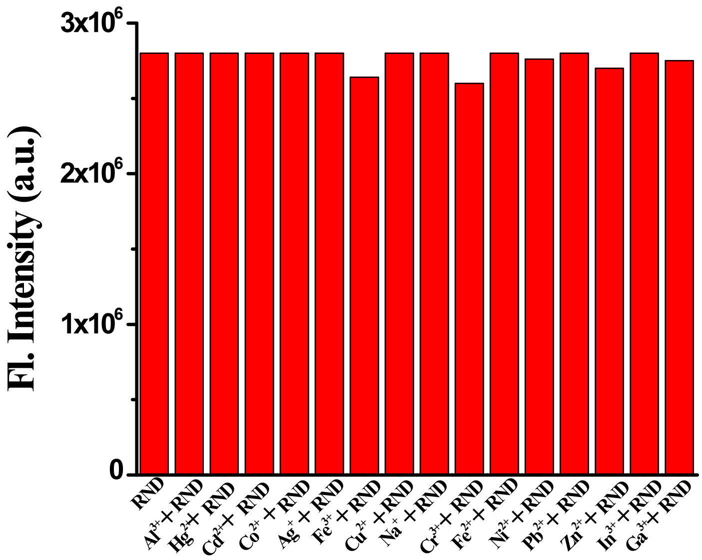


Figure S7: Fluorescence response of probe RDN in presence of Al^{3+} (1 equiv.) additional various metal ions (10 equiv.) in 20 mM HEPES buffer at pH =7.1

6. Spectra of receptor (RDN) and three trivalent ions (Al^{3+}, Cr^{3+} and Fe^{3+}):

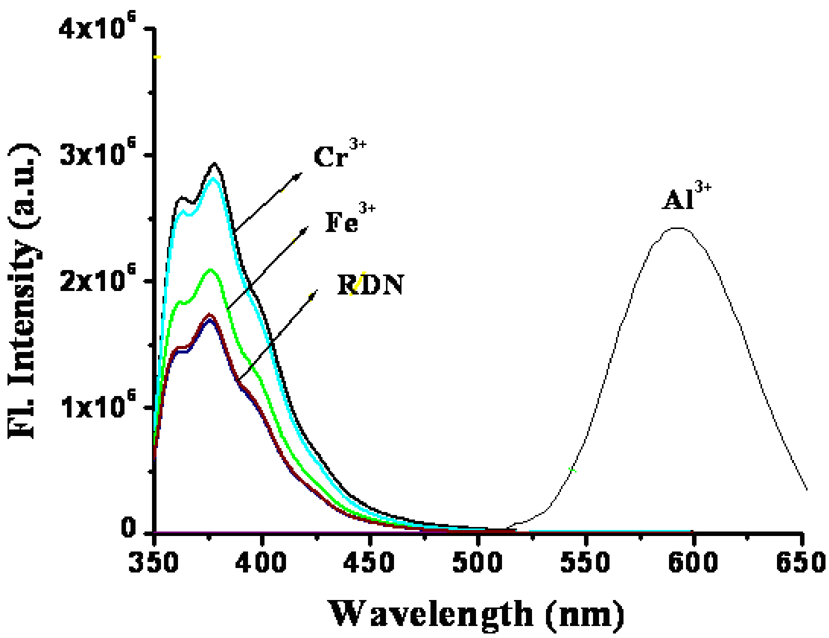
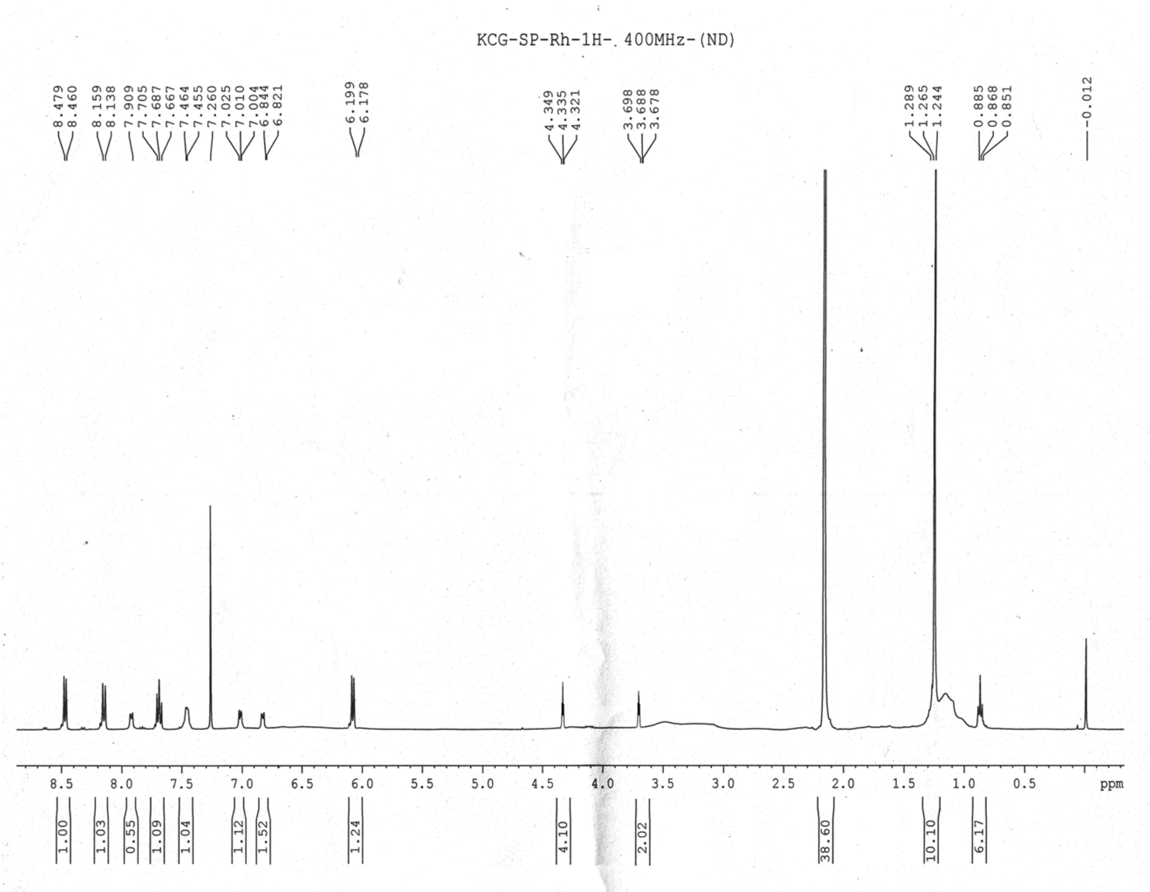


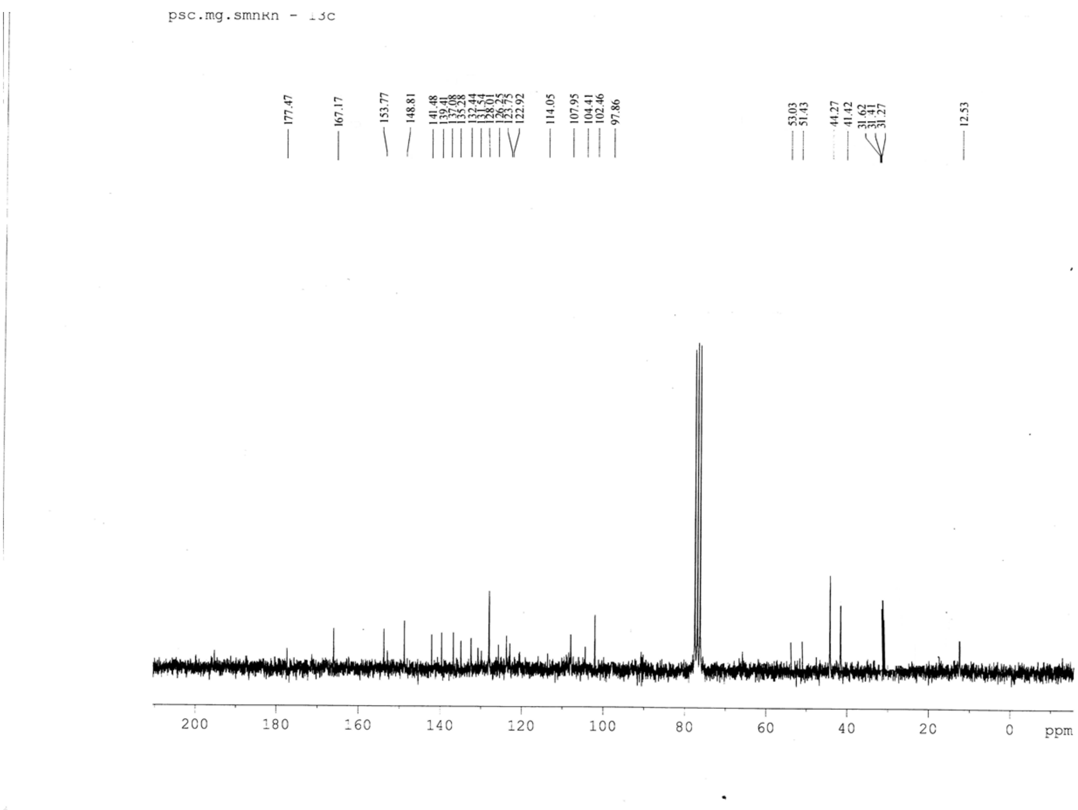
Figure S8: Fluorescence emission spectra of RDN (c = 2.0 X10^{-5} M) with Al^{3+}, Cr^{3+} and Fe^{3+} (c =2.0 X10^{-5} M) at pH 7.1 in CH_3OH :H_2O (6 : 4, v/v)

7. ¹H NMR, ¹³C NMR and HRMS spectra of RDN, RDN-Al^{3+}, RDN-Cr^{3+} and RDN-Fe^{3+}complex:

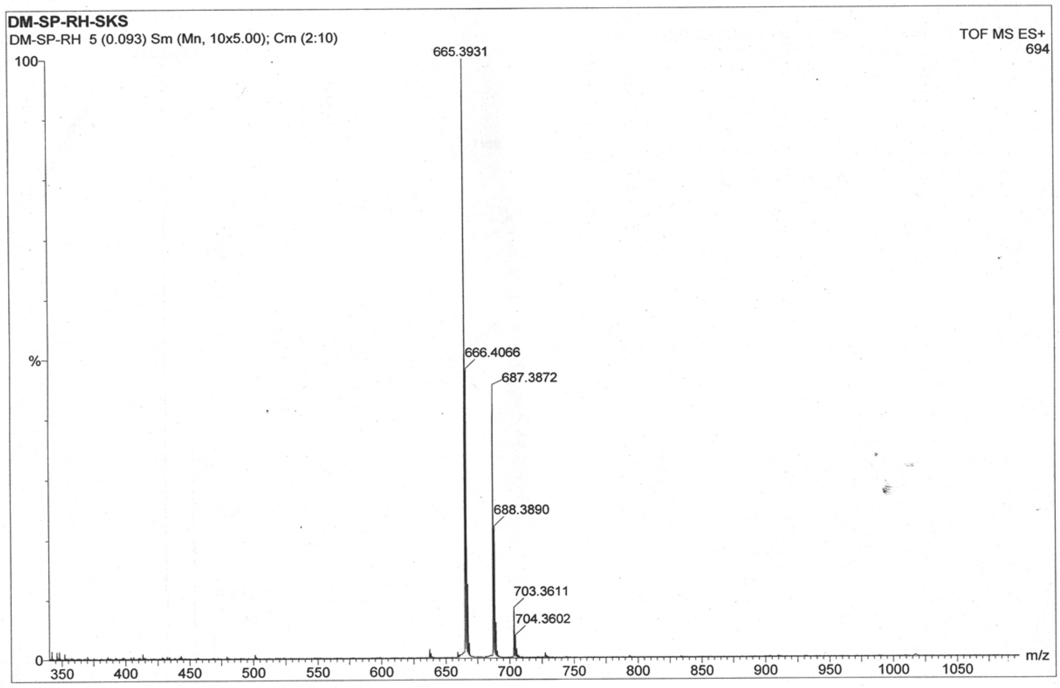
¹H NMR spectrum of Receptor i.e. RDN:



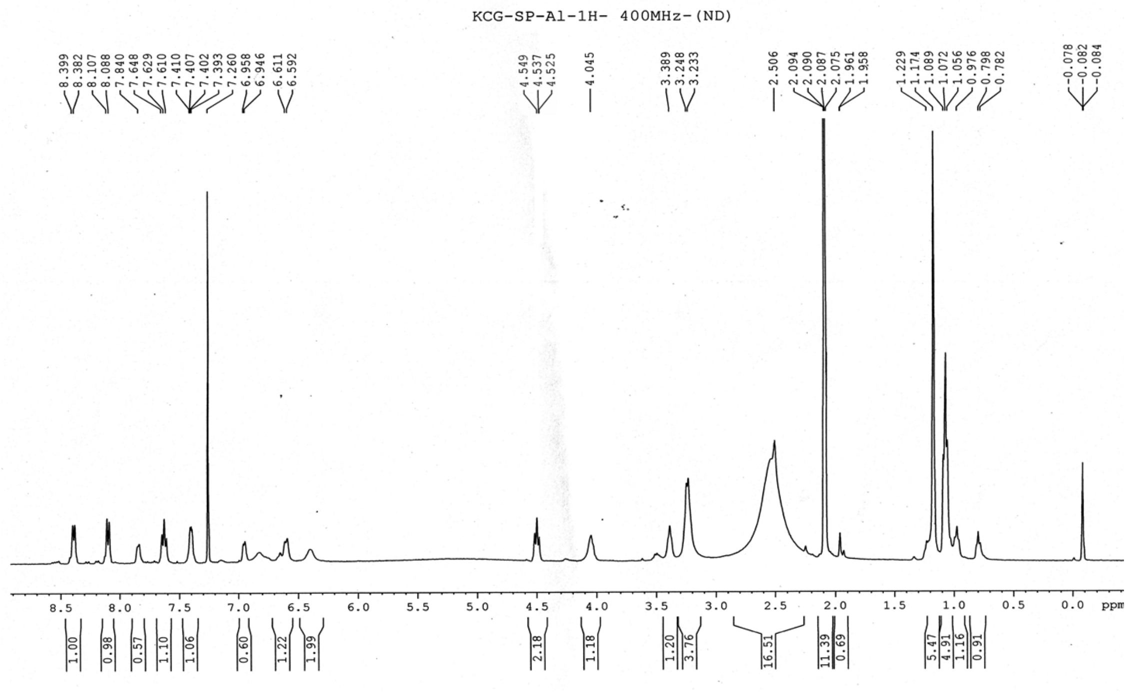
¹³C NMR spectrum of RDN:



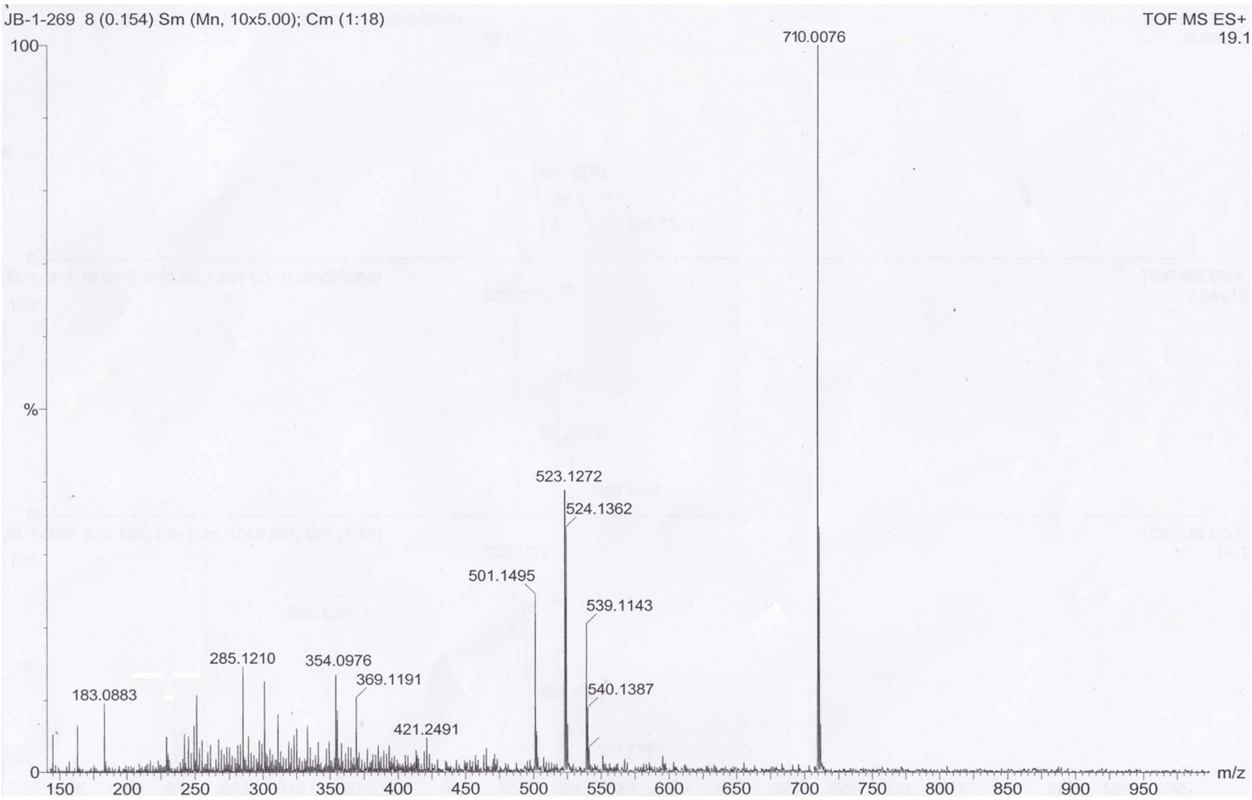
HR Mass Spectra of RDN:



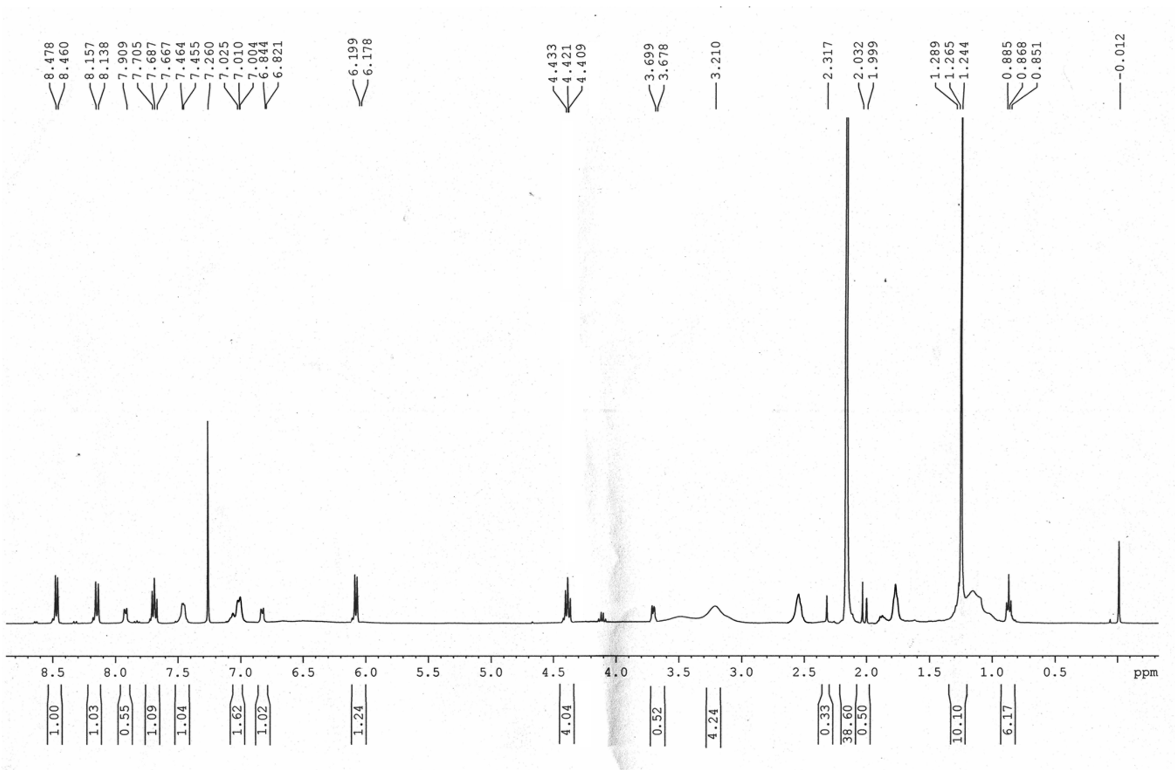
^{1}H NMR spectrum of RDN-Al^{3+} complex:



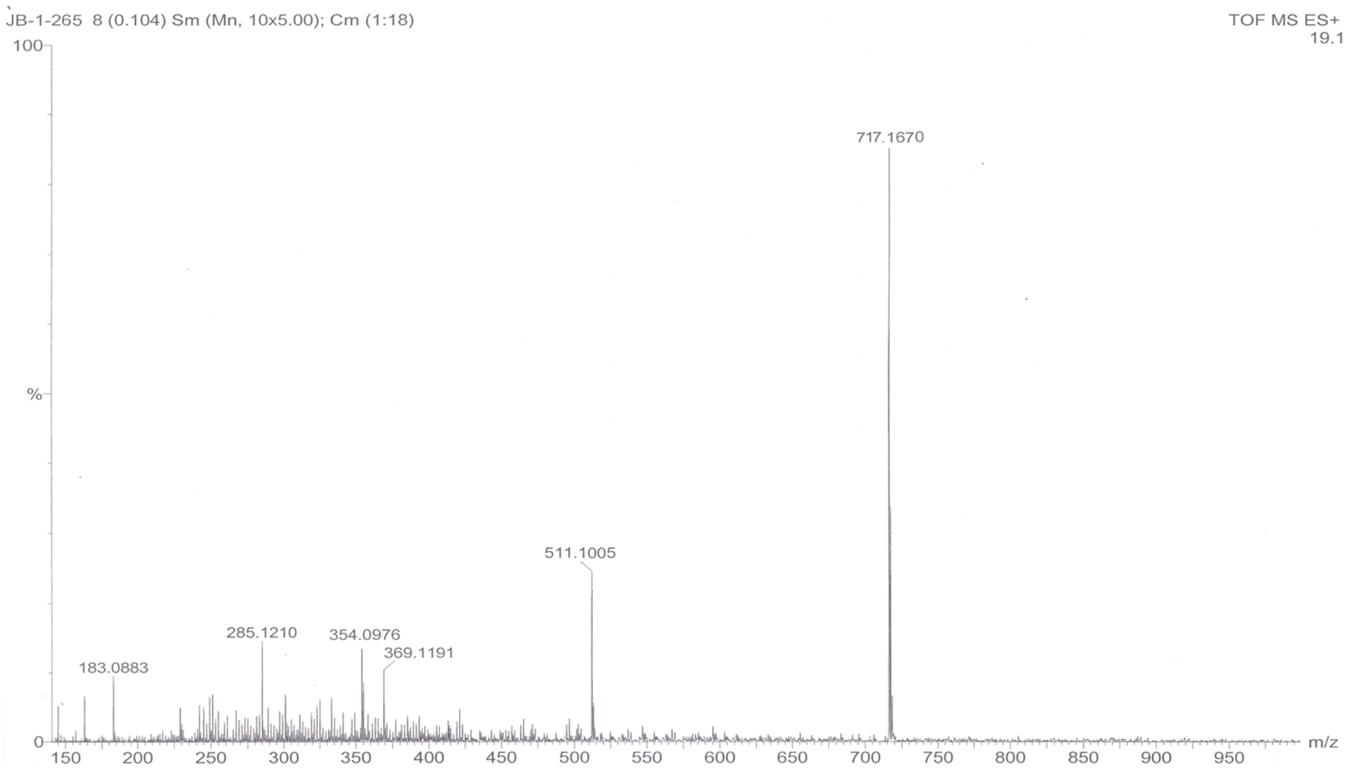
HRMS Spectra of RDN-Al^{3+} complex:



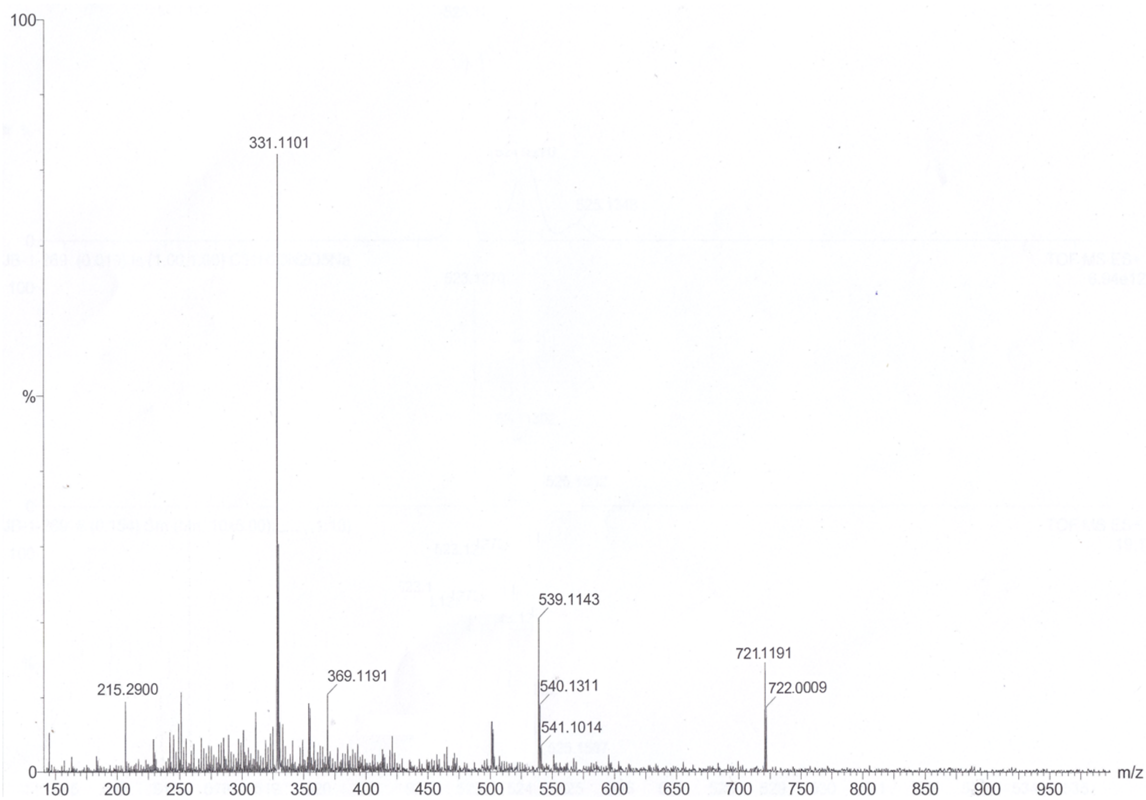
^1H NMR spectrum of RDN-Cr^{3+} complex:



HRMS Spectra of RDN-Cr^{3+} complex:

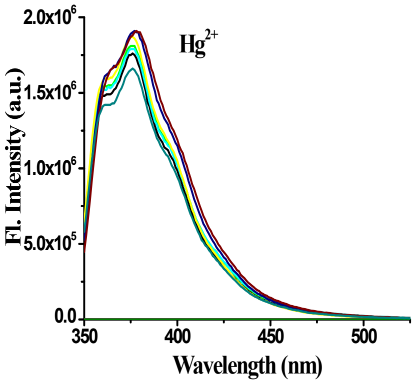


HRMS Spectra of RDN-Fe^{3+} complex:



8. Fluorescence emission spectra of RDN with different cations Hg^{2+}, Cd^{2+}, Co^{2+}, Ag^{+}, Fe^{3+},Cu^{2+}, Na^{+}, Cr^{3+}, Fe^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, In^{3+}, Ga^{3+} . The solutions of anions and oxidants were prepared from $HgCl_2$, $Cd(ClO_4)_2{\cdot}H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $AgNO_3$, $ZnCl_2$, $FeCl_3$, $Cu(ClO_4)_2{\cdot}6H_2O$, NaCl, $CrCl_3.6H_2O$, $FeCl_2$, $Ni(ClO_4)_2{\cdot}6H_2O$, $Pb(ClO_4)_2$, $GaCl_3$ $InCl_3$ respectively in CH_3CN-H_2O.

(a)



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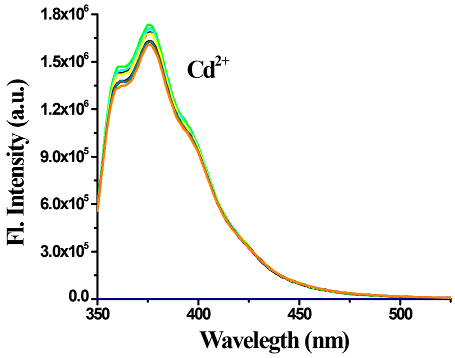

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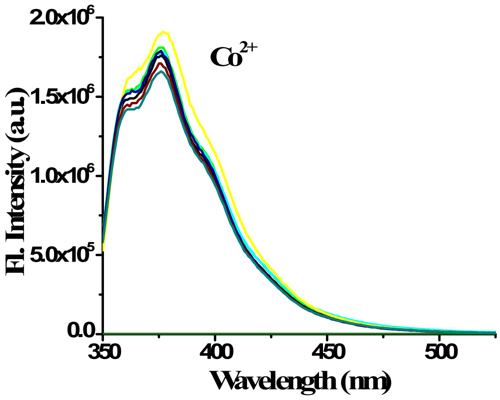

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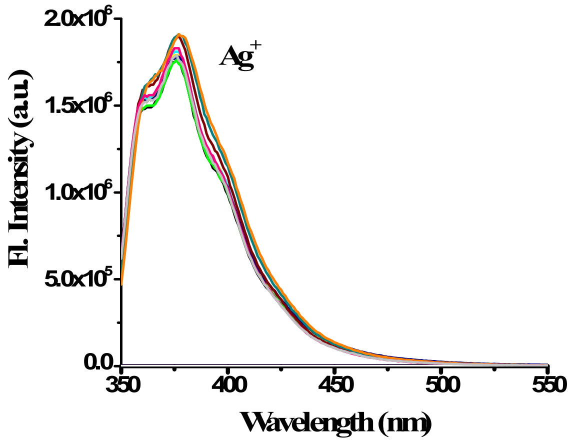

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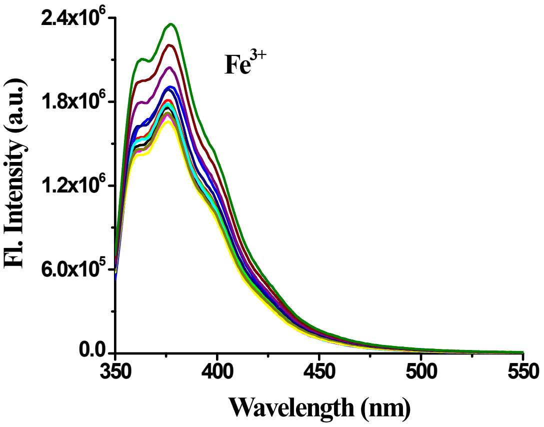

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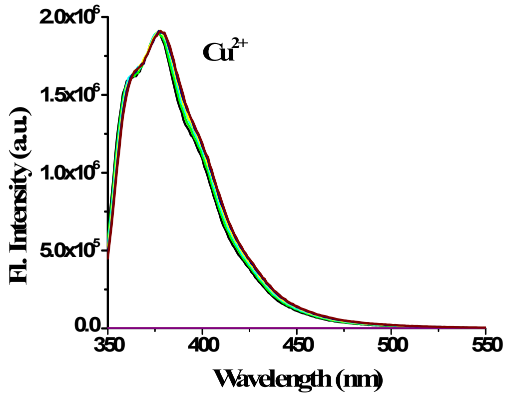

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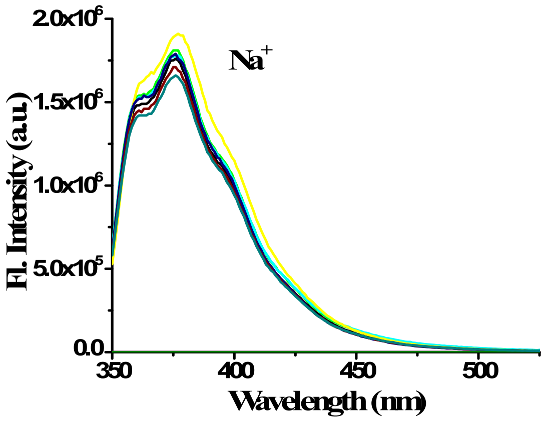
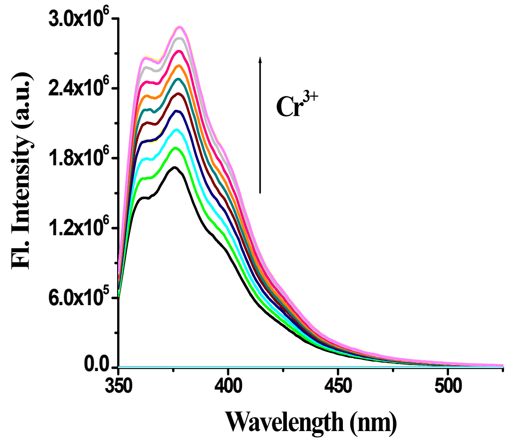
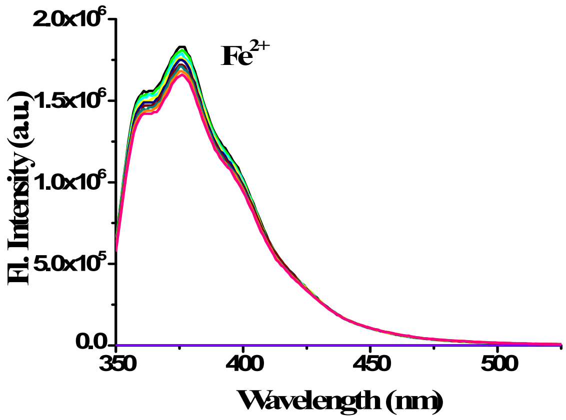

Na+
Fl. Intensity (a.u.)
Wavelength (nm)

(h)

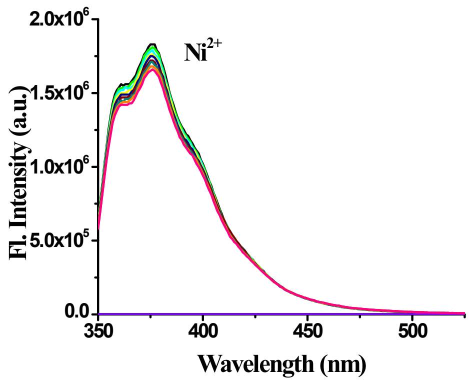
(


Cr3+
Fl. Intensity (a.u.)
Wavelength (nm)

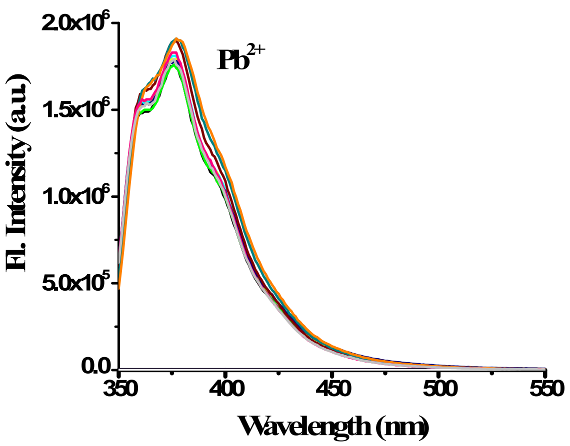
(i)


Fe2+
Fl. Intensity (a.u.)
Wavelength (nm)

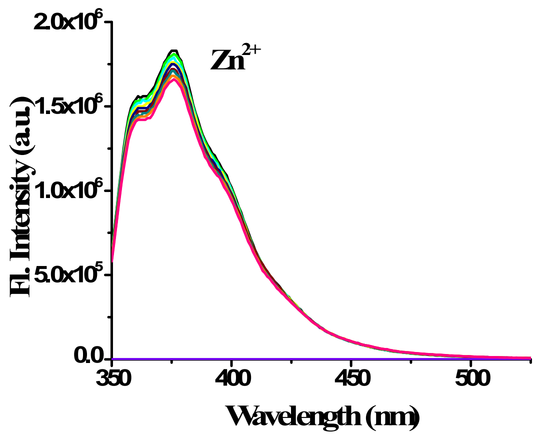
(j)


Ni2+
Fl. Intensity (a.u.)
Wavelength (nm)

(k)


Pb2+
Fl. Intensity (a.u.)
Wavelength (nm)

(l)


Zn2+
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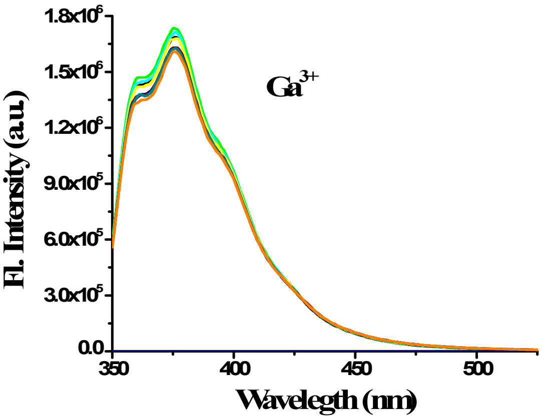
Wavelength (nm)

(m)



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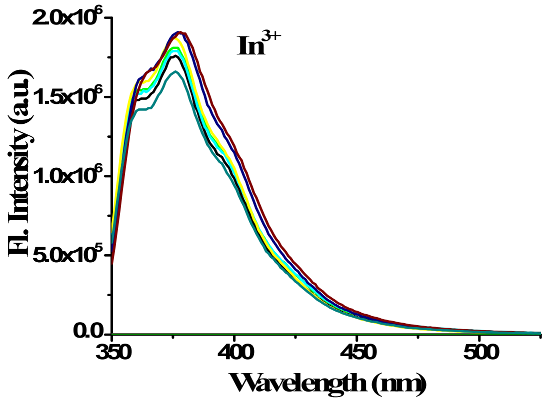

9. References :

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