Supporting Information

A highly reactive (<1min.) ratiometric chemodosimeter for selective "naked eye" and fluorogenic detection of hydrazine

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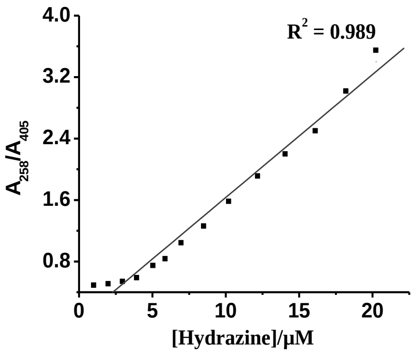
CONTENTS

1. The sensitivity of the CBM (Linear dynamic Curve):

(a)



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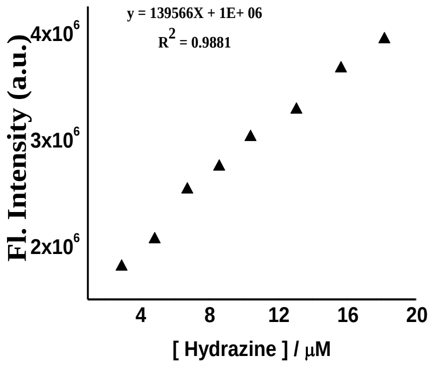
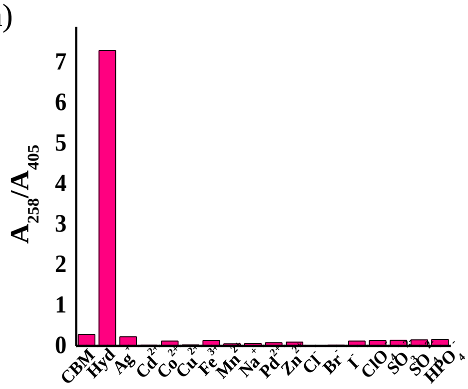


Figure S1: (a) Absorbance ratio changes (A_{258}/A_{405}) of CBM upon gradual addition of hydrazine. (b) The plot of fluorescence intensity vs. the whole range of hydrazine concentration tested at 413 nm.

2. Bar Diagram of UV-vis and fluorescence titration method :

(a)



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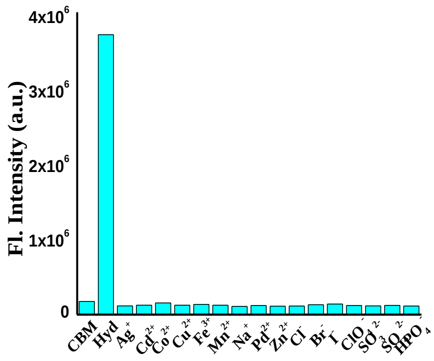
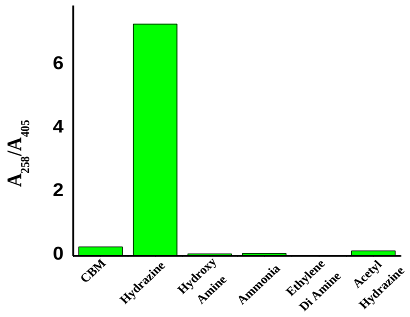


Figure S2: (a) Ratiometric response of CBM (2.0 x 10^{-5} M) towards metal ions and anions (2 eqiv.) with the naked eye color change (A_{258}/A_{405}) (b) Fluorescence response of CBM (2.0 x 10^{-5} M) towards metal ions and anions (2 eqiv.) with emission spectroscopy at 413nm.

3. Bar Diagram of CBM towards different amine containing compound in UV-vis and fluorescence titration method:

(a)



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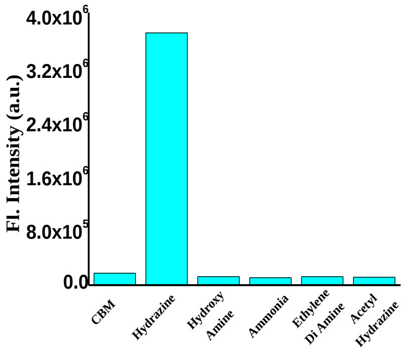


Figure S3: (a) Relative absorbance of the CBM in presence of other amine containing compounds (b) Bar chart illustrating fluorescence response of free ligand and two equivalent of other amine containing compounds in CH_3CN-H_2O (8:2, v/v, 25 ° C) at 413 nm.

4. Determination of fluorescence quantum yield:

The quantum yield of **CBM** itself is 0.123 is remarkably change into 0.466.

5. Calculation of the detection limit:

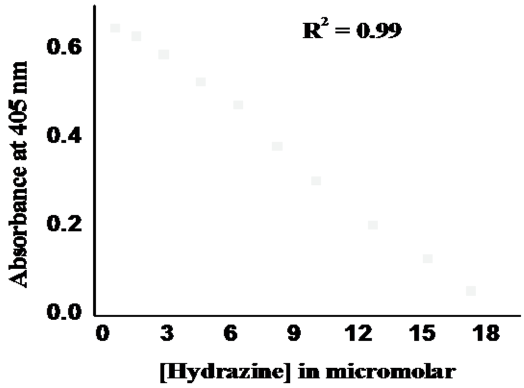


Figure S4: Absorbance vs. concentration of hydrazine plot at 405 nm

The detection limit DL of CBM for hydrazine 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.

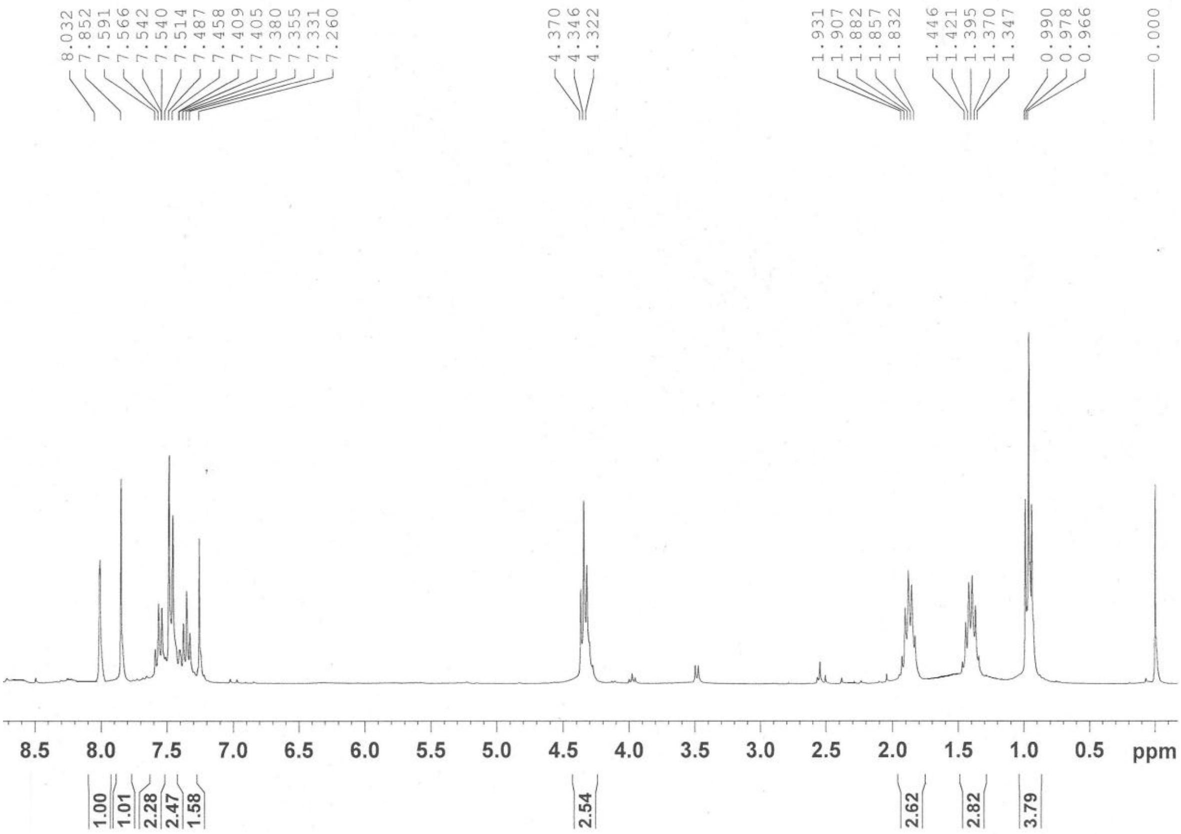
From the graph we get slope = 0.0361, and Sb1 value is 0.018588347
.
Thus using the formula we get the Detection Limit = 1.02 µM i.e. CBM can detect hydrazine in this minimum concentration.

6. Calculation of rate constant:

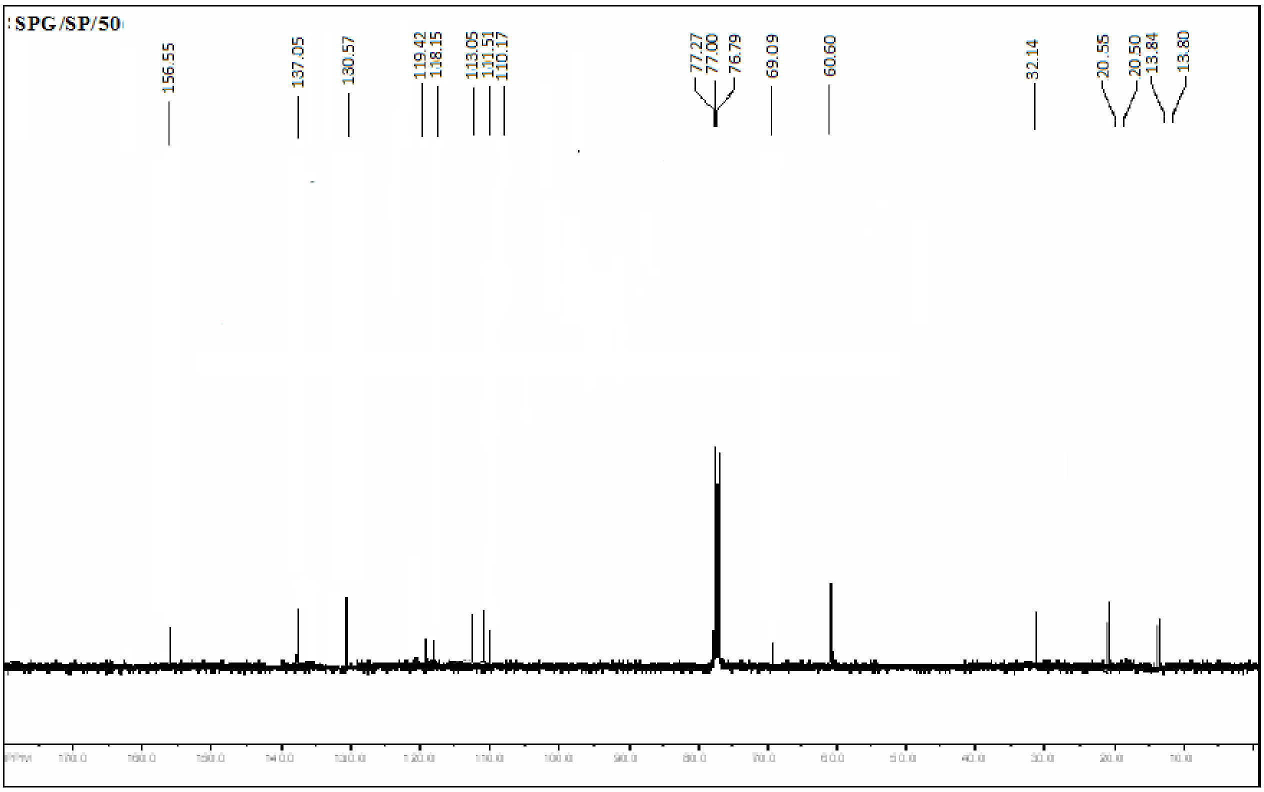
From the time vs. Fl. Intensity vs. time (sec.) plot at fixed wavelength (413nm) using first order rate equation (Figure S5), we get rate constant K = slope X 2.303 = 0.0226 X 2.303 = 5.2 X 10^{-2} sec^{-1}

7. ^{1}H NMR, ^{13}C NMR and ESI MS spectra of CBM and corresponding hydrazone product:

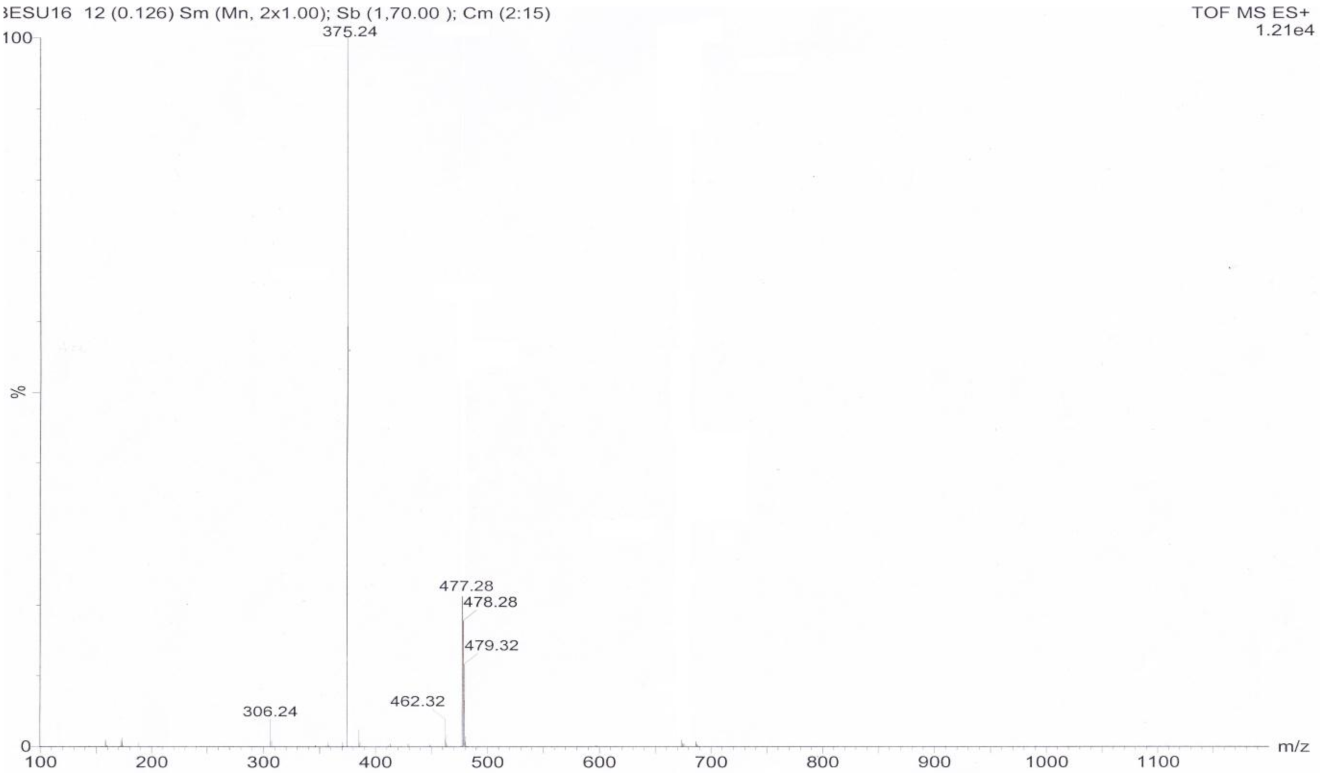
^{1}H NMR spectrum of Receptor i.e. CBM:



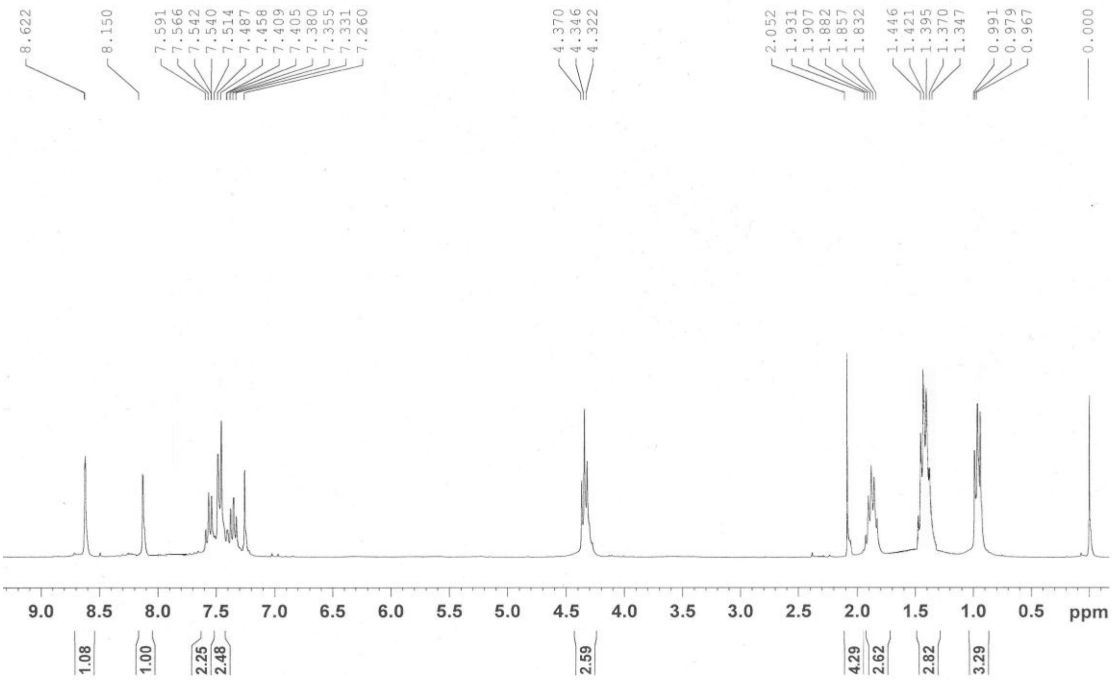
^{13}C NMR spectrum of CBM:



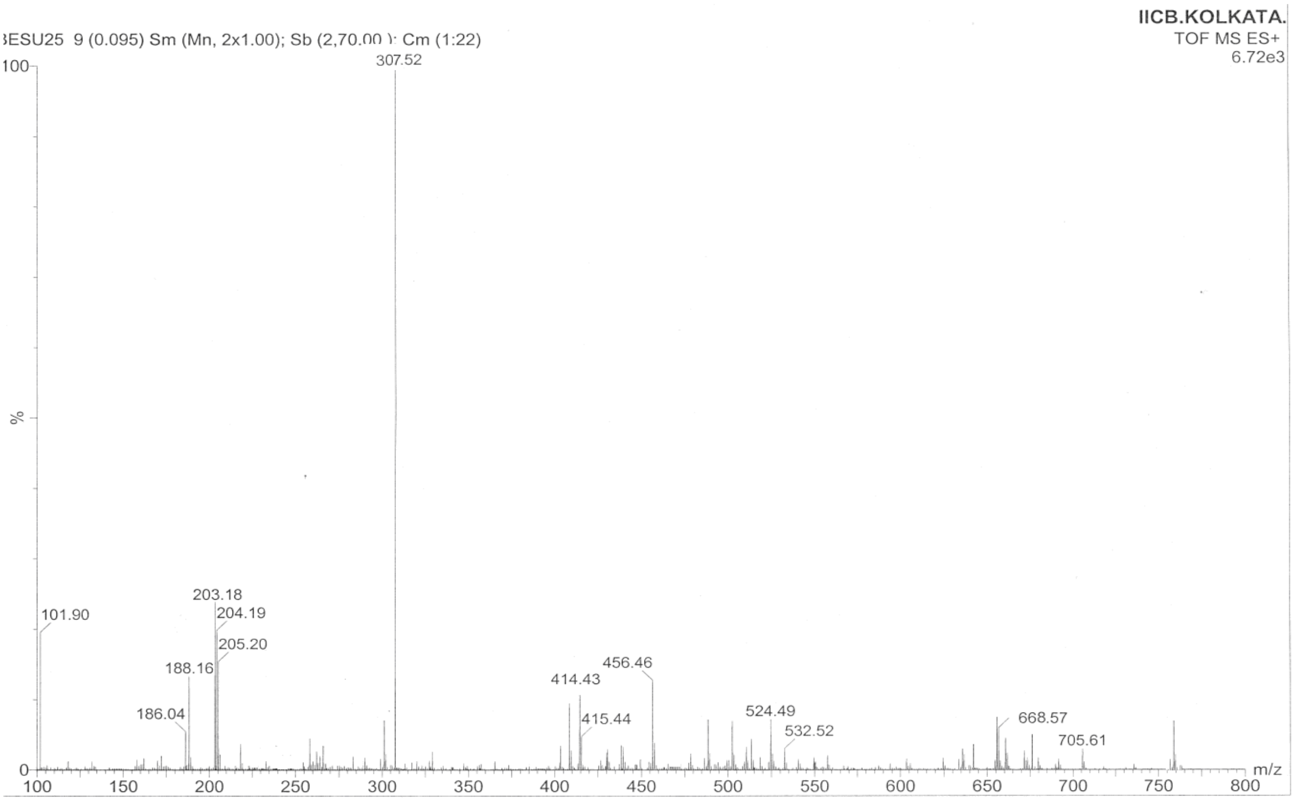
ESI MS Mass Spectra of CBM:



^{1}H NMR spectrum of Hydrazone product i.e. CBM + Hyd:

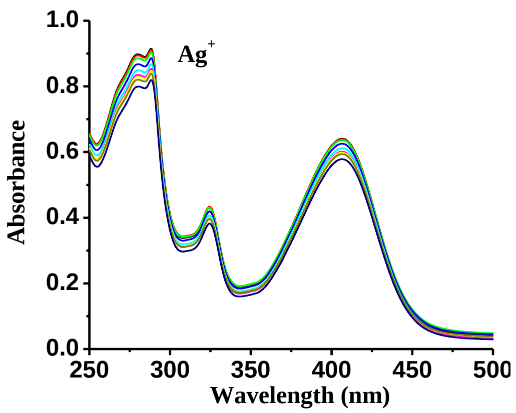


ESI MS Spectra of CBM+ Hyd:



8. UV-vis absorption spectra of CBM with different cations as Ag^{+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} , Pb^{2+}, Zn^{2+}, Na^{+} (The solutions of metal ions were prepared from $AgNO_3$, $Cd(ClO_4)_2{\cdot}H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$, $FeCl_3$, $MnCl_2$, $Pb(ClO_4)_2$, $Zn(ClO_4)_2{\cdot}6H_2O$, and $NaClO_4$, respectively in CH_3CN-H_2O), different anions Cl^-, Br^-, I^- as their tetra butyl salt and ClO_4^{2-}, HPO_4^{2-}, SO_3^{2-}, SO_4^{2-} as their sodium salt in CH_3CN : H_2O (8:2, v/v).

(a)



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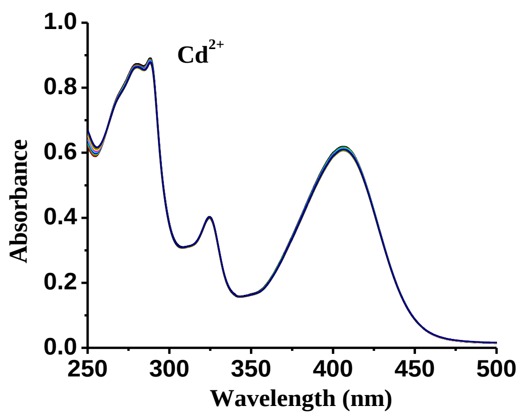

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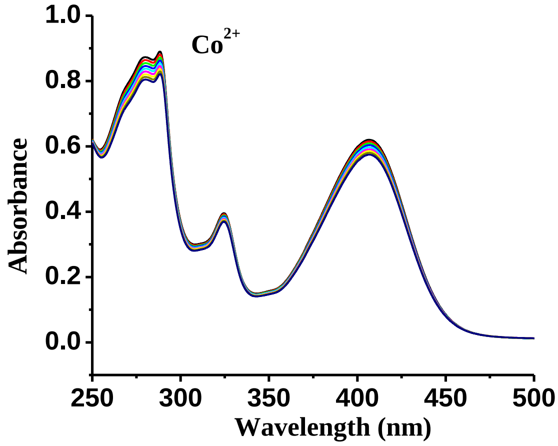
Co2+
Absorbance
Wavelength (nm)
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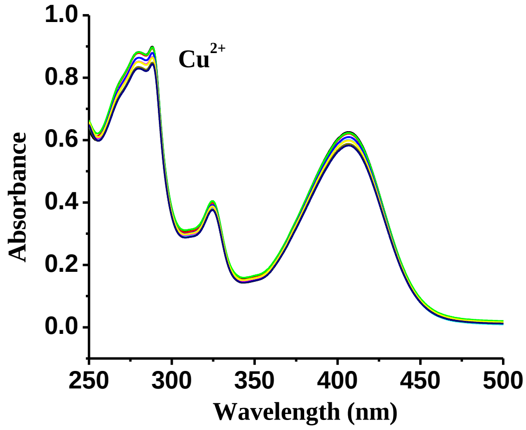
0.6
0.4
0.2
0.0
250
300
350
400
450
500

(d)


Cu2+
Absorbance
Wavelength (nm)
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0.6
0.4
0.2
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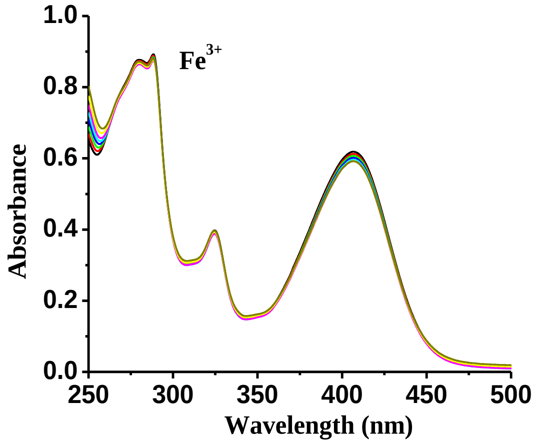
400
450
500

(e)


Fe3+
Absorbance
Wavelength (nm)
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300
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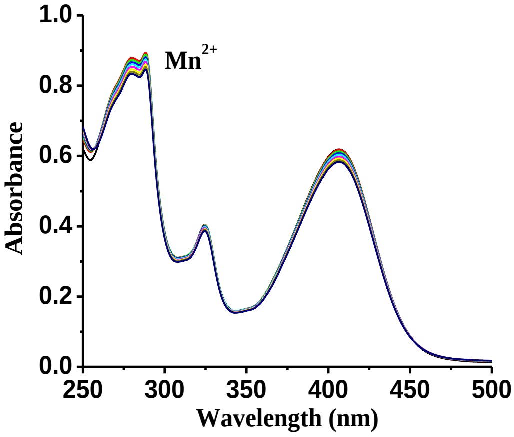
400
450
500

(f)


Mn2+
Absorbance
Wavelength (nm)
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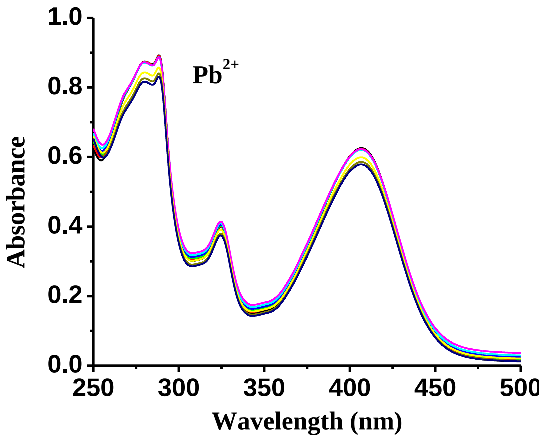
0.0
250
300
350
400
450
500

(g)


Pb2+
Absorbance
Wavelength (nm)
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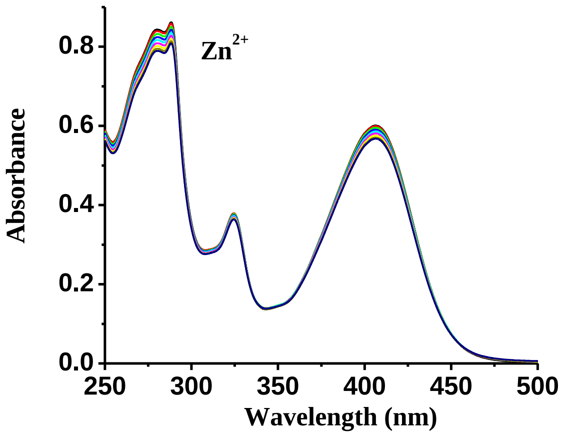
0.6
0.4
0.2
0.0
250
300
350
400
450
500

(h)


Zn2+
Absorbance
Wavelength (nm)
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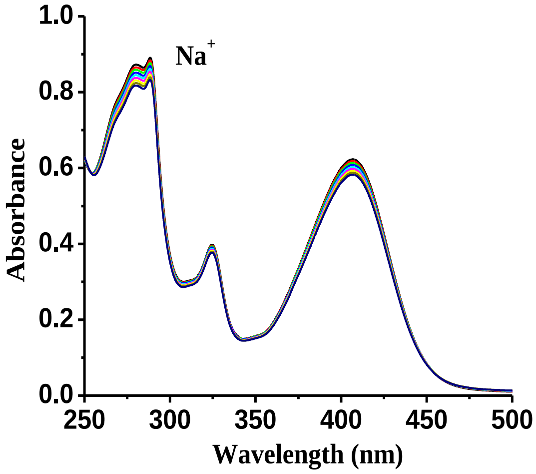
0.4
0.2
0.0
250
300
350
400
450
500

(i)


Na^{+}
Absorbance
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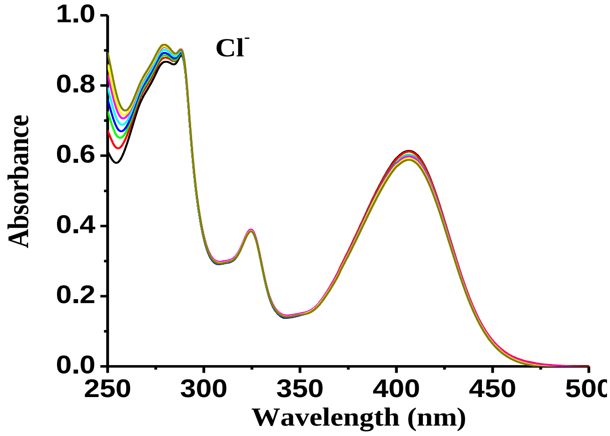
500
Wavelength (nm)

(j)


Cl^{-}
Absorbance
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0.4
0.2
0.0
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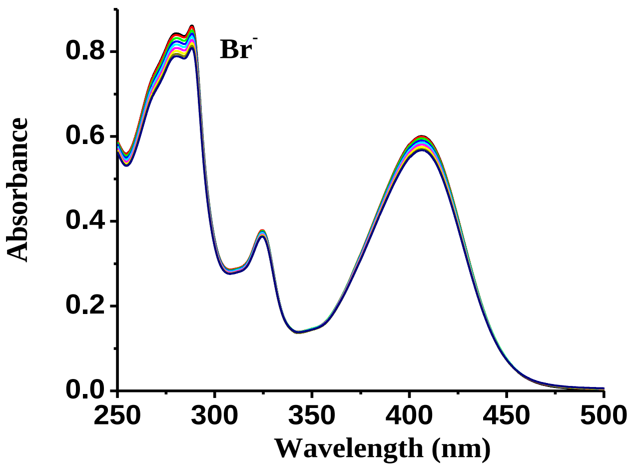
300
350
400
450
50C
Wavelength (nm)

(k)


Br^{-}
Absorbance
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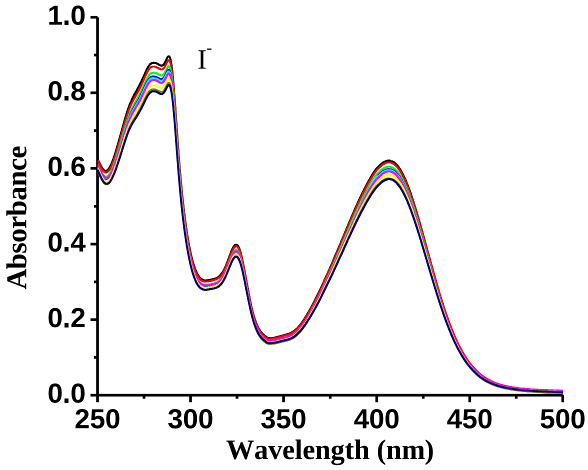
0.0
250
300
350
400
450
500
Wavelength (nm)

(l)


I^{-}
Absorbance
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0.4
0.2
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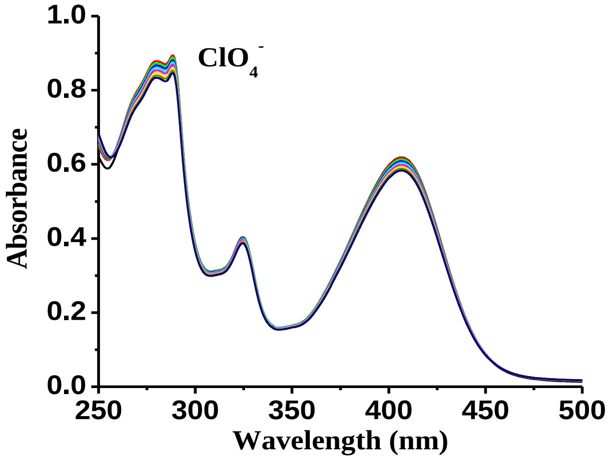
300
350
400
450
500
Wavelength (nm)

(m)


ClO$_4^{-}$
Absorbance
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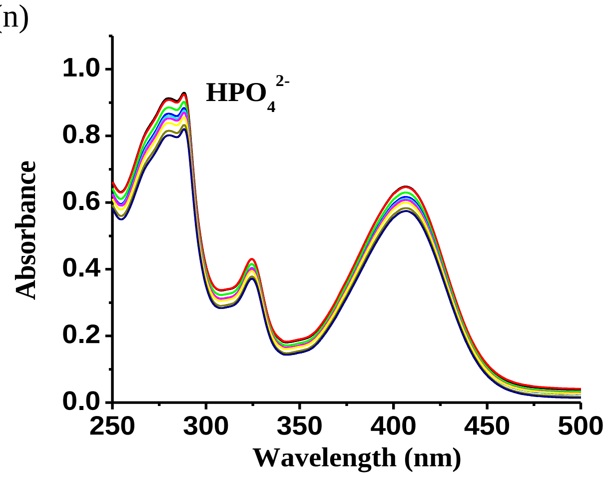
0.6
0.4
0.2
0.0
250
300
350
400
450
500
Wavelength (nm)

(n)


HPO$_4^{2-}$
Absorbance
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0.6
0.4
0.2
0.0
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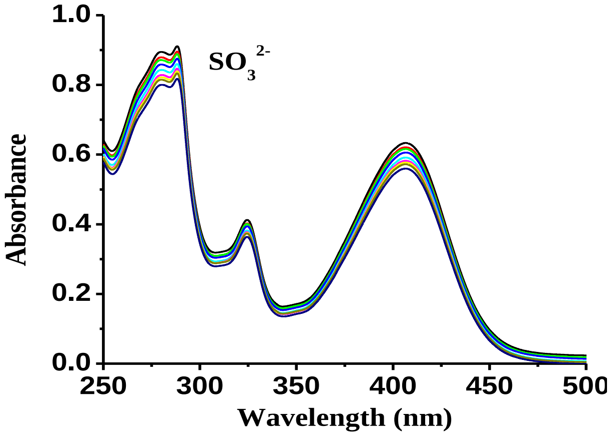
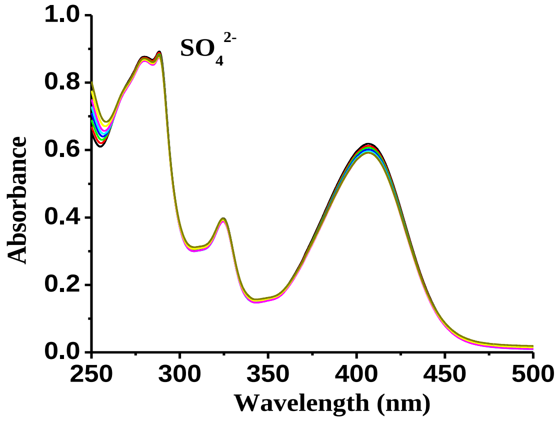
300
350
400
450
500
Wavelength (nm)

(o)

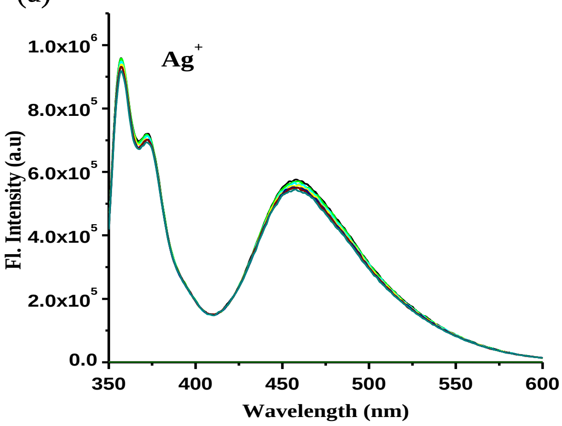


(p)



9. Fluorescence emission spectra of CBM with different cations as Ag^{+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} , Pb^{2+}, Zn^{2+}, Na^{+} (The solutions of metal ions were prepared from $AgNO_3$, $Cd(ClO_4)_2\cdot H_2O$, $Co(ClO_4)_2\cdot 6H_2O$, $Cu(ClO_4)_2\cdot 6H_2O$, $FeCl_3$, $MnCl_2$, $Pb(ClO_4)_2$, $Zn(ClO_4)_2\cdot 6H_2O$, and $NaClO_4$, respectively in CH_3CN-H_2O), different anions Cl^-, Br^-, I^- as their tetra butyl salt and ClO_4^-, HPO_4^{2-}, SO_3^{2-}, SO_4^{2-} as their sodium salt in CH_3CN : H_2O (8:2, v/v).

(a)



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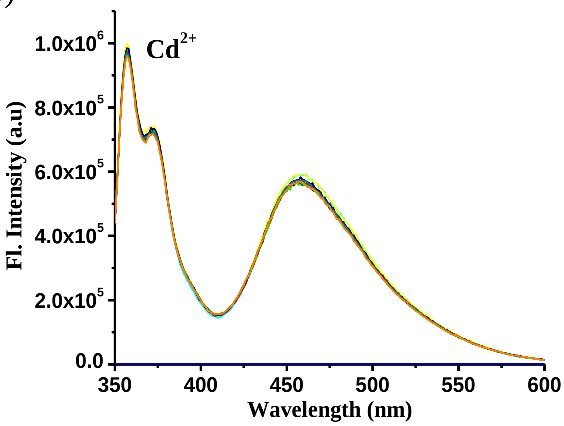

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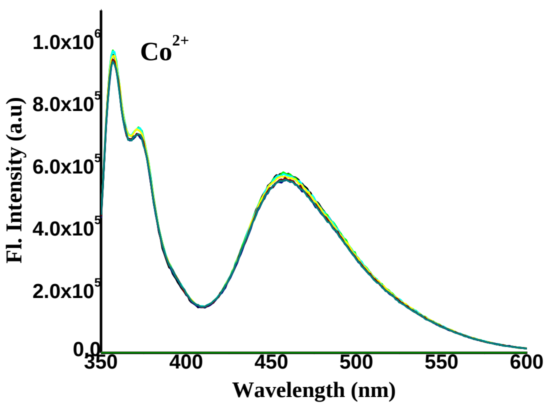

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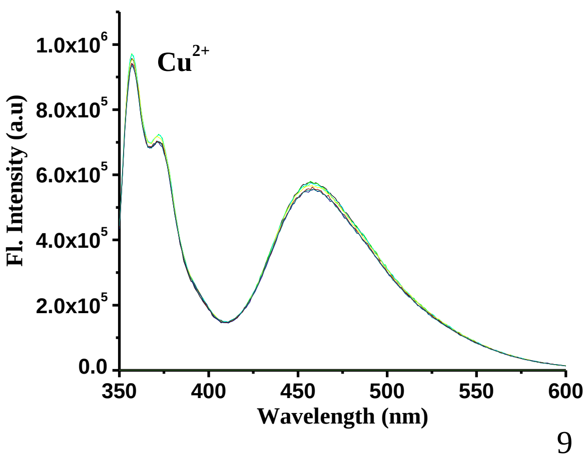

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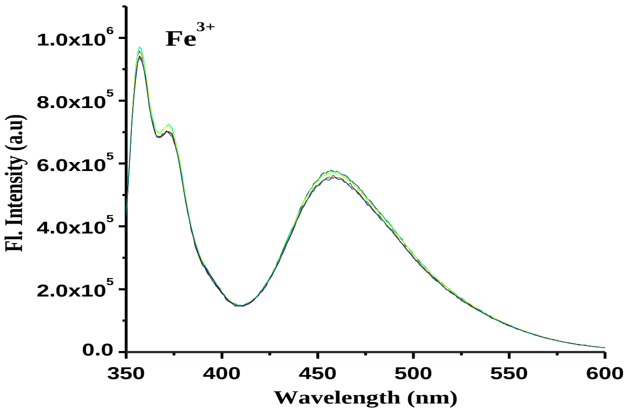
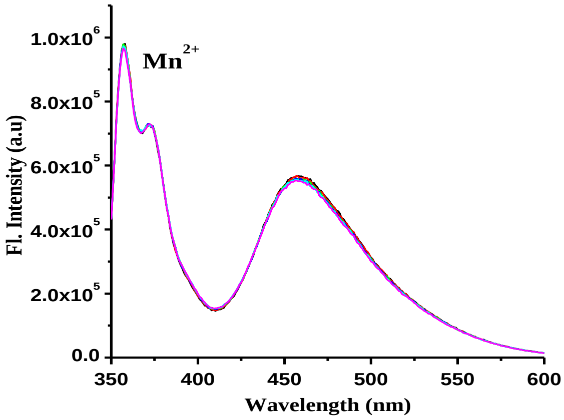
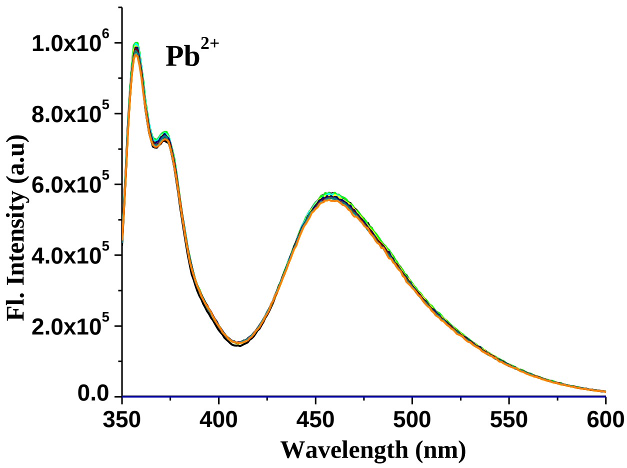

Fe^{3+}
Fl. Intensity (a.u)
Wavelength (nm)
$1.0x10^6$
$8.0x10^5$
$6.0x10^5$
$4.0x10^5$
$2.0x10^5$
0.0
350 400 450 500 550 600

(f)


Mn^{2+}
Fl. Intensity (a.u)
Wavelength (nm)
$1.0x10^6$
$8.0x10^5$
$6.0x10^5$
$4.0x10^5$
$2.0x10^5$
0.0
350 400 450 500 550 600

(g)


Pb^{2+}
Fl. Intensity (a.u)
Wavelength (nm)
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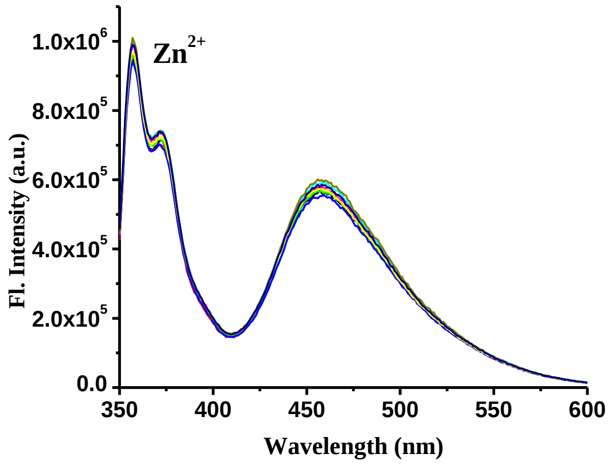
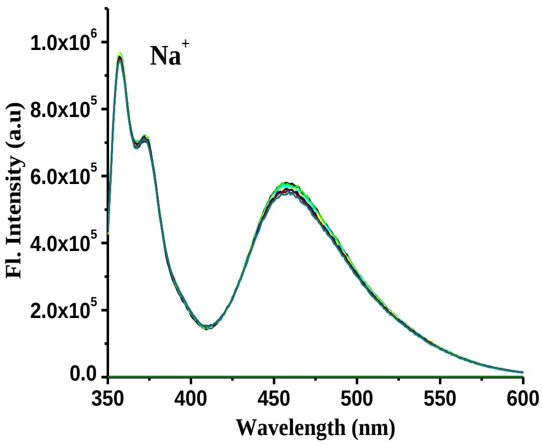
$8.0x10^5$
$6.0x10^5$
$4.0x10^5$
$2.0x10^5$
0.0
350 400 450 500 550 600

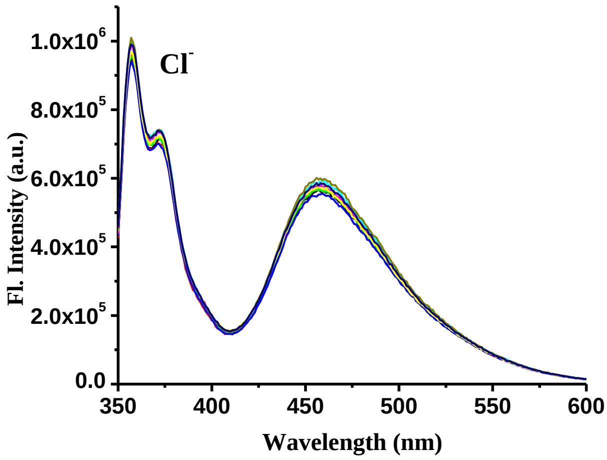
(h)


Zn^{2+}
Fl. Intensity (a.u.)
Wavelength (nm)
$1.0x10^6$
$8.0x10^5$
$6.0x10^5$
$4.0x10^5$
$2.0x10^5$
0.0
350 400 450 500 550 600

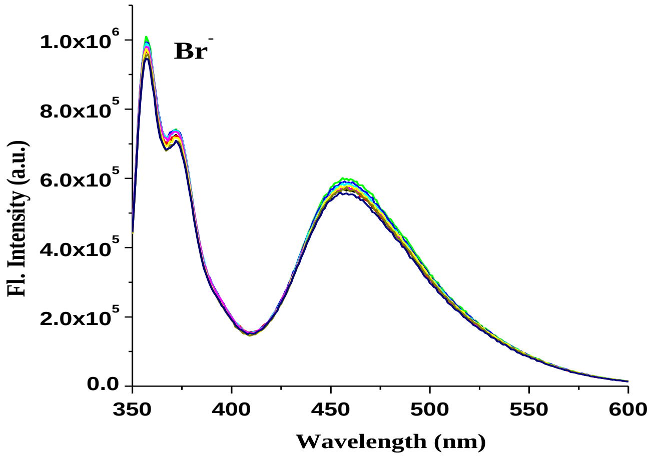
(i)


Na^{+}
Fl. Intensity (a.u)
Wavelength (nm)
$1.0x10^6$
$8.0x10^5$
$6.0x10^5$
$4.0x10^5$
$2.0x10^5$
0.0
350 400 450 500 550 600

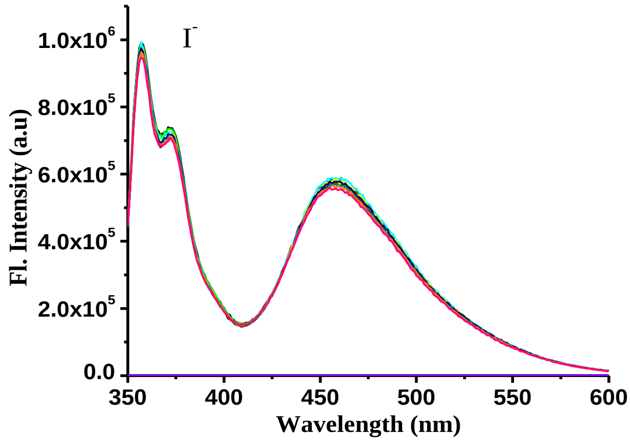
(j)


Cl^{-}
Fl. Intensity (a.u.)
Wavelength (nm)
$1.0x10^6$
$8.0x10^5$
$6.0x10^5$
$4.0x10^5$
$2.0x10^5$
0.0
350 400 450 500 550 600

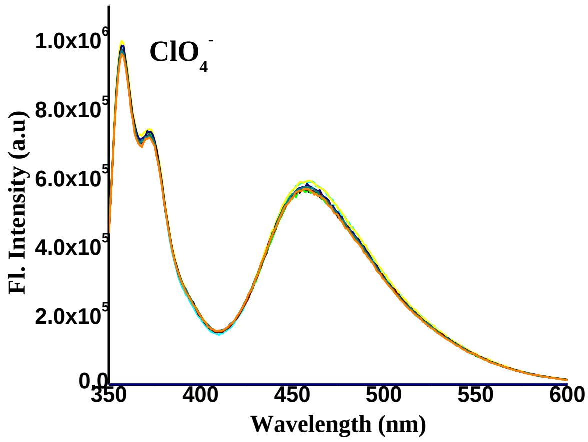
(k)


Br⁻
Fl. Intensity (a.u.)
Wavelength (nm)

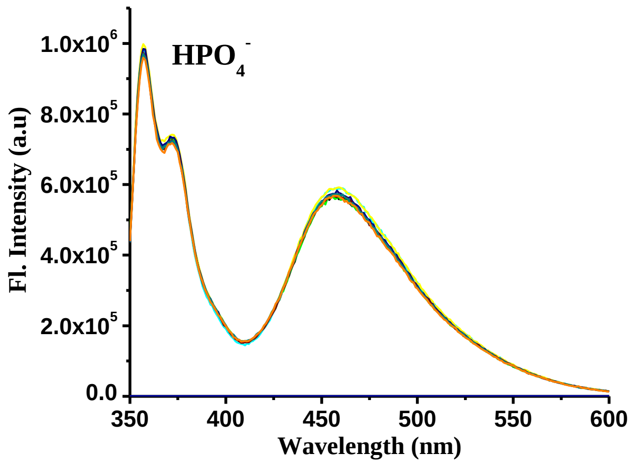
(l)


I⁻
Fl. Intensity (a.u)
Wavelength (nm)

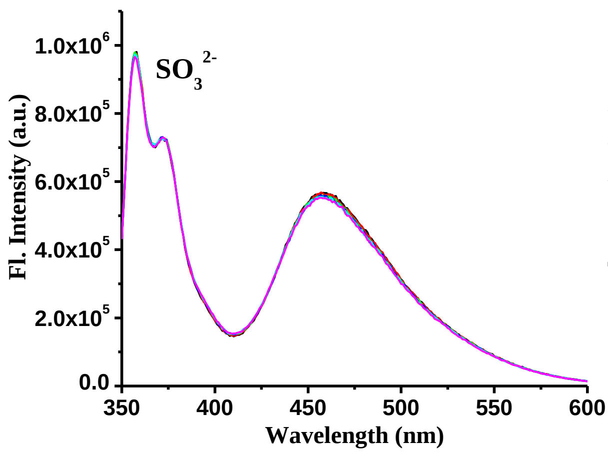
(m)


ClO_4^-
Fl. Intensity (a.u)
Wavelength (nm)

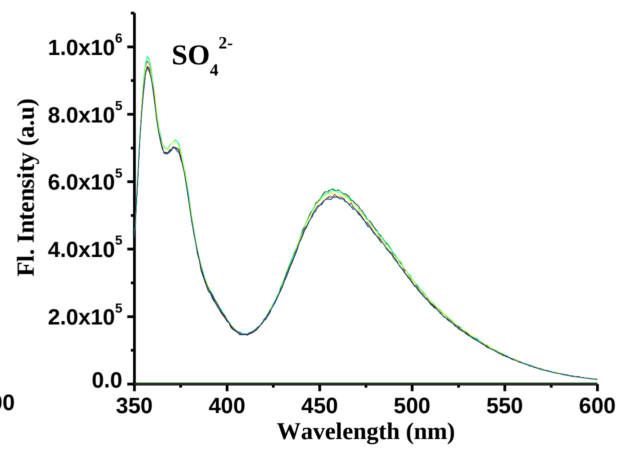
(n)


HPO_4^-
Fl. Intensity (a.u)
Wavelength (nm)

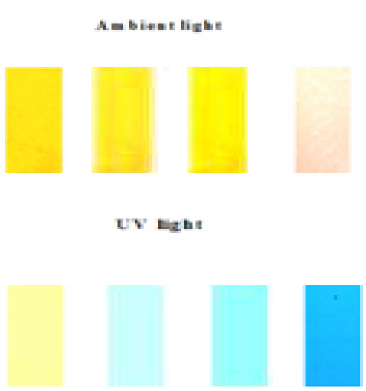
(o)


SO_3^{2-}
Fl. Intensity (a.u.)
Wavelength (nm)

(p)


SO_4^{2-}
Fl. Intensity (a.u)
Wavelength (nm)

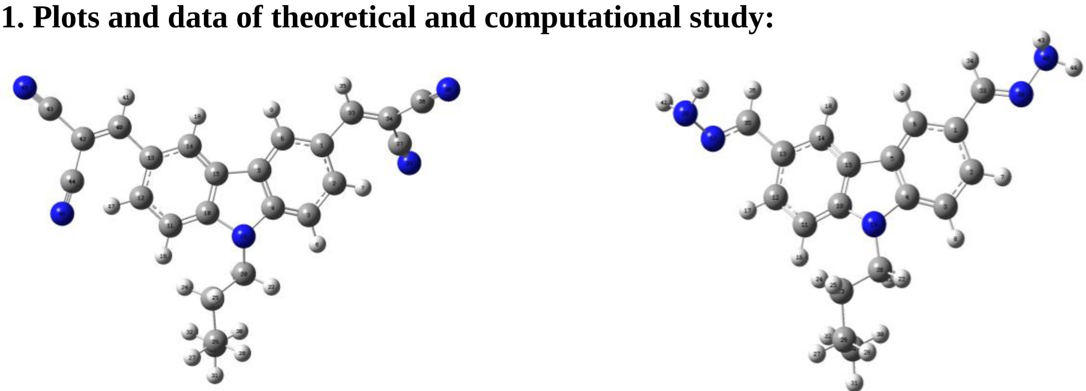
10. Photograph of CBM towards various concentration of hydrazine in TLC plate:



(A) **(B)** **(C)** **(D)**

Figure S5: Photograph of CBM towards various concentration of hydrazine (A) 0 , (B) 2 X 10^{-5} (C) 2 X 10^{-4} (D) 2 X 10^{-3} in TLC plate in presence of Ambient light and UV light.

11. Plots and data of theoretical and computational study:



CBM **CBM + Hyd**

Figure S6: Optimized ground state geometries of receptor (CBM) and corresponding hydrazone product (CBM + Hyd)

Cartesian coordinates for the Starting substrate i.e. CBM :

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.42318139
C	1.22831809	0.00000000	2.12560392
C	2.35695171	0.03309607	1.39944009
C	2.33587245	0.28320768	0.04736298
C	1.19771636	0.27107309	-0.68732878
H	-0.91469675	-0.02083462	1.96157974
H	1.26683042	-0.03725392	3.19352701
H	1.21058096	0.43157911	-1.74434207
C	4.56507130	0.36095347	0.76456933

C	5.88755512	0.65868427	0.75991943
C	6.47616586	1.03672998	-0.45246688
C	5.66974257	1.13961705	-1.60513328
C	4.29236904	0.87914544	-1.53897004
C	3.77832334	0.53943355	-0.35510902
H	6.47840501	0.59681004	1.64525783
H	7.52095034	1.25704595	-0.51708087
H	3.67522920	0.94357870	-2.39861611
N	3.74708975	-0.22980990	1.86024959
C	4.03677336	0.19895113	3.23105737
H	3.89663520	1.26641119	3.37325399
H	3.37580284	-0.31181090	3.88992332
C	5.48942356	-0.17912579	3.50728913
H	6.12977997	0.47046403	2.93724320
H	5.64227177	-1.18982433	3.20763273
C	5.81733972	-0.04749235	5.00674914
H	6.85242813	-0.26214947	5.14709378
H	5.22926117	-0.76974738	5.54449022
C	5.50933396	1.35004486	5.52831537
H	4.46569477	1.50799445	5.45361558
H	5.81905227	1.42341715	6.54680208
H	6.02325568	2.08061060	4.95511022
C	-1.27472504	-0.36008885	-0.77700307
C	-2.45041386	-0.54984159	-0.11366913
H	-1.23936580	-0.50429853	-1.82780069
C	-3.47156224	-1.62555216	-0.54557292
C	-2.74615778	0.28207204	1.10654948
N	-4.27397233	-2.42231623	-0.82116450
N	-3.02005677	0.89025354	2.05329084
C	6.30229392	1.53635506	-2.93223294
H	5.70082602	1.70357019	-3.78453968
C	7.64635525	1.66626202	-3.01358793
C	8.31078689	2.12379600	-4.32219208
C	8.55514891	1.39168516	-1.84016675
N	8.84856385	2.45774449	-5.27114813
N	9.31015505	1.18937177	-0.96436995

Cartesian coordinates for the hydrazone product i.e. CBM + Hyd :

C	3.41291100	-0.54038800	0.02782000
C	3.45564200	0.87917900	0.18332700
C	2.25334500	1.62867400	0.05456000
C	1.14627300	0.92338000	-0.17675300
C	1.08116000	-0.42118500	-0.08297000
C	2.17352100	-1.18469400	-0.07849600
H	4.38072500	1.37314500	0.36519300
H	2.22745900	2.69842800	0.14467000
H	2.09848000	-2.26545100	-0.13449100
C	-1.10225300	0.37792000	-0.11330800
C	-2.43414600	0.48087100	0.17740300
C	-3.08729700	-0.72635900	0.53070600
C	-2.37956400	-1.93774300	0.48286600
C	-0.97890900	-1.94376800	0.39652700
C	-0.38469100	-0.77618600	0.08619200
H	-2.95087900	1.40571900	0.13665100

H	-4.12576200	-0.70426900	0.80455500
H	-0.41099300	-2.83844500	0.54025100
N	-0.18940500	1.41544000	-0.69249000
C	-0.49343300	2.81434000	-0.48005600
H	-0.34037100	3.05584000	0.52975000
H	0.13392700	3.42739100	-1.07807500
C	-1.94870900	3.04790600	-0.83236400
H	-2.53158200	2.35221500	-0.30248300
H	-2.08519000	2.91939900	-1.86395500
C	-2.39083000	4.47606200	-0.39502100
H	-3.40158400	4.61598000	-0.69212200
H	-1.76111500	5.19051100	-0.87629000
C	-2.28507900	4.62370100	1.14777300
H	-1.25766900	4.47508000	1.46515000
H	-2.60666300	5.63401600	1.44951600
H	-2.95036700	3.89391500	1.59667500
C	4.69855400	-1.39513400	-0.00152400
H	4.61699600	-2.43790700	-0.04136700
C	-3.16062000	-3.26820900	0.43322400
H	-2.67184200	-4.21295400	0.58908800
N	-4.44250200	-3.16264900	0.11381000
N	5.87671700	-0.83604300	0.02495900
N	-5.01333400	-4.12175400	-0.77201600
N	7.06155200	-1.63987300	0.08891700
H	-5.59079600	-4.77576200	-0.27679100
H	-4.25850100	-4.60474200	-1.20973400
H	7.14192800	-2.09436000	-0.86241000
H	7.83734300	-1.04381200	0.21453400

12. 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