Supporting Information

A reaction based colorimetric as well as fluorescence *'turn on'* probe for the rapid detection of hydrazine

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1. General:

Chemicals and solvents used for the synthesis of receptor were purchased from Sigma-Aldrich chemicals Private Limited and used without further purification. Silica gel (100-200 mesh size, Merck) was used for column chromatography. Melting points were determined on a hot-plate melting point apparatus in an open-mouth capillary and are uncorrected. ^{1}H-NMR and ^{13}C NMR spectra were recorded on Brucker 300 MHz and 75 MHz instruments respectively. For NMR spectra, $CDCl_3$ was used as solvent using TMS as an internal standard. Chemical shifts are expressed in δ units and ^{1}H–^{1}H and ^{1}H–C coupling constants in Hz. UV-vis titration experiments was performed on a JASCO UV-V530 spectrophotometer using a dissolution cell of 10 mm path and fluorescence experiment was done using PTI (Photon Technology International) fluorescence spectrophotometer using a fluorescence cell of 10 mm path.

2. General method of UV-vis and fluorescence titration:

By UV-vis method

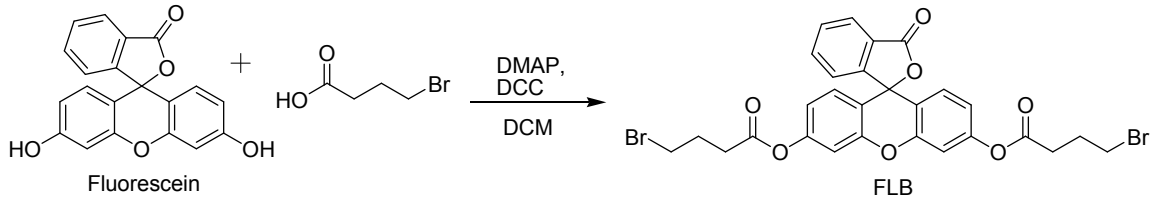
For UV-vis titrations, stock solution of the receptor (20 μM) was prepared in [(CH_3OH / water), 1:1, *v/v*] (at 25°C) using HEPES buffered solution. The solutions of the guest analytes [Cd^{2+}, Cu^{2+}, Mn^{2+}, Mg^{2+}, Fe^{3+}, Co^{2+}, Ag^{+}, Ni^{2+}, Cr^{3+}, Pd^{2+}, Zn^{2+}, Hg^{2+} (as their chloride salts); F^{-}, NO_3^{-}, OCl^{-}, HSO_4^{-}, HSO_3^{-}, SO_3^{2-}, SO_4^{2-} (as their sodium salts); $NH_2(CH_2)_2NH_2$, NH_3 and NH_2OH] in the order of 2×10^{-4} M, were prepared in deionized water using HEPES buffer at pH = 7.1. Solutions of various concentrations containing the

sensor and increasing concentrations of analytes were prepared separately. The spectra of these solutions were recorded by means of UV-vis method.

By fluorescence method

For fluorescence titrations, stock solution of the sensor (20 μM) was prepared in the same way as in the case of UV-vis titration. The solutions of the guest analytes in the order of 2 × 10^{-4} M, were prepared in deionised water. Solutions of various concentrations containing sensor and increasing concentrations of analytes were prepared separately. The spectra of these solutions were recorded by means of fluorescence method.

Synthetic method for the preparation of FLB:



Synthesis of FLB:

Fluorescein (500 mg, 1.5 mmol) and DMAP (50 mg, 0.41 mmol), were added to 4-bromobutyric acid (1.0 g, 5.9 mmol). The mixture was dissolved in dry dicholoromethane (25 mL) and chilled at 0^0 C followed by the addition of a solution of DCC (930 mg, 4.5 mmol) in dry dichloromethane. The reaction mixture was stirred under nitrogen atmosphere at 0^0C for 15 minutes and at room temperature for 12 hrs. The precipitate of urea was removed by filtration and the filtrate was concentrated in high vacuum to give an oily residue. This residue was purified by column chromatography using silica gel (100-200 mesh size) and 10% ethyl acetate in pet ether (v/v) as eluent to give a white color solid (760 mg, yield = 81%).

Mp= 70-72^0 C

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (m, 4H), 2.79 (t, *J* = 5Hz, 4H), 3.53 (t, *J* = 5Hz,

4H), 6.81 (m, 4H), 7.09 (d, J = 1.5 Hz, 2H), 7.17 (d, J = 5Hz, 1H), 7.66 (m, 2H), 8.03 (d, J = 10 Hz, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 27.5, 27. 8, 31.0, 32.4, 32.6, 68.6, 81.7, 110.4, 116.6, 117.7, 124.1, 125.3, 126.1, 129.1, 130.2, 135.4, 151.6, 152.0, 152.9, 169.2, 170.6

TOF MS (ESI, positive): Calculated for $C_{28}H_{23}Br_2O_7$ $[M + H]^+$ (m/z): 628.9811; found: 628.9819.

3. Time dependent fluorescence and absorbance change of FLB upon addition of hydrazine:

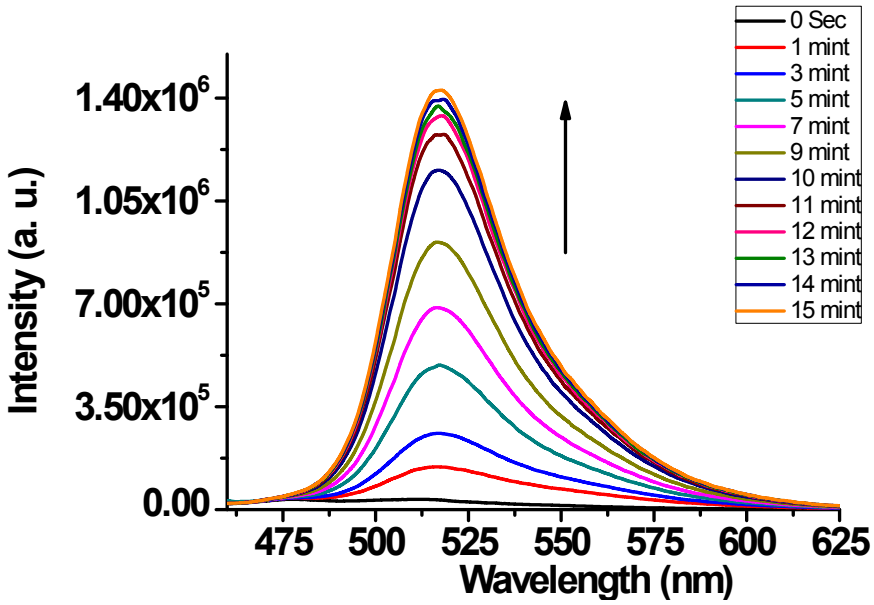


Figure S1: Change of emission spectra of FLB (20 μM) after addition of hydrazine (4 equivalents) with different time interval.

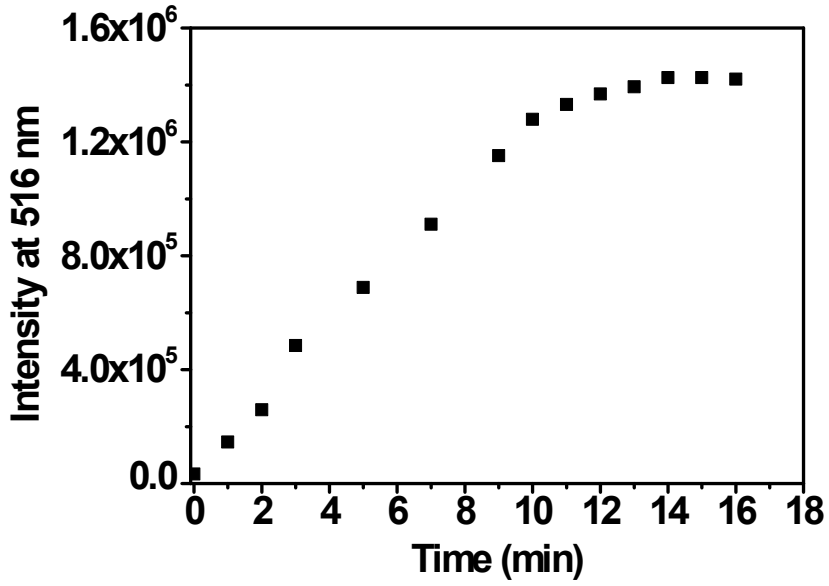


Figure S2: Time (min) vs. emission intensity plot

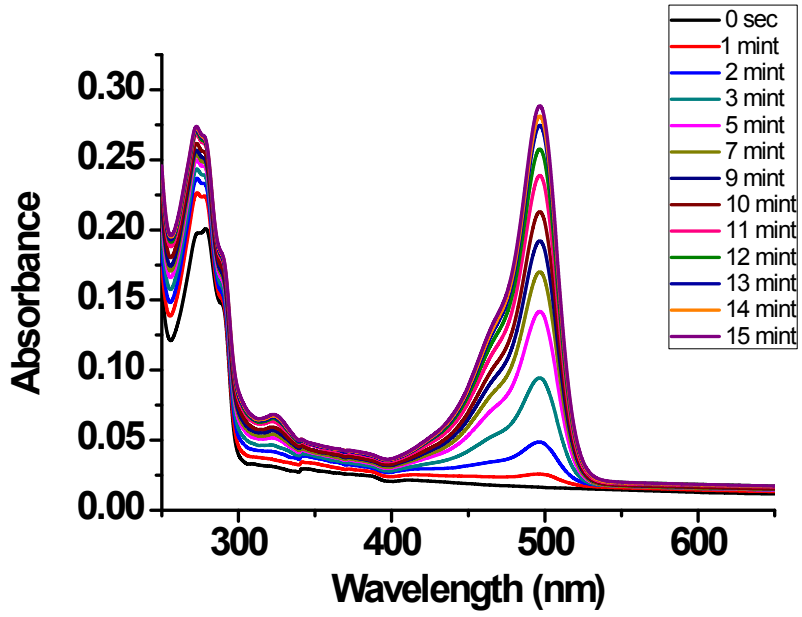


Figure S3: Change of absorbance spectra of FLB (20 μM) after addition of hydrazine (4 equivalents) with different time interval.

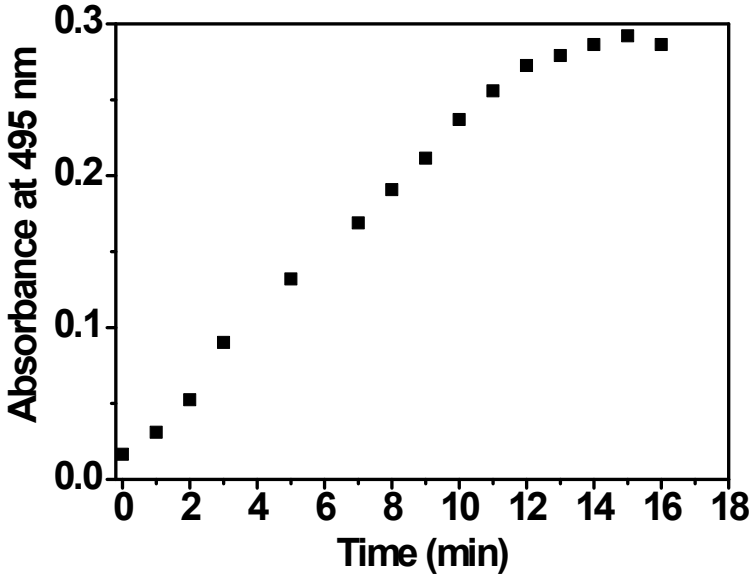


Figure S4: Time (min) vs. absorbance intensity plot

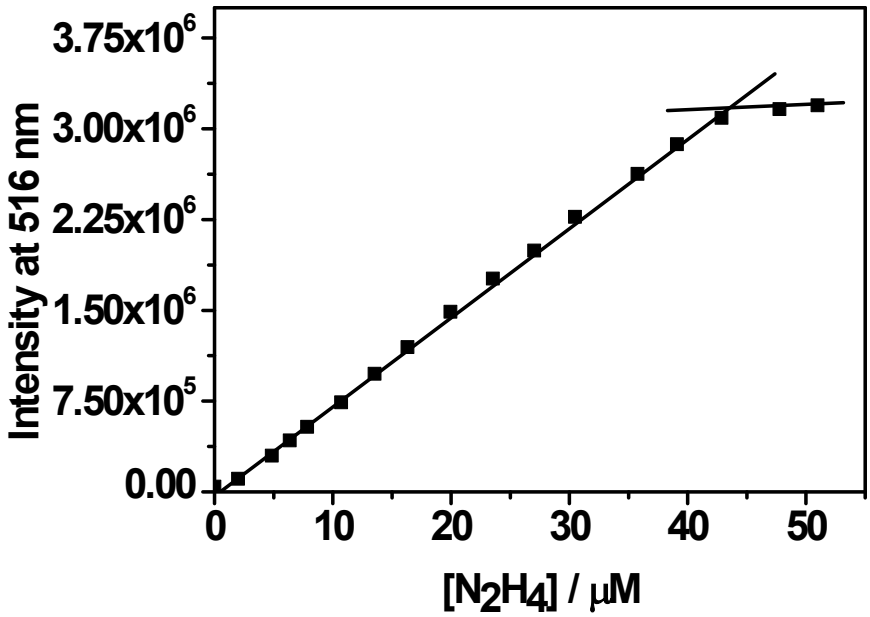


Figure S5: The response curve of emission at 516 nm of FLB depending on N_2H_4 concentration

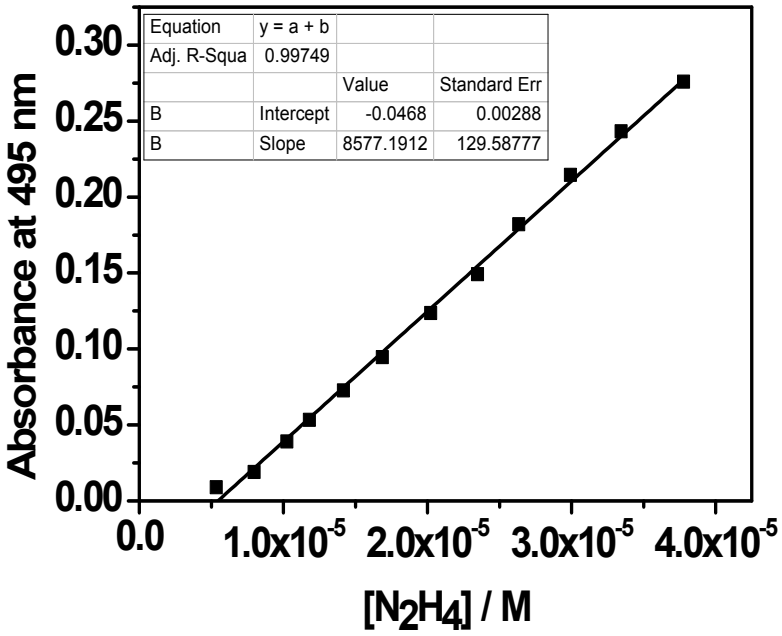


Figure S6: The linear response curve of absorbance of FLB depending on N_2H_4 concentration.

4. Determination of detection limit:

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of FLB without hydrazine was measured by 10 times and the standard deviation of blank measurements was determined.

The detection limit (DL) of **FLB** for hydrazine was determined from the following equation: $DL = K \times Sb_1/S$

Where K = 2 or 3 (we take 3 in this case); Sb_1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

From the graph we get slope = 7.7801×10^{10}, and Sb_1 value is 1006.6056

Thus using the formula we get the Detection Limit = 3.881×10^{-8} M i.e. FLB can detect N_2H_4 in this minimum concentration by fluorescence techniques.

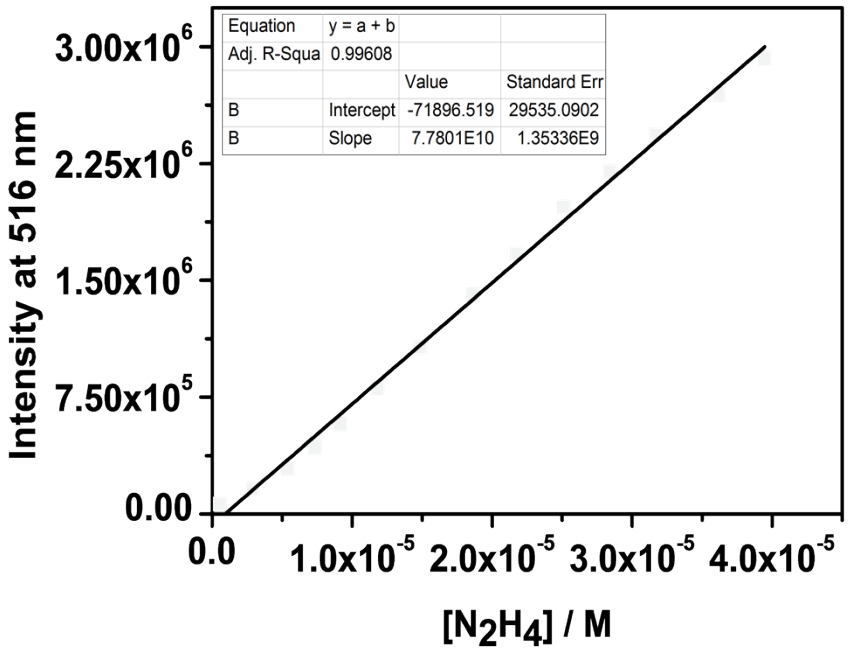


Figure S7: Linear response curve of FLB of fluorescence intensity at 516 nm depending on the N_2H_4 concentration.

5. Effect of pH:

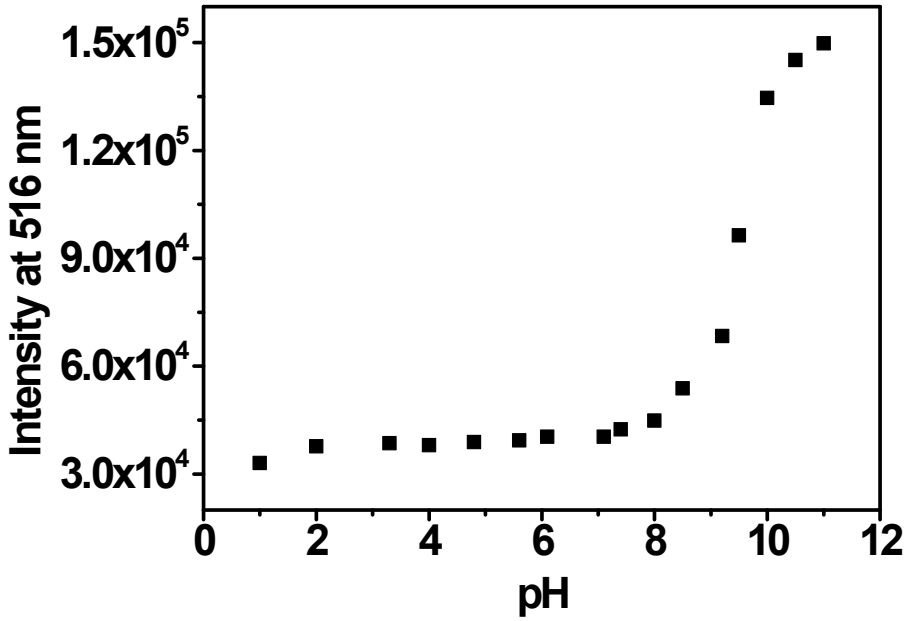


Figure S8: Effects of pH on the fluorescence spectra (λ_{ex} = 450 nm) of FLB (20 μM) in a mixture of methanol and water (1:1, v/v).

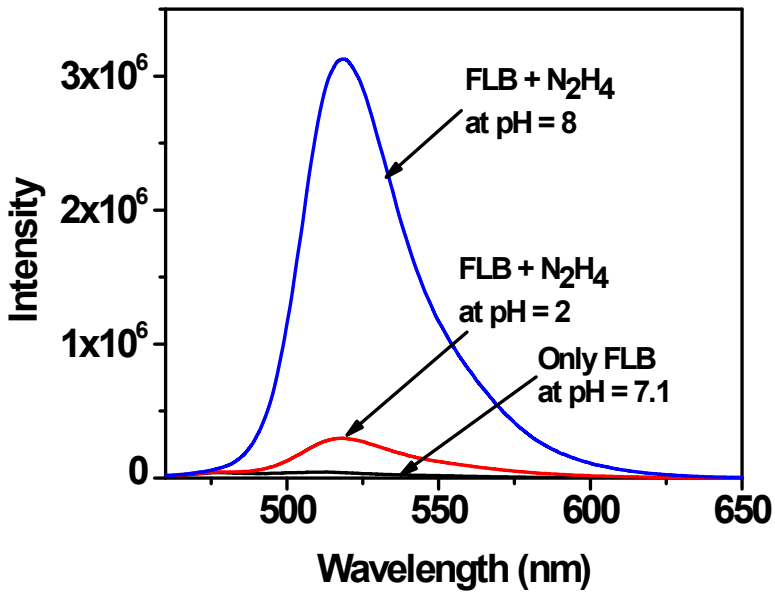


Figure S9: Effects of pH on the emission spectra (λ_{ex} = 450 nm) of FLB (20 μM) after addition of hydrazine (4 equiv.) in a mixture of methanol and water (1:1, v/v).

6. Determination of fluorescence Quantum Yields (Φ):

For measurement of the quantum yields of FLB and its reaction product with hydrazine (in situ, after addition of 4 equivalents of hydrazine), we recorded the absorbance of the compounds in methanol solution. The emission spectra were recorded using the maximal excitation wavelengths, and the integrated areas of the fluorescence-corrected spectra were measured. The quantum yields were then calculated by comparison with anthracene (Φs = 0.27 in ethanol) as reference using the following equation:

$$\Phi X = \Phi S \times \left(\frac{Ix}{Is}\right) \times \left(\frac{As}{Ax}\right) \times \left(\frac{nx}{ns}\right)^2$$

Where, x & s indicate the unknown and standard solution respectively, Φ is the quantum yield, *I* is the integrated area under the fluorescence spectra, *A* is the absorbance and *n* is

the refractive index of the solvent. We calculated the quantum yields of FLB and FLB + N_2H_4 using the above equation and the values are 0.01 and 0.54 respectively.

7. Comparison of absorption and fluorescence spectra of FLB with Fluorescein after addition of hydrazine:

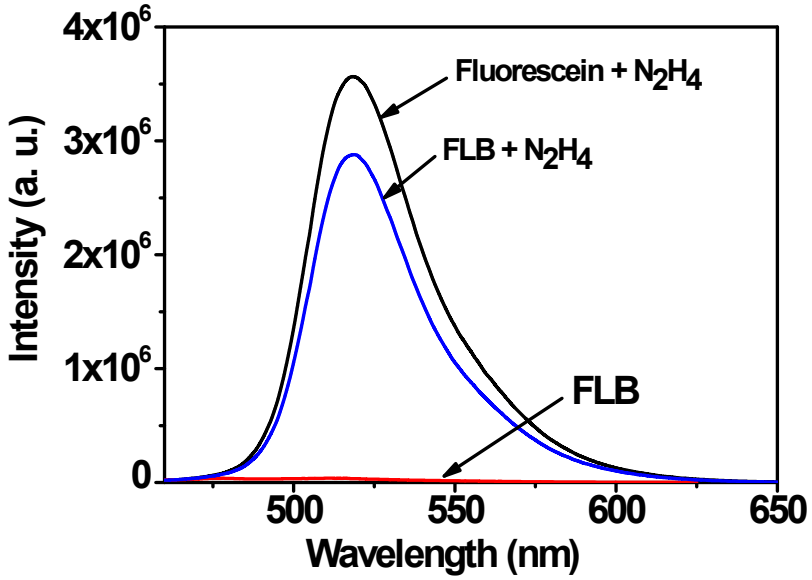


Figure S10: Comparison of emission spectra of FLB, (FLB+N_2H_4) and (fluorescein + N_2H_4) in methanol: water (1:1, v/v, λ_{ex}= 450 nm) solution.

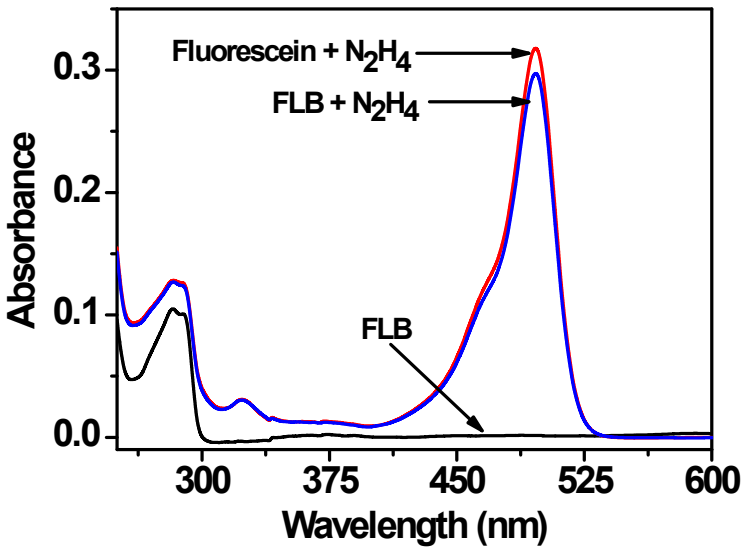


Figure S11: Comparison of absorption spectra of FLB, (FLB+N_2H_4) and (fluorescein + N_2H_4) in methanol: water (1:1, v/v, pH = 7.1) solution.

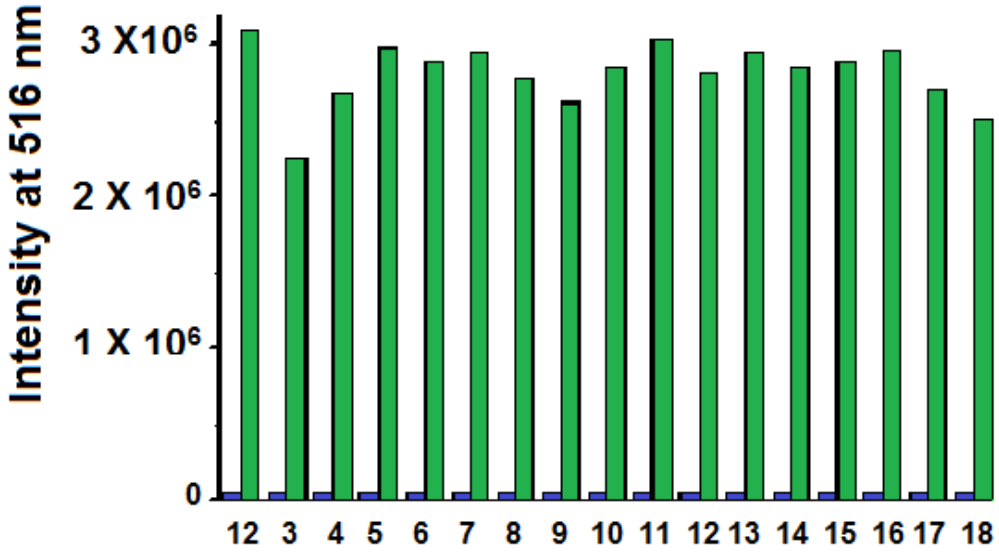


Figure S12: Fluorescence intensity of FLB (20 μM) at 516 nm upon addition of different analytes itself (blue bar) and hydrazine + different analytes (green bar).
1 blank, 2 N_2H_4, 3 Cu^{2+}, 4 Cd^{2+}, 5 Mn^{2+}, 6 Mg^{2+}, 7 Cr^{3+}, 8 Fe^{3+}, 9 Co^{2+}, 10 Hg^{2+}, 11 F^-, 12 NO_3^-, 13 HSO_4^-, 14 HSO_3^-, 15 SO_3^{2-}, 16 SO_4^{2-}, 17 $NH_2(CH_2)_2NH_2$, 18 NH_2OH

8. Computational study:

Computational Details: DFT calculations were performed using the Gaussian 03 (Revision B.04)[1] package. "Gauss View" is used for visualization of Molecular orbital. The method used was Becke's three parameter hybrid-exchange functional, the nonlocal correlation provided by the Lee, Yang, and Parr expression, and the Vosko, Wilk, and Nuair 1980 local correlation functional (III) (B3LYP).[2] The 6-311+G(d,p) basis set was used for calculations. Single-point calculations were done in the gas phase .Molecular orbitals were analysed using the AOMix program.[3] All the structure were optimized with B3LYP functional and 6-311+G (d,p) basis with no symmetry constrain. Time

dependent DFT calculations were also carried out using the same functional. For these calculations, singlet excited states were calculated based on the singlet ground state geometry.

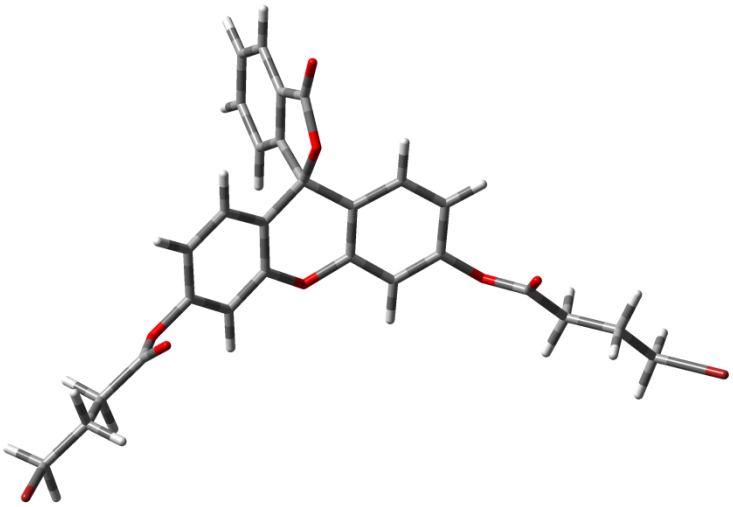


Figure S13: Energy minimized form of FLB calculated by B3LYP/6-31+G method basis set using the Gaussian 03W, Revision-D.01 program

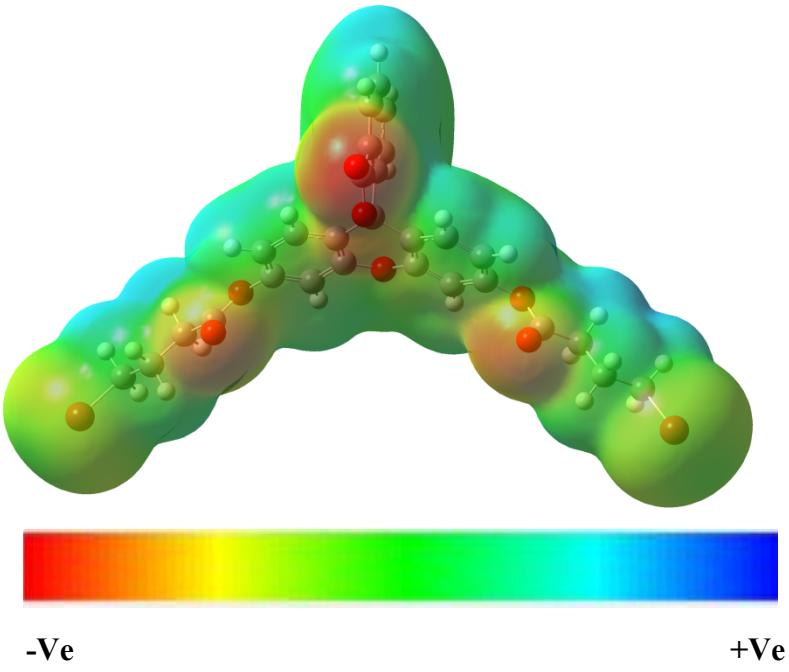


Figure S14: Charge surface diagram of FLB

Table S1: Electronic excitations of FLB and fluorescein calculated from TDDFT

Name of molecule	Transition	Wave length
FLB	HOMO→ LUMO	264.5nm
Fluorescein	HOMO → LUMO	475.1 nm
	HOMO-2→ LUMO	304.23nm

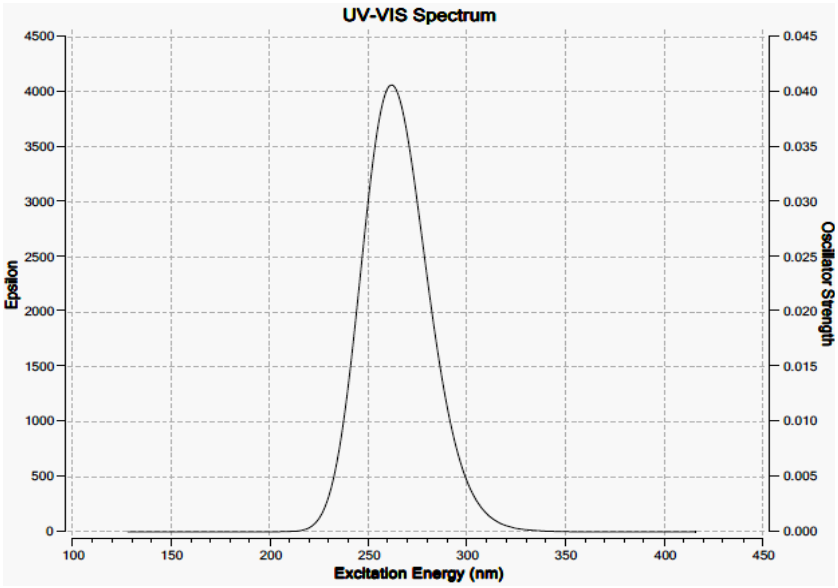


Figure S15: Electronic transition spectra of FLB obtained by TD-DFT study in gas phase.

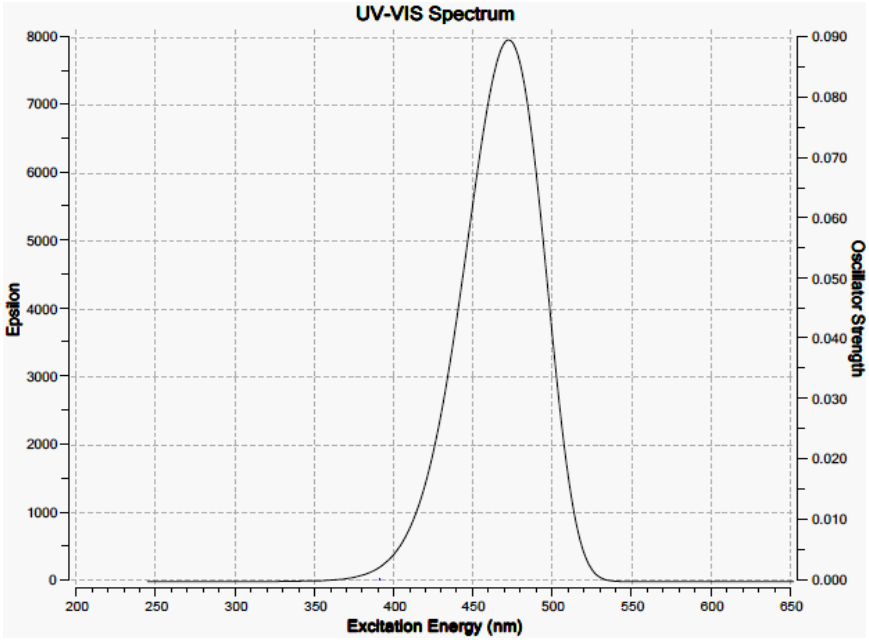


Figure S16: Electronic transition spectra of fluorescein obtained by TD-DFT study in gas phase.

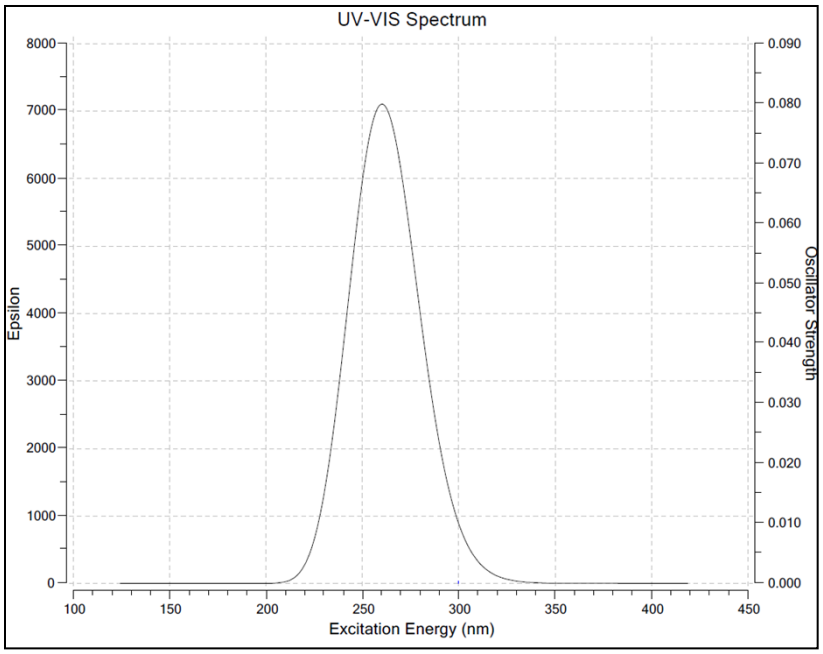


Figure S17: Electronic transition spectra of FLB obtained by TD-DFT study in water/methanol (1:1) mixture.

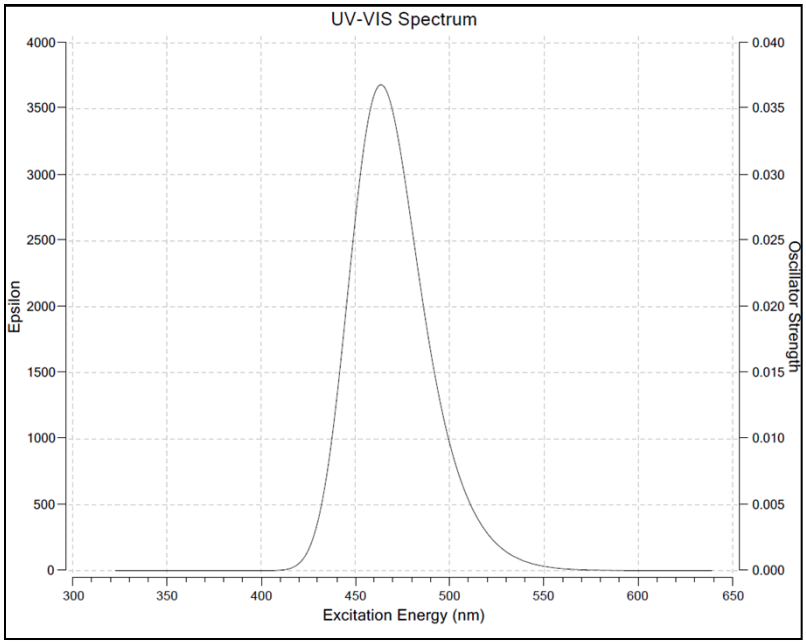


Figure S18: Electronic transition spectra of fluorescein obtained by TD-DFT study in water/methanol (1:1) mixture.

9. ^{1}H NMR, HRMS and ^{13}C NMR spectra of FLB:

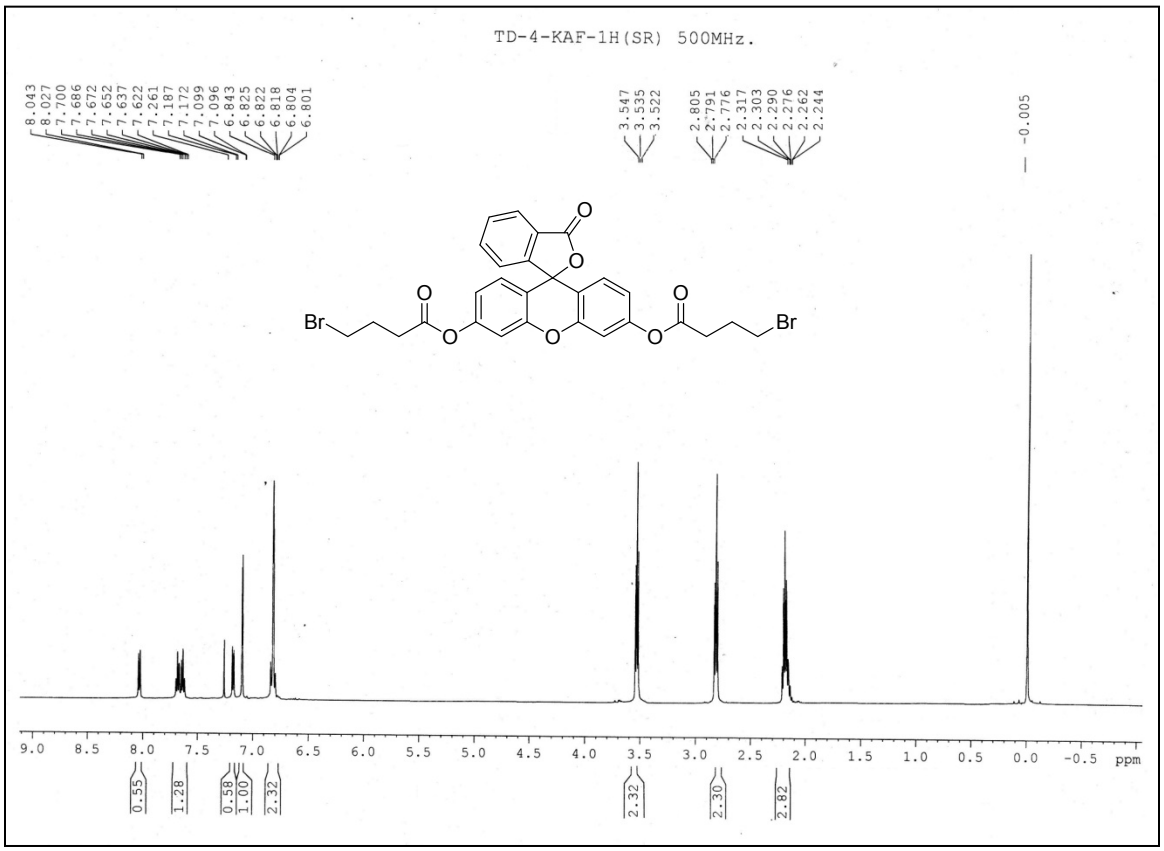


Figure S19: ^{1}H NMR spectrum (500 MHz) of FLB in $CDCl_3$

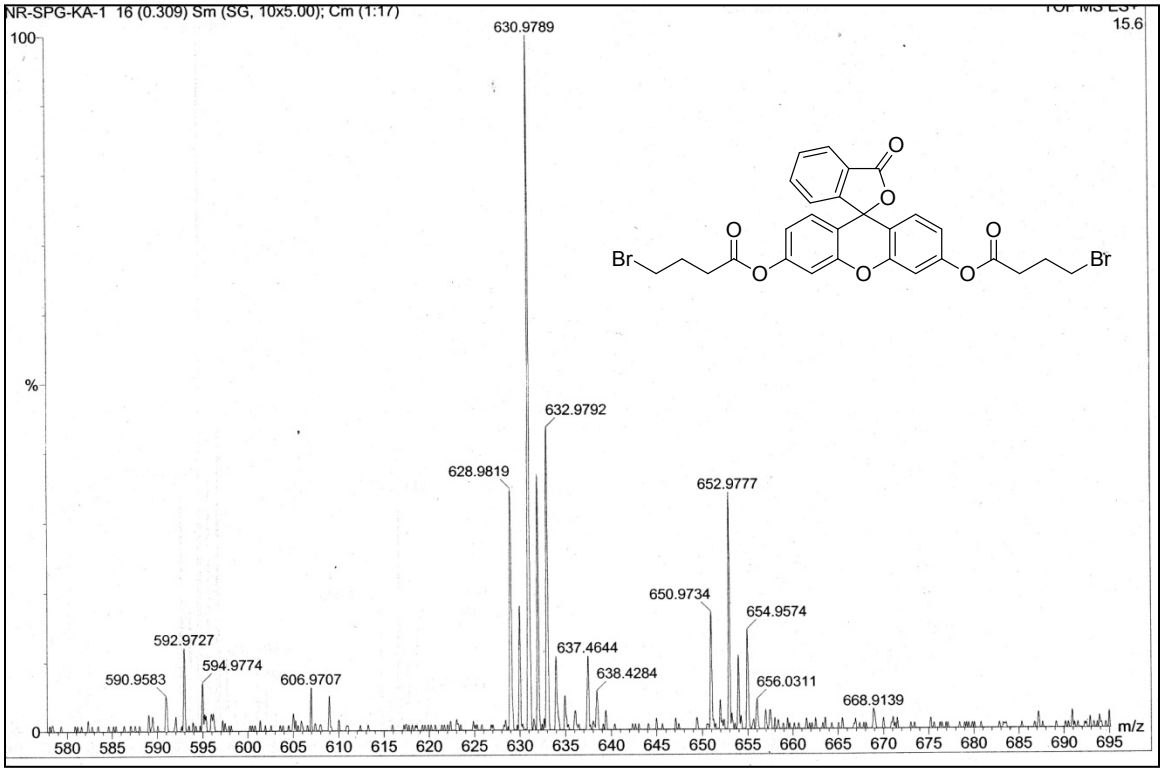


Figure S20: HRMS spectrum of FLB.

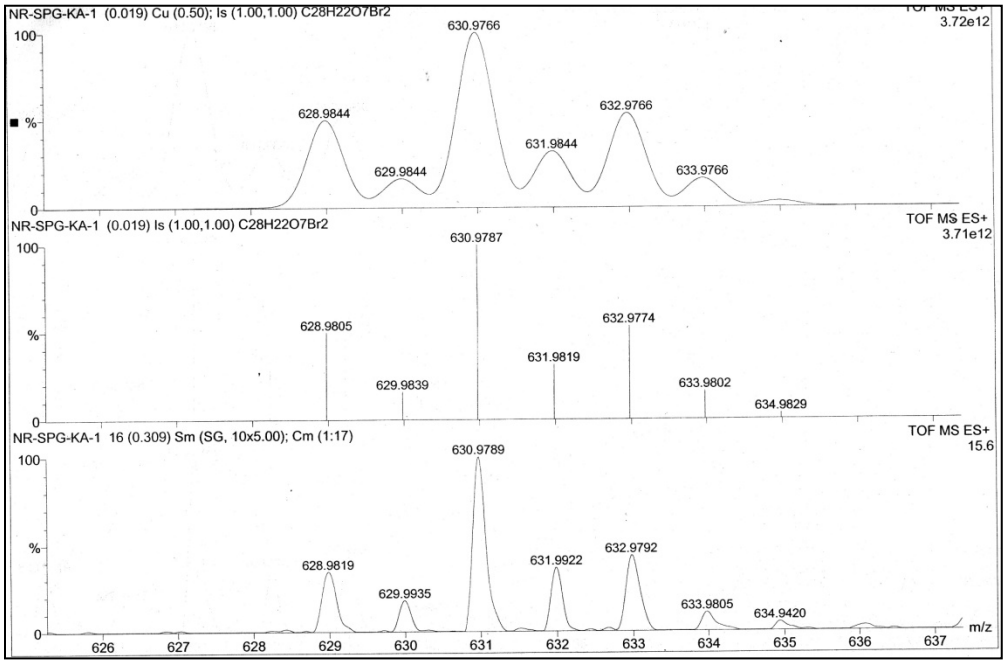


Figure S21: Expansion mode of the HRMS of FLB

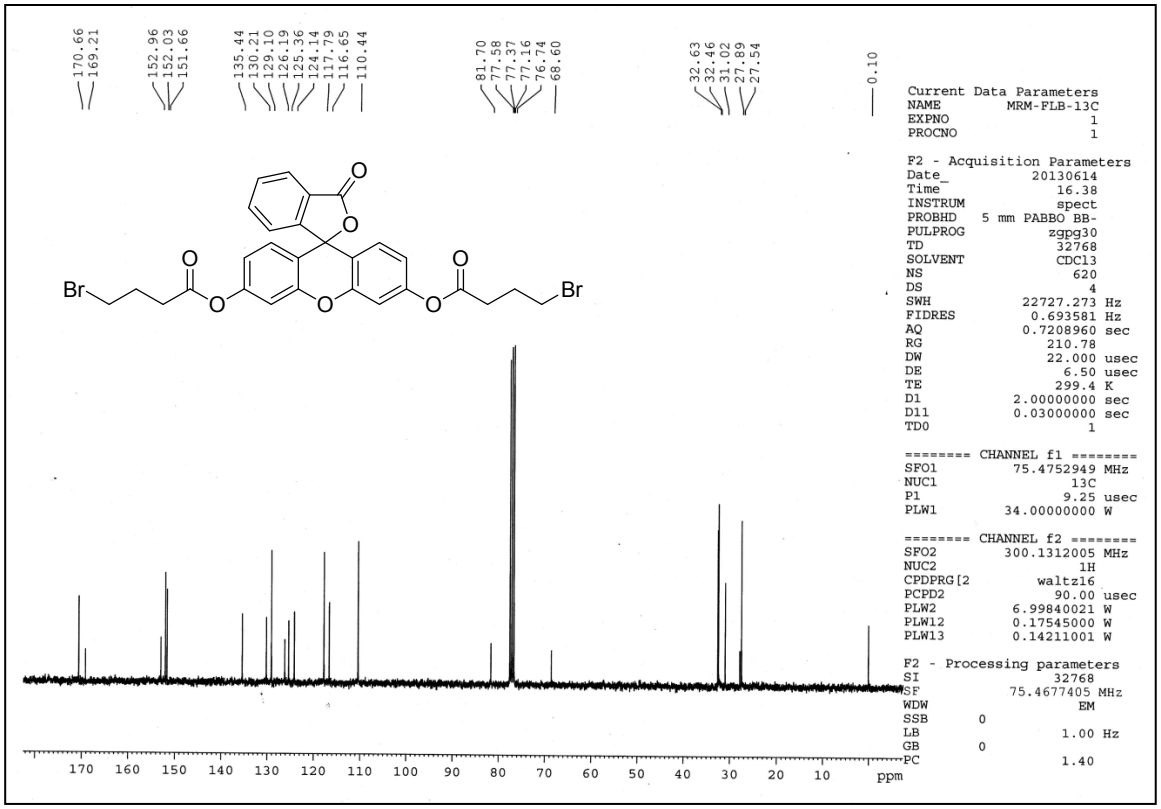


Figure S22: ^{13}C NMR (75 MHz) spectrum of FLB in $CDCl_3$

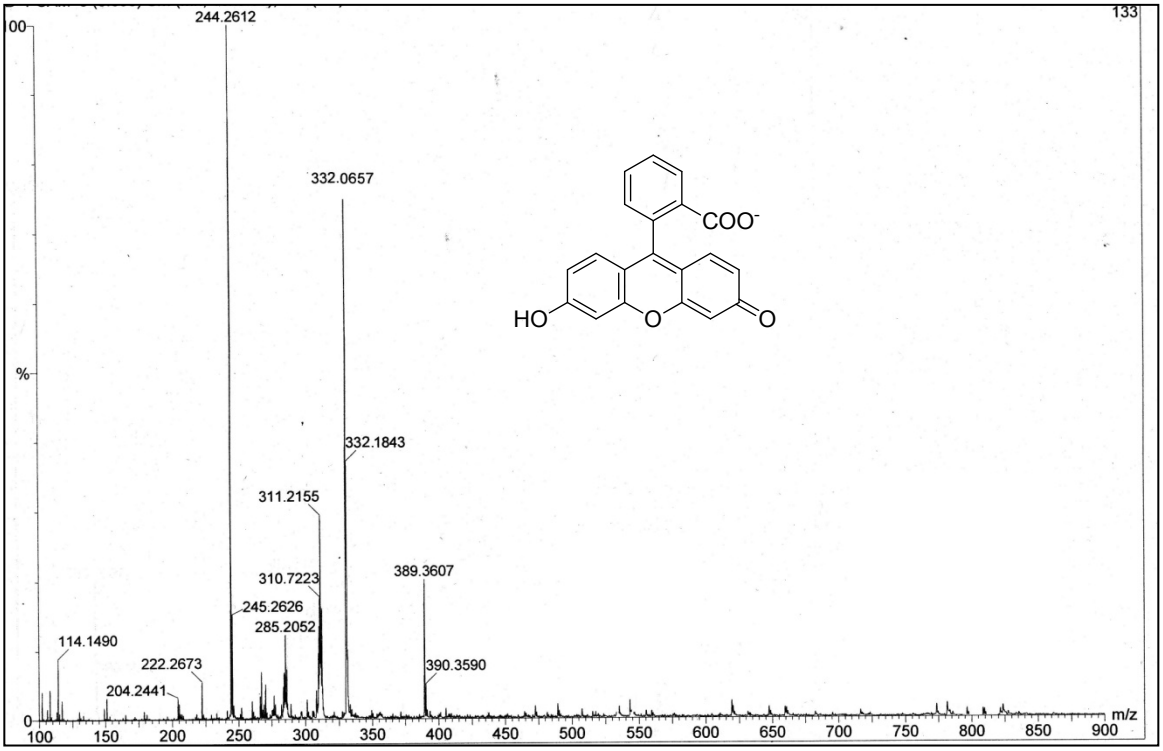


Figure S23: ESI MS spectrum of FLB after reaction with hydrazine.

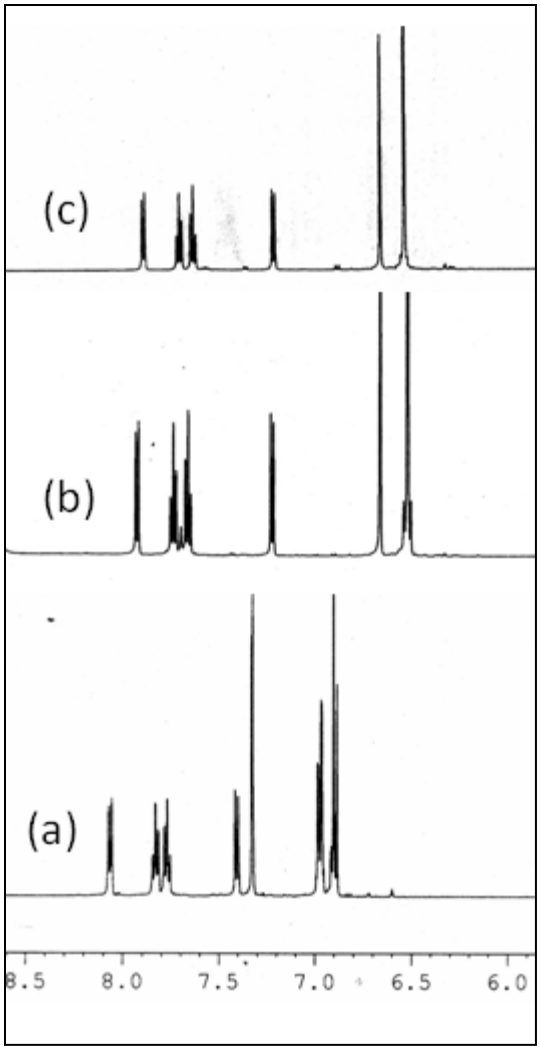
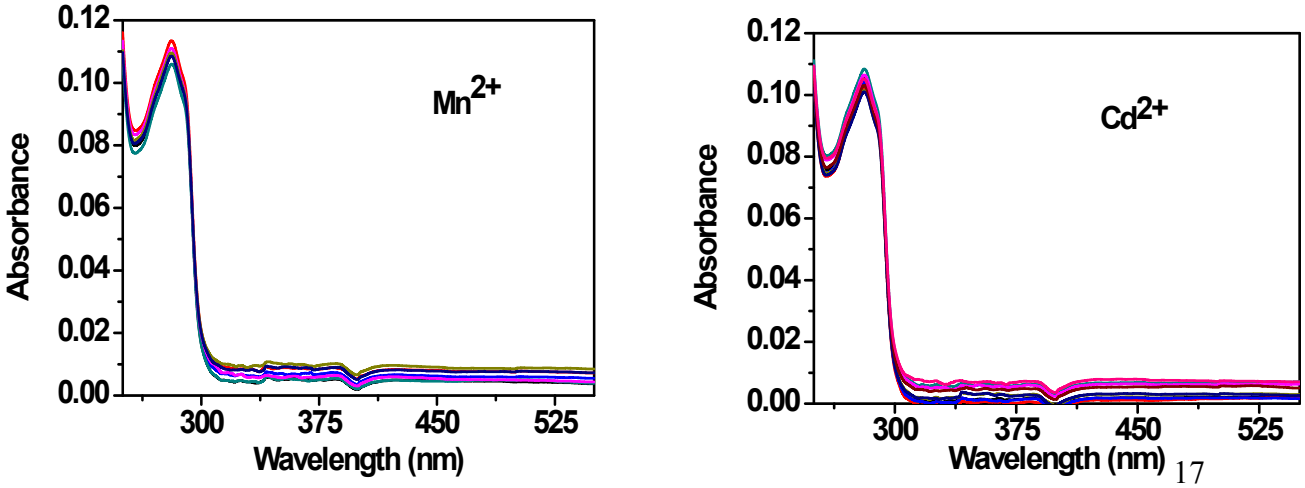
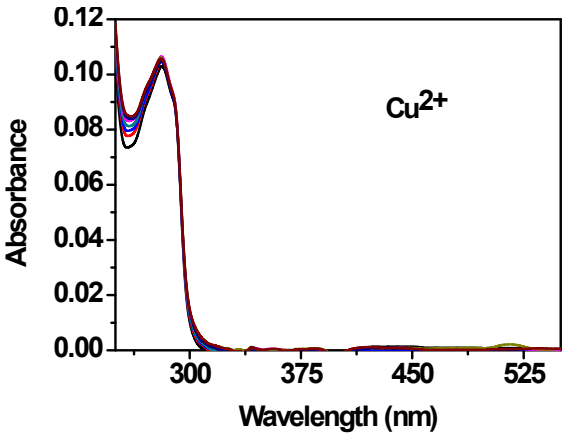


Figure S24: Partial ^{1}H NMR (300 MHz) spectra of (a) FLB, (b) [FLB + N_2H_4] and (c) [fluorescein + N_2H_4] in d^6 DMSO containing 1% D_2O. [FLB] = [fluorescein] = 2.4×10^{-2} M; [N_2H_4] = 1.2×10^{-1} M

UV-vis titration spectra of FLB with different guest anions, neutral molecule and cations:

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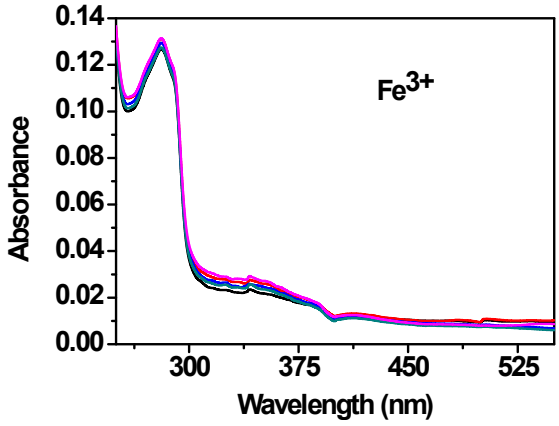
0.08
0.06
0.04
0.02
0.00
300
375
450
525
Wavelength (nm)
Cu2+


Absorbance
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0.06
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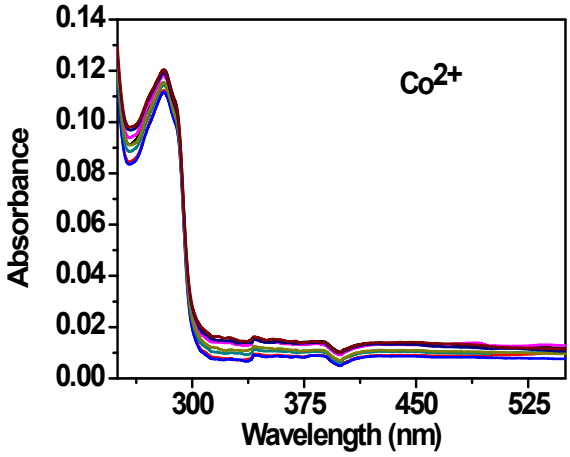
300
375
450
525
Wavelength (nm)
Fe3+


Absorbance
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300
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450
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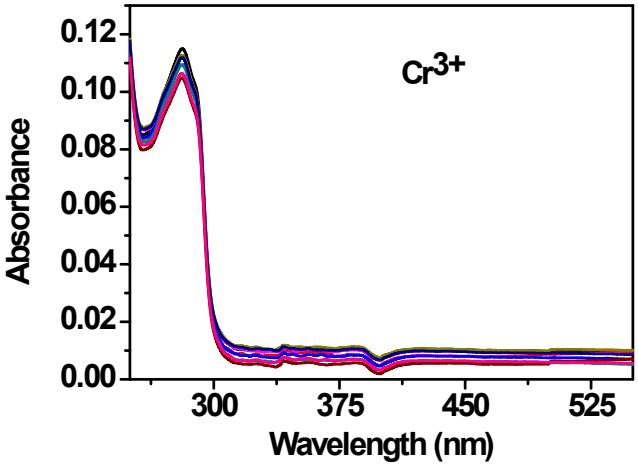
Wavelength (nm)
Co2+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300
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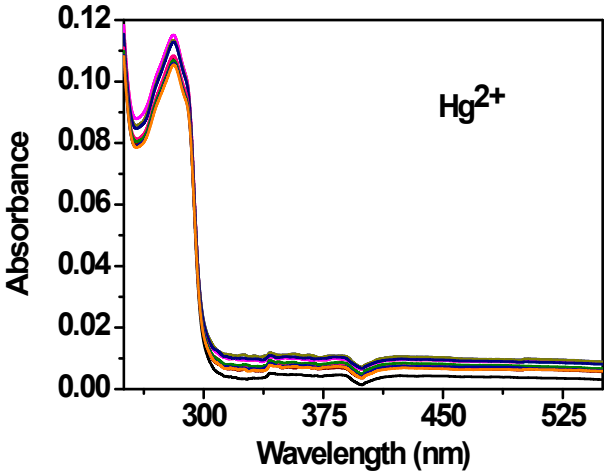
Wavelength (nm)
Cr3+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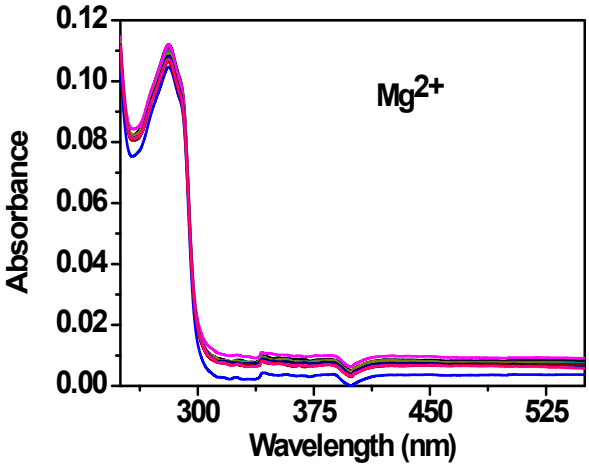
0.04
0.02
0.00
300
375
450
525
Wavelength (nm)
Hg2+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300
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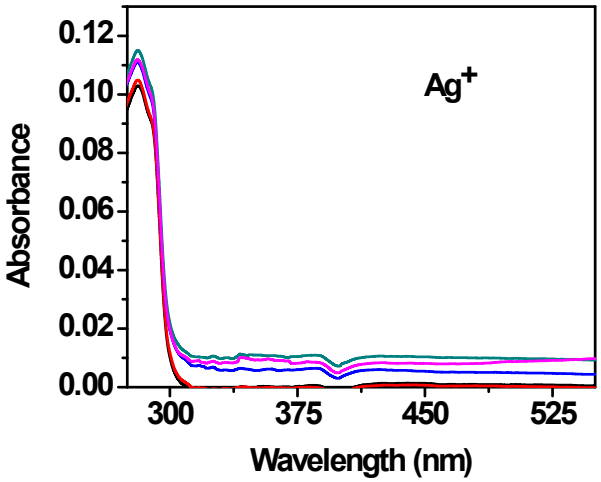
450
525
Wavelength (nm)
Mg2+


Ag+
Absorbance
Wavelength (nm)
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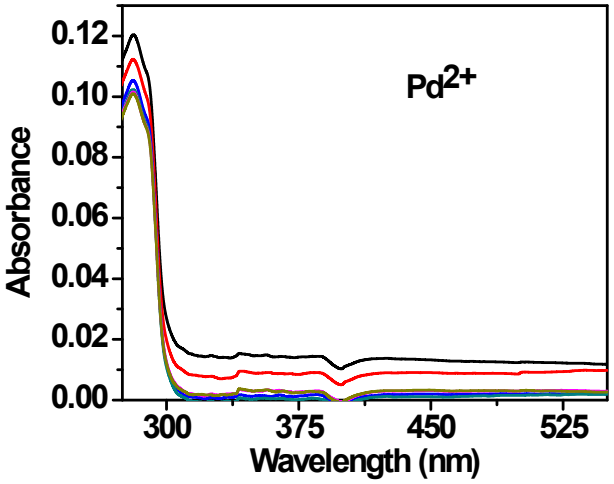
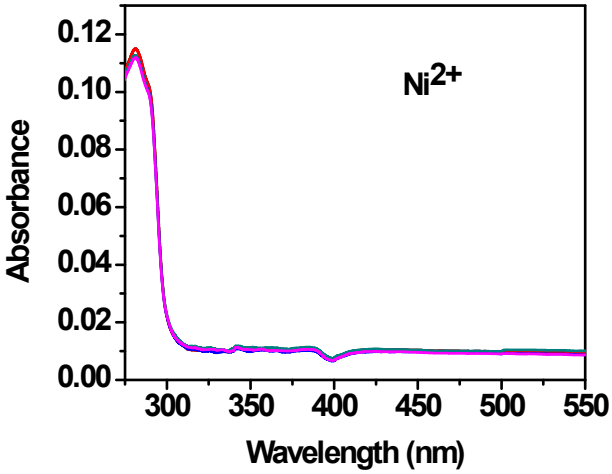
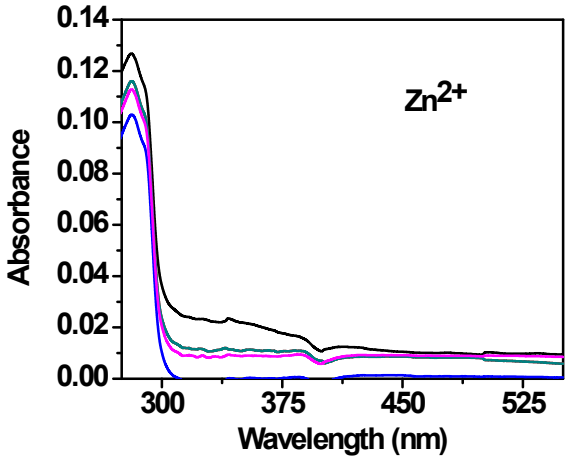
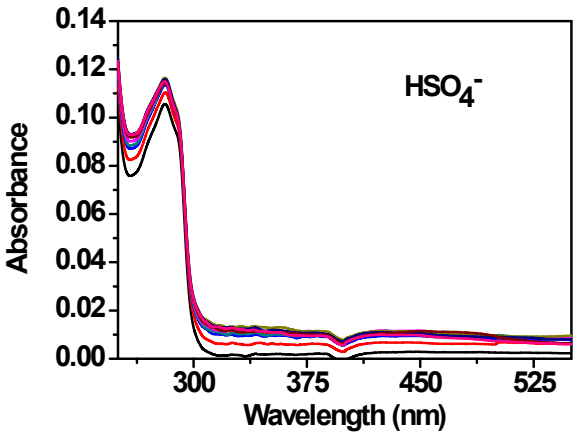
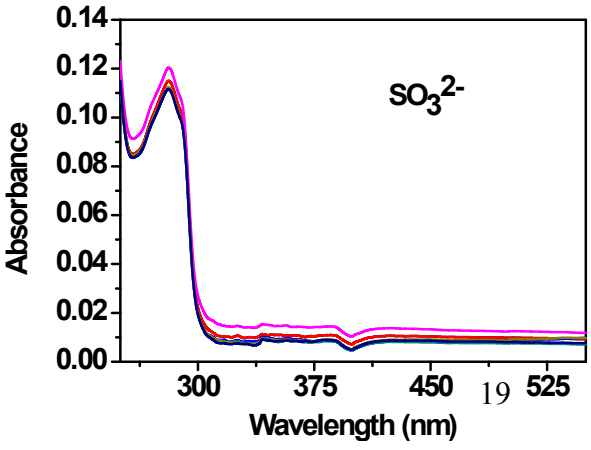
0.02
0.04
0.06
0.08
0.10
0.12
300
375
450
525

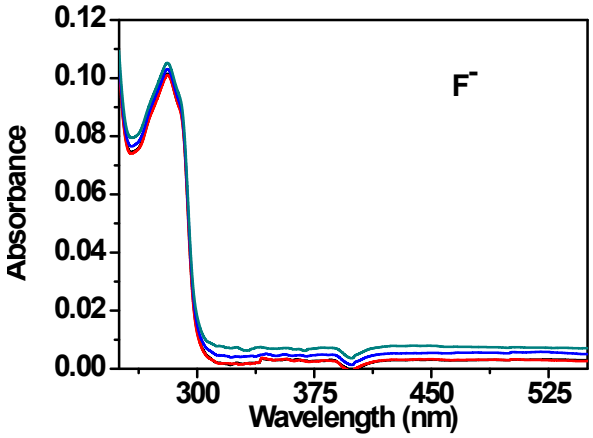

Pd2+
Absorbance
Wavelength (nm)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
300
375
450
525

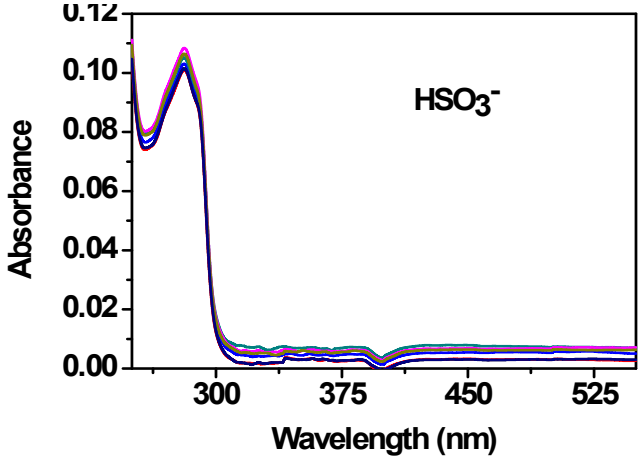

Ni2+
Absorbance
Wavelength (nm)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
300
350
400
450
500
550

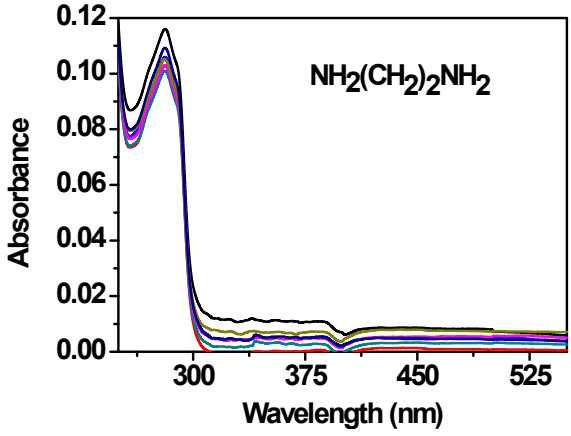

Zn2+
Absorbance
Wavelength (nm)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
300
375
450
525

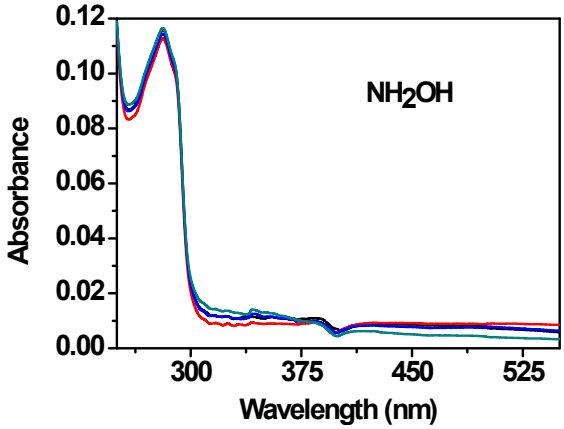

HSO4-
Absorbance
Wavelength (nm)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
300
375
450
525

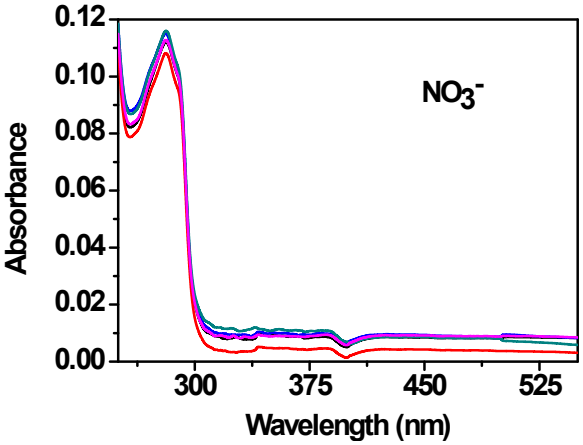

SO32-
Absorbance
Wavelength (nm)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
300
375
450
525

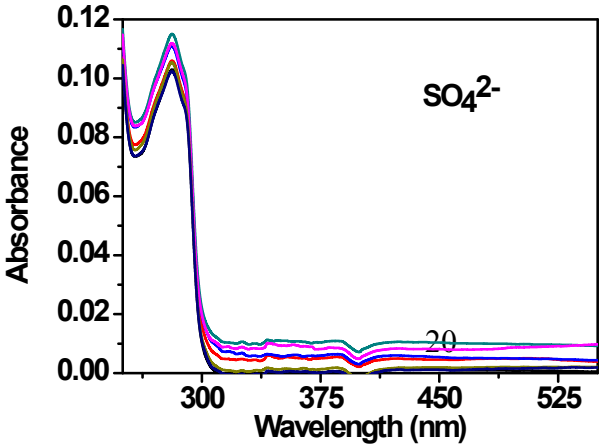

F-
Absorbance
Wavelength (nm)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
300
375
450
525

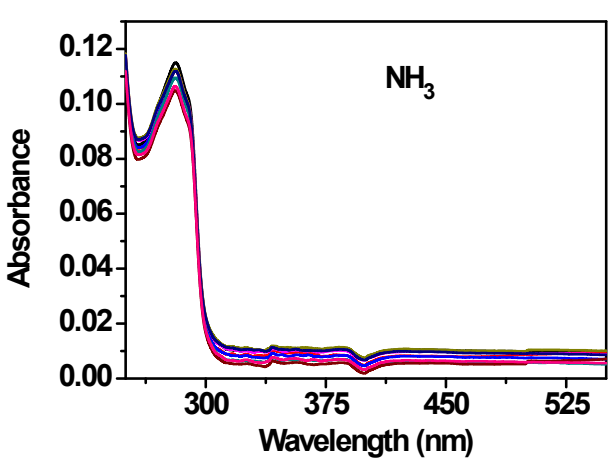

HSO3-
Absorbance
Wavelength (nm)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
300
375
450
525

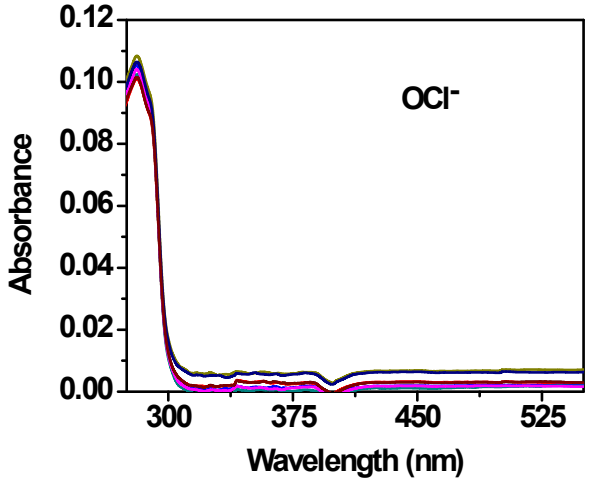

NH2(CH2)2NH2
Absorbance
Wavelength (nm)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
300
375
450
525


NH2OH
Absorbance
Wavelength (nm)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
300
375
450
525

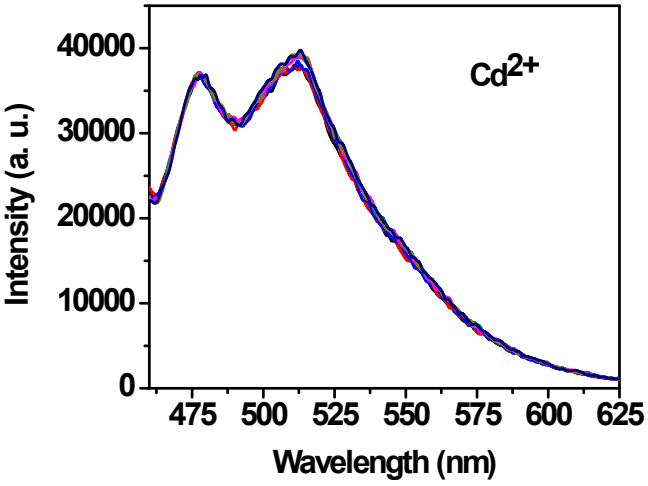

NO3-
Absorbance
Wavelength (nm)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
300
375
450
525

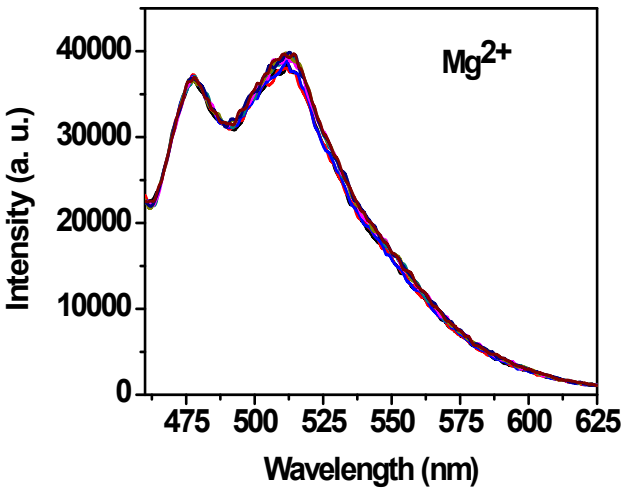

SO4 2-
Absorbance
Wavelength (nm)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
300
375
450
525

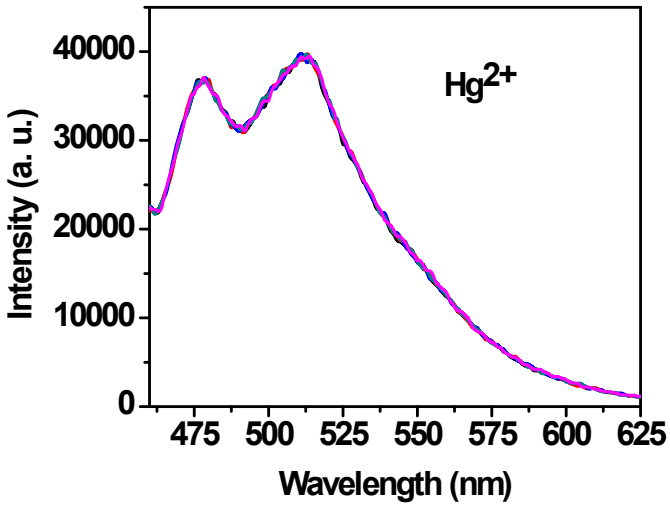


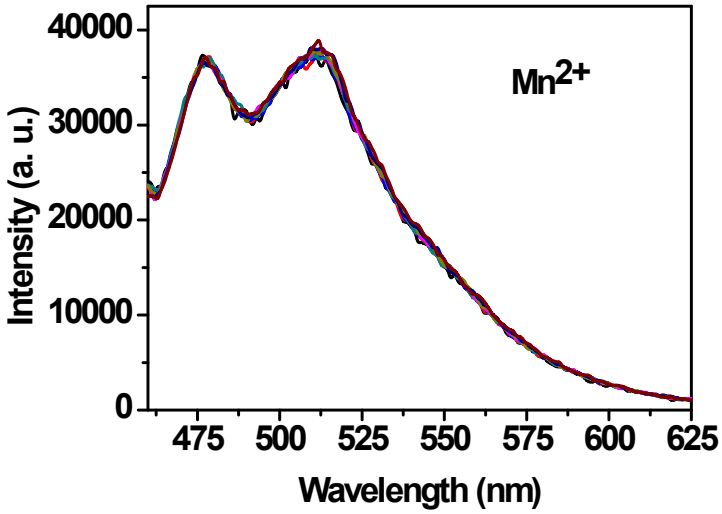


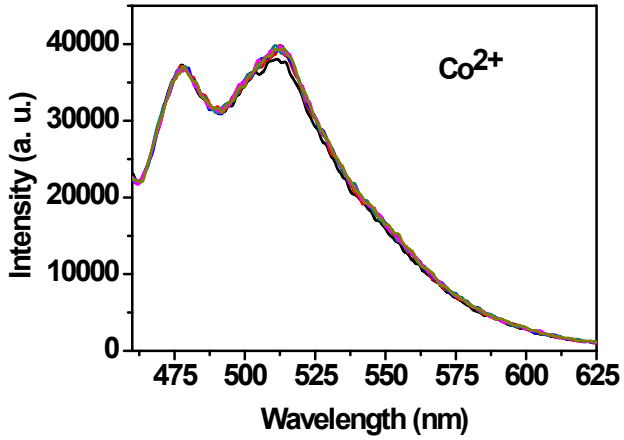
Fluorescence titration spectra of FLB with different guest:

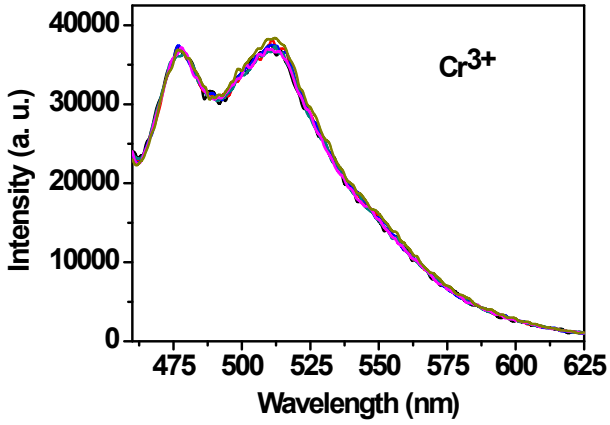


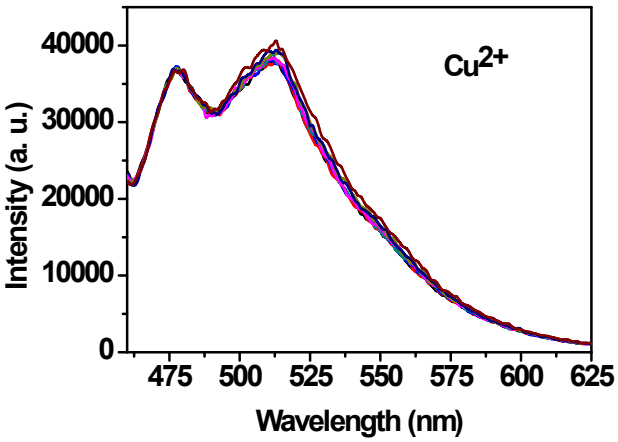


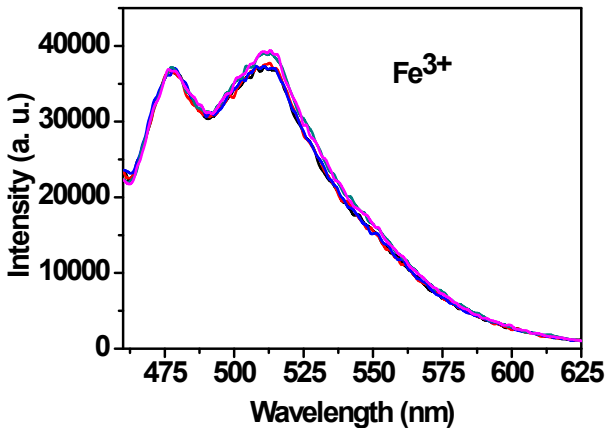

Hg2+
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

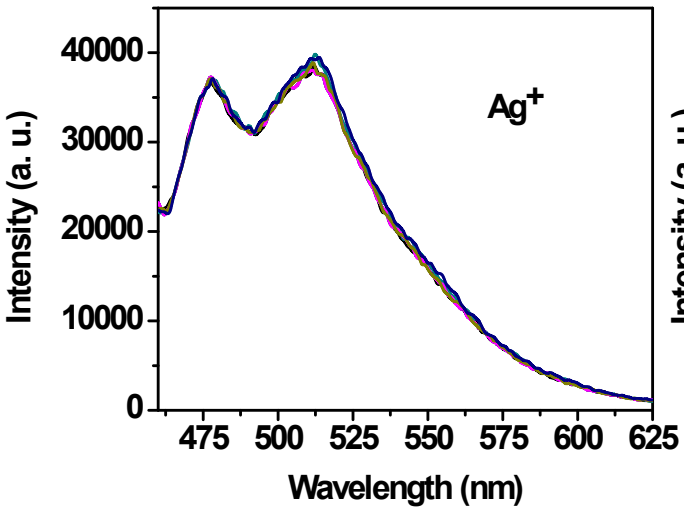

Mn2+
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

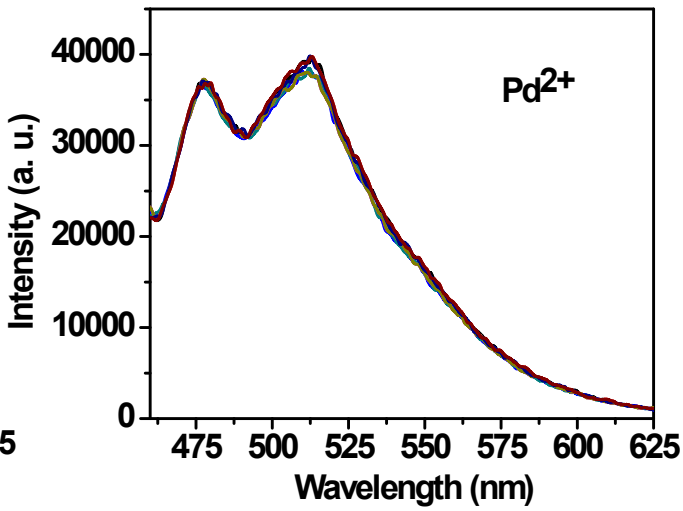

Co2+
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

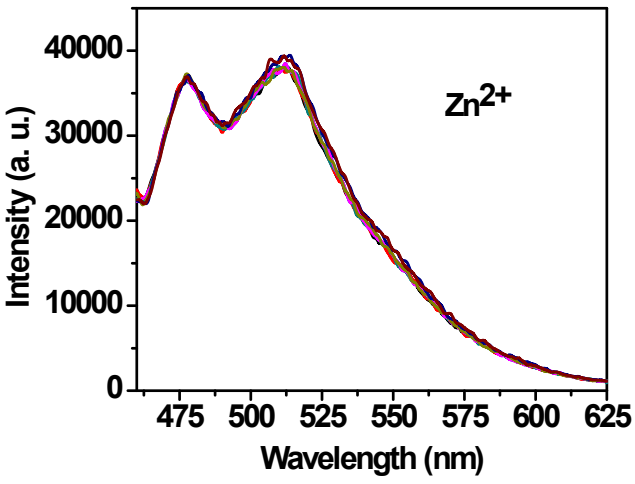

Cr3+
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

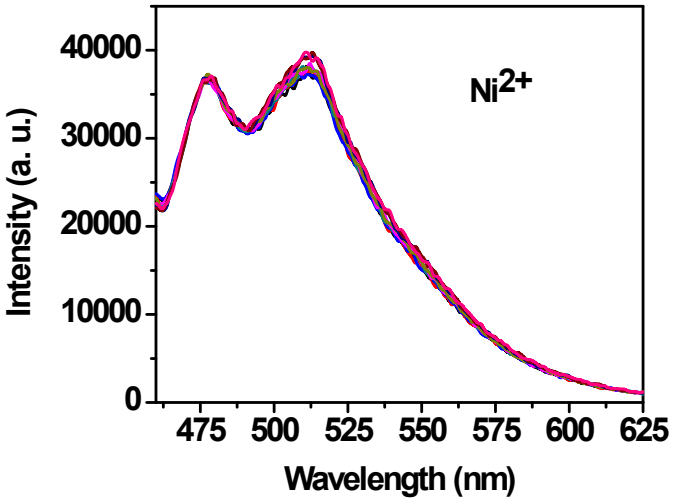

Cu2+
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

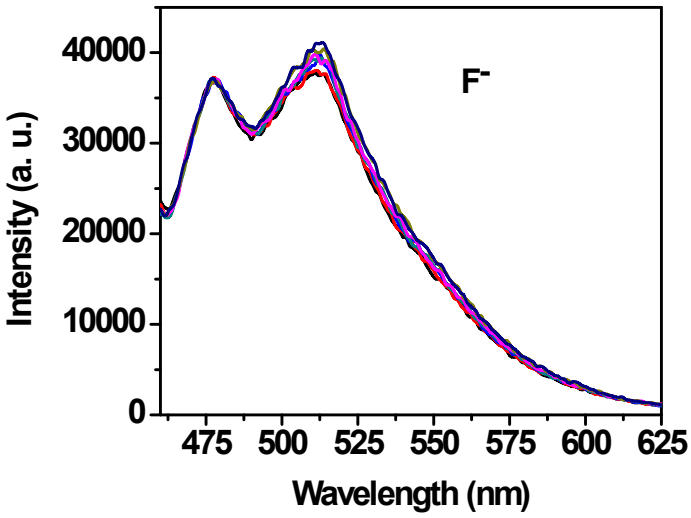

Fe3+
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

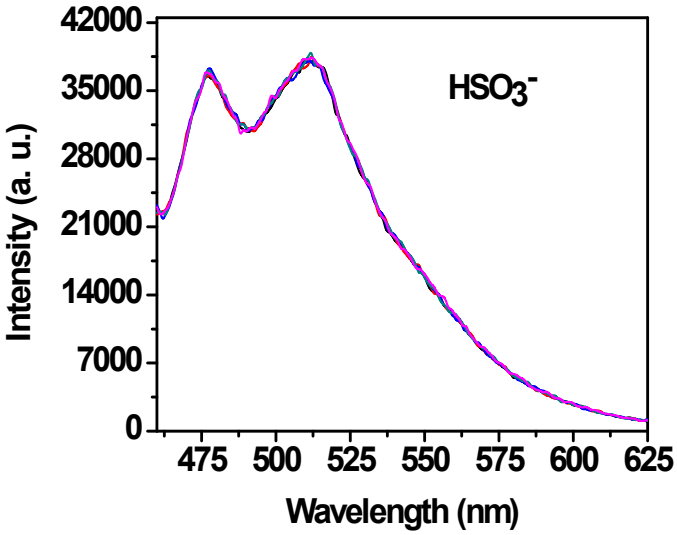

Ag+
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

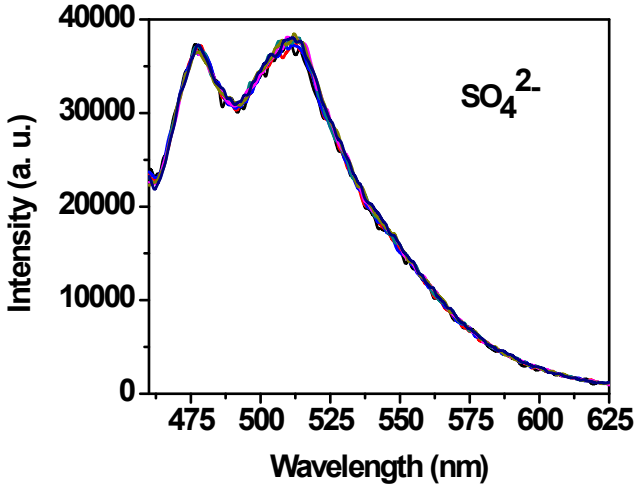

Pd2+
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

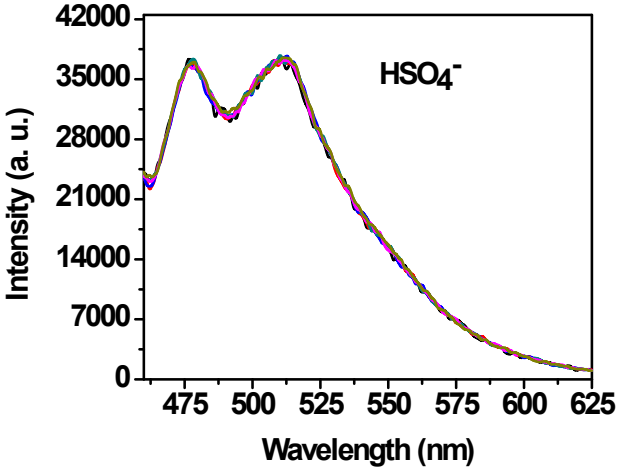

Zn2+
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

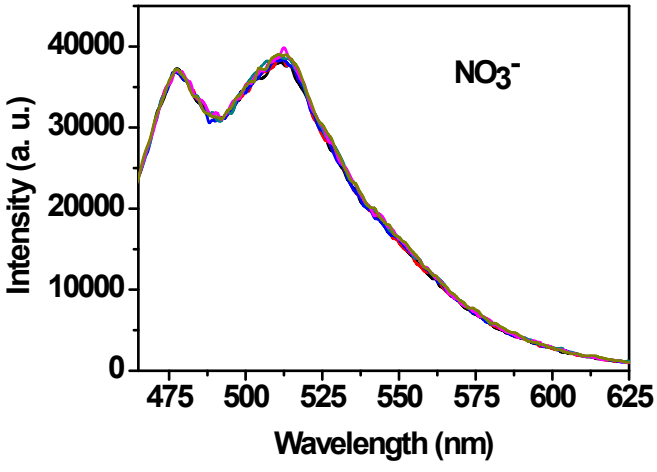

Ni2+
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

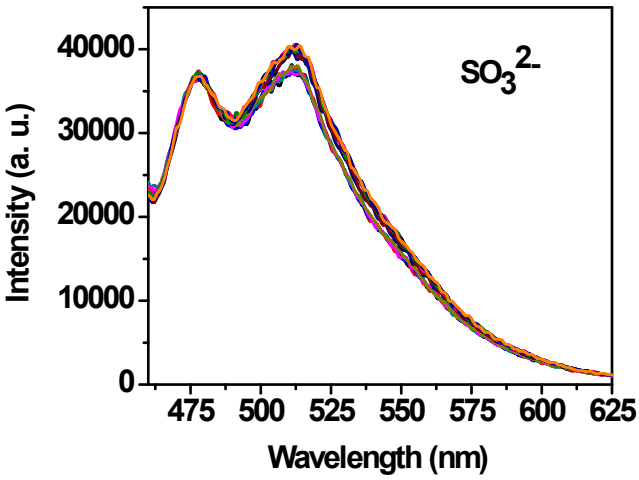

F-
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

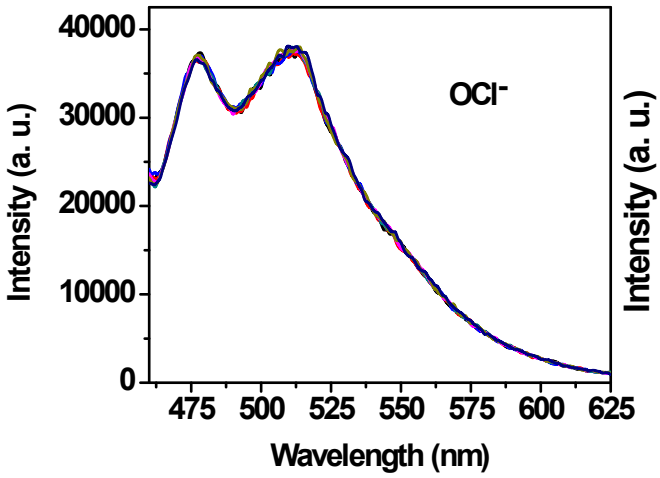

HSO3-
Intensity (a. u.)
Wavelength (nm)
0
7000
14000
21000
28000
35000
42000
475
500
525
550
575
600
625

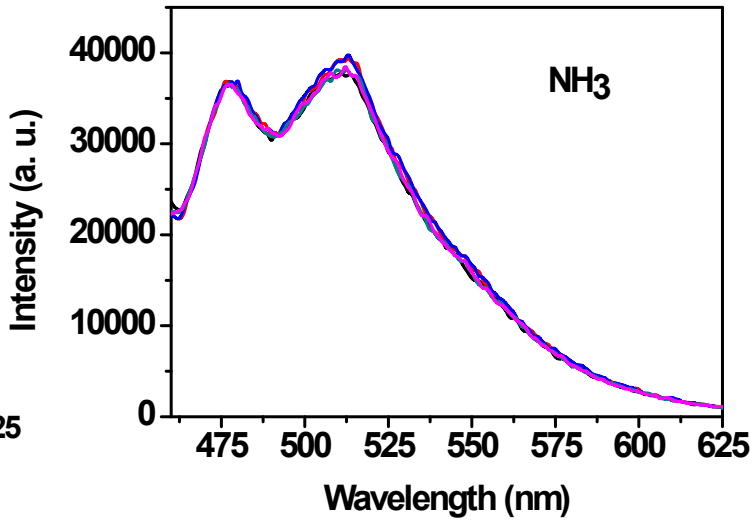

SO4 2-
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625

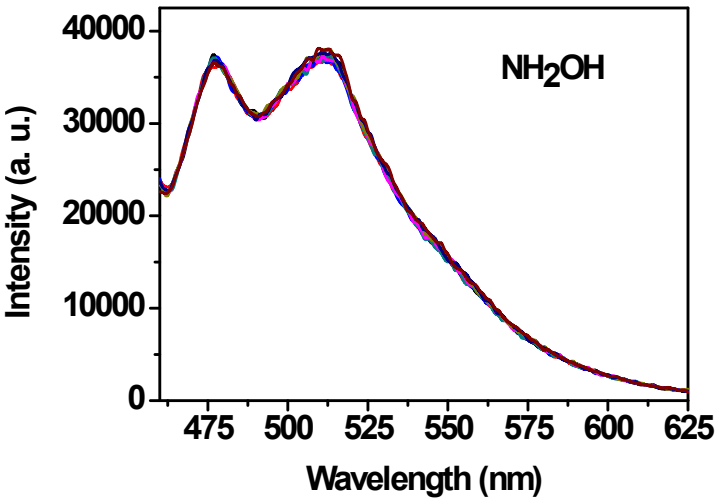

HSO4-
Intensity (a. u.)
Wavelength (nm)
0
7000
14000
21000
28000
35000
42000
475
500
525
550
575
600
625

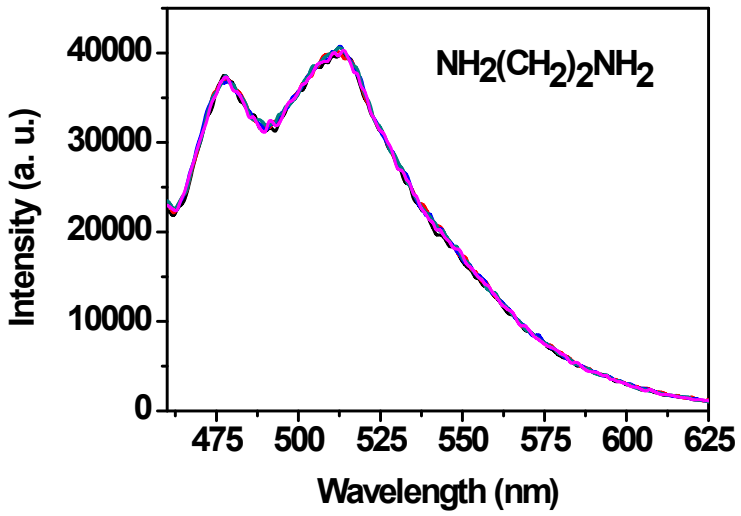

NO3-
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625


SO3 2-
Intensity (a. u.)
Wavelength (nm)
0
10000
20000
30000
40000
475
500
525
550
575
600
625









Coordinates Geometry:

Coordinate of FLB:

C	-5.32440600	-2.02046900	1.41681000
C	-4.17565100	-1.84799400	0.68360000

C	-3.87045400	-0.57567500	0.23301900
C	-4.67653600	0.51152700	0.50760800
C	-5.84304800	0.29602300	1.23535900
C	-6.17276000	-0.96194700	1.69783200
C	-3.33051300	1.79503700	-1.15340200
C	-2.58750600	0.64769400	-1.35018800
C	-1.68389000	0.52809500	-2.39137800
H	-1.11965200	-0.36982200	-2.51436100
C	-1.54007700	1.58811500	-3.25320500
C	-2.28011400	2.74993300	-3.10572700
C	-3.17411900	2.84093400	-2.05806500
H	-3.52964400	-2.66795500	0.45979500
H	-6.50201900	1.11457500	1.43118200
H	-7.07396900	-1.12191800	2.24774700
H	-2.17206100	3.55257200	-3.80156700
H	-3.76308300	3.72623600	-1.94859900
C	-4.24847400	1.89017000	0.04801400
C	-3.64690600	2.72242000	1.17857400
C	-4.43455500	3.83278400	1.39826500
C	-2.50916500	2.50606900	1.93336900
C	-5.56227000	3.80188300	0.46058200
C	-4.13001100	4.77073400	2.36979200
C	-2.19255900	3.43949100	2.91116800
H	-1.88610800	1.64966300	1.77652800
C	-2.99187900	4.56226800	3.13099400
H	-4.75851500	5.62393900	2.51974500
H	-1.31644200	3.29562900	3.50996500
H	-2.72100500	5.26362100	3.89241800
O	-2.71321500	-0.43666000	-0.50586800
O	-5.42208300	2.67245500	-0.29850800
O	-6.47360900	4.57071000	0.31619500
O	-5.57239900	-3.29840400	1.91955600
C	-6.67922000	-4.02618000	1.61389600
O	-7.55565100	-3.61591900	0.89856400
O	-0.57169400	1.46906200	-4.25087200
C	-0.84630800	1.54068600	-5.58034000
O	-1.95235500	1.73946700	-6.01081800
C	-6.63311800	-5.36199500	2.28481500
C	-7.88003400	-6.20521600	2.01696100
H	-6.49388500	-5.18833100	3.34442400
H	-5.73711400	-5.86523700	1.94231100
C	-7.76809600	-7.54562900	2.71841500
H	-8.75883700	-5.68065200	2.36076600
H	-8.00314000	-6.35208300	0.95476400
H	-6.94809300	-8.13698600	2.35517900
H	-7.71339500	-7.45191400	3.78718100
C	0.39778000	1.34295100	-6.38646100
C	0.15672200	1.46444300	-7.89134900

H	0.79833000	0.36980000	-6.12971100
H	1.12543600	2.06755300	-6.04325400
C	1.45264100	1.24856800	-8.64981300
H	-0.58089100	0.74154000	-8.20492200
H	-0.24772900	2.43879900	-8.12093800
H	2.19622500	1.98936900	-8.42104900
H	1.85578300	0.26260000	-8.51055600
Br	1.17011600	1.40646200	-10.61864800
Br	-9.38528100	-8.66749100	2.39100900

Coordinate of fluorescein:

C	-5.32440600	-2.02046900	1.41681000
C	-4.17565100	-1.84799400	0.68360000
C	-3.87045400	-0.57567500	0.23301900
C	-4.67653600	0.51152700	0.50760800
C	-5.84304800	0.29602300	1.23535900
C	-6.17276000	-0.96194700	1.69783200
C	-3.33051300	1.79503700	-1.15340200
C	-2.58750600	0.64769400	-1.35018800
C	-1.68389000	0.52809500	-2.39137800
H	-1.11965200	-0.36982200	-2.51436100
C	-1.54007700	1.58811500	-3.25320500
C	-2.28011400	2.74993300	-3.10572700
C	-3.17411900	2.84093400	-2.05806500
H	-3.52964400	-2.66795500	0.45979500
H	-6.50201900	1.11457500	1.43118200
H	-7.07396900	-1.12191800	2.24774700
H	-2.17206100	3.55257200	-3.80156700
H	-3.76308300	3.72623600	-1.94859900
C	-4.24847400	1.89017000	0.04801400
C	-3.64690600	2.72242000	1.17857400
C	-4.43455500	3.83278400	1.39826500
C	-2.50916500	2.50606900	1.93336900
C	-5.56227000	3.80188300	0.46058200
C	-4.13001100	4.77073400	2.36979200
C	-2.19255900	3.43949100	2.91116800
H	-1.88610800	1.64966300	1.77652800
C	-2.99187900	4.56226800	3.13099400
H	-4.75851500	5.62393900	2.51974500
H	-1.31644200	3.29562900	3.50996500
H	-2.72100500	5.26362100	3.89241800
O	-2.71321500	-0.43666000	-0.50586800
O	-5.42208300	2.67245500	-0.29850800
O	-6.47360900	4.57071000	0.31619500
O	-5.57239900	-3.29840400	1.91955600
O	-0.57169400	1.46906200	-4.25087200
H	-0.76562160	1.51964162	-5.18971905

H -6.35399323 -3.81233130 1.70371072

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