Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2015

Dual-mode chemodosimetric response of dibromo-BODIPY with anions

Adiki Raja Sekhar, Masood Ayoub Kaloo and Jeyaraman Sankar
Department of Chemistry, IISER Bhopal, India – 462066

sankar@iiserb.ac.in

Supplementary Information

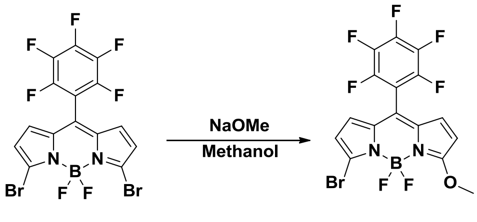
1. General Information:

All solvents and reagents were purchased from commercial sources and used without further purification except for dry THF which was further distilled over sodium metal. Mass spectra were recorded on a Bruker HR-LCMS spectrometer using CH_3OH and $CHCl_3$ as solvents. 100 MHz for ^{13}C, 376 MHz for ^{19}F, 128 MHz for ^{11}B and 400 MHz for ^{1}H NMR spectra were recorded using a Bruker instrument operating at 400 MHz in $CDCl_3$ with TMS as internal reference. UV/Vis spectra were recorded on Cary 100. Fluorescence emission spectra were recorded on a Horiba Jovin Vyon Fluoro log 3-111 spectrophotometer.

UV-Vis and fluorescence titration experiments were carried out with a solution of R (1.2 μM) and gradual addition of anions for further analysis, prepared in dichloromethane (HPLC grade). In fluorescence experiment **R** was titrated with various equivalents of anions and excited at 400 nm. Experiments were carried out under ambient conditions. All anions for the titration experiments were conducted with a stock solution in DCM. alkoxide stock solution was prepared in respective alcohols (HPLC grade) to avoid solubility issues.

Data collection was performed using φ and ω scans. The structure was solved using a direct method followed by full-matrix least square refinements against F2 (all data HKLF 4 format) using SHELXTL. Subsequent difference Fourier synthesis and the least-square refinement revealed the positions of the remaining non-hydrogen atoms. Determinations of the crystal system, an orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and multi-scan absorption correction applied. Non-hydrogen atoms refined with independent anisotropic displacement parameters and hydrogen atoms placed geometrically and refined using the riding model. All calculations were carried out using SHELXL 97, PLATON 99, and WinGXsystemVer-1.6414.

2. Preparation of R_{OMe}:



Pentafluorophenyl dibromo-BODIPY (100 mg) was dissolved in 10 ml of dry methanol. Then 2 equivalents of sodium methoxide salt was added to the reaction mixture at room temperature, stirred this mixture for 5 min in open atmospheric condition. The reaction mixture was concentrated by evaporation of solvent under reduced pressure. The crude mixture was subjected to silica column chromatography. The desired compound was purified using ethyl acetate and hexane as elutants as red colour powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85–6.84 (d, J= 4.84, 1H), 6.41 (m, 2H), 6.26–6.25

(d, *J*= 4.84, 2H), 4.20 (s, 3H); ^{19}F NMR (376 MHz, CDCl$_3$): -δ 136.9-137.0 (2F, *ortho*), 147.45-147.67 (2F, BF), 149.75-149.87 (1F, *para*), 159.42-159.58 (2F, *meta*); ^{11}B NMR (128 MHz, CDCl$_3$): δ 0.64-0.21. MS (LR-MS): Anal. Calc. for $C_{16}H_7BBrF_7N_2O$ requires 466, found –CH$_3$ 451.

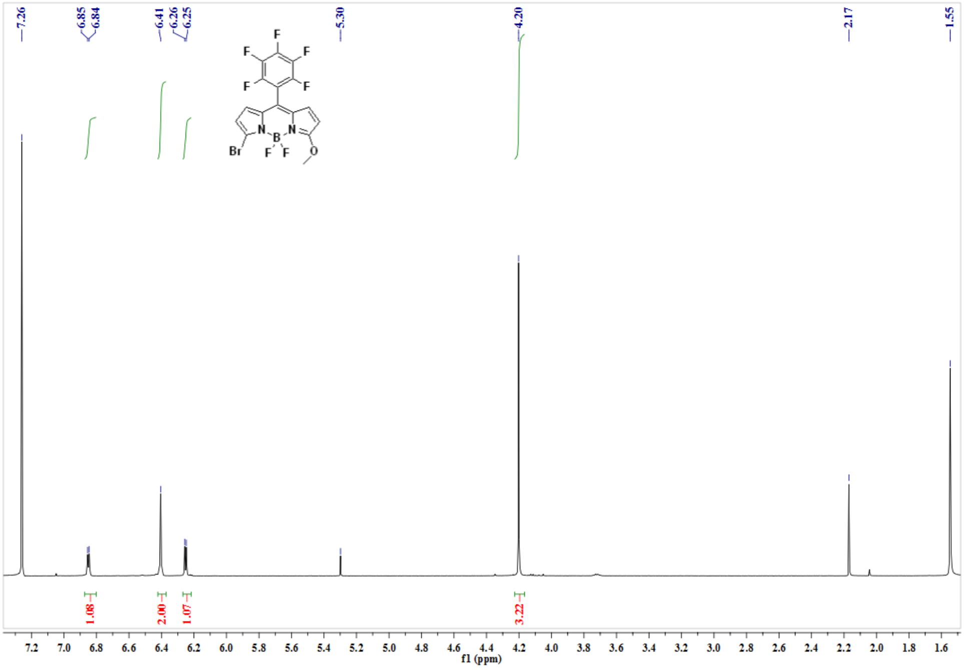


Figure 1. 400 MHz ^{1}H NMR of $\mathbf{R_{OMe}}$

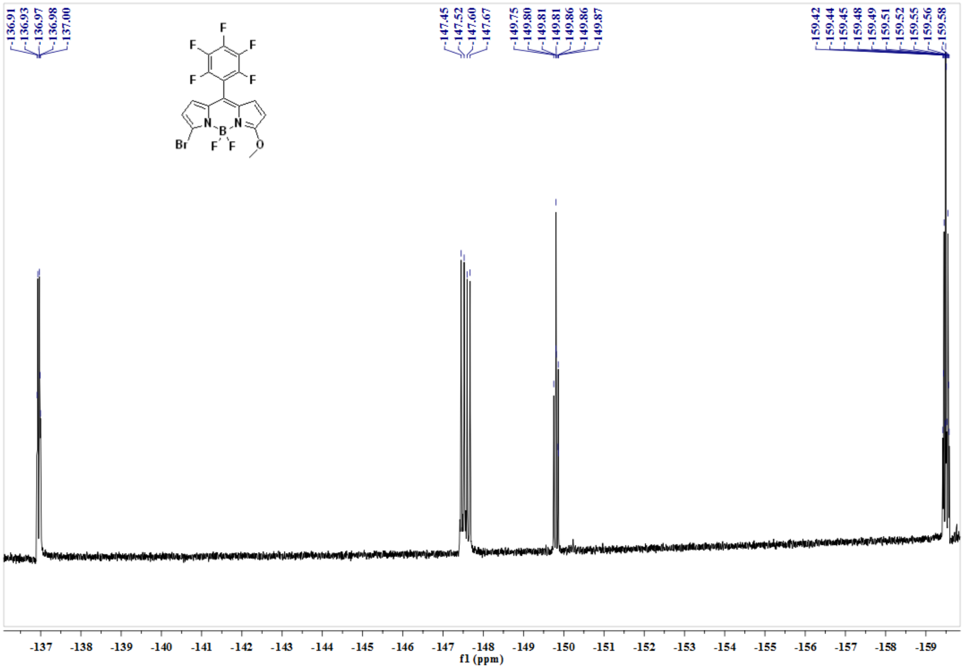


Figure 2. 376 MHz ^{19}F NMR of $\mathbf{R_{OMe}}$.

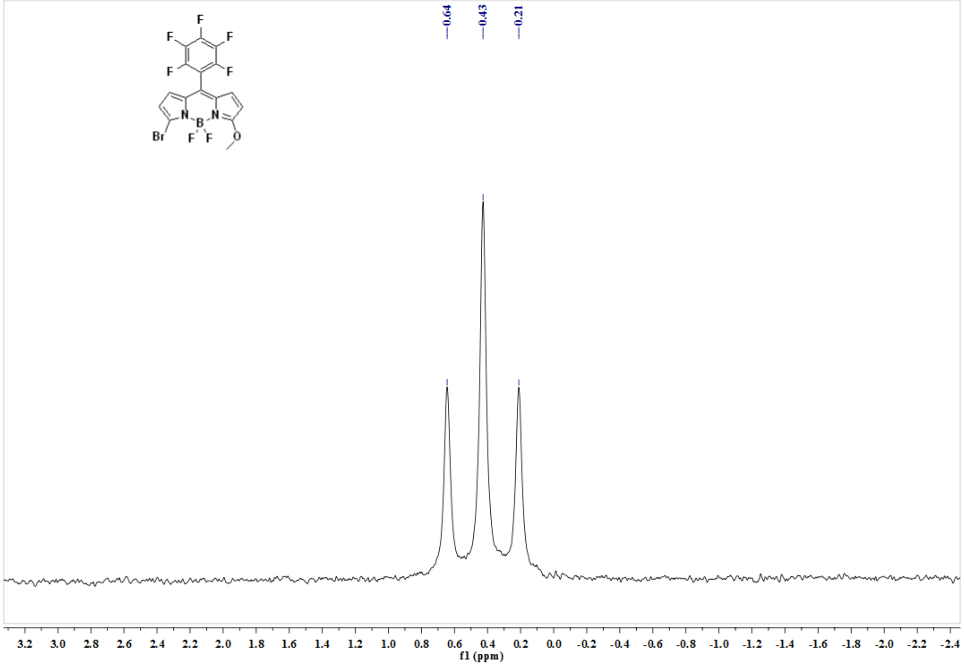


Figure 3. 128 MHz ^{11}B NMR of $\mathbf{R_{OMe}}$.

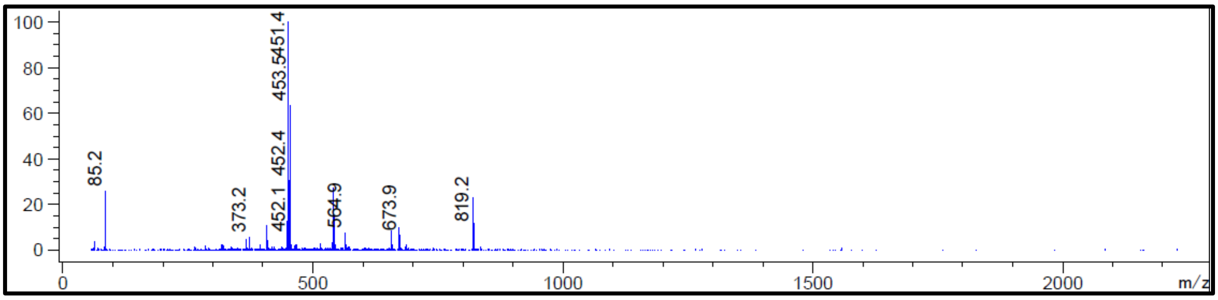
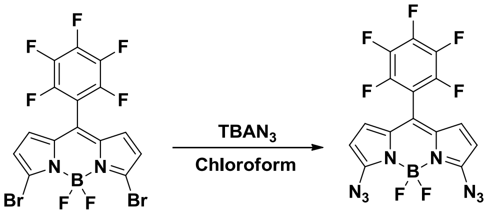


Figure 4. Mass (LR-MS) of $\mathbf{R_{OMe}}$.

Preparation of Azide BODIPY ($\mathbf{R_{[N3]2}}$):



Pentafluorophenyl dibromo-BODIPY (100 mg) was dissolved in 10 ml of dry chloroform. Then higher equivalents of tetrabutyl ammonium azide added to the reaction mixture at room temperature, stirred this mixture for 10 min in dark condition. Then solvent was evaporated under reduced pressure. By performing column chromatography we purified desire compound by using ethyl acetate and hexane as elutants. The total procedure performed under dark condition, to avoid the decomposition of resultant product. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.69–6.68 (d, J= 4.83, 2H), 6.33–6.32 (d, J= 4.32, 2H), ^{11}B NMR (128 MHz, CDCl$_3$): δ 0.44-0.02. MS (LR-MS): Anal. Calc. for $C_{15}H_4BF_7N_8$ requires 388.0727, found $C_{15}H_4N_4BF_7$ + 4H-N$_4$ is 388.0746.

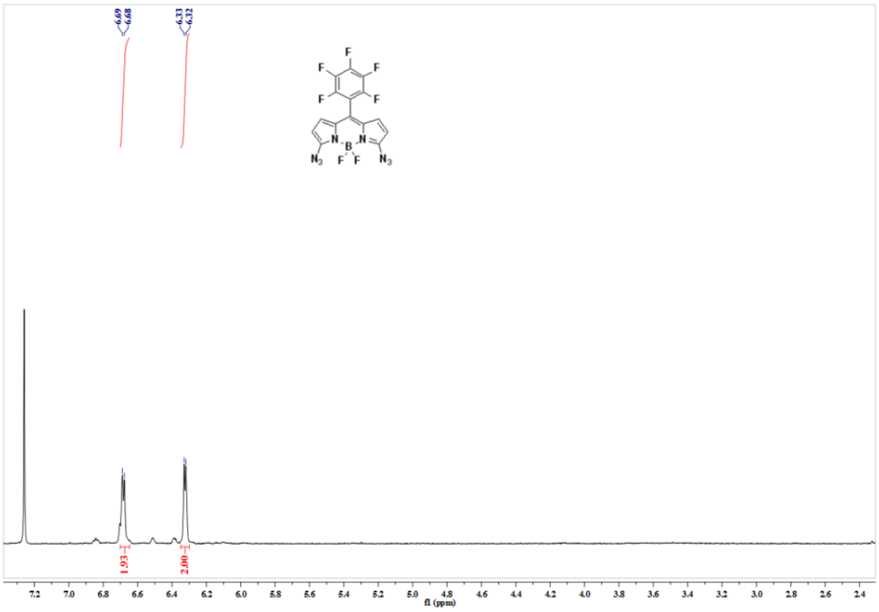


Figure 5. 400 MHz ^{1}H NMR of $\mathbf{R}_{[N3]2}$

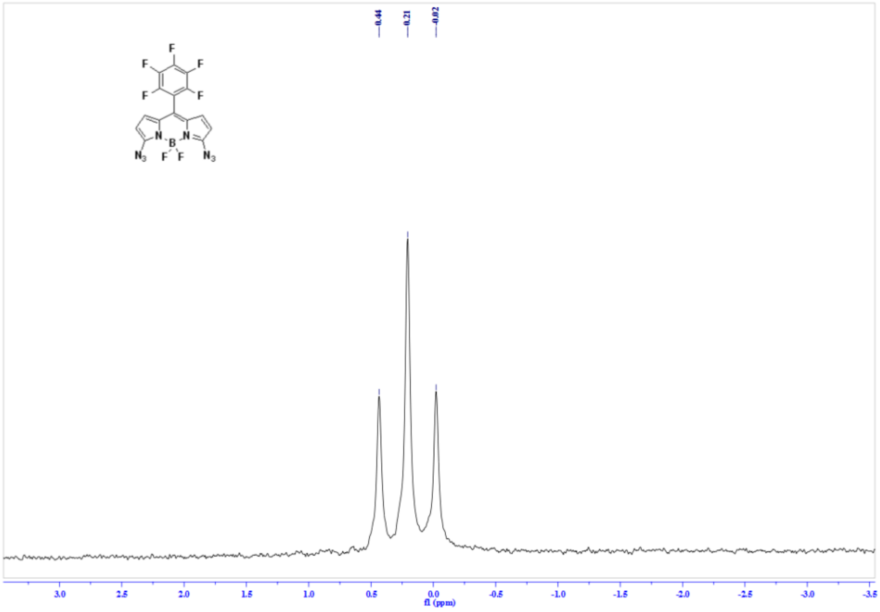


Figure 6. 128 MHz ^{11}B NMR of $\mathbf{R}_{[N3]2}$

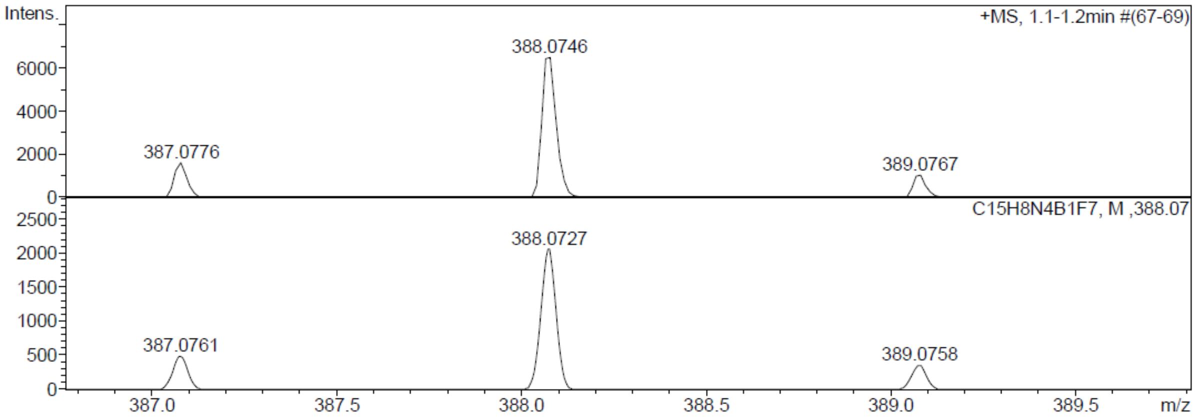
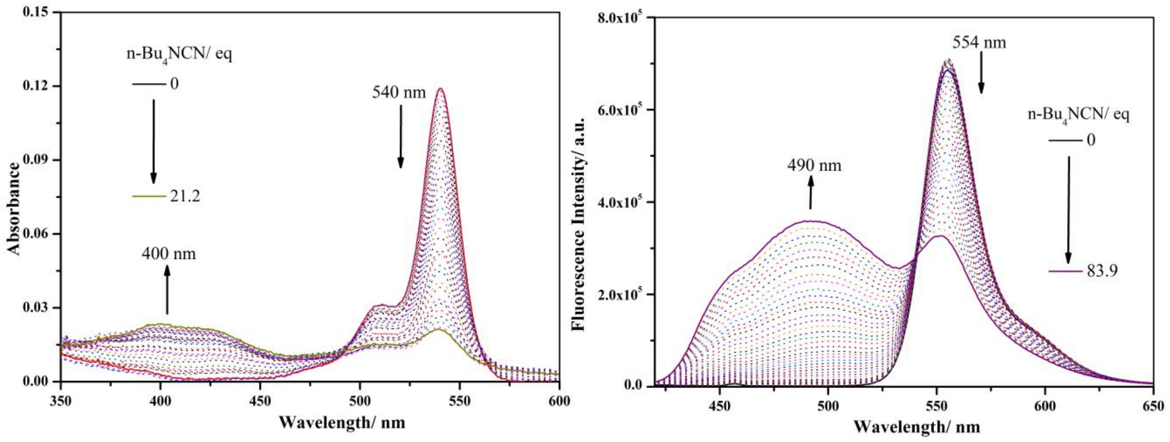


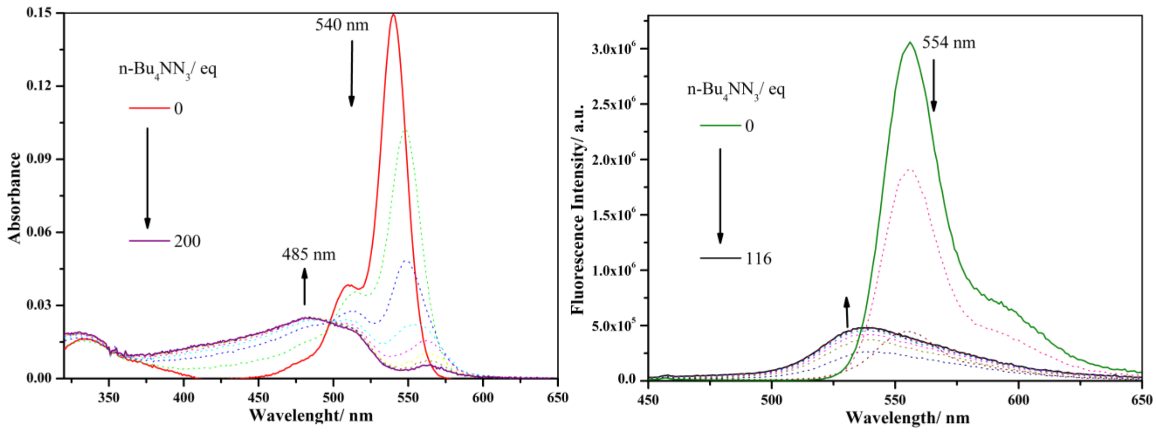
Figure 7. Mass spectra of $\mathbf{R}_{[N3]2}$

3. Absorption and fluorescence titration profiles:



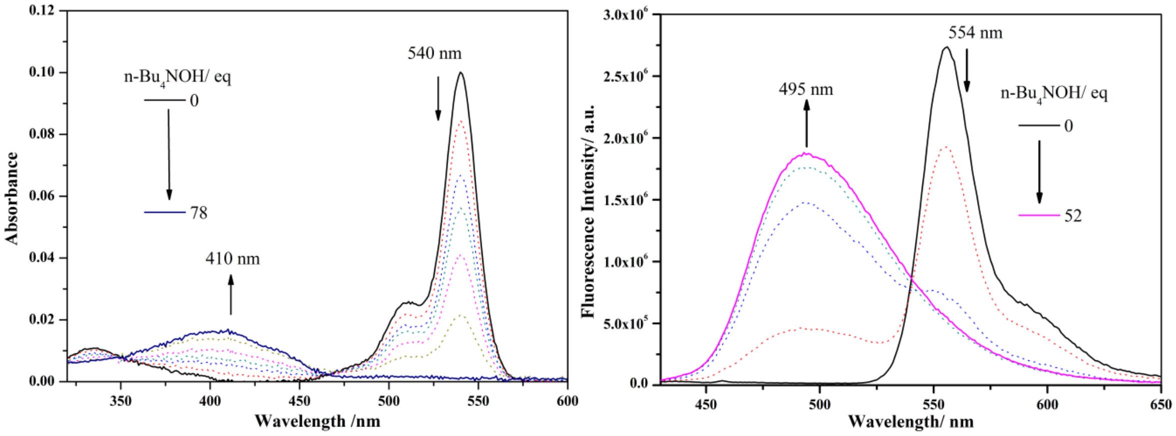
a **b**

Figure 8. Titration profiles of **R** upon addition of various equivalents of cyanide, (a) Absorption profile, (b)Emission profile in DCM.



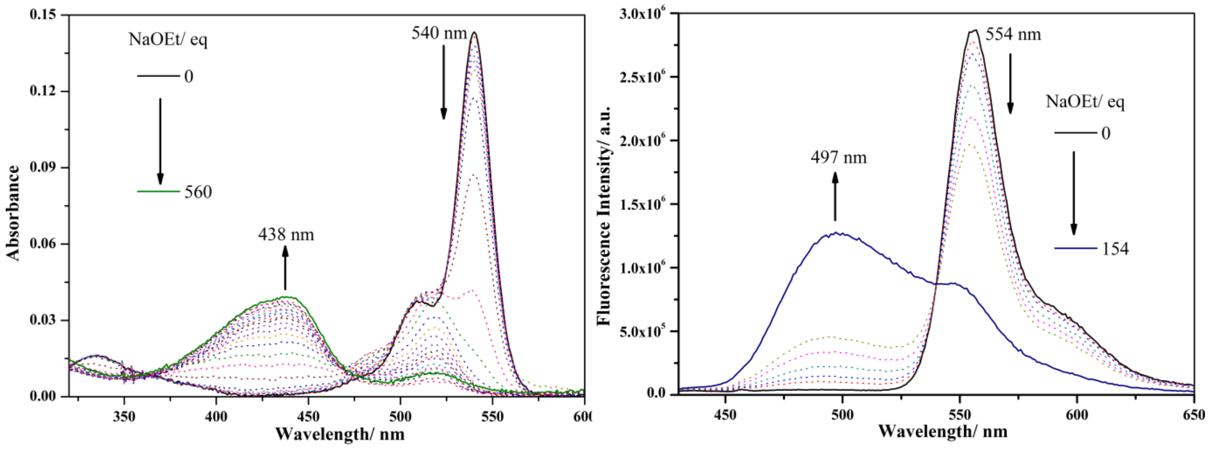
a **b**

Figure 9. Absorption (a) and Emission (b) titration profiles of **R** upon addition of various equivalents of azide in DCM.



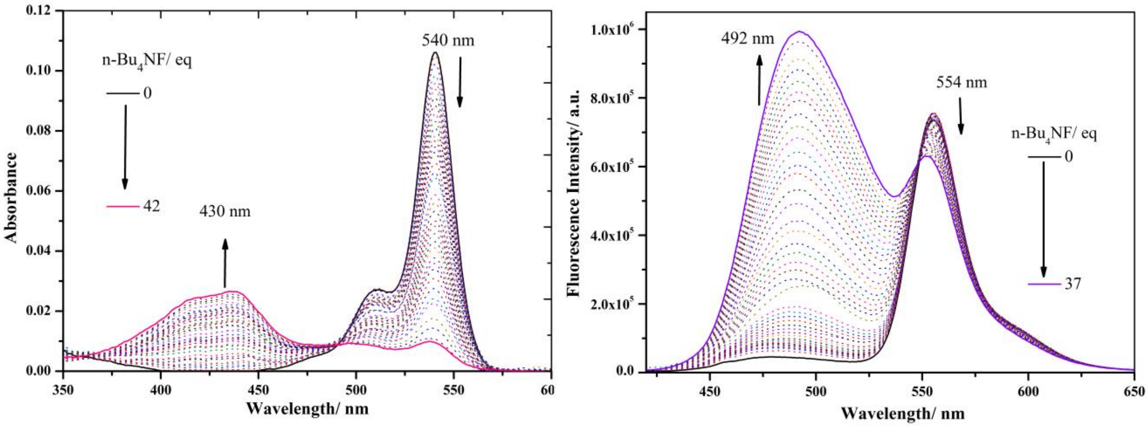
a **b**

Figure 10. Titration profiles of **R** upon addition of various equivalents of hydroxide anion (a) absorption, (b) Emission profile.



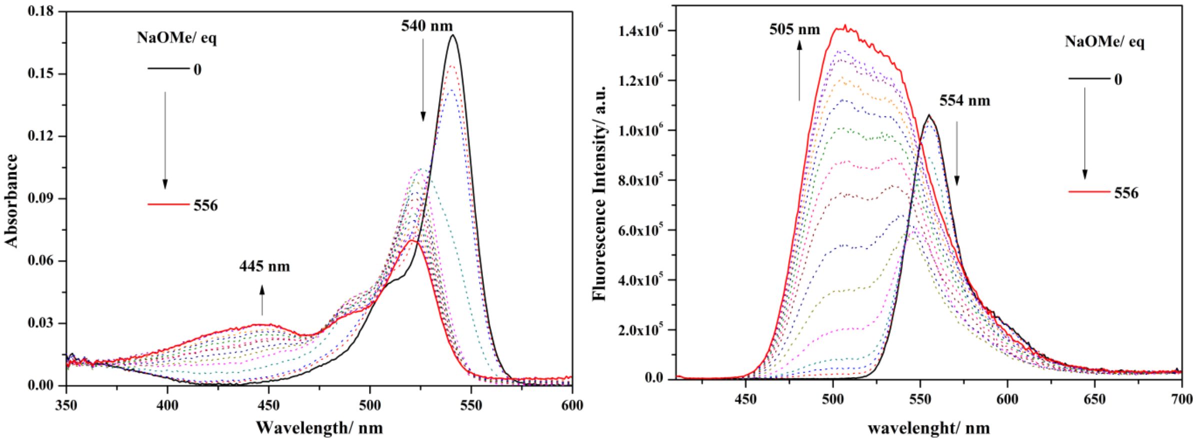
a **b**

Figure 11. Titration profiles of **R** upon addition of various equivalents of Ethoxide anion (a) absorption, (b) Emission profile.



a **b**

Figure 12. Titration profiles of **R** upon addition of various equivalents of fluoride anion absorption (a), Emission (b) profile.



a **b**

Figure 13. Titration profiles of **R** upon addition of various equivalents of methoxide anion absorption (a), Emission (b) profile.

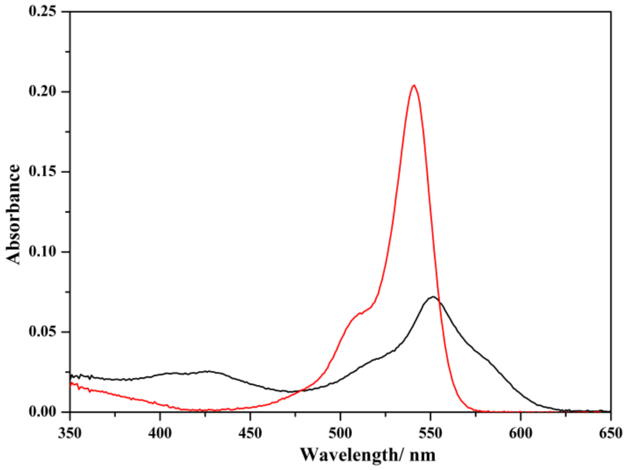
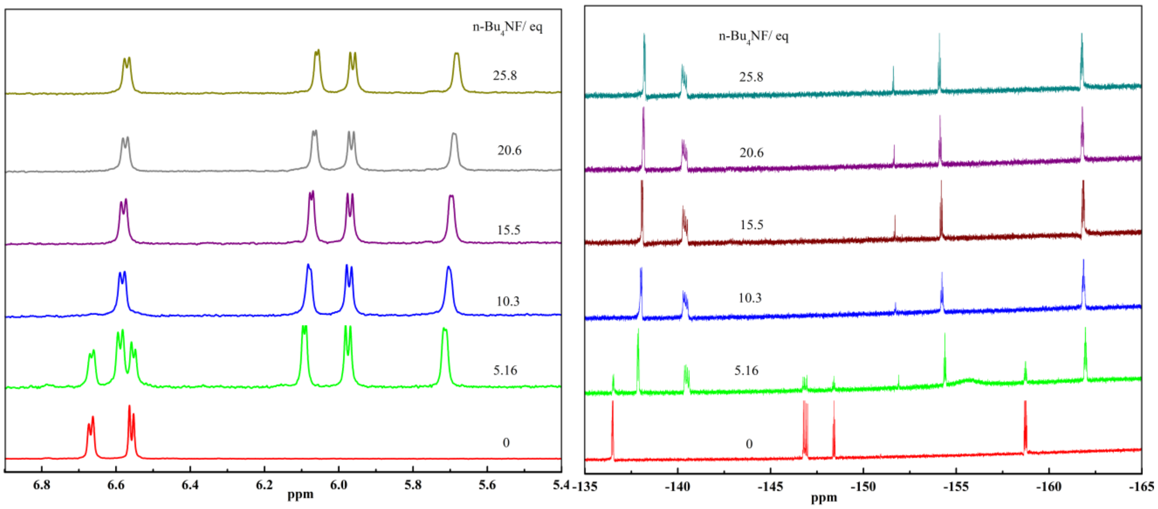


Figure 14. Behaviour of **R** in presence of all anions.

4. NMR (^{1}H, ^{11}B & ^{19}F NMR) titration



a **b**

Figure 15. ^{1}H- NMR (a) and ^{19}F- NMR (b) titration profiles of **R** upon addition of various equivalents of fluoride in $CDCl_3$.

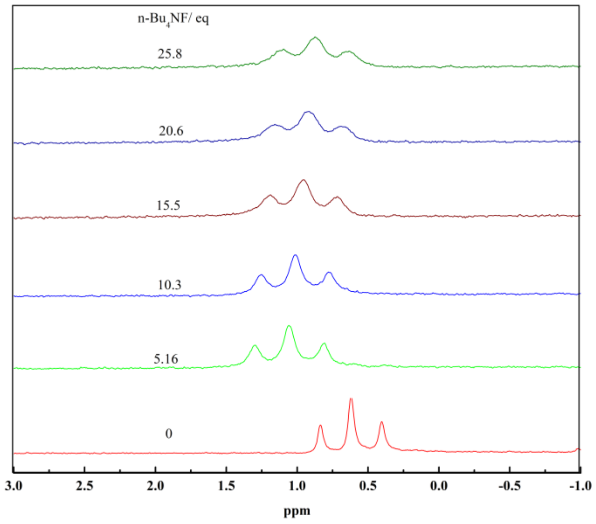
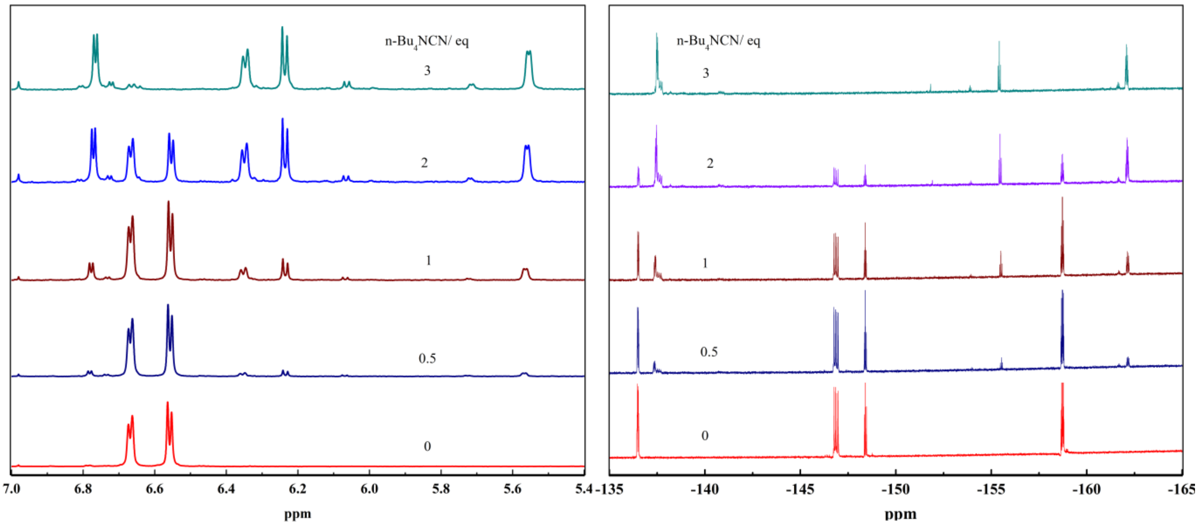
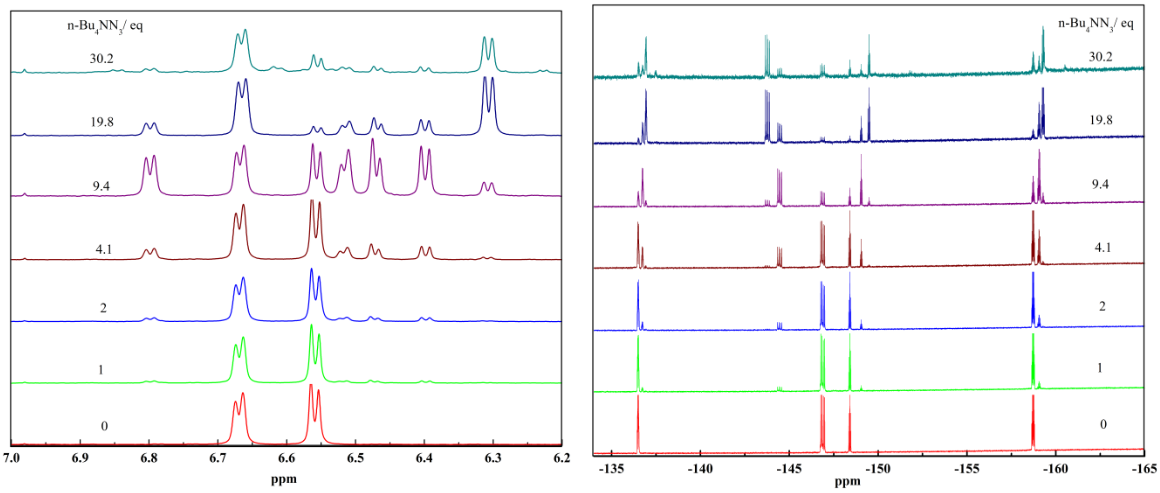


Figure 16. ^{11}B- NMR titration profile of **R** upon addition of various equivalents of fluoride in $CDCl_3$.



a **b**

Figure 17. ^{1}H- NMR (a) and ^{19}F- NMR (b) titration profiles of **R** upon addition of various equivalents of cyanide in $CDCl_3$.



a **b**

Figure 18. ^{1}H- NMR (a) and ^{19}F- NMR (b) titration profiles of **R** upon addition of various equivalents of azide in $CDCl_3$.

5. Stability of R_{CN} and $R_{[N3]2}$ products.

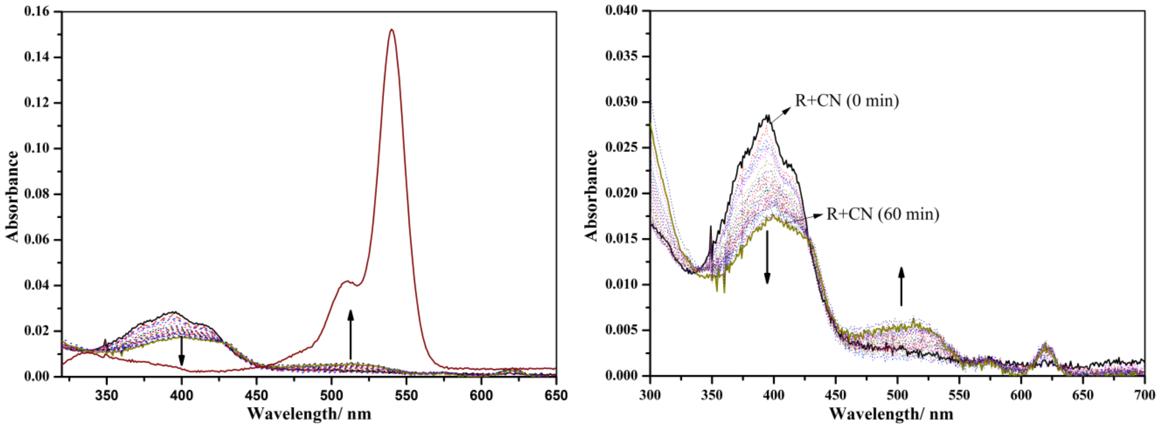


Figure 19. Time dependent decomposition of $\mathbf{R_{CN}}$ monitored by UV-Vis spectrophotometry.

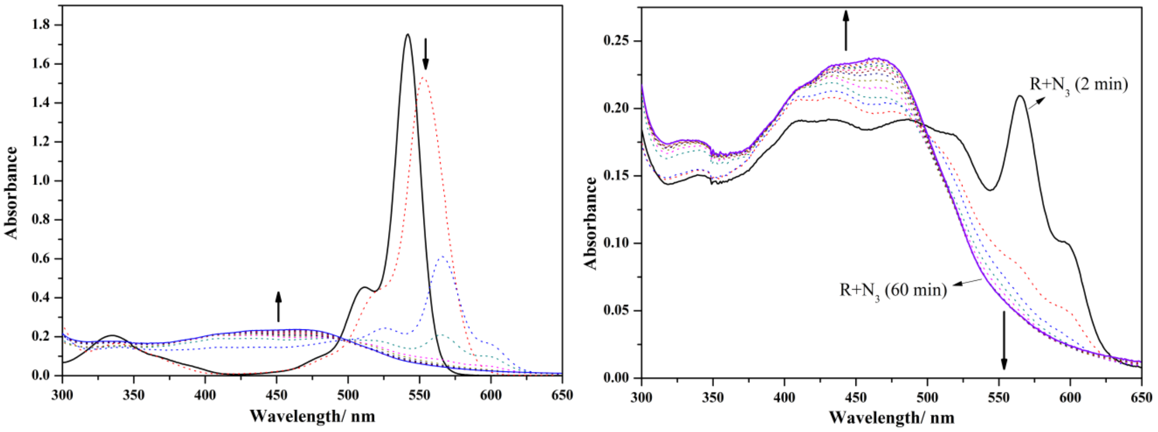


Figure 20. Time dependent decomposition of $\mathbf{R_{[N3]2}}$ monitored by UV-Vis spectrophotometry.

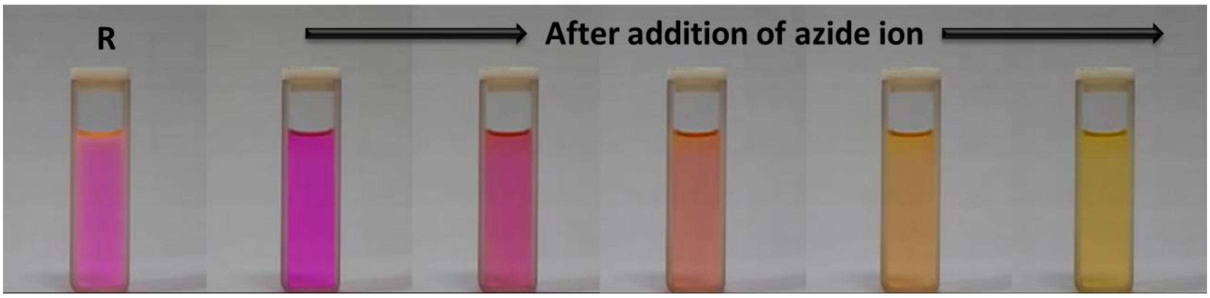


Figure 21. Decomposition of **R + TBAN$_3$** monitored visual colour changes from pink (0 min) to yellow (2 min).

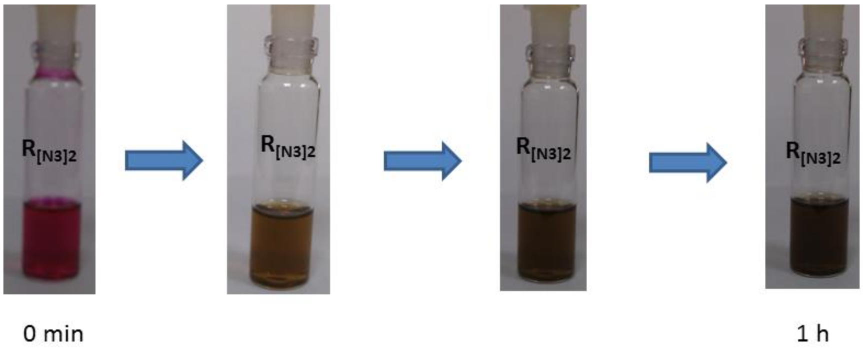
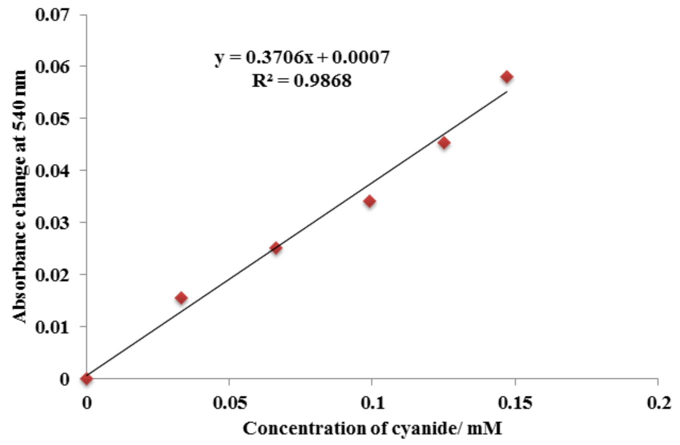
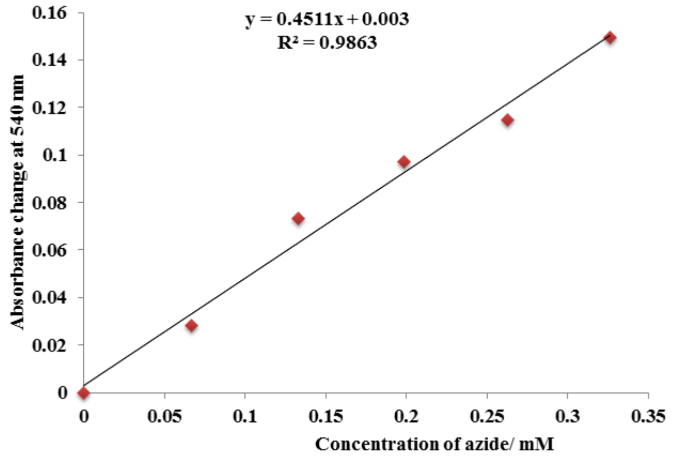
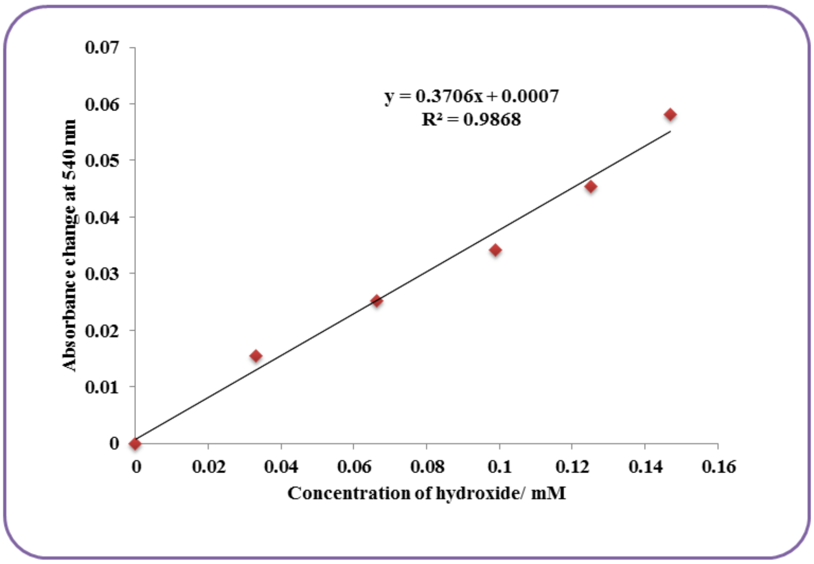


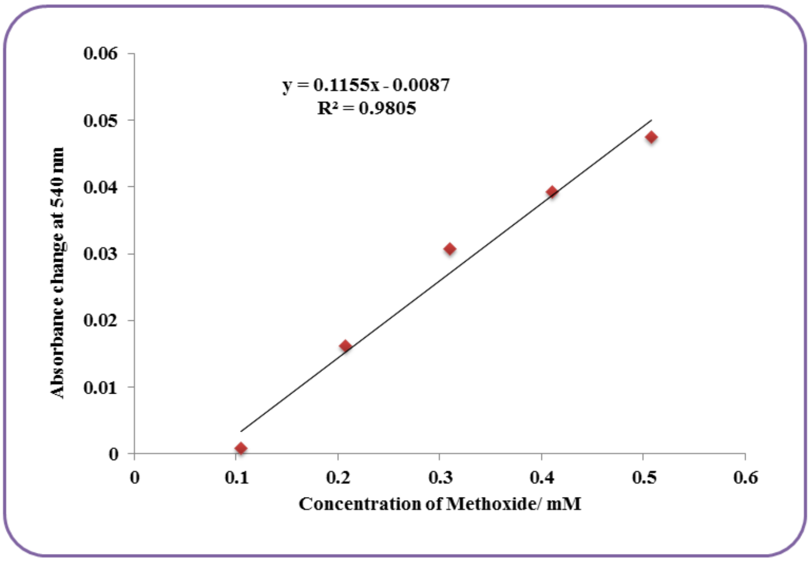
Figure 22. Decomposition of $\mathbf{R_{[N3]2}}$ monitored via visual colour changes from pink (0 min) to dark precipitation (1 h).

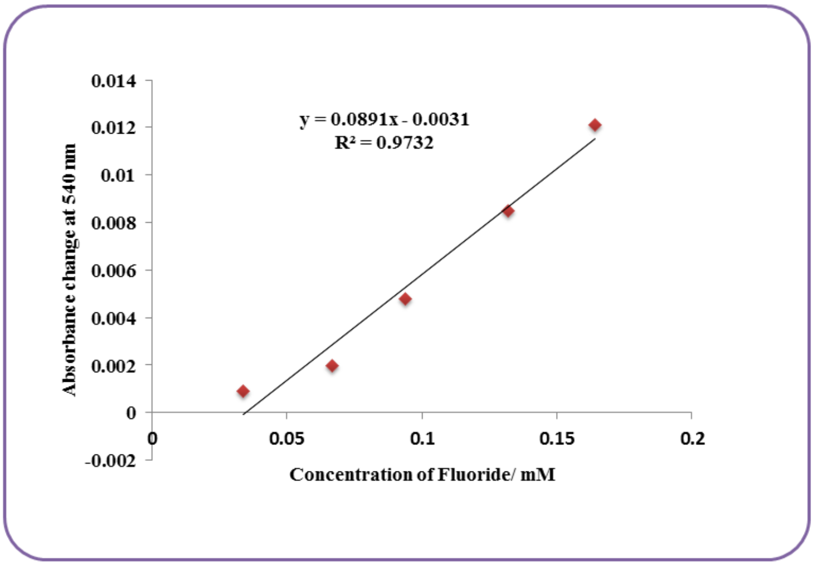
6. Calibration curves.






y = 0.3706x + 0.0007
R² = 0.9868
Absorbance change at 540 nm
Concentration of hydroxide/ mM
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16


y = 0.1155x - 0.0087
R² = 0.9805
Absorbance change at 540 nm
Concentration of Methoxide/ mM
0
0.01
0.02
0.03
0.04
0.05
0.06
0
0.1
0.2
0.3
0.4
0.5
0.6


y = 0.0891x - 0.0031
R² = 0.9732
Absorbance change at 540 nm
Concentration of Fluoride/ mM
-0.002
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0
0.05
0.1
0.15
0.2

7. Crystallographic data

	R_{OMe}
CCDC	1042078
Formula	C_{16} H_7 B Br F_7 N_2 O
Formula mass (g/mol)	466.95
Crystal system	Monoclinic
Space group	$P_2(1)/c$
a(Å)	11.3455(12)
b(Å)	10.2153(10)
c(Å)	14.3393(13)
α(°)	90.00
β(°)	94.725(5)
γ(°)	90.00
$V(Å^3)$	1656.2(3)
Z	4
D_{calc} (g/cm^5)	1.873
F_{000}	912.0
Crystal size (mm)	0.46x0.34x0.23
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Measured reflection	2243
Unique reflection [I>2σ(I)]	2011
$R_1[I>2\sigma(I)]^a$	0.0354
$R_w[I>2\sigma(I)]^b$	0.0944

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o$, $^bR_w=[\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$

Possible Hydrogen bonds by Methoxy group

Donor-H	**Donor...Acceptor**	**H...Acceptor**	**Donor-H......Acceptor**
C00R -H00B	C00R ...F003 (1)	H00B ...F003 (1)	C00R -H00B ...F003 (1)
0.98	3.562	2.857	129.54
C00R -H00C	C00R ...F007 (2)	H00C ...F007 (2)	C00R -H00C ...F007 (2)
0.98	3.614	2.986	122.99
C00R -H00C	C00R ...F009 (3)	H00C ...F009 (3)	C00R -H00C ...F009 (3)
0.98	3.202	2.39	139.86

(1) x,-y+1/2+1,+z+1/2

(2) -x+2,-y+1,-z+1

(3) -x+2,+y-1/2,-z+1/2+1