Supporting Information

Chromofluorescent Probes for Selective Detection of Fluoride and Acetate ions

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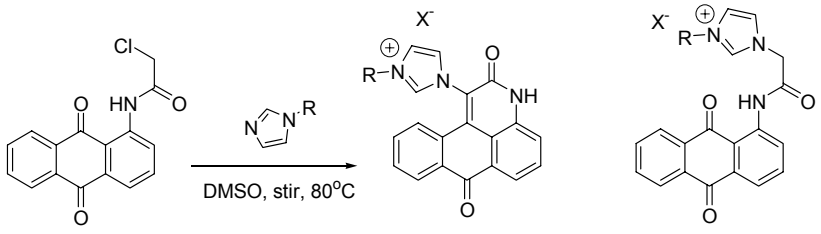
1. **General Experiment Conditions:** ^{1}H NMR Spectra and titrations were carried out at temperature 25 ^{o}C using JEOL A1 spectrometer operating at 300 MHz. ^{13}C NMR sepctra were recorded at 75 MHz. All chemical shifts are reported in ppm relative to the TMS as an internal reference. UV-Vis studies were carried out on a Shimadzu UV-1601 PC or Shimadzu UV-2400 machines using slit width of 1.0 nm and matched quartz cells. The fluorescence experiments were performed on Shimadzu 1501 fluorescence spectrophotometer. Elemental analysis were performed on Flash EA-1112 series CHNS-O analyser instrument.

2. **Synthesis of receptors 2 and 3**



1 **2 R = Benzyl,X = Cl** **4**
3 R = dodecyl,X = Br
2.PF_6 R = Benzyl, X = PF_6

The mixture of 1-aminoanthraquinone (3 mmol) and K_2CO_3 (3 mmol) in acetonitrile was stirred and chloroacetyl chloride (4 mmol) was added dropwise. The stirring was continued for 12 hours. The rection mixture was diluted with water, the solid separated was filtered and washed with water and then with ethanol. The residual solid was found to be pure 1-chloroacetamide anthraquinone **1**, mp. 217 ^{o}C, 80%. The solution of **1** (1 mmol) in DMSO was heated to 80 ^{o}C. 1-

benzyl-imidazole (2 mmol) was added and solution was heated for 2h. The reaction mixture was cooled to RT and solid separated was filtered off to isolate pure **2** and similarly by using the dodecyl imidazole instead of bezylimidazole the chemosensor **3** was isolated.

Chemosensor 2: Yield 80 %, mp.> 300 ^{o}C, M+ m/z 404 ^{1}H NMR (DMSO-d_6, 300 MHz) : δ 5.65 (s, 2H, CH_2), 6.70 (d, *J* = 8.1 Hz, 1H, ArH), 7.43-7.51 (m ,7H, 7 x ArH), 7.77 (t, *J* = 7.2 Hz, H, ArH), 7.85 (d, *J* = 7.2 Hz, 1H, ArH), 7.93 (d, *J* = 7.5 Hz, 1H, ArH), 7.98 (s, 1H, ArH), 8.16 (d, *J* = 6.9 Hz, 2H, 2 x ArH), 8.37 (d, *J* = 7.8 Hz, 1H, ArH), 9.72 (s, 1H, NH) ^{13}C NMR (DMSO-d_6, 75 MHz): δ 52.86 (CH_2), 116.05, 120.33, 121.88, 123.21, 124.18, 124.46, 127.41, 128.43, 128.56, 129.21, 129.38, 130.46, 132.41, 132.64, 133.84, 134.15, 134.85, 137.44, 138.64, 151.19, 157.97, 167.64, 181.75. Elemental analysis: $C_{26}H_{18}ClN_3O_2$ requires, C, 70.99; H, 4.12; N, 9.55; O, 7.27; found C, 70.76; H, 4.08; N, 9.39 %.

Chemosensor 3: Yield 78 %, mp.> 300 ^{o}C, M+ m/z 482 ^{1}H NMR (DMSO-d_6) δ: 0.83 (t, *J* = 6.6 Hz, 3H, CH_3), 1.20-1.24 (m, 18H, 9CH_2), 1.88 (t, *J* = 6.6 Hz, 2H, CH_2), 4.37 (t, *J* = 6.9 Hz, 2H, CH_2), 6.78 (d, *J* = 8.1 Hz, 1H, ArH), 7.62 (t, *J* = 7.5 Hz, 1H, ArH), 7.79 (t, *J* = 7.5 Hz, 1H, ArH), 7.84 (d, *J* = 8.1 Hz, 1H, ArH), 7.96 (t, *J* = 7.8 Hz, 2H, 2 x ArH), 8.18 (d, *J* = 8.7 Hz, 2H, 2 x ArH), 8.38 (d, *J* = 8.1 Hz, 1H, ArH), 9.60 (s, 1H, ArH). ^{13}C NMR, DMSO δ: 13.96 (CH_3), 18.05 (CH_2), 22.09(CH_2), 25.40 (CH_2), 28.31 (CH_2), 28.72 (CH_2), 28.93 (CH_2), 29.02 (CH_2), 29.21 (CH_2), 31.30 (CH_2), 49.60 (CH_2), 121.65, 122.96, 126.65, 127.87, 128.43, 130.39, 132.17, 132.53, 133.98, 138.31, 157.83, 181.55. Elemental analysis: $C_{31}H_{36}BrN_3O_2$ requires, C, 66.19; H, 6.45; N, 7.47; O, 5.69 found C, 66.31; H, 6.43; N, 7.35 %

Chemosensor 2PF_6: The receptor **2** (0.5 mmol) was dissolved in ethanol at RT and solution of NH_4PF_6 (0.5 mmol) in water was added drop wise. The solution was allowed to stir for 1 h. The separated yellow solid was filtered to isolate pure 4. Yield 88 %, mp.> 300 ^{o}C, M^+ m/z 404, ^{1}H NMR (CD_3CN) δ**:** 5.49 (s, 2H, CH_2), 6.79 (d, *J* = 9 Hz, 1H, ArH), 7.43-7.54 (m, 7H, 7xArH), 7.70-7.75 (m, 3H, ArH), 7.89 (t, *J* = 6.0 Hz, 1H, ArH), 8.23 (d, *J* = 6.0 Hz, 1H, ArH), 8.42 (d, *J* = 6.0 Hz, 1H, ArH), 8.85 (s, 1H, ArH), ^{13}C NMR (DMSO-d_6, 75 MHz): δ 53.34 (CH_2), 116.9, 120.88, 123.01, 123.45, 124.11, 127.21, 128.2, 128.3, 128.7, 129.21, 129.81, 132.04, 132.27, 132.83, 133.20, 133.6, 134.59, 136.74, 137.42, 151.19, 157.22, 181.44. Elemental analysis: $C_{26}H_{18}F_6N_3O_2P$; requires, C, 56.84; H, 3.30; N, 7.65; O, 5.82; found C, 56.81; H, 3.29; N, 7.62 %

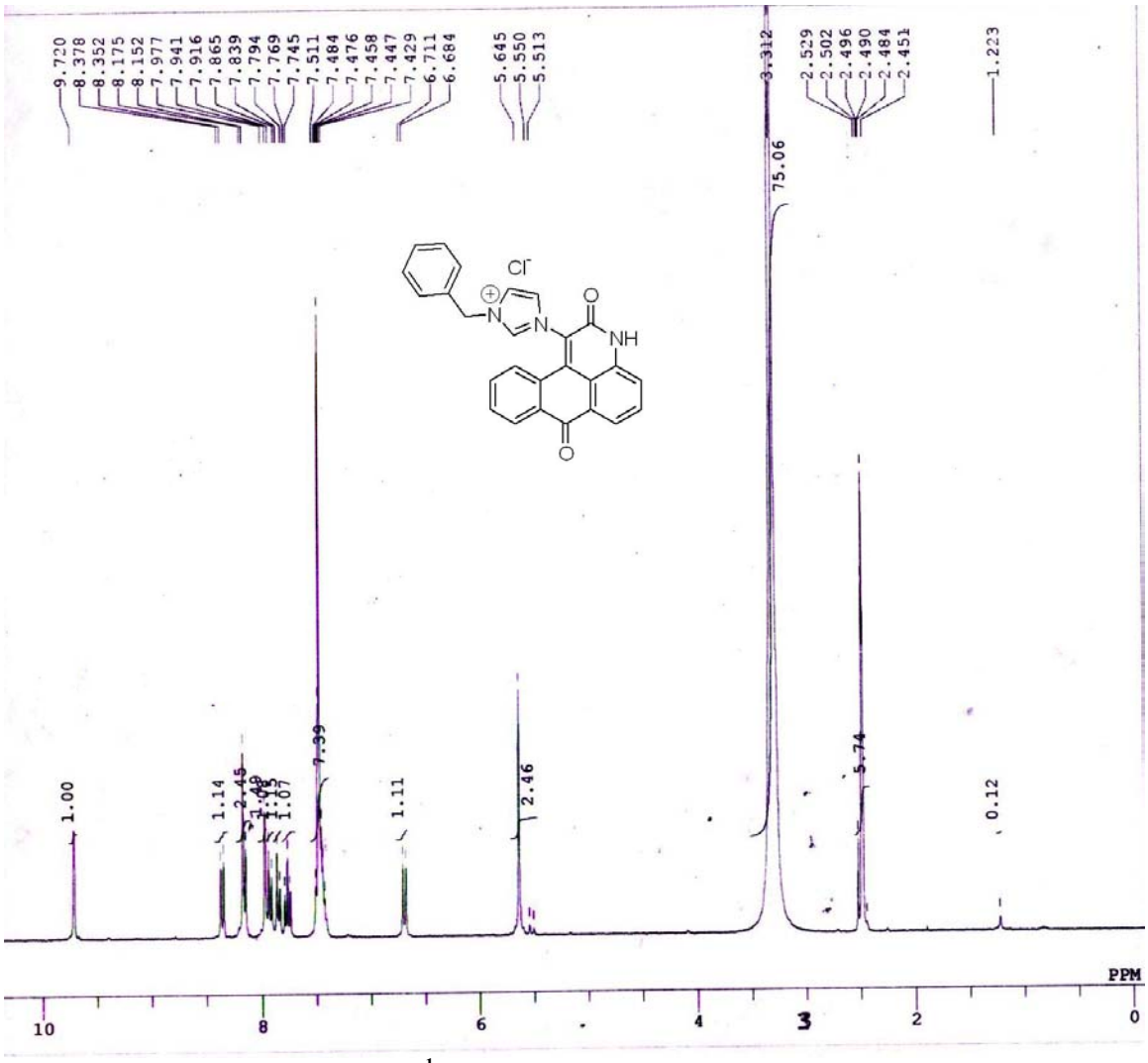


Figure S1: ^{1}H NMR Spectrum of Chemosensor 2

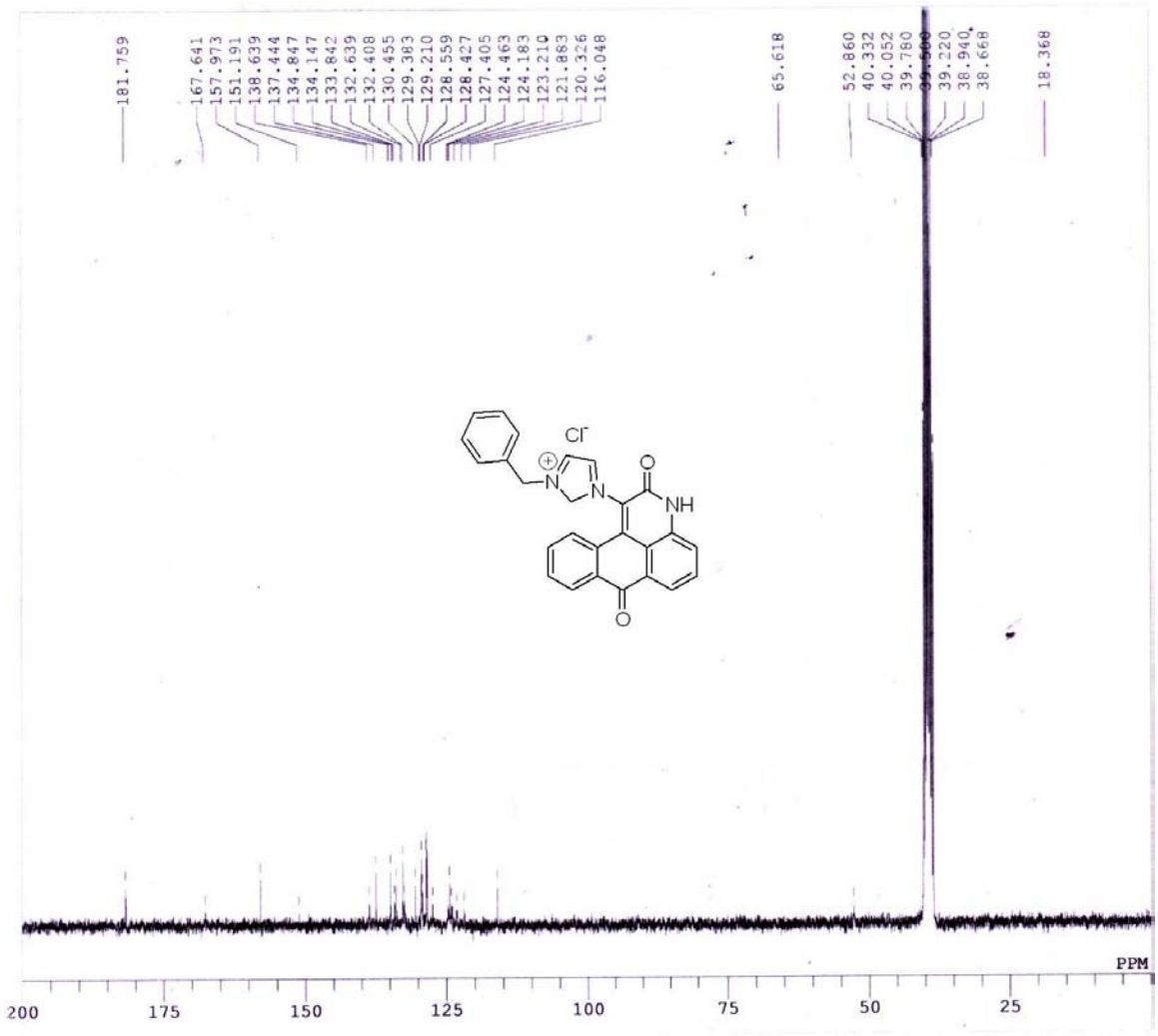


Figure S2: ^{13}C NMR Spectrum of Chemosensor 2

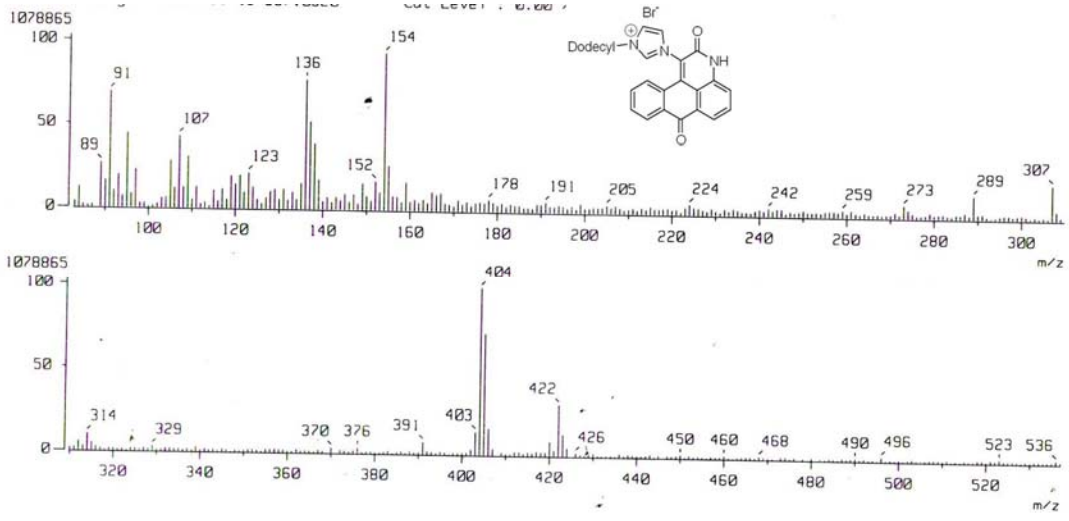


Figure S3: Mass Spectrum for Chemosensor 2

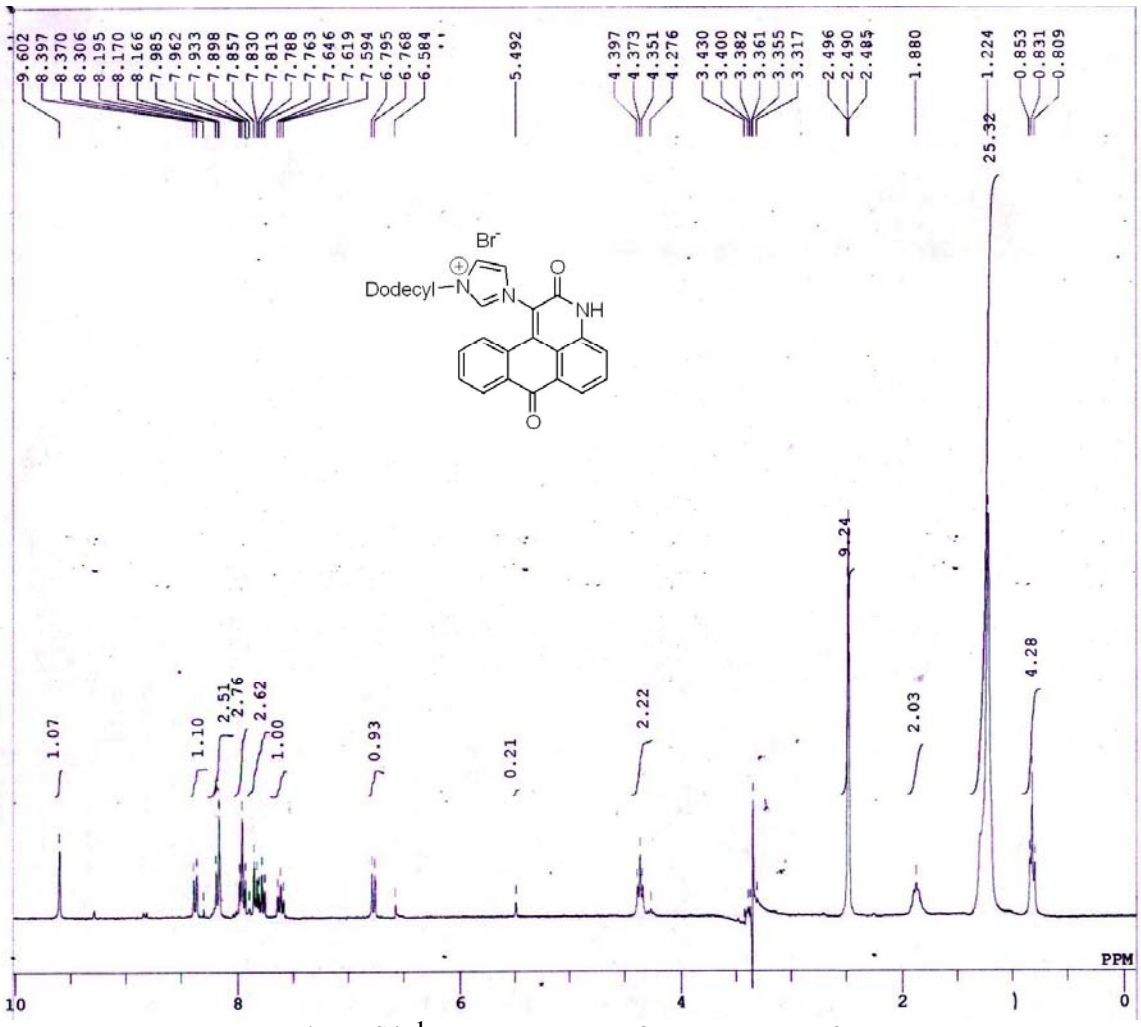


Figure S4: ^{1}H NMR spectrum for chemosensor 3

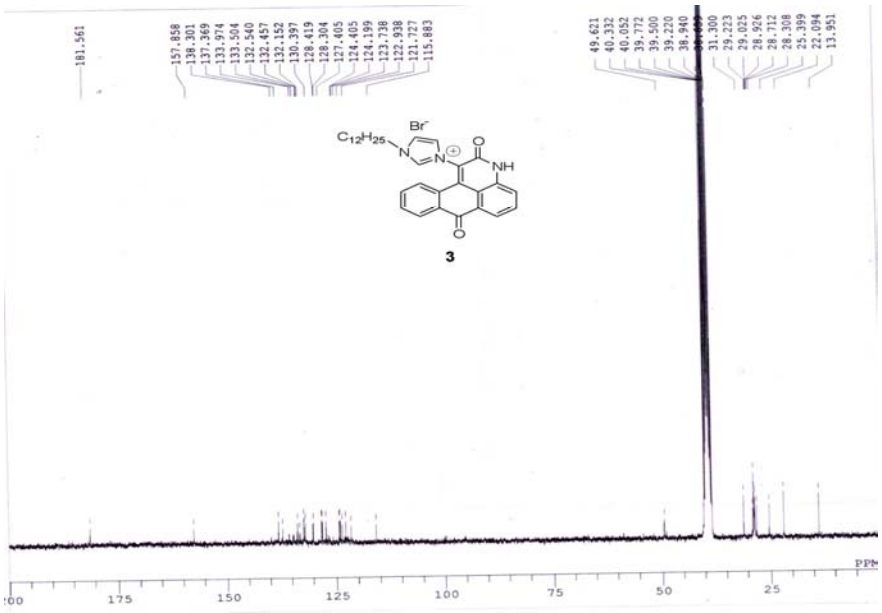


Figure S5: ^{13}C NMR for chemosensor 3

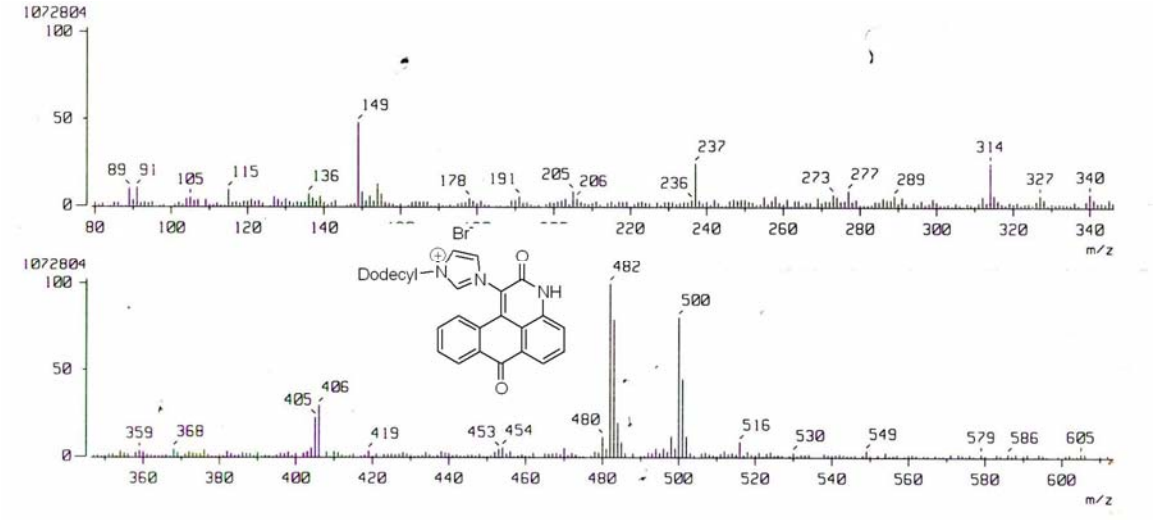


Figure S6: Mass spectrum for chemosensor 3

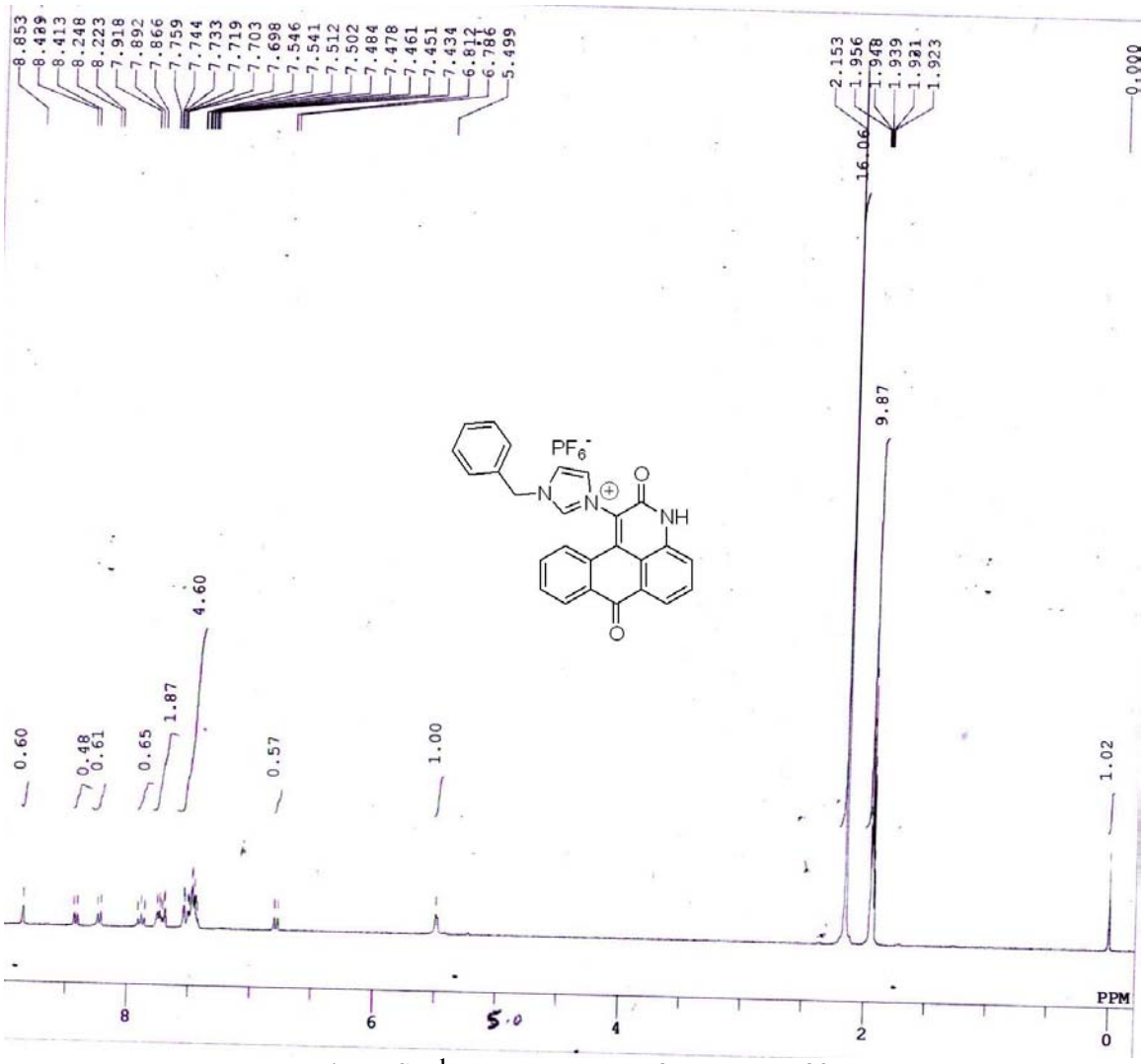


Figure S7: ^{1}H NMR spectrum for PF_6 salt of 2

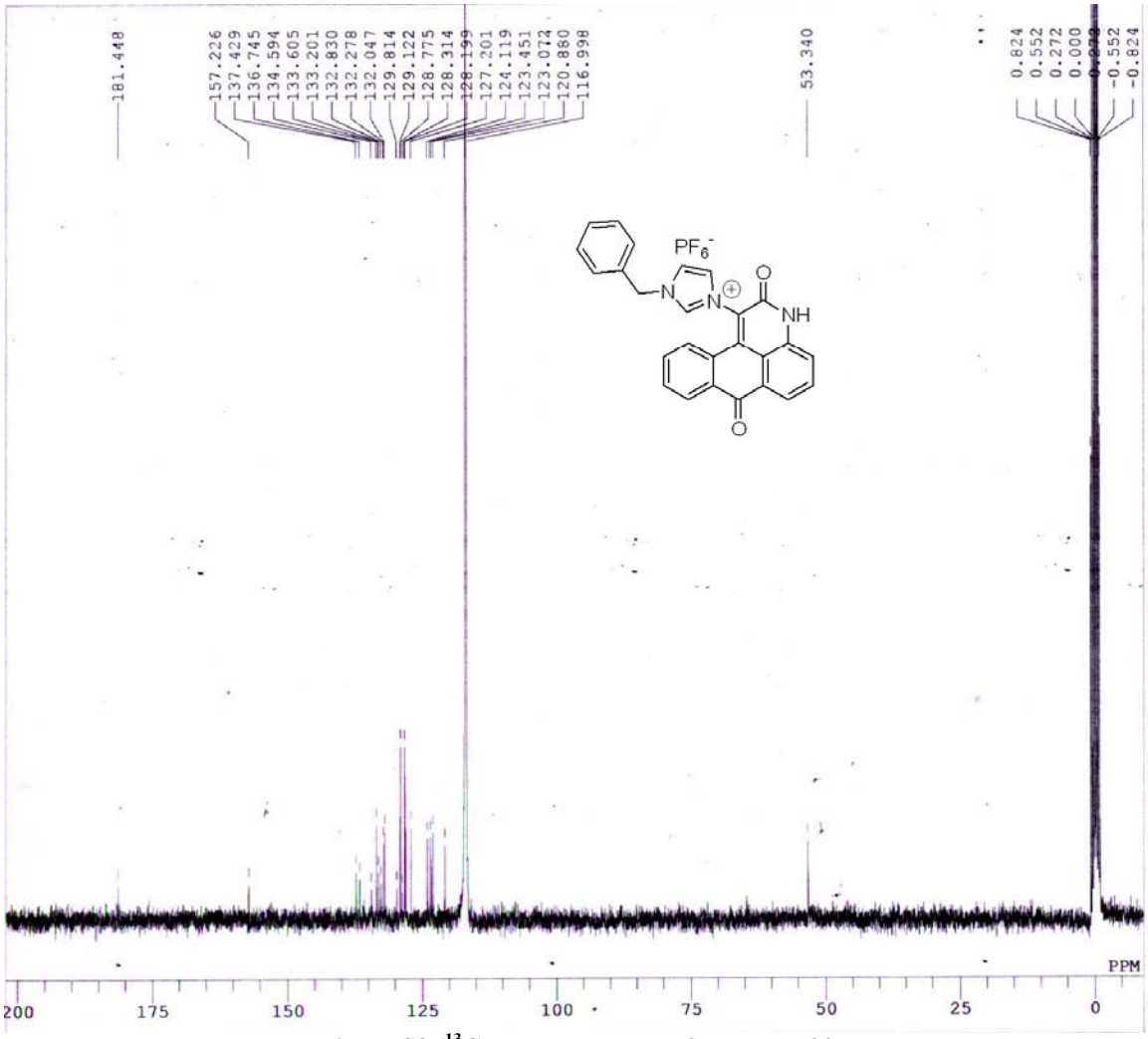


Figure S8: ^{13}C NMR spectrum of PF_6 salt of 2

X-Ray Crystal structure for chemosensor 2 PF_6:

Single crystal was obtained in CH_3CN: $C_{26}H_{18}F_6N_3O_2P$. M = 549.4, yellow colored, 0.23 x 0.18 x 0.15 mm, Monoclinic, space group P21/c, a = 16.36, b = 15.516, c = 9.214, α = 90, β = 98.51, γ = 90, V = 2314, γ = 90, Z = 4, reflection collected = 15915, unique = 4069[R(int) = 0.2177, final GoF = 1.023 R1 =0.1214, wR2 = 0.2531, T = 150K with CrysALis CCD diffractometer with graphite monochromated Mo-Kα irradiation (λ = 0.7103 Å) using SHELX-97, Full-matrix least square on F2 refinement methods.

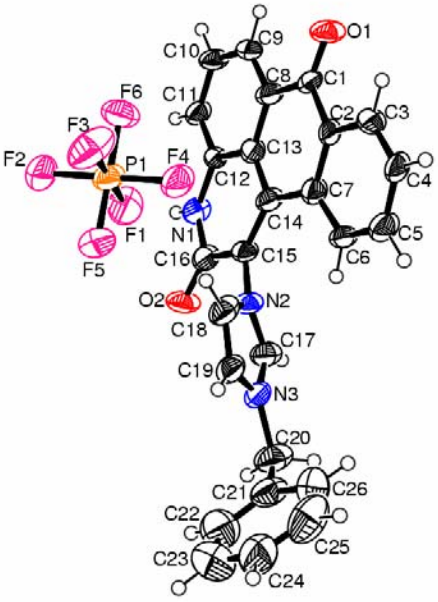


Figure S 9: X-Ray Crystal structure for chemosensor **2** PF_6 shows that H-6 faces imidazolium ring and so is shifted upfield in its ^{1}H NMR spectrum.

3. Photophysical studies – Parameters and Conditions

All anion stimulated colour changes and UV-studies have been studied in CH_3CN-DMSO (20:1) or in $CHCl_3$-MeOH (1:1) and fluorescence studies have been performed in CH_3CN and $CHCl_3$-MeOH (1:1). All absorption scans and fluorescence spectra were saved as ACS II files and were further processed in Excel™ to produce graphs shown. Solutions of **2** and **3** were typically 50 μM for UV-Vis studies and 10 μM for fluorescence studies. Stability constants were determined by fitting the absorption and fluorescence spectra recorded during the titrations of the probes with tetrabutylammonium fluoride and acetate. The data was fitted with the global analysis program SPECFIT[1]-32.

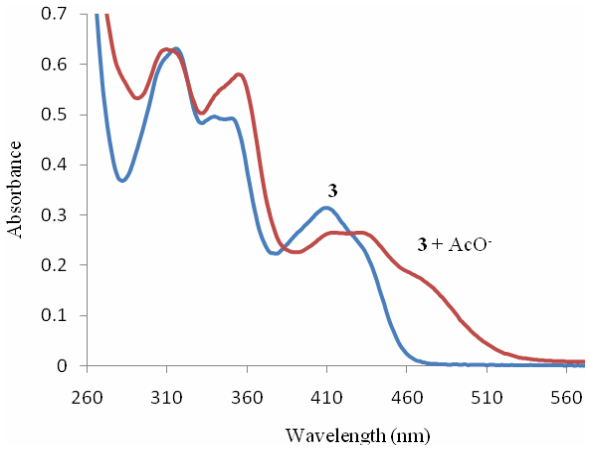
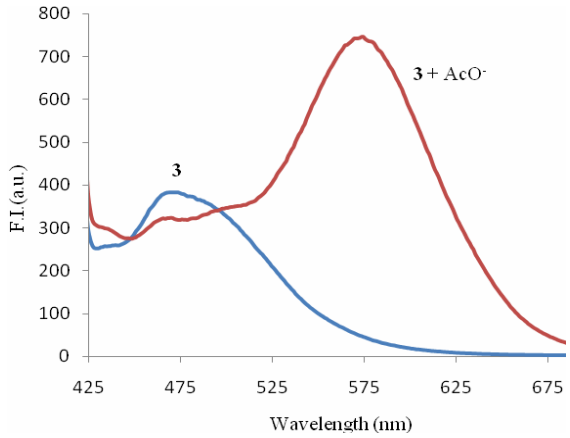


Figure S10A: UV-Vis spectra of **3** (50 µM) in $CHCl_3$-MeOH (1:1) and **3** + AcO^- (100 µM)



FigureS10B: UV-Vis spectra of **3** (50 µM) in $CHCl_3$-MeOH (1:1) and **3** + AcO^- (20 µM)

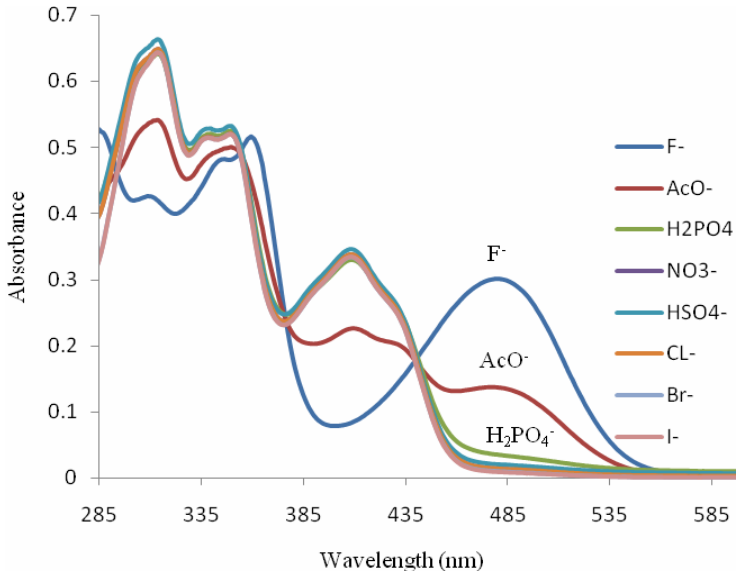


Figure S11: Effect of all anions on UV-Vis Spectrum to the solution of chemosensor **2**.

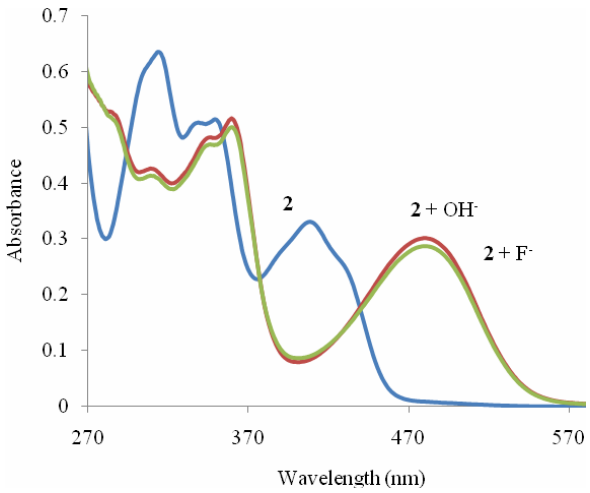


Figure S12: Effect of addition of TBA OH on UV-Vis spectrum of chemosensor **2**

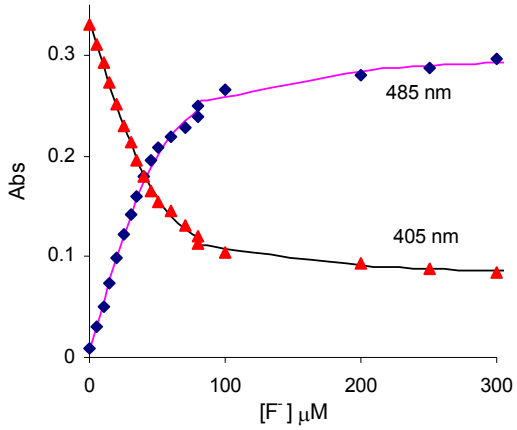


Figure S13: Plot of Absorbance of chemosensor **2** Vs [F^-] in CH_3CN (points show the experimental results and line is curve fit)

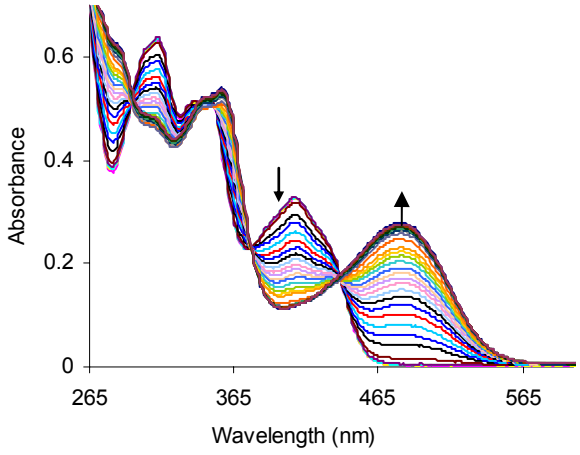


Figure S14: Effect of incremental addition of acetate ions on UV-Visible spectrum of **3** (50μM) in CH_3CN

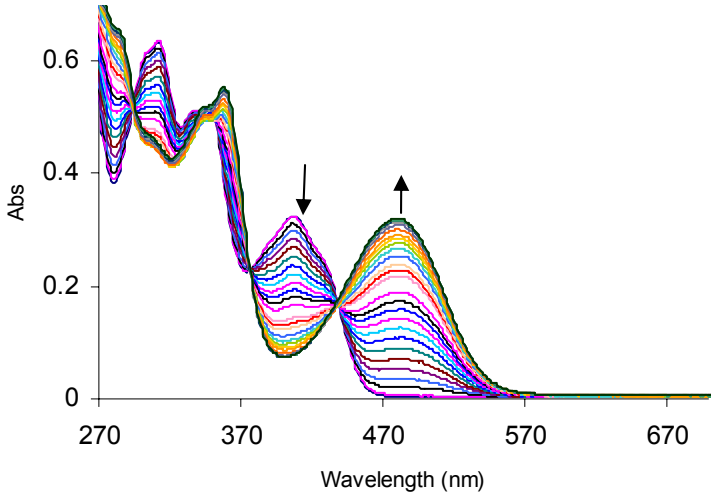


Figure S15: Effect of incremental addition of fluoride on UV-Visible spectrum of **3** (50μM) in CH_3CN

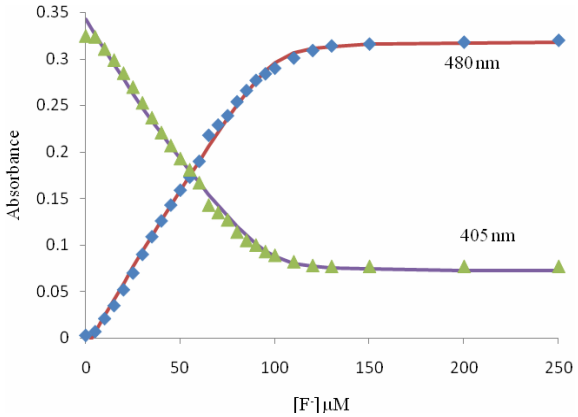


Figure S16: Plot of Absorbance Vs [F^-] on addition of F^- ions to solution of **3** in CH_3CN (points show the experimental results and line is curve fit)

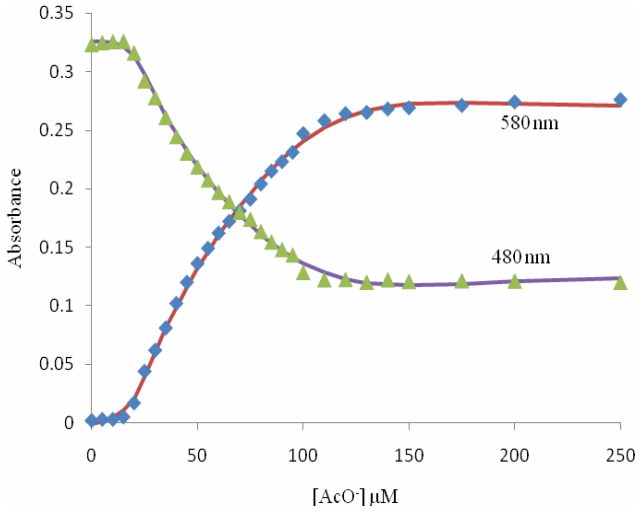


Figure S17: Plot of Absorbance Vs [F^-] on addition of F^- ions to solution of **3** in CH_3CN (points show the experimental results and line is curve fit)

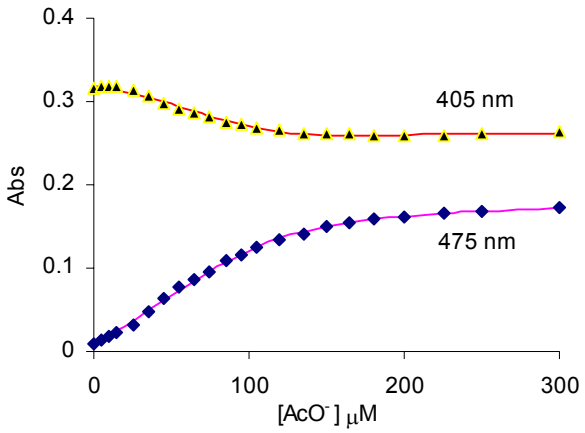


Figure S18: Plot of Absorbance Vs [AcO^-] on addition of AcO^- ions to solution of **3** in $CHCl_3$-MeOH (1:1) (points show the experimental results and line is curve fit)

Table S1. Binding Constants (k_a) of **2** (DMSO-CH_3CN; 20 :1 based on UV-Vis[a] and fluorescence[b] methods

Guest anion	K_a (M^{-1})[a]	K_a (M^{-1})[b]
F^-	1.62×10^5	1.21×10^5
AcO^-	1.54×10^4	-----
$H_2PO_4^-$	3.16×10^2	-----

----- could not be determined.

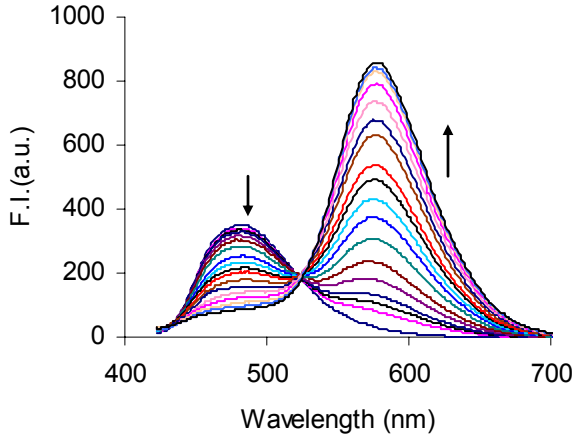


Figure S19: Effect of Acetate ions on Fluorescence spectrum of **3** (CH_3CN)

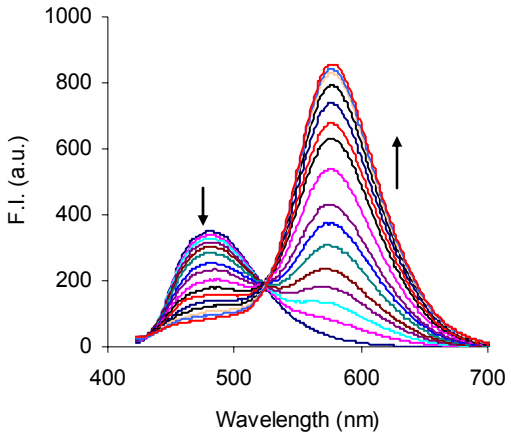


Figure S20: Effect of Fluoride ions on Fluorescence spectrum of **3** in CH_3CN

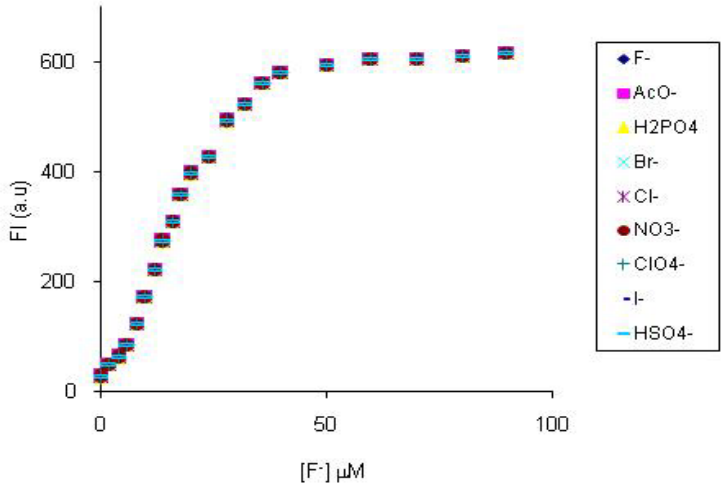


Figure S21. Estimation of fluoride ions using probe **2** (CH_3CN) in the presence of other anions

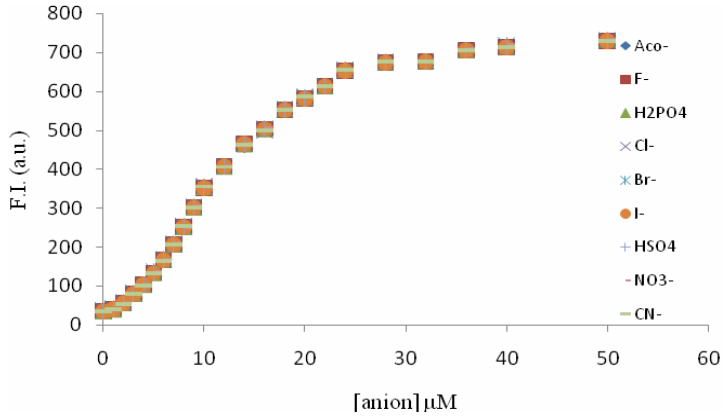


Figure S22. Estimation of acetate ions using probe **3** ($CHCl_3$ – MeOH, 1:1) in the presence of other anions

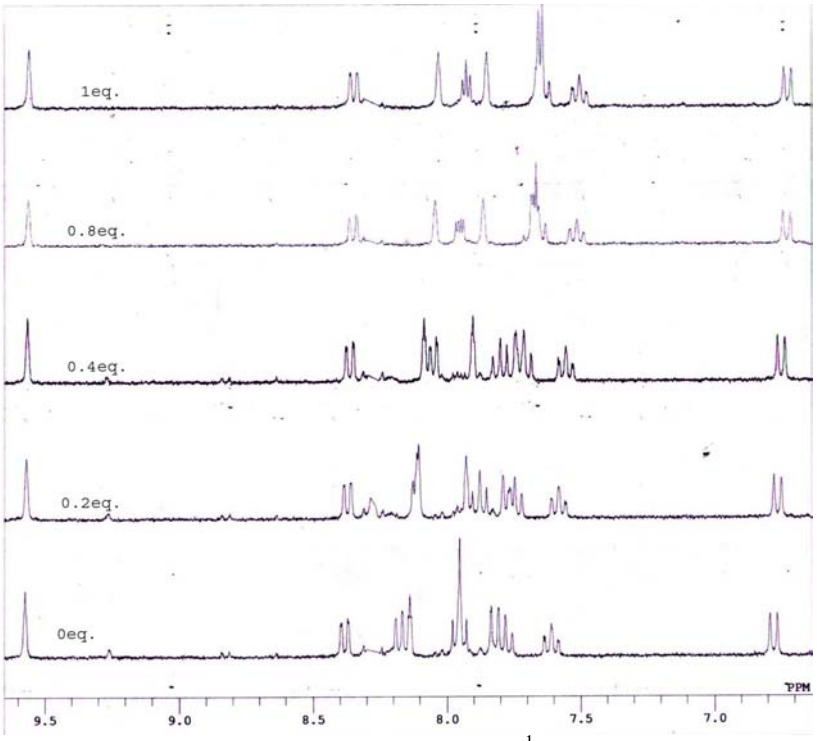


Figure S23: Effect of incremental addition of AcO^- on ^1H NMR Spectra of Chemosensor **3** (DMSO-d_6)

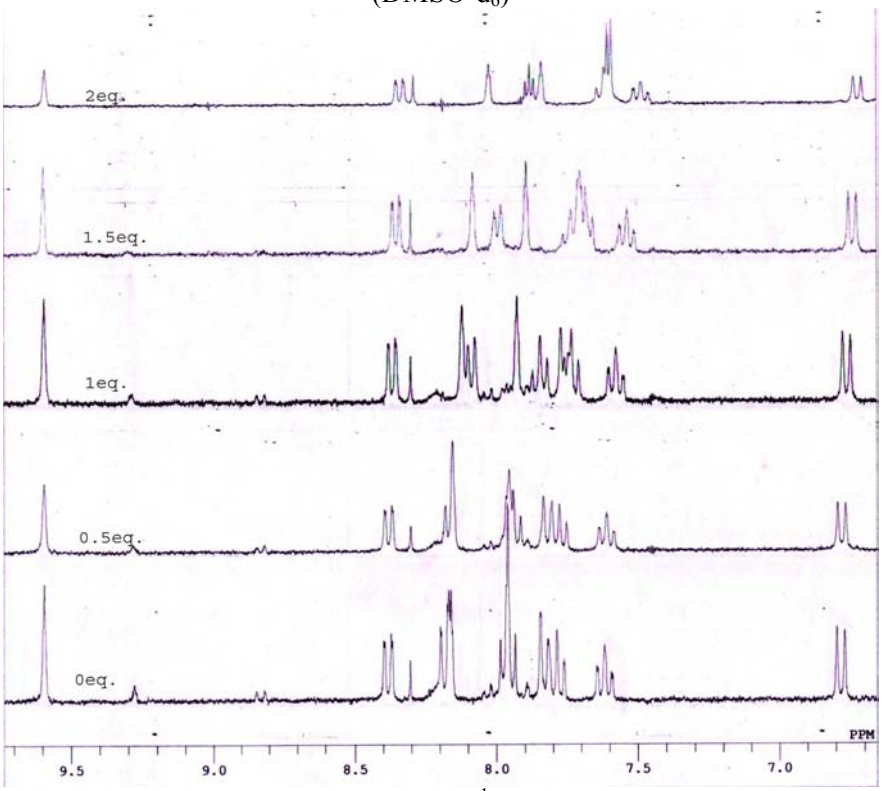


Figure S24: Effect of incremental addition of F^- on ^1H NMR Spectra of Chemosensor **3** (DMSO-d_6)