

Exclusive fluoride ion recognition and Fluorescence “turn-on” response with a label-free DMN Schiff base

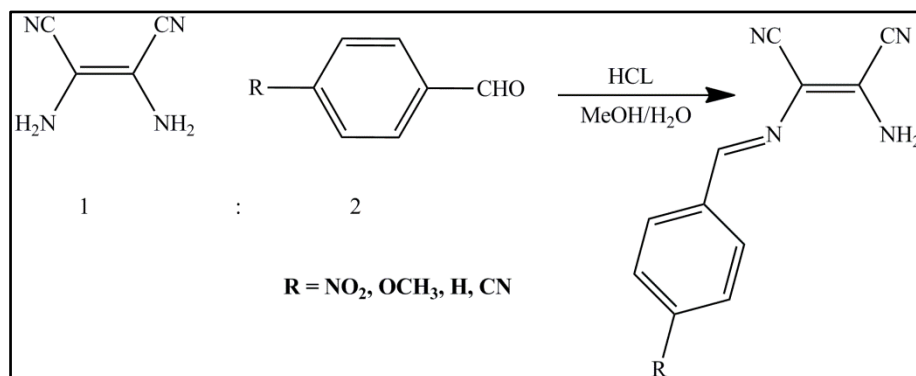
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1. General Information

All solvents and reagents were purchased from commercial sources and used without further purification except for dry THF which was further distilled. However anions in the form of Tetra butyl ammonium (TBA) salts were stored in a desiccator under vacuum containing silica. Mass spectra were recorded on a Bruker HR-MS spectrometer using CH₃CN as solvent. ¹³C and ¹H nmr spectra were recorded using a Bruker instrument operating at 400 and 500MHz. UV/Vis spectra were recorded on Perkin Elmer spectrophotometer, lambda 25. Fluorescence emission spectra were recorded on a Horiba Jovin Vyon Fluoro log 3-111 spectrophotometer. Titration were performed on 2.5mL samples of solutions of receptors (10, 20 or 30μM) in dry THF, by addition of THF (dry) stock solutions of the appropriate anions. The synthesis of all the receptor derivatives was carried out openly in the ambient lab conditions.

2. Synthesis and characterisation of compounds



All the receptor derivatives (**1-4**) were synthesised by the same procedure mentioned below:

To the stirring solution of 2-equivalents of aldehyde (para substituted benzaldehydes) in distilled water. Add 2-3 drops of conc. HCl, followed by drop wise addition of methanolic solution of 1 equivalents of diaminomalenonitrile (DMN). The resulted imine solidifies within a minute, was filtered, washed with water and recrystalized with ethanol, and finally characterised with standard spectroscopic techniques like NMR and HR MS.

Receptor 1.

(Yellow colour, 95% yield); ^1H NMR- (500MHz; d_6 -DMSO): δ 8.38 (s, 1H), 8.36 (s, 2H), 8.31 (d, $J = 5\text{Hz}$, 2H), 8.33 (d, $J = 5\text{Hz}$, 2H). ^{13}C NMR- (500MHz; d_6 -DMSO): δ 152.68, 149.00, 141.74, 130.22, 129.07, 124.20, 114.58, 113.97, 102.36. MS (HRMS, negative mode) found 241.061. $\text{C}_{11}\text{H}_7\text{N}_5\text{O}_2$ requires 241.060.

Receptor 2.

(Yellow colour, 95% yield); ^1H NMR- (500MHz; d_6 -DMSO): δ 8.22 (s, 1H), 7.78 (s, 2H), 3.84 (s, 3H), 8.00 (d, $J = 10\text{Hz}$, 2H), 7.04 (d, $J = 10\text{Hz}$, 2H). ^{13}C NMR- (500MHz; d_6 -DMSO): δ 162.52, 155.13, 131.44, 128.81, 126.40, 115.09, 114.76, 114.29, 103.50, 55.86. MS (HRMS, positive mode) found 227.092. $\text{C}_{12}\text{H}_{11}\text{N}_4\text{O}$ requires 227.093.

Receptor 3.

(Yellow colour, 90% yield); ^1H NMR- (500MHz; CDCl_3): δ 8.46 (s, 2H), 7.29 (s, 1H), 7.86 (d, J = 5Hz, 2H), 7.54 (d, J = 5Hz, 2H), 7.49 (t, J = 15Hz, 1H). ^{13}C NMR- (500MHz; d_6 -DMSO): δ 159.19, 134.67, 132.53, 129.30, 129.21, 129.04, 124.61, 113.47, 112.29. MS (HRMS, negative mode) found 196.076. $\text{C}_{11}\text{H}_9\text{N}_4$ requires 196.075.

Receptor 4.

(Yellow colour, 95% yield); ^1H NMR- (500MHz; d_6 -DMSO): δ 8.31 (s, 1H), 8.26 (s, 2H), 8.23 (d, J = 5Hz, 2H), 7.93 (d, J = 10Hz, 2H). ^{13}C NMR- (500MHz; d_6 -DMSO): δ 153.13, 140.05, 133.02, 129.81, 128.89, 119.12, 114.58, 113.94, 113.30, 102.33. MS (HRMS, negative mode) found 221.071. $\text{C}_{12}\text{H}_7\text{N}_5$ requires 221.070.

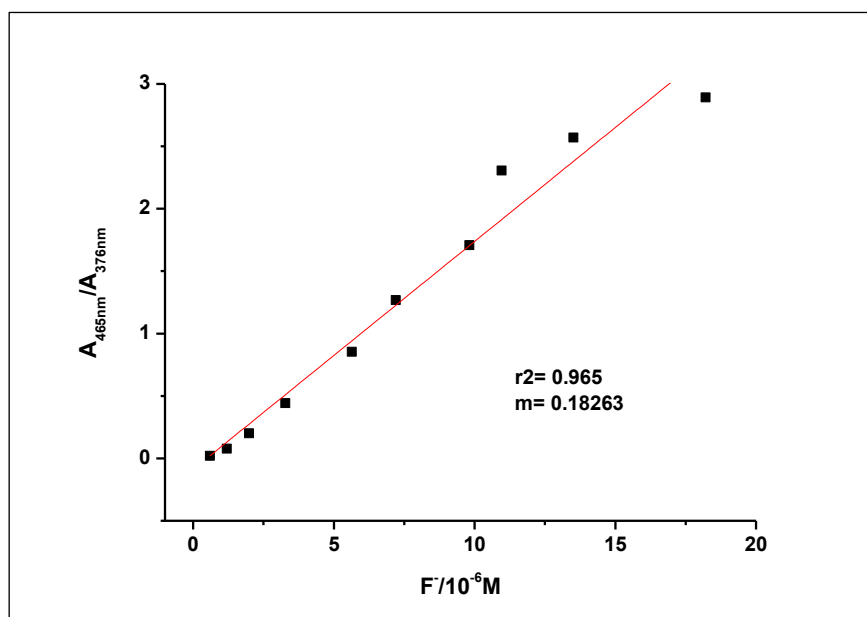
3. Photo physical properties of all receptor derivatives

Receptor	λ_{abs} (nm)	E ($\text{Lmol}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{abs}}\text{F}$ (nm)	$\Delta\lambda$ (nm)	λ_{em} (nm)	$\lambda_{\text{em}}\text{F}$ (nm)
CN	376	33160	465	89	404(w) , 426(m)	404(h), 423(h)
NO_2	393	34894	650	167	501(w)	485(w)
H	363	20841	422	59	428(w)	425(w)
OCH_3	373	43885	423	50	438(w)	436(w)

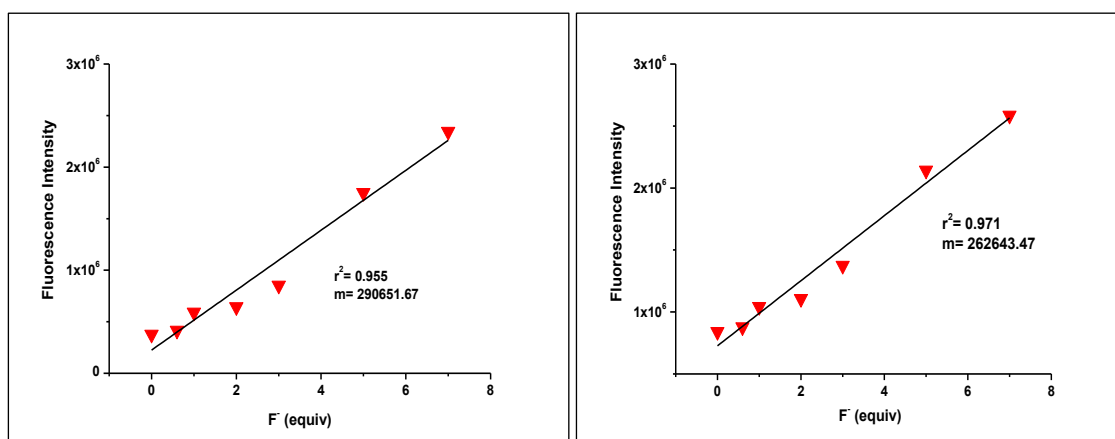
Table 1. Photo physical properties of receptors (1-4).

Where λ_{abs} (nm), λ_{em} (nm), $\lambda_{\text{em}}\text{F}$ (nm) and $\lambda_{\text{abs}}\text{F}$ (nm) refers to the absorption and emission bands of each receptor derivatives in the absence and presence of the fluoride ion respectively. **E** represents the extinction coefficient and $\Delta\lambda$ (nm) indicates the red shift of the absorption bands. The blue shift of the emission band mentioned here has been observed with the addition of just 10 equivalents of the TBAF (10 μM) and continues with the further additions. ‘w’, ‘m’ and ‘h’ refers to the weak, moderate and high intensity of the emission bands.

4. Ratiometric responses of receptor 4 with fluoride ion

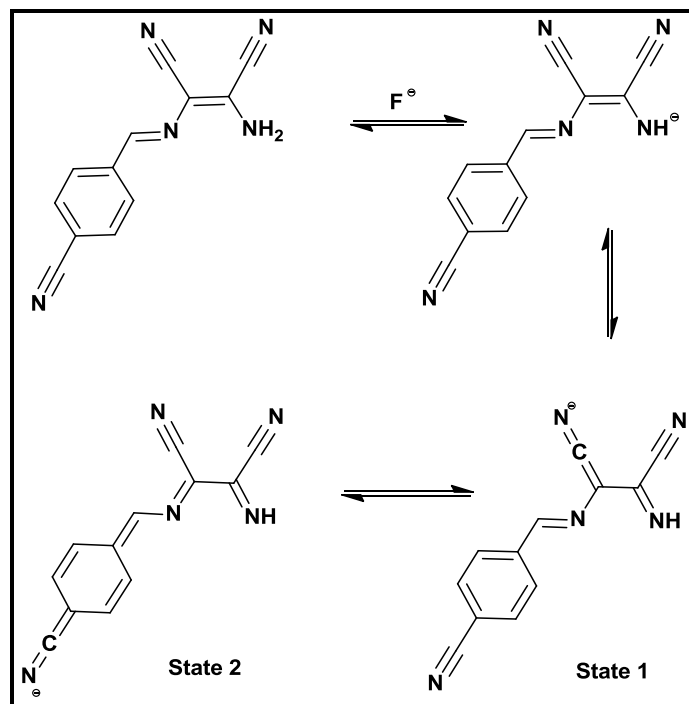


- (a) Absorbance ratio metric plot ($A_{465\text{nm}}/A_{376\text{nm}}$) Vs. F , demonstrating the potential utility of receptor for calibrating and determining fluoride ion concentration in Micro molar range.

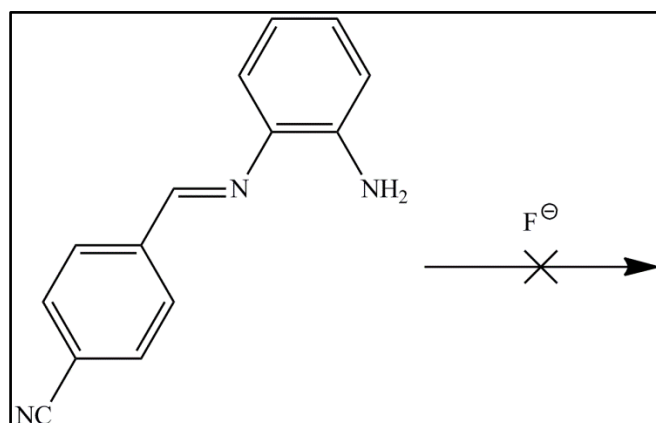


- (b) Plot showing variation of Fluorescence intensity at the two wavelengths (404 and 426nm) with respect to the various equivalent additions of Fluoride ion ($10\mu\text{M}$).

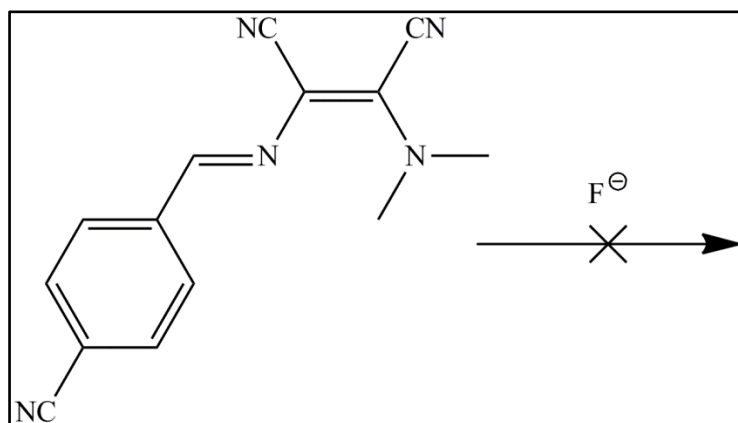
5. Proton transfer signalling mechanism



6. Schemes to cross check proposed recognition mechanism

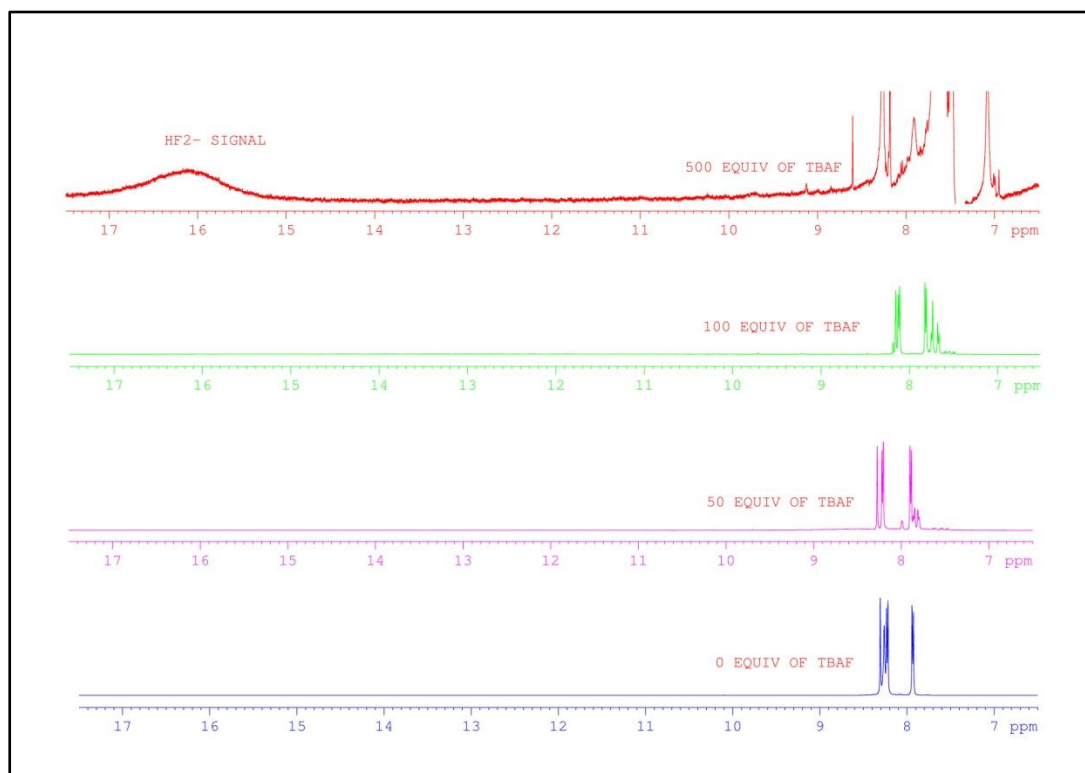


Scheme 1A. Cross checking the acidic nature of receptor **4**



Scheme 1B. N-dimethylated derivative **4** remains inactive with F^- .

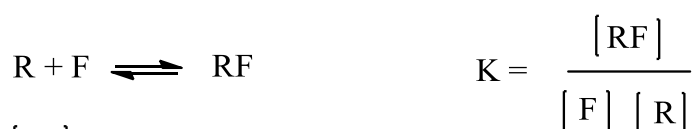
7. ^1H NMR Titration of **4** with fluoride.



^1H NMR titration of Receptor **4** with 0-500 Equivalents of TBAF reporting formation of HF_2^- dimer at high concentrations.

8. Binding constant calculations and nonlinear curve fittings

On the basis of 1:1 stoichiometry, the binding constants (K) of receptors (**1-4**) with fluoride were calculated from absorption studies by below equation, using the nonlinear least squares curve-fitting, of (ΔA vs. F) with the help of Pro FIT software, Version 6.1.16.

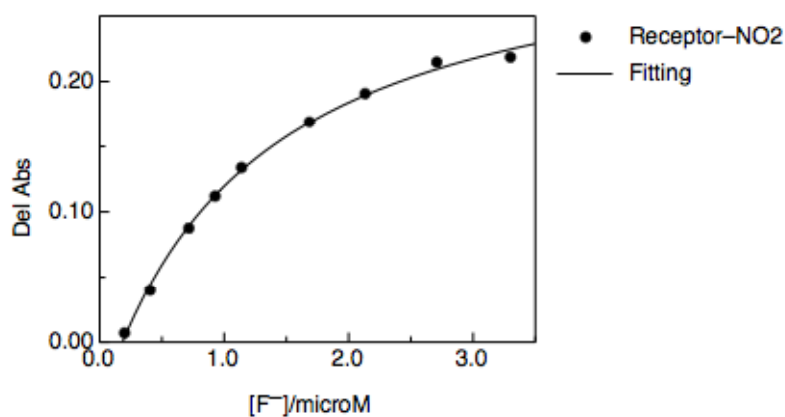


[R] = Receptor concentration

[F] = Fluoride concentration

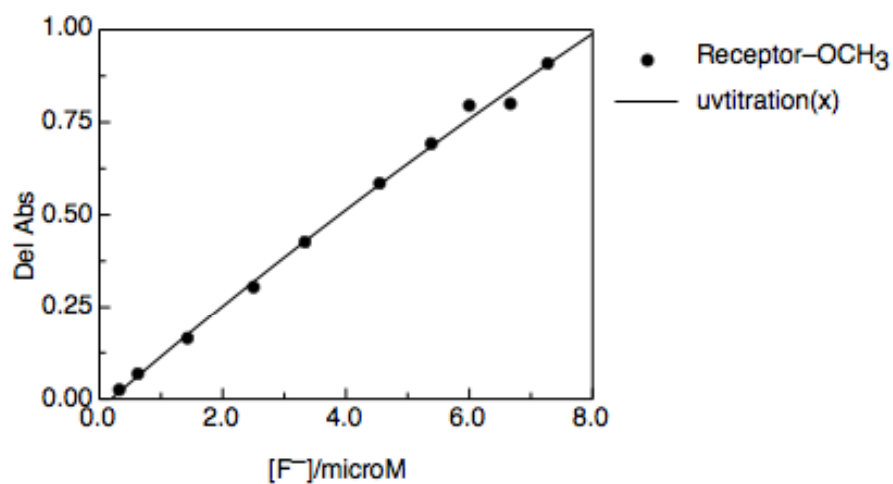
After solution, we have;

$$[R] = ([R]_0 - [F]_0 - 1/K) / 2 \pm \sqrt{([R]_0 + [F]_0 + 1/K)^2 / 4 - [R]_0 [F]_0}$$



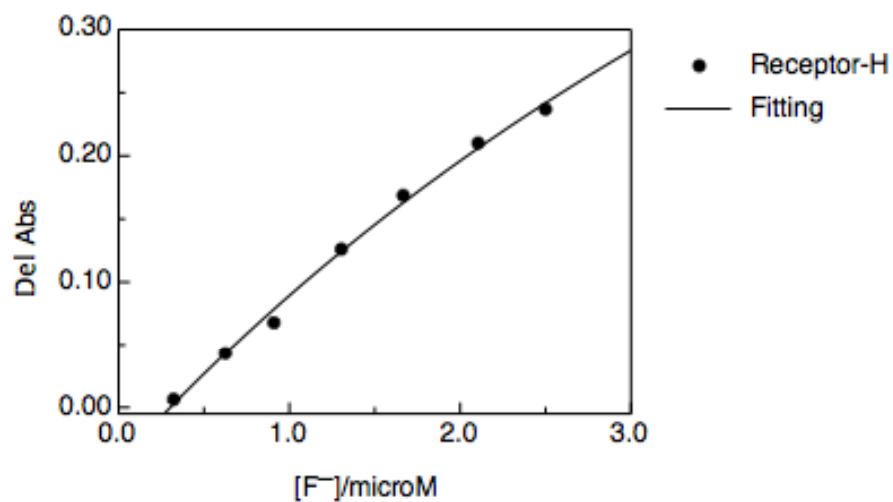
Parameters:		Standard deviations:	
K	= 8588.0415	ΔK	= 976.8324
Guesto	= 1.0000e-5		
AbsComp	= 0.3697	ΔAbsComp	= 8.7319e-3

(a) Nitro derivative (**1**)



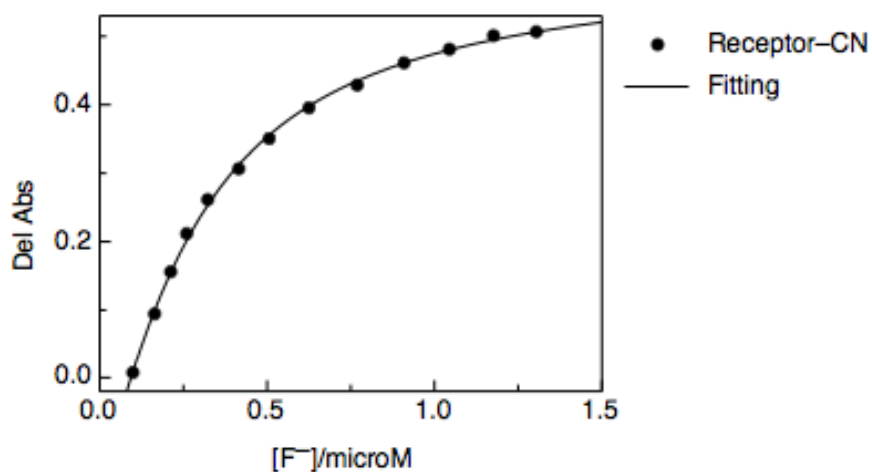
Parameters:		Standard deviations:	
K	= 170.2059	ΔK	= 138.6586
Guesto	= 2.0000e-5		
AbsComp	= 8.5028	$\Delta\text{AbsComp}$	= 6.1270

(b) Methoxy derivative (2)



Parameters:		Standard deviations:	
K	= 1291.0248	ΔK	= 809.7425
Guesto	= 2.5000e-5		
AbsComp	= 1.1912	$\Delta\text{AbsComp}$	= 0.5317

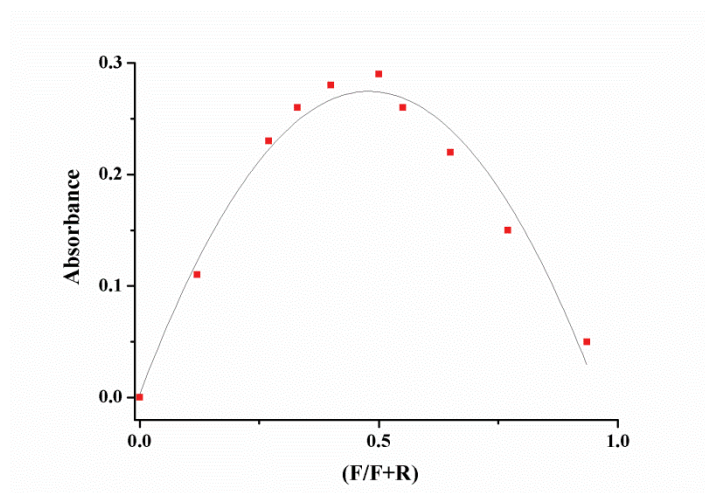
(c) Unsubstituted receptor derivative (**3**)



Parameters:		Standard deviations:	
K	= 5.3567e+4	ΔK	= 3459.1312
Guesto	= 2.0000e-5		
AbsComp	= 0.7845	$\Delta\text{AbsComp}$	= 8.0371e-3

(d) Cyano derivative (**4**)

9. Jobs plot of receptor 4 with fluoride ion



Jobs plot for receptor **4** and F⁻ ion confirming 1:1 stoichiometry. F= moles of F⁻ and R= moles of receptor.