Supplementary Material (ESI) for RSC Advances

Colorimetric receptors for naked eye detection of inorganic fluoride ion in aqueous media using ICT mechanism

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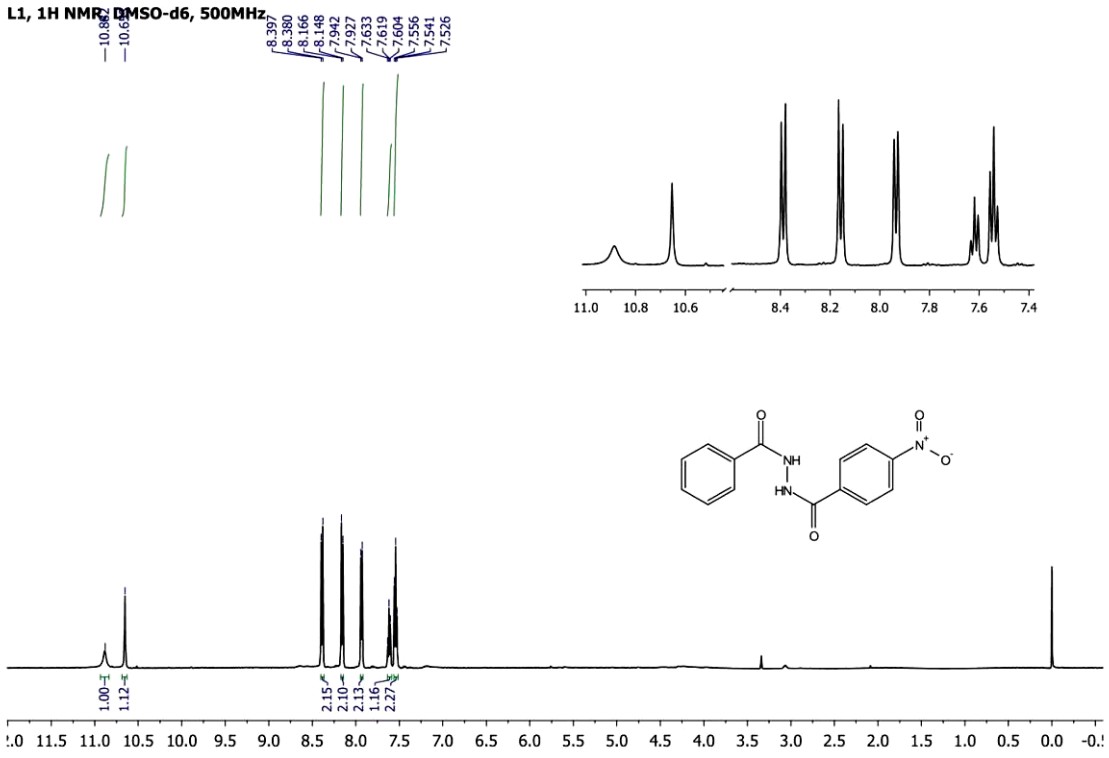

Figure S1. ^{1}H NMR spectra of L1.

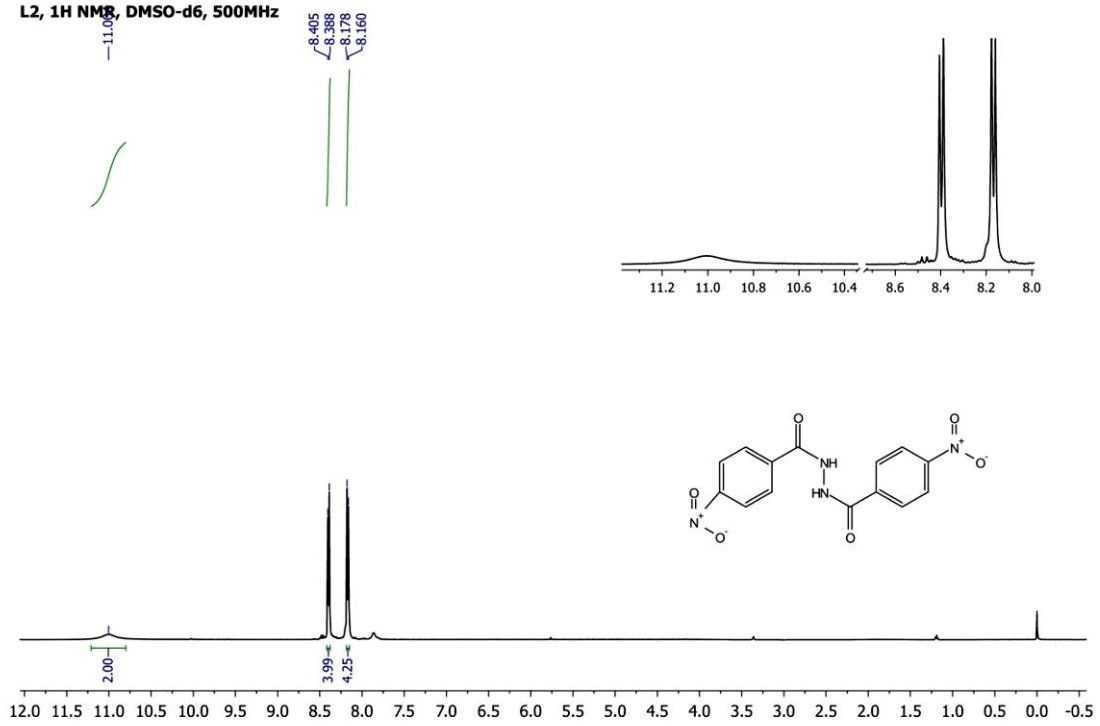

Figure S2. ^{1}H NMR spectra of L2.

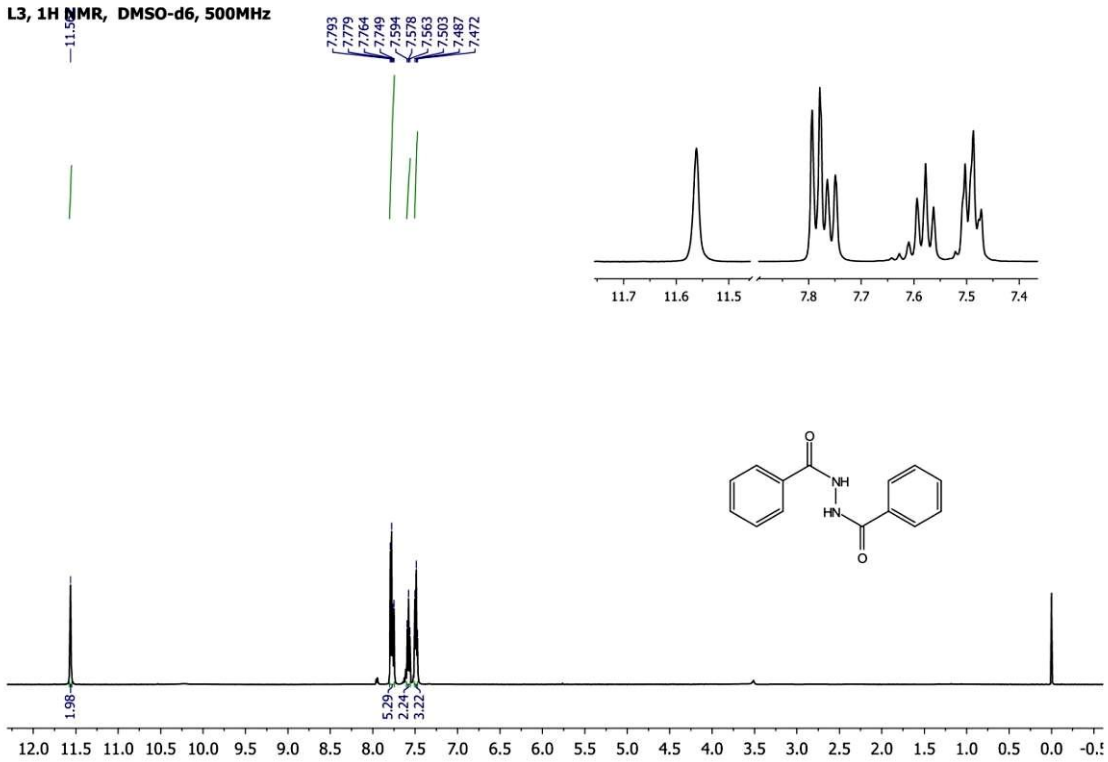

Figure S3. ^{1}H NMR spectra of L3.

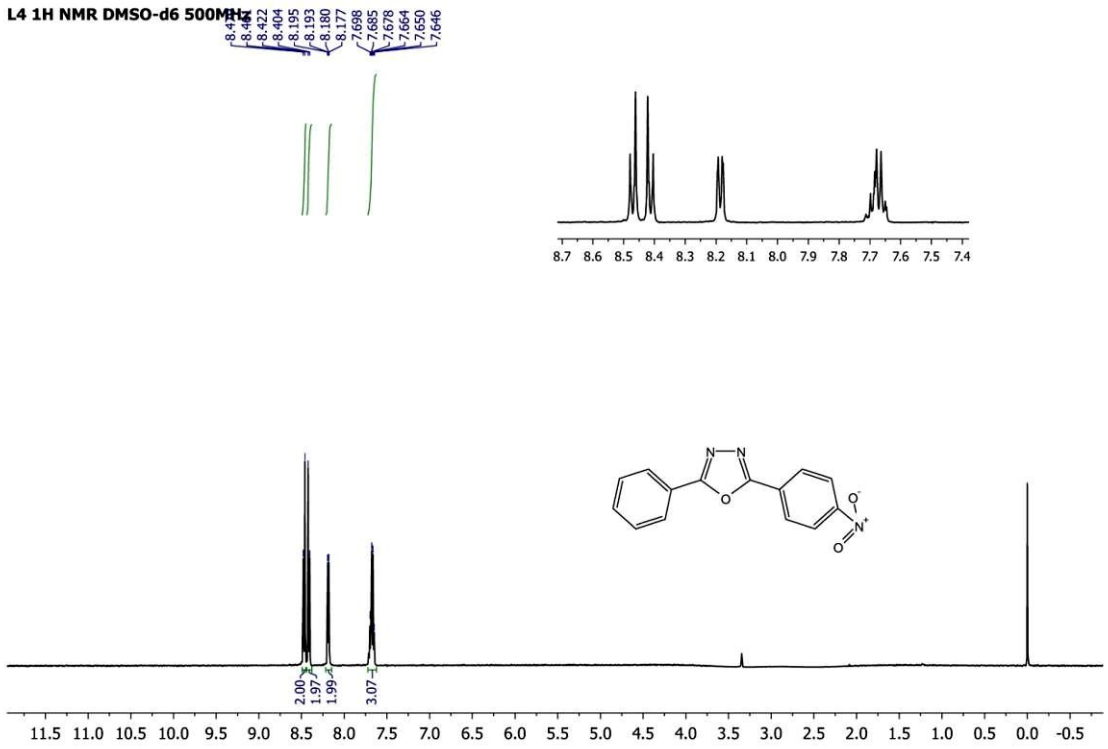

Figure S4. ^{1}H NMR spectra of L4.

Photographs:

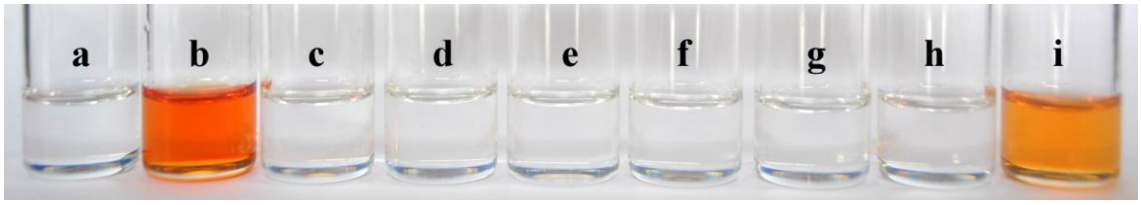

Figure S5. Change in colour of L1 (2.5×10^{-5}M) in DMSO solution with the addition of 1 equiv. of tetrabutylammonium anions. (a)Free Receptor L1, (b) F^-, (c) Cl^-, (d) Br^- (e) I^-, (f) NO_3^-, (g) HSO_4^-, (h) $H_2PO_4^-$ and (i) AcO^-.

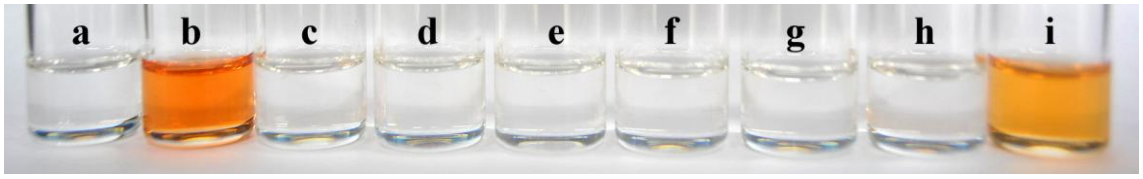

Figure S6. Change in colour of L2 (2.5×10^{-5}M) in DMSO solution with the addition of 1 equiv. of tetrabutylammonium anions. (a) Free Receptor L2, (b) F^-, (c) Cl^-, (d) Br^- (e) I^-, (f) NO_3^-, (g) HSO_4^-, (h) $H_2PO_4^-$ and (i) AcO^-.

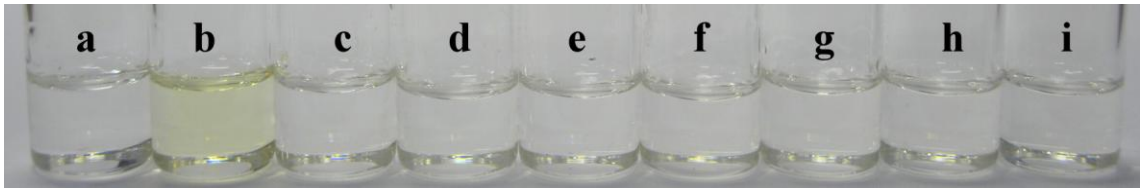

Figure S7. Change in colour of L3 (5×10^{-5}M) in DMSO solution with the addition of 10 equiv. of tetrabutylammonium anions. (a) Free Receptor L3, (b) F^-, (c) Cl^-, (d) Br^- (e) I^-, (f) NO_3^-, (g) HSO_4^-, (h) $H_2PO_4^-$ and (i) AcO^-.

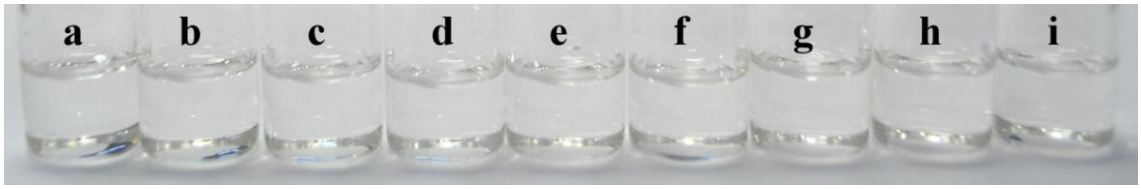

Figure S8. Change in colour of L4 (5×10^{-5}M) in DMSO solution with the addition of 10 equiv. of tetrabutylammonium anions. (a) Free Receptor L4, (b) F^-, (c) Cl^-, (d) Br^- (e) I^-, (f) NO_3^-, (g) HSO_4^-, (h) $H_2PO_4^-$ and (i) AcO^-.

On addition of 1 equiv. of TBA salts of anions to the receptors L3 and L4, change in the colour was not observed and hence used 10 equiv. of TBA salts of anion. Receptor L3 showed a slight colour change from colourless to yellow on addition of F^- ions. However, in case of L4 no colour change was observed which confirms the role of –NH in binding process of F^- ion.

Figure S9. Photograph of L1 solution (2.5×10^{-5}M) in DMSO after the addition of 1 equiv. of tetrabutylammonium fluoride and 1 equiv. of other anions. (a) Free Receptor L1, (b) F^-, (c) Cl^- + F^-, (d) Br^- + F^- (e) I^- + F^-, (f) NO_3^-+F^-, (g) HSO_4^-+F^- and (h) H_2PO_4+F^-.

Figure S10: Photograph of L2 solution (2.5×10^{-5}M) in DMSO after the addition of 1 equiv. of tetrabutylammonium fluoride and 1 equiv. of other anions. (a) Free Receptor L2, (b) F^-, (c) Cl^- + F^-, (d) Br^- + F^-, (e) I^- + F^-, (f) NO_3^-+F^-, (g) HSO_4^-+F^- and (h) H_2PO_4+F^-.

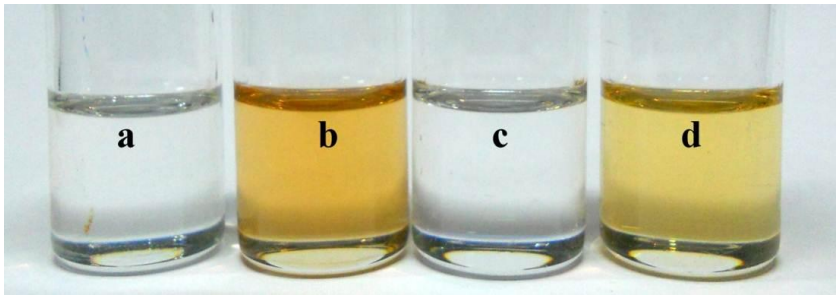

Figure S11: Change in colour after addition of 1 equiv. of NaF solution in H_2O to the receptor solution (2.5×10^{-5}M) in DMSO:H_2O (9:1 v/v). (a) Receptor L1, (b) L1+NaF, (c) Receptor L2 and (d) L2+NaF.

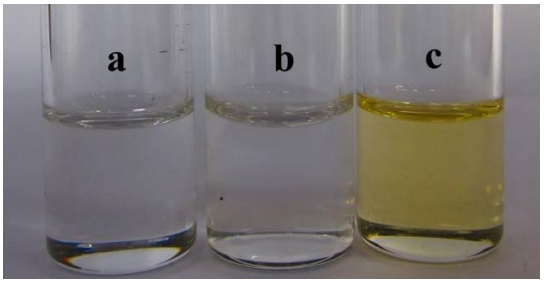

Figure S12: Change in colour after addition of a drop of sea water to the receptor solution (5×10^{-5}M) in DMSO:H_2O (9:1 v/v). (a) Receptor L1, (b) Sea water and (c) L1+ a drop of Sea water.

The sea water was collected from Arabian Sea at National Institute of Technology Karnataka, Surathkal. (latitude13°0'33.99", longitude 74°47'17.23").

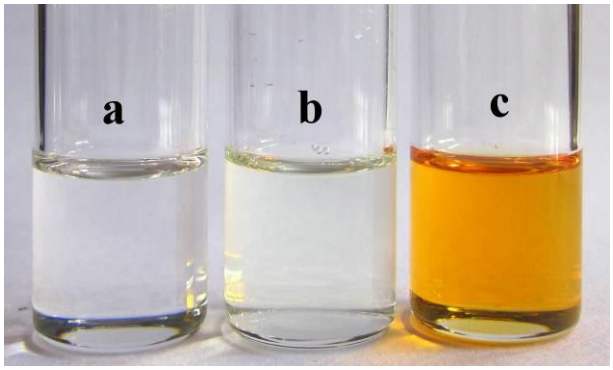

Figure S13: Change in colour after addition of a drop of commercial mouthwash to the receptor solution (5×10^{-5}M) in DMSO:H_2O (9:1 v/v). (a) Receptor L1, (b) Commercial mouthwash and (c) L1+ a drop of commercial mouthwash.

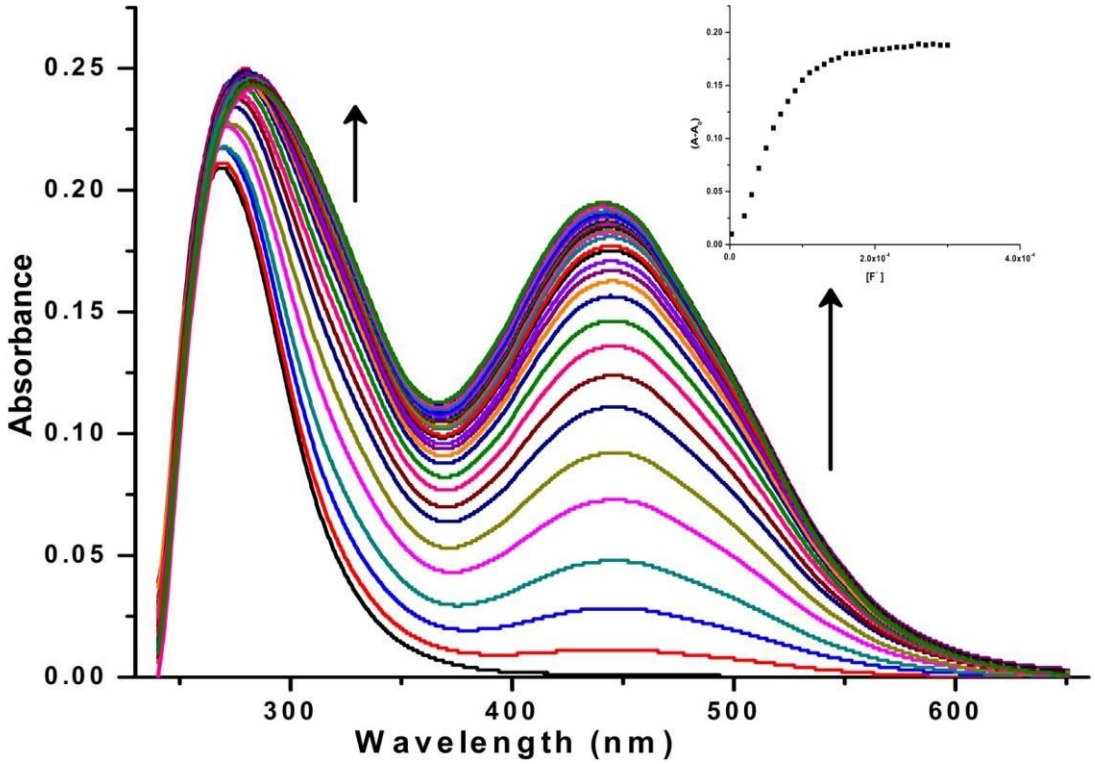

Figure S14: UV-Vis spectra of L1 (2.5×10^{-5}M) with the increasing concentration of TBAF (0–10 equiv.) in dry DMSO. Inset: corresponding titration plot of L1 at 446 nm ($A-A_0$) vs [F^-].

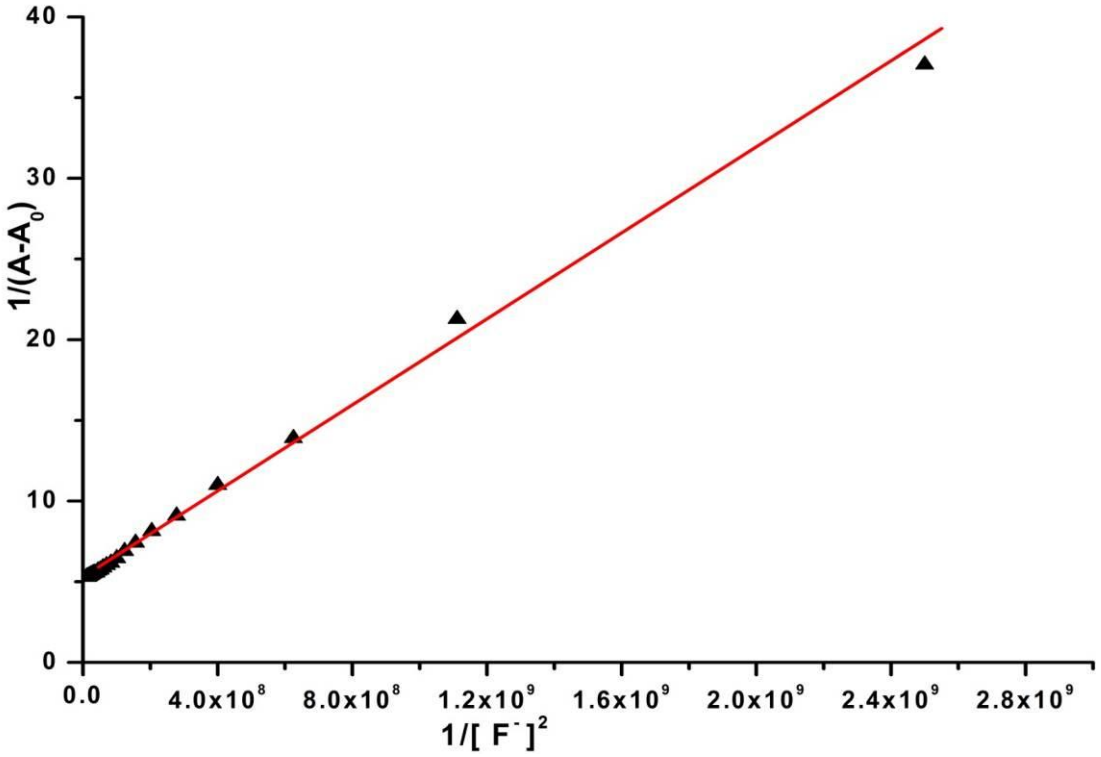

Figure S15: Benesi - Hildebrand plot of receptor L1 binding with F^- ion associated with absorbance change at 446 nm in dry DMSO solvent.

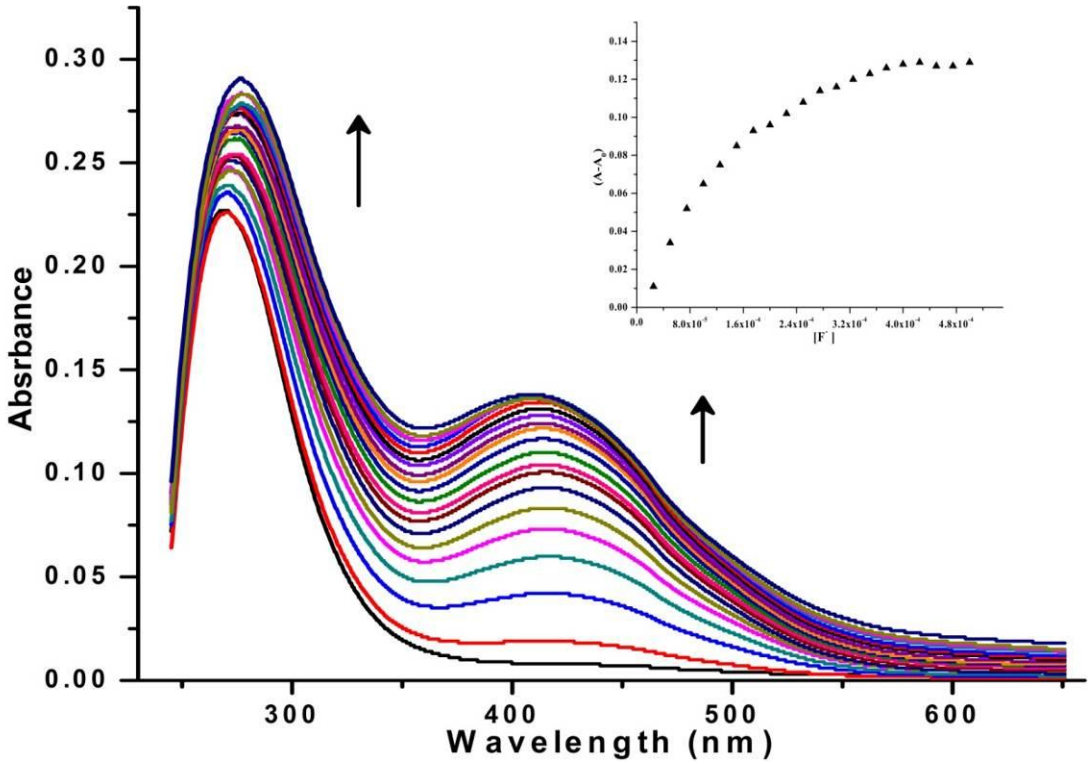

Figure S16: UV-Vis spectra of L1 (2.5×10^{-5}M) with the increasing concentration of NaF (0–20 equiv.) in DMSO:H_2O (9:1 v/v). Inset: corresponding titration plot of L1 at 417 nm (A-A_0) vs. [F^-].

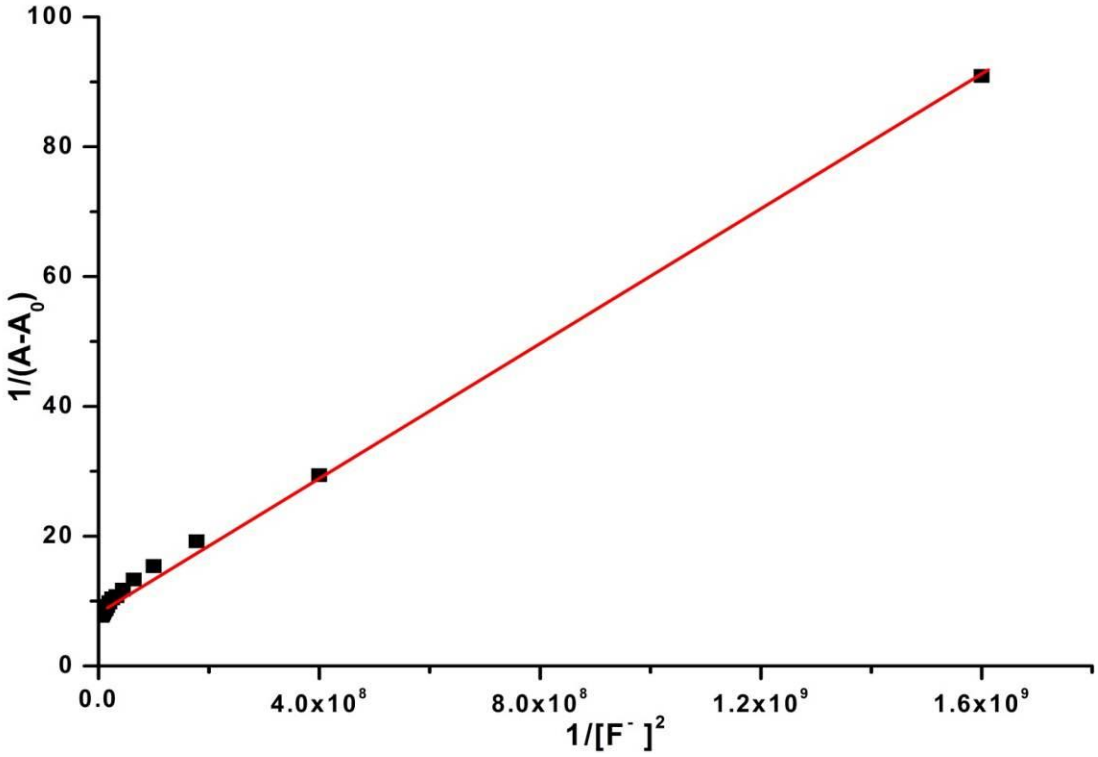

Figure S17: Benesi - Hildebrand plot of receptor L1 binding with F^- ion associated with absorbance change at 417 nm in DMSO:H_2O (9:1 v/v) solvent.

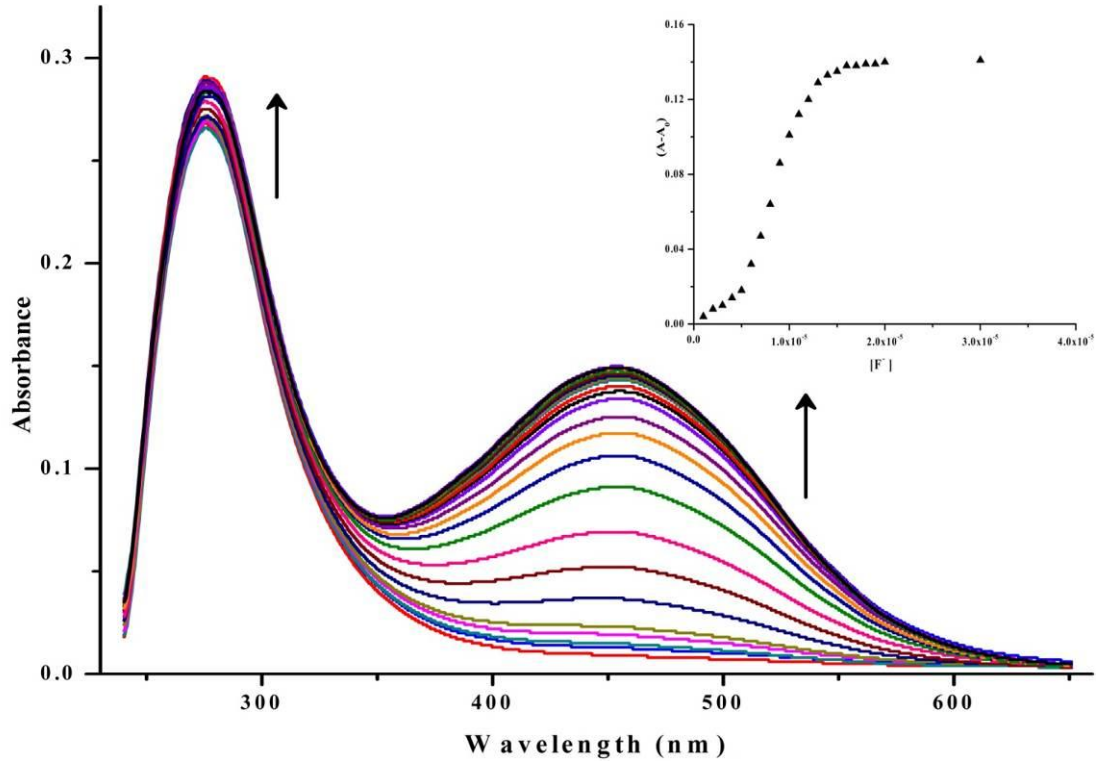

Figure S18: UV-Vis spectra of L2 (2.5×10^{-5}M) with the increasing concentration of TBAF (0–10 equiv.) in dry DMSO. Inset: corresponding titration plot of L2 at 452 nm ($A-A_0$) vs. [F^-].

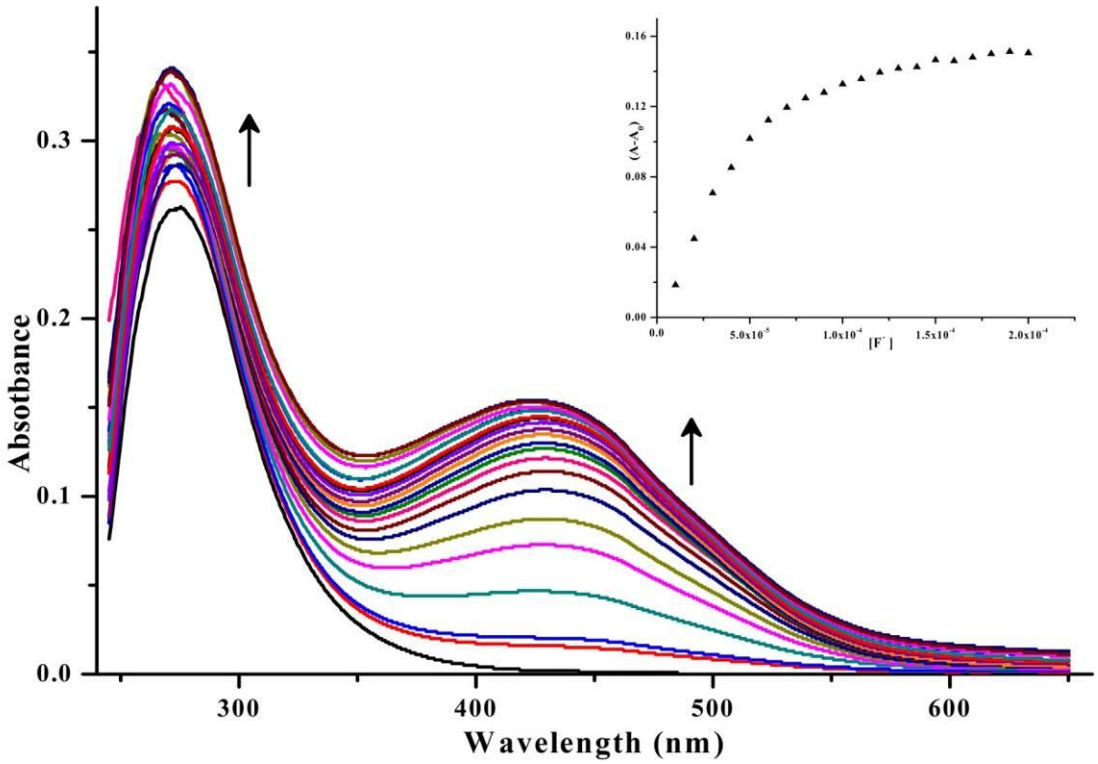

Figure S19: UV-Vis spectra of L2 (2.5×10^{-5}M) with the increasing concentration of NaF (0–20 equiv.) in DMSO:H_2O (9:1 v/v). Inset: corresponding titration plot of L2 at 431 nm ($A-A_0$) vs. [F^-].

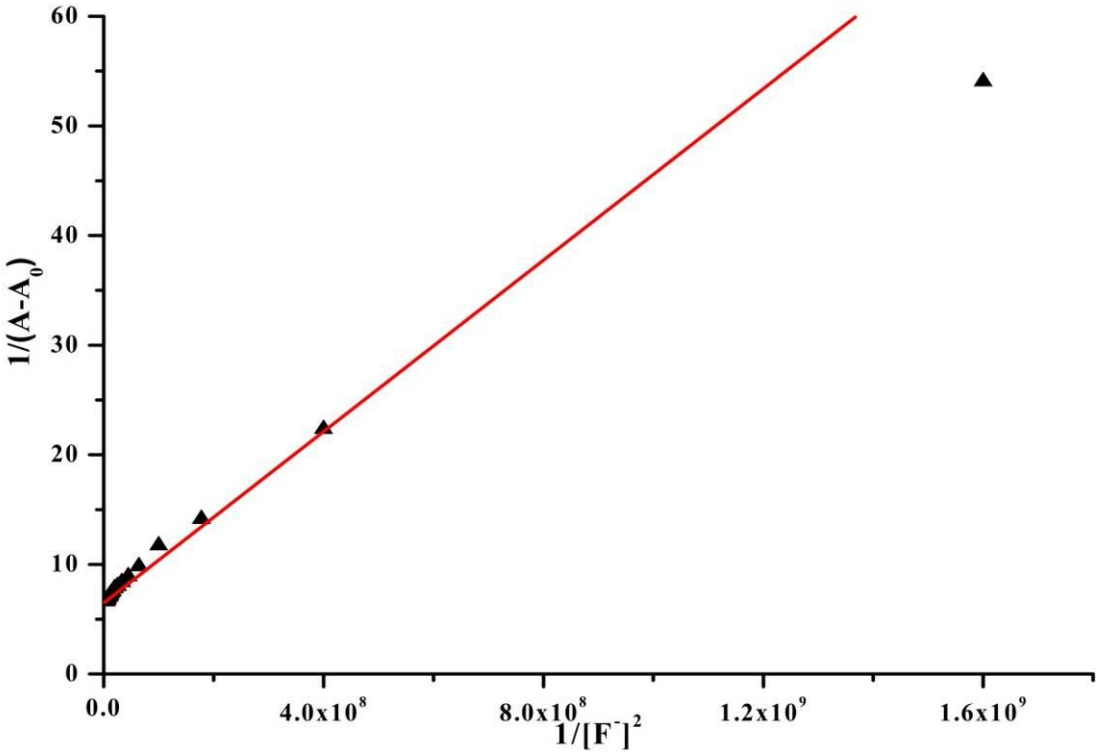

Figure S20: Benesi - Hildebrand plot of receptor L2 binding with F^- ion associated with absorbance change at 431 nm in DMSO:H_2O (9:1 v/v) solvent.

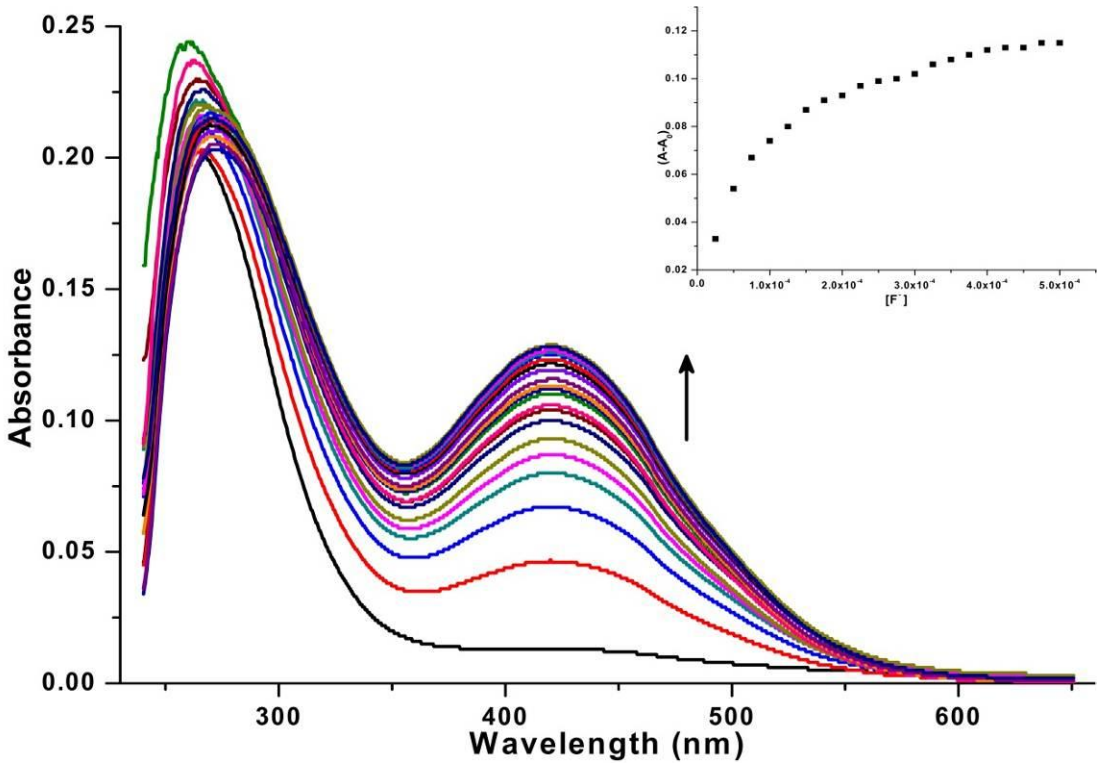

Figure S21: UV-Vis spectra of L1 (2.5×10^{-5}M) with the increasing concentration of TBAF (0–20 equiv.) in DMSO:H_2O (9:1 v/v). Inset: corresponding titration plot of L1 at 421 nm ($A-A_0$) vs. [F^-].

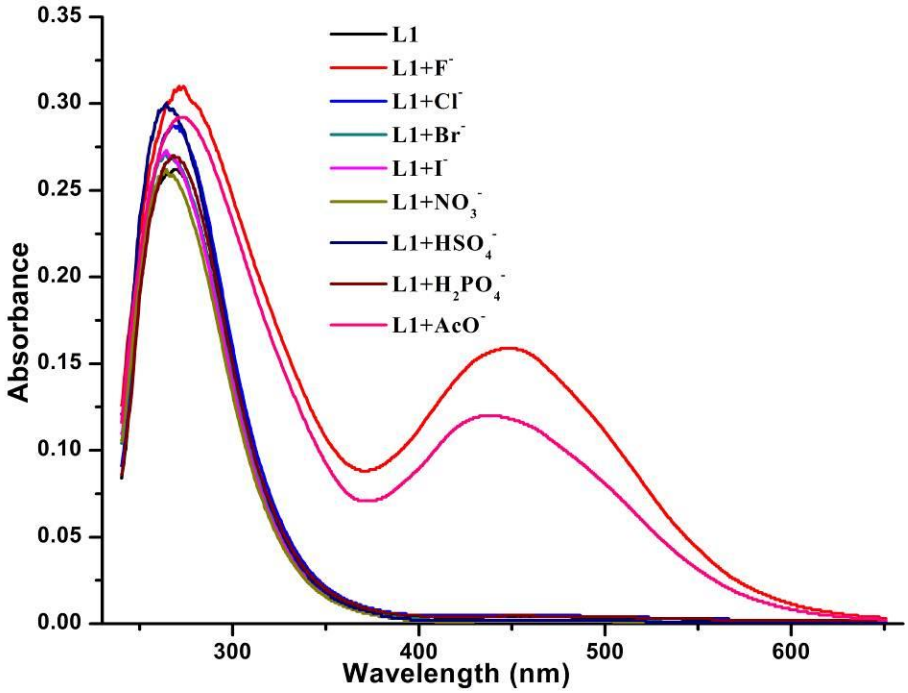

Figure S22: UV–Vis changes of L1 in DMSO ($2.5 \text{ X } 10^{-5}$M) after addition of 10 equiv of different anions in the form of TBA salts.

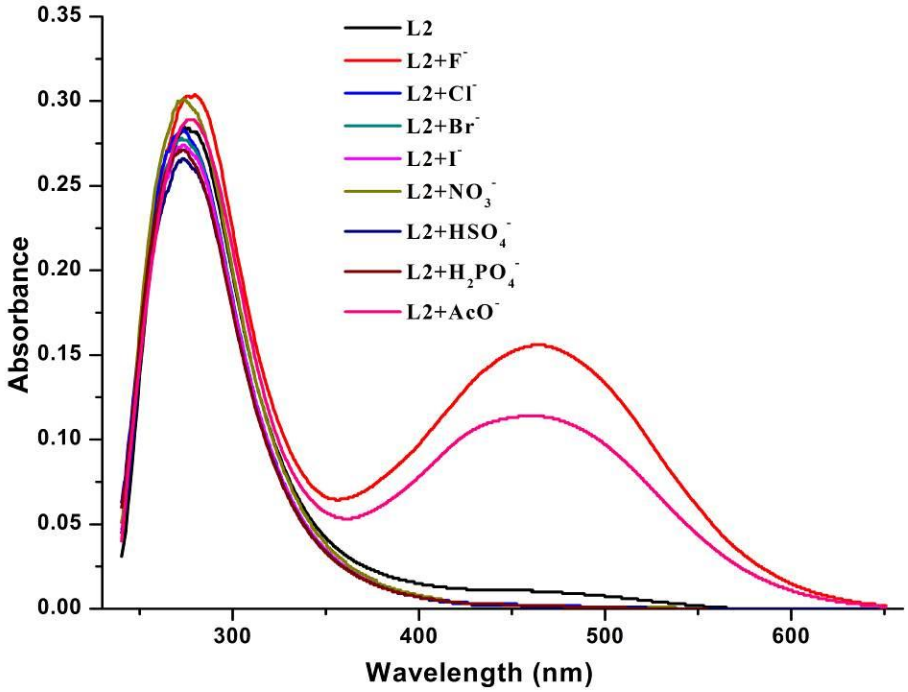

Figure S23: UV–Vis changes of L2 in DMSO (2.5 X 10^{-5}M) after addition of 10 equiv of different anions in the form of TBA salts.

Calibration curve:

The calibration curve was established by plotting a graph of absorbance vs concentration of F^- ion. A set of standard solutions of NaF was prepared in standard flasks. Absorbance at 417 nm for each standard solution was recorded.

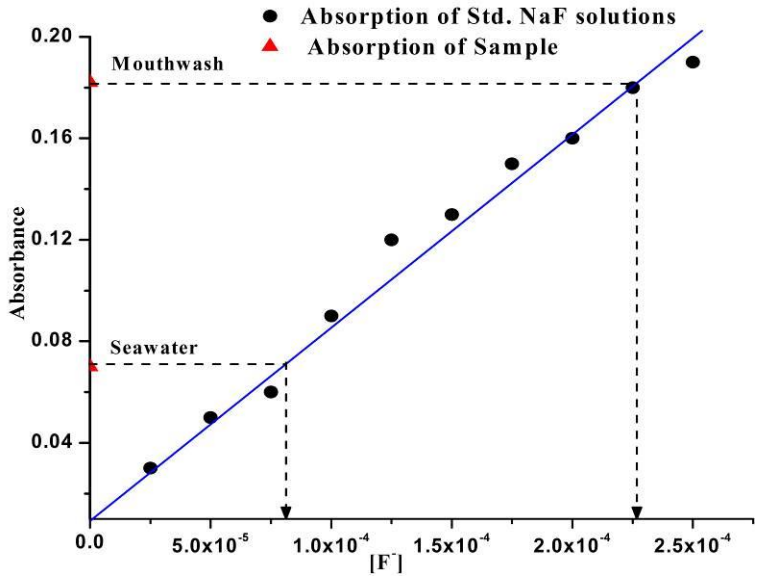

Fig. S24: Calibration curve to detrmine the amount of F^- ions in seawater/mouthwash sample.

The mouthwash sample was diluted by 50 times before analysis. Hence the value obtained from the standard plot was multiplied by the proper dilution factor to calculate actual fluoride ion concentration in mouthwash.

Binding constant:

Binding constant was calculated using equation (1).

$$\frac{1}{(A - A_0)} = \frac{1}{(A_{max} - A_0)} + \frac{1}{K[F^-]^n(A_{max} - A_0)} \quad \ldots\ldots\ldots\ldots (1)$$

Where, A_0, A, A_{max} are the absorption considered in the absence of F^-, at an intermediate, and at a concentration of saturation. K is binding constant, $[F^-]$ is concentration of F^- ion and n is the stoichiometric ratio.