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Supporting Information

Naked-eye detection of inorganic fluoride in aqueous media using a new azo-azomethine colorimetric receptor enhanced by electron withdrawing groups

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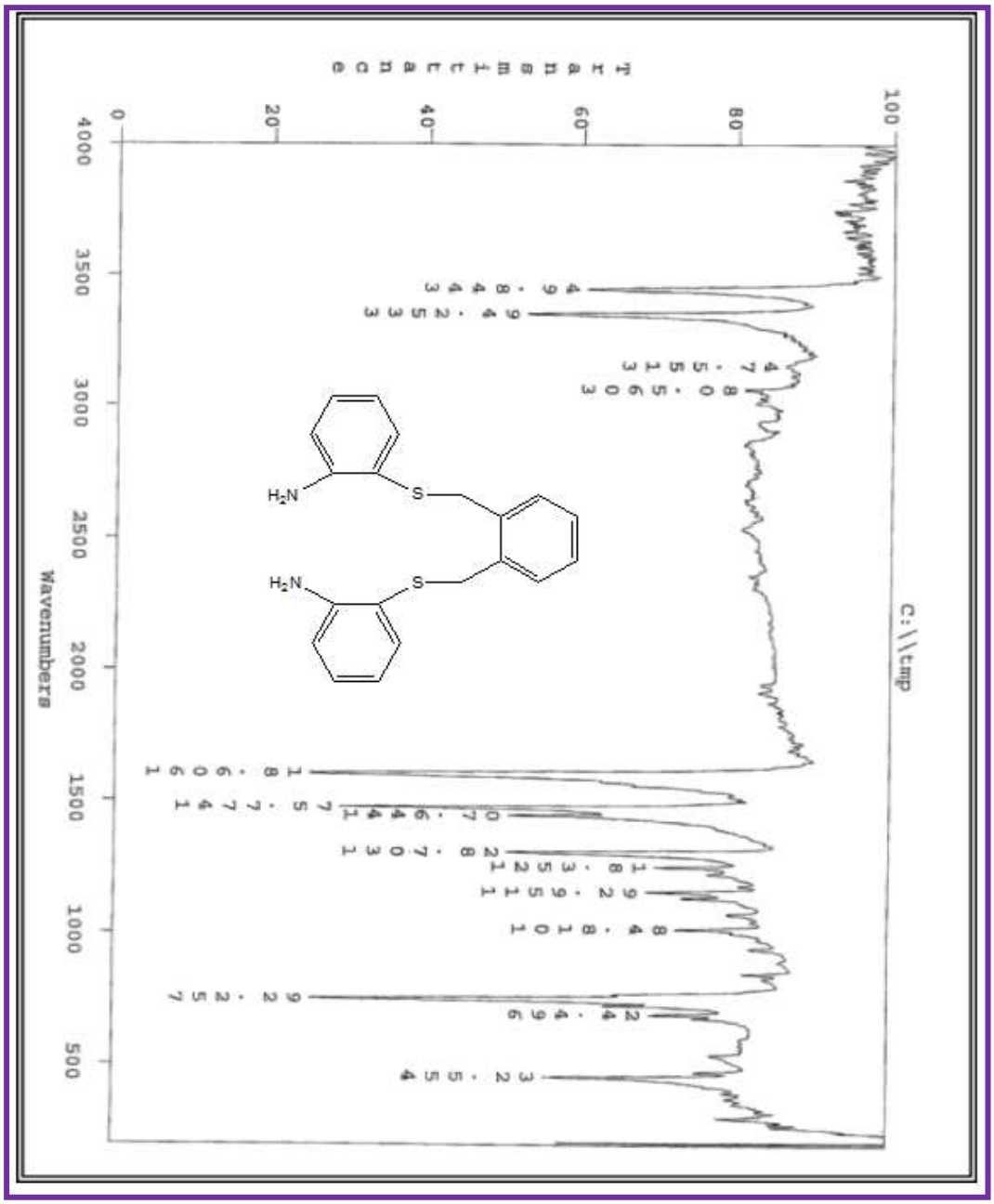

Figure S1. IR spectrum of α,α′-Bis(o-aminophenylthio)-1,2-xylene

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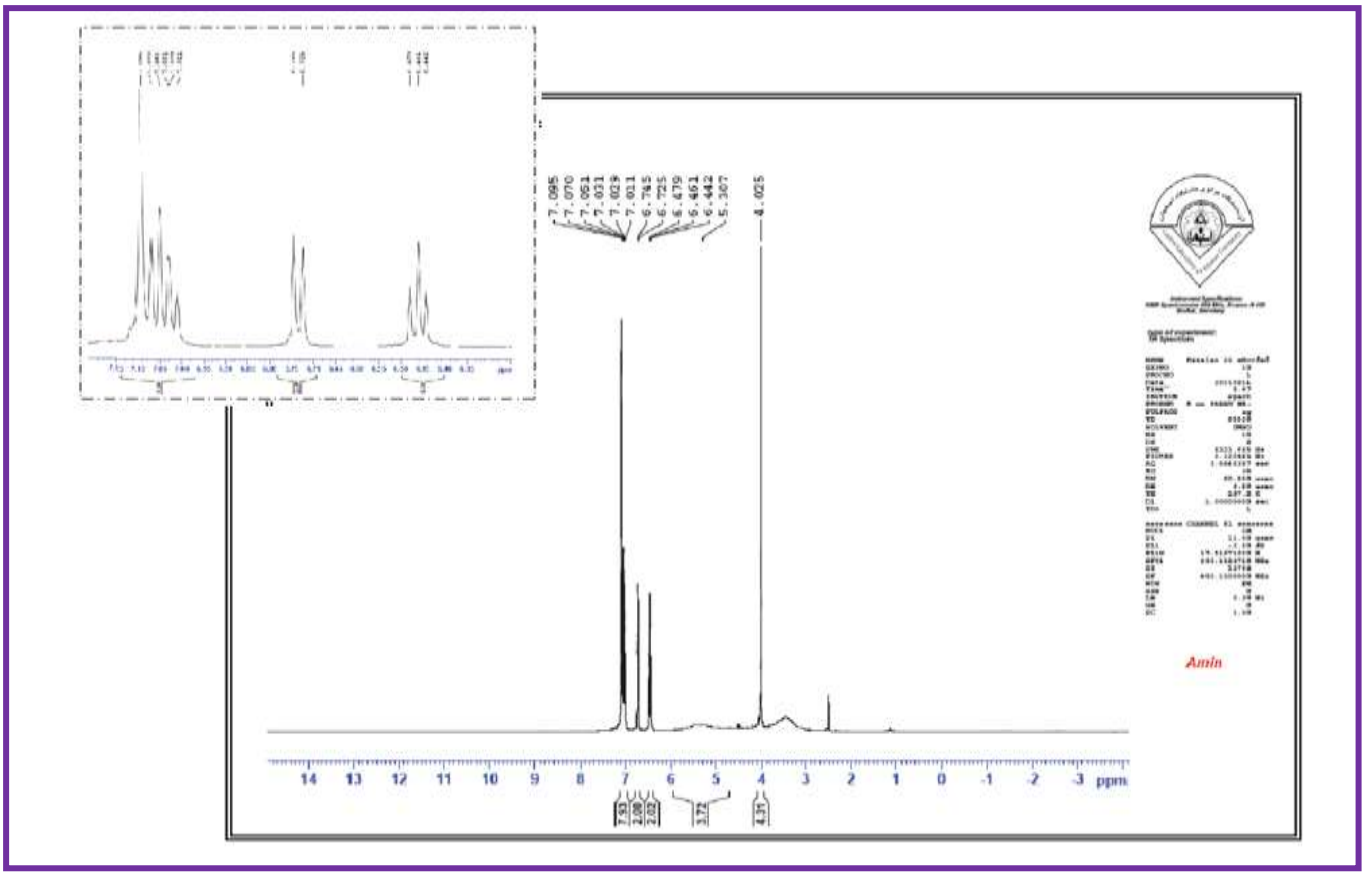

Figure S2. ^{1}H NMR spectrum of α,α′-Bis(o-aminophenylthio)-1,2-xylene

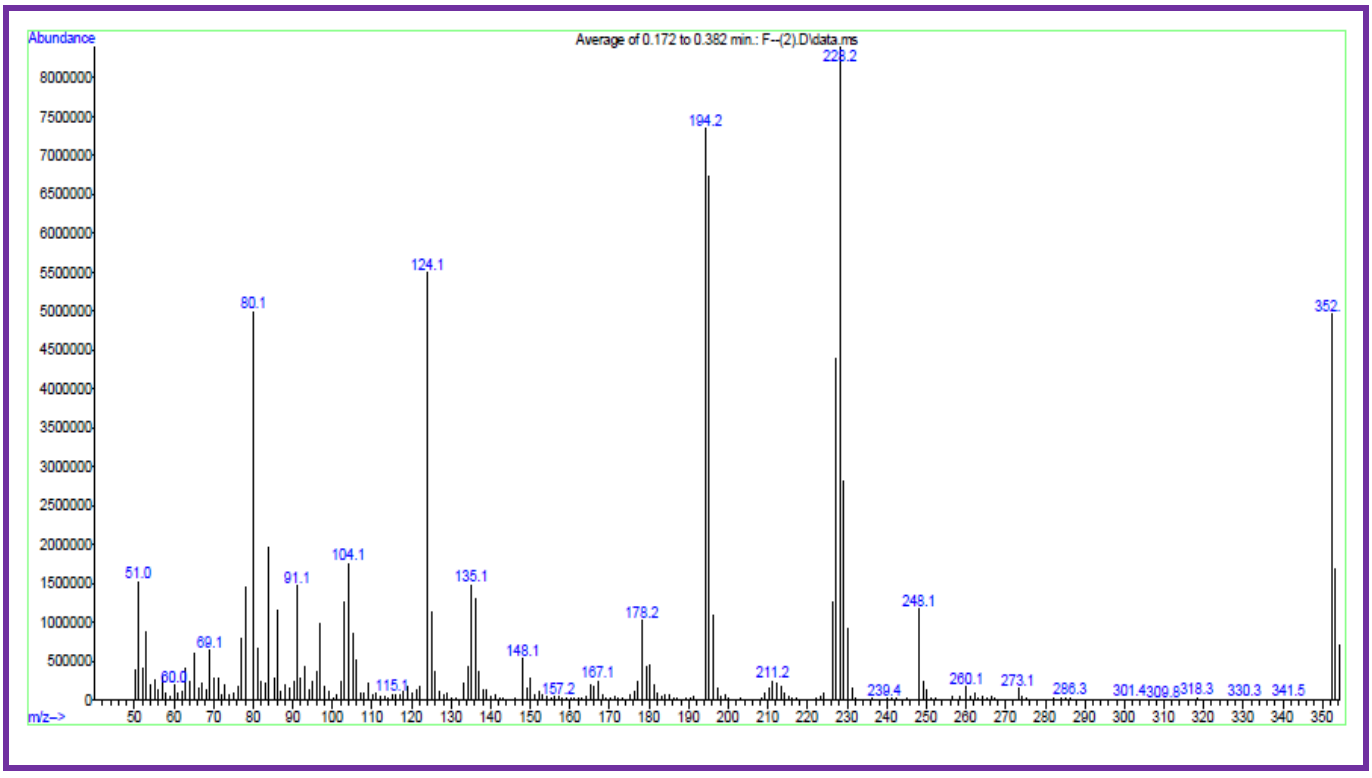

Figure S3. EI-mass spectrum of α,α′-Bis(o-aminophenylthio)-1,2-xylene

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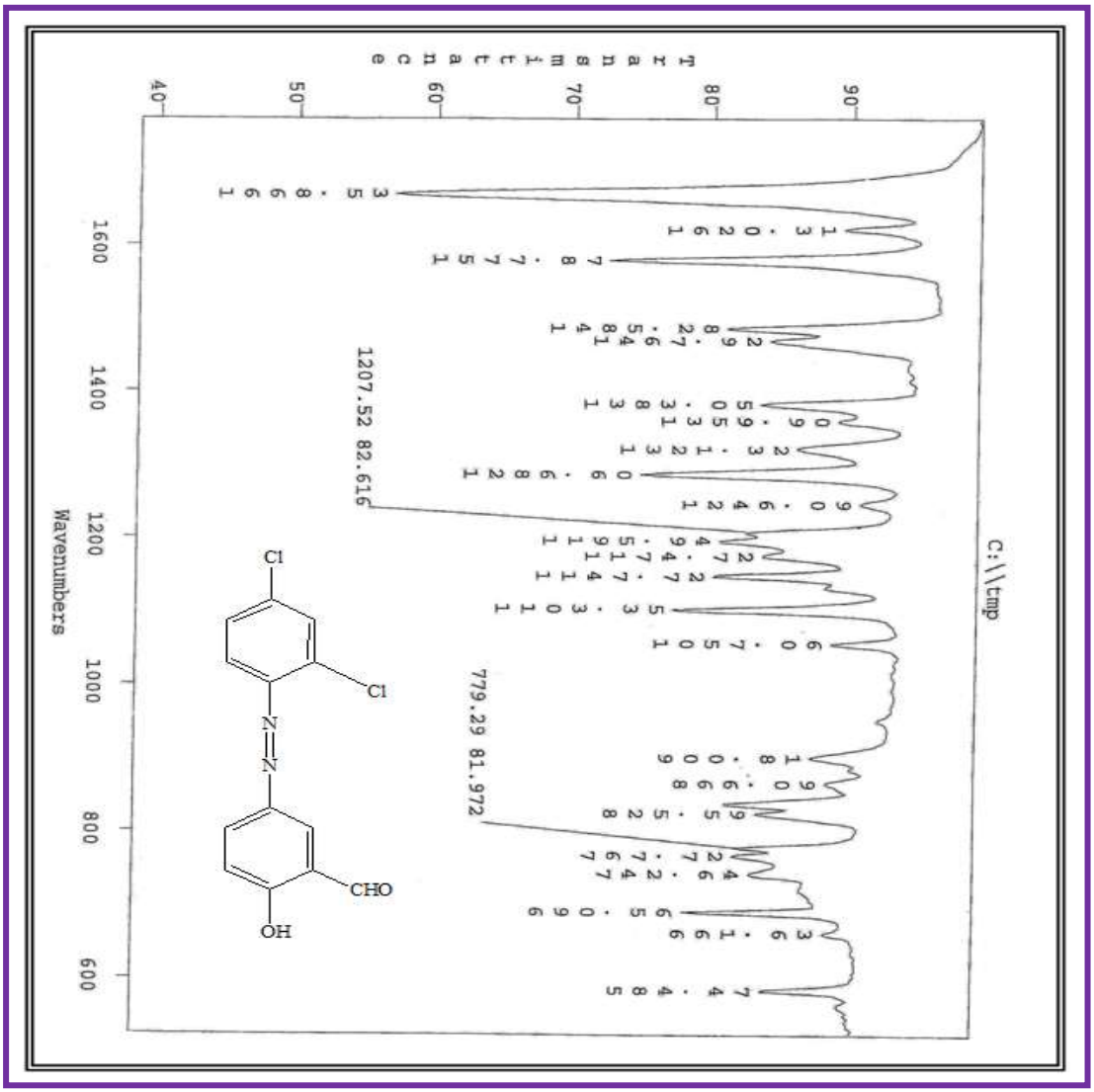

Figure S4. IR spectrum of 1-(3-Formyl-4-hydroxyphenylazo)-2,4-dichlorobenzene

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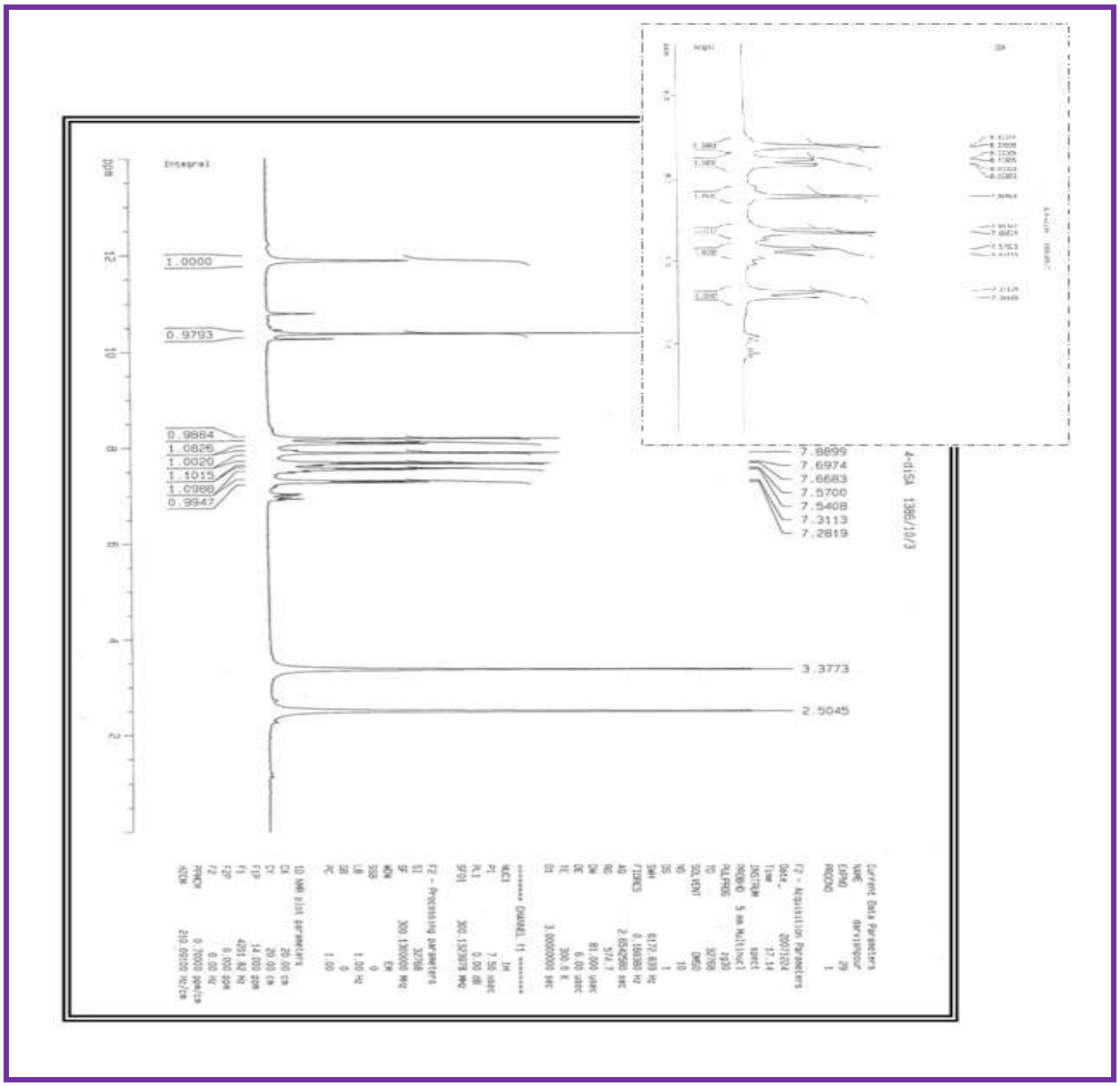

Figure S5. ^{1}H NMR spectrum of 1-(3-Formyl-4-hydroxyphenylazo)-2,4-dichlorobenzene

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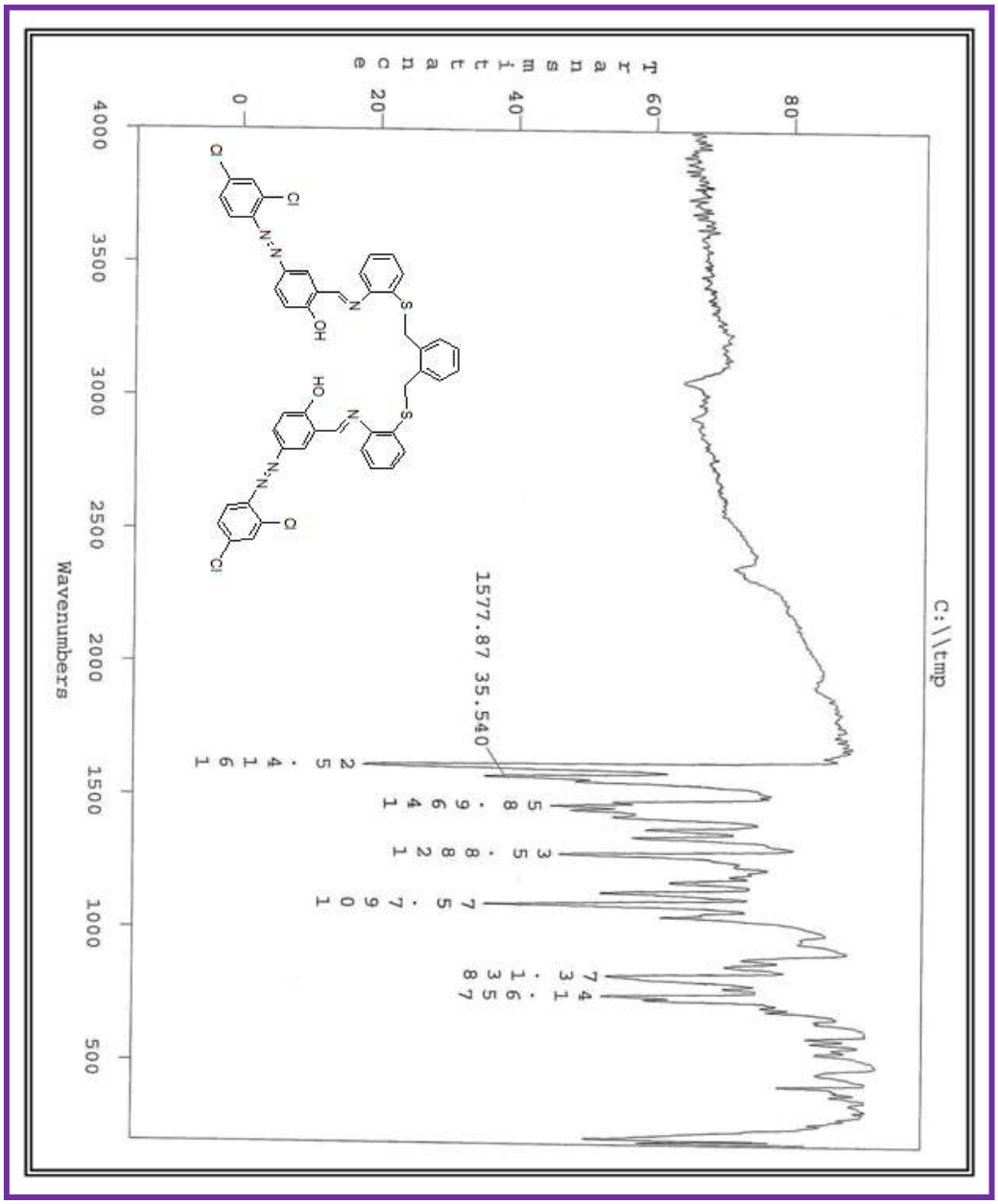

Figure S6. IR spectrum of **1**

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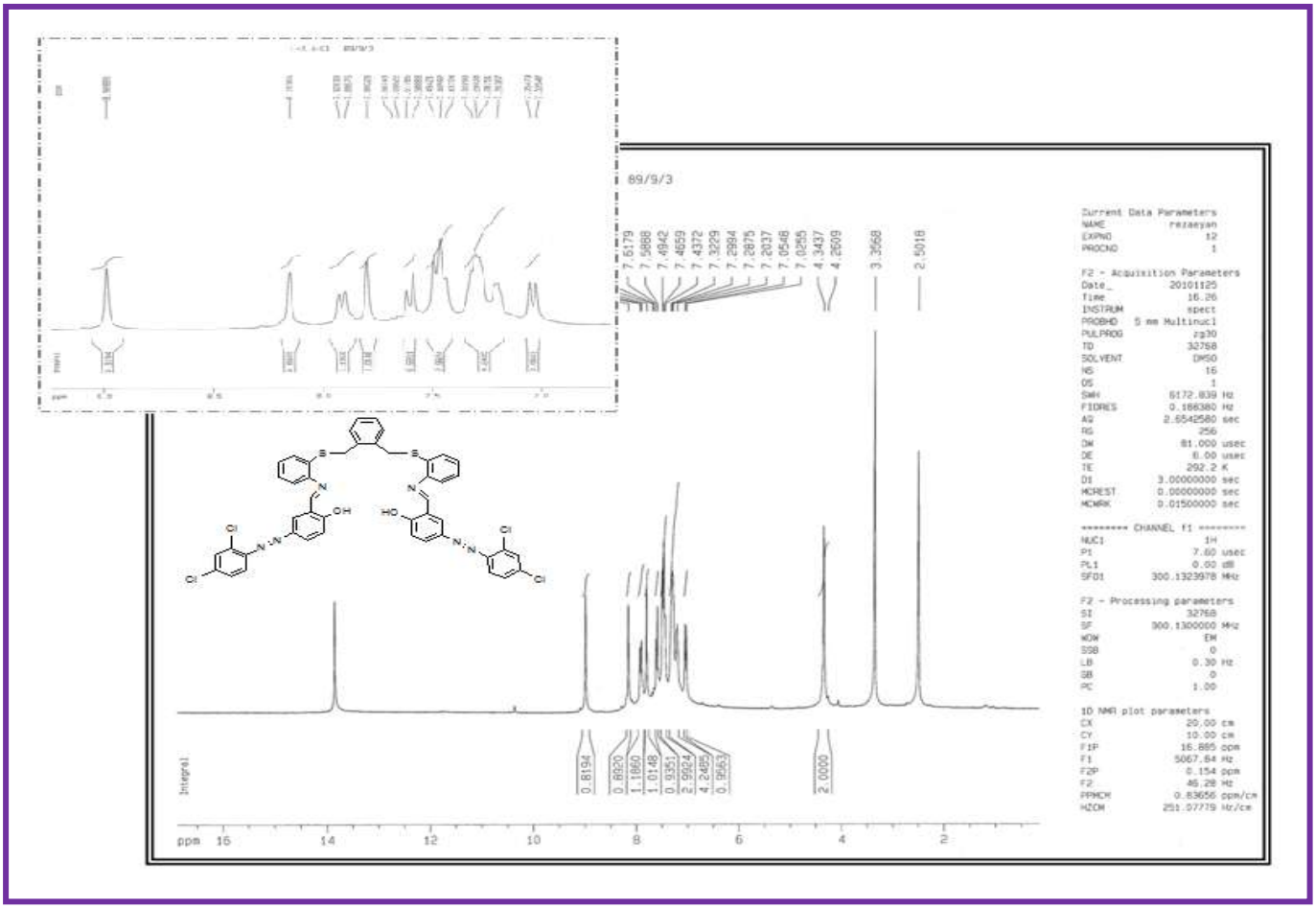

Figure S7. ^{1}H NMR spectrum of **1**

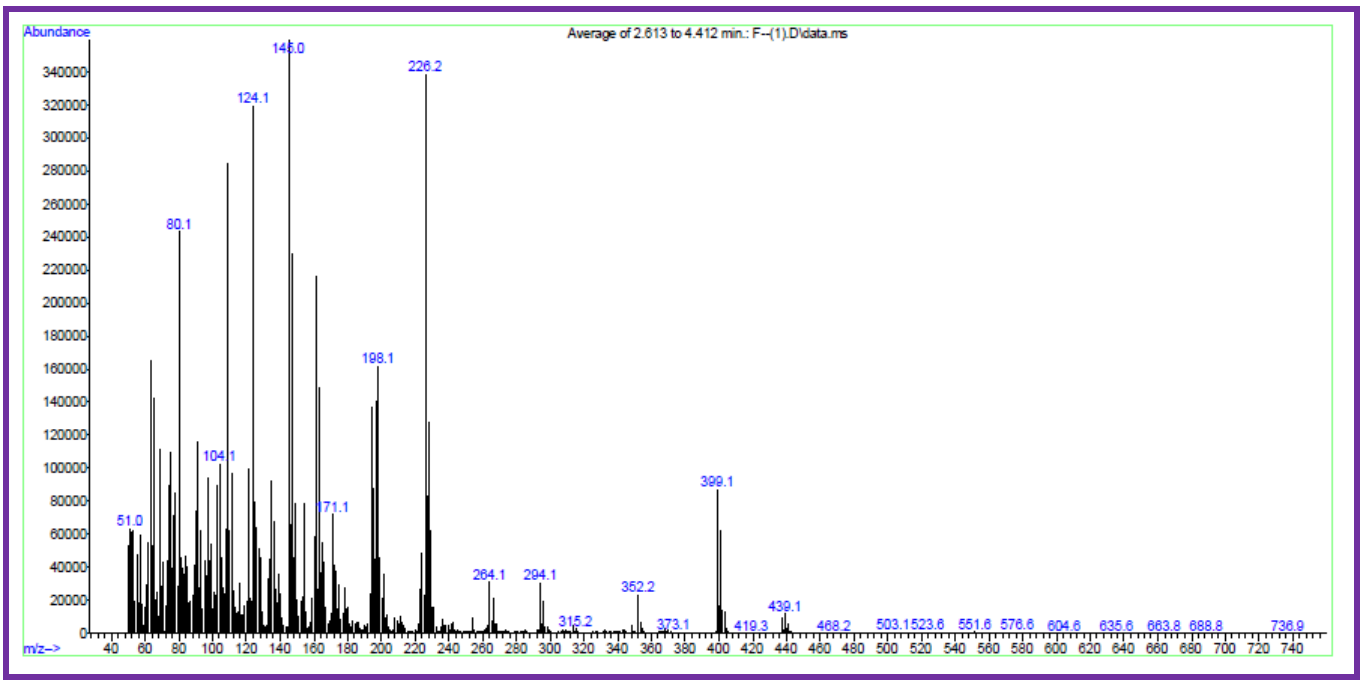

Figure S8. EI-mass spectrum of **1**

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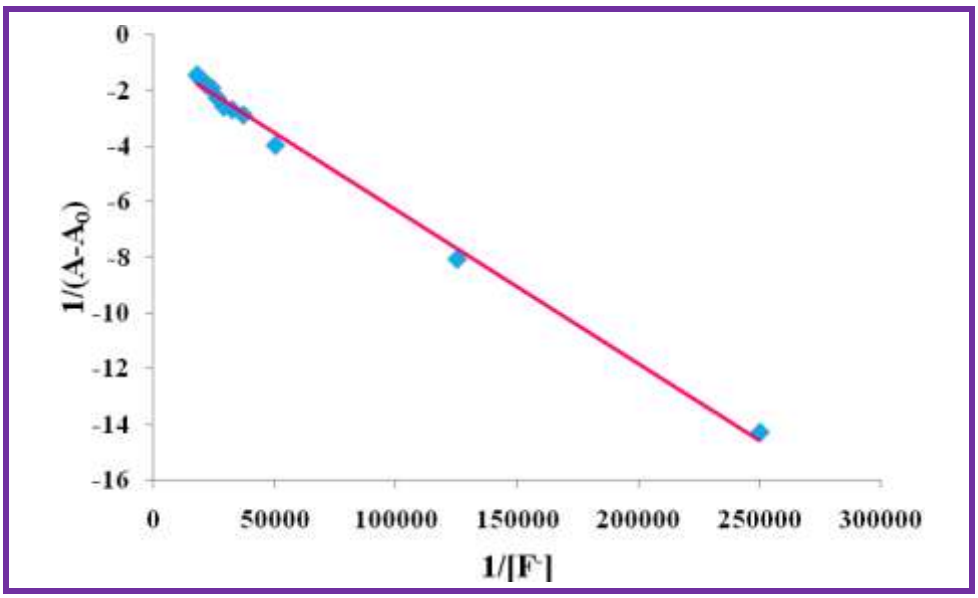

Figure S9. Benesi–Hildebrand plot of receptor **1** binding with F^- anion associated with absorbance change at 369 nm in DMSO.

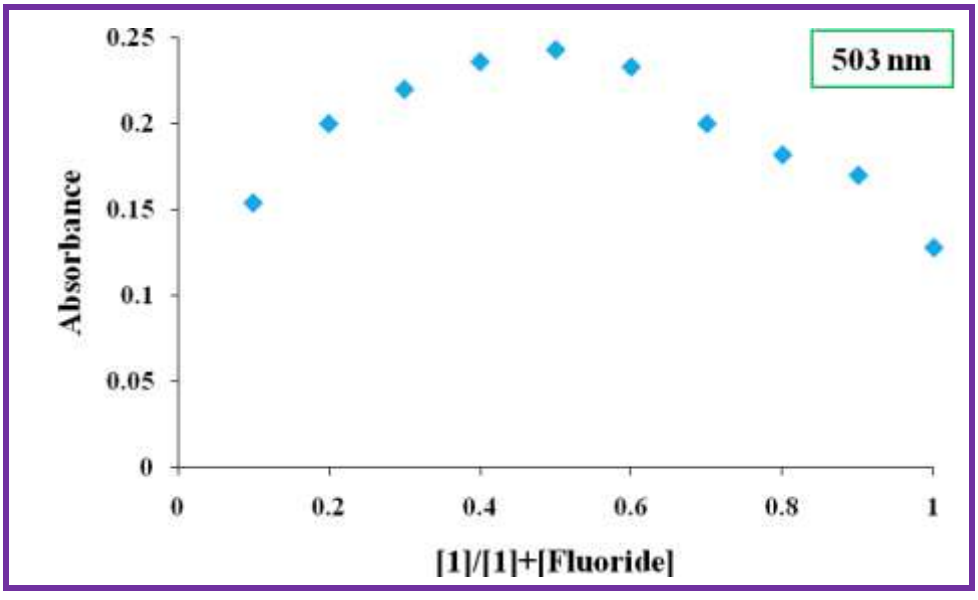

Figure S10. Job's plot for sensor **1** and fluoride anion with a total concentration of 2.0×10^{-5} M in DMSO.

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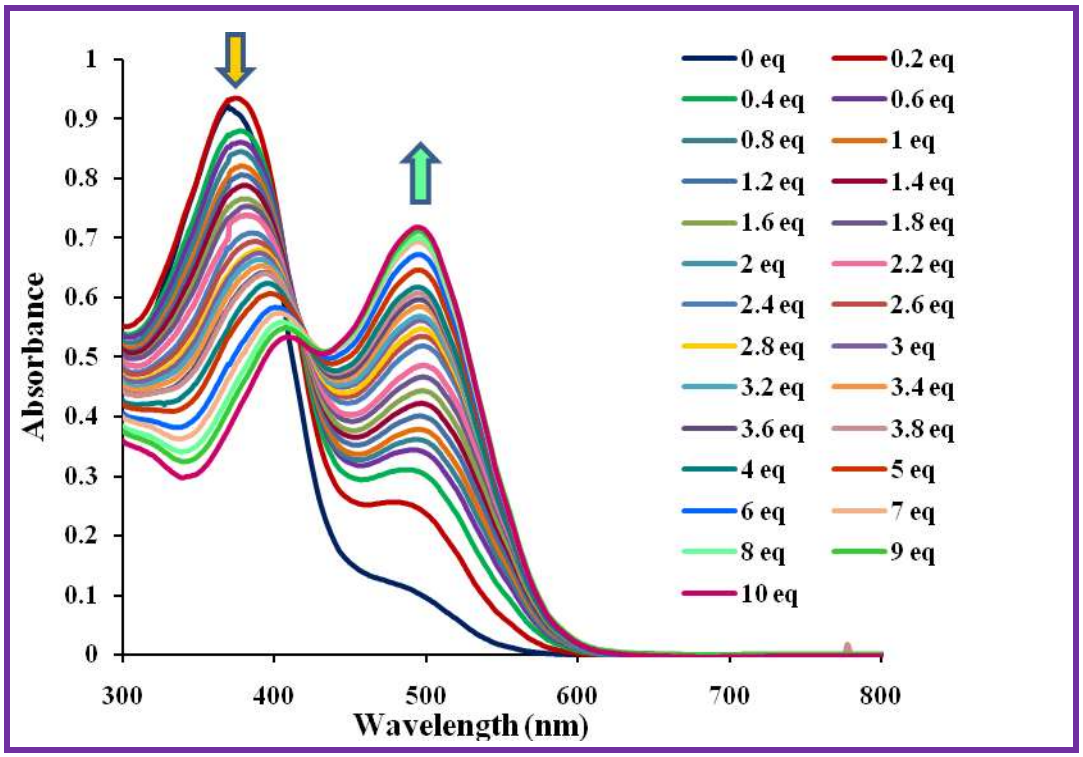

Figure S11. UV-Vis absorption spectra of receptor **1** (2×10^{-5} mol L^{-1}) in dry DMSO upon addition of $H_2PO_4^-$ (0-10 equiv.).

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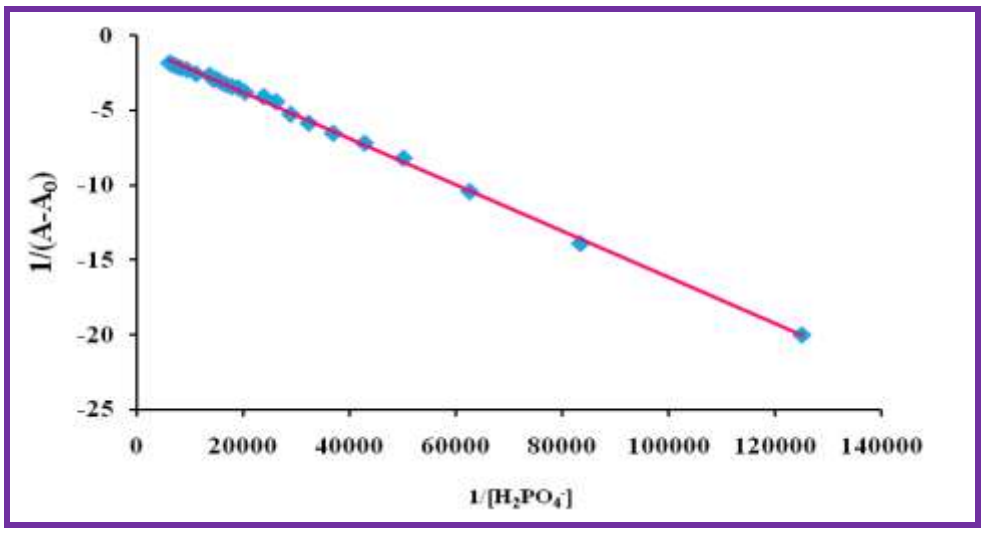

Figure S12. Benesi–Hildebrand plot of receptor **1** binding with $H_2PO_4^-$ anion associated with absorbance change at 369 nm in DMSO.

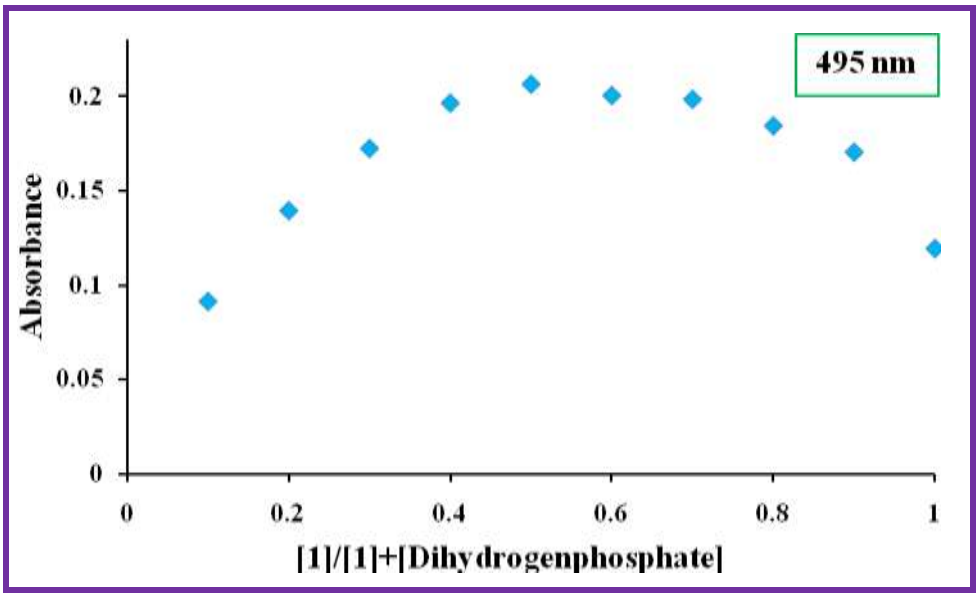

Figure S13. Job's plot for sensor **1** and dihydrogenphosphate anion with a total concentration of 2.0×10^{-5} M in DMSO.

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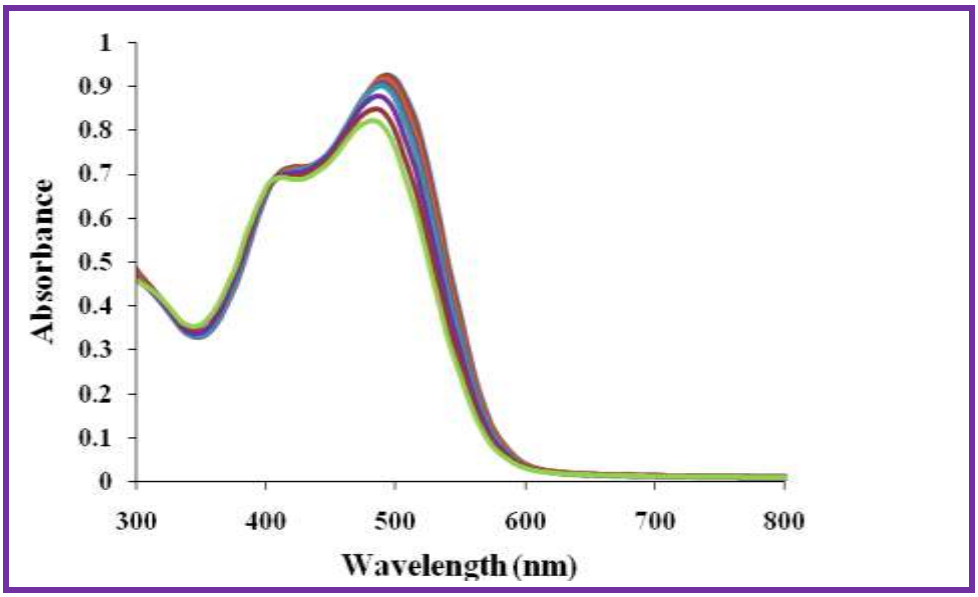

Figure S14. Changes in UV-Vis spectra of **1** +10 equiv F^- recorded in DMSO (2.0×10^{-5} M) after addition of 0, 2, 10, 20, 40, 80, 140 and 200 μL of CH_3OH.

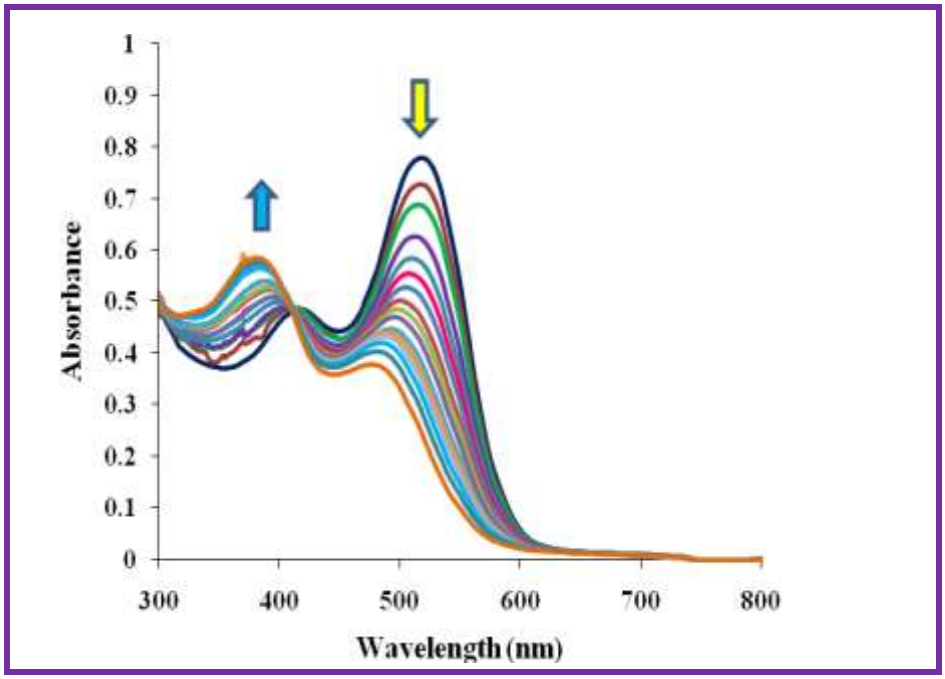

Figure S15. Changes in UV-Vis spectra of **1** +10 equiv $H_2PO_4^-$ recorded in DMSO (2.0×10^{-5} M) after addition of 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 100, 120, 140, 180, 240 and 360 μL of CH_3OH.

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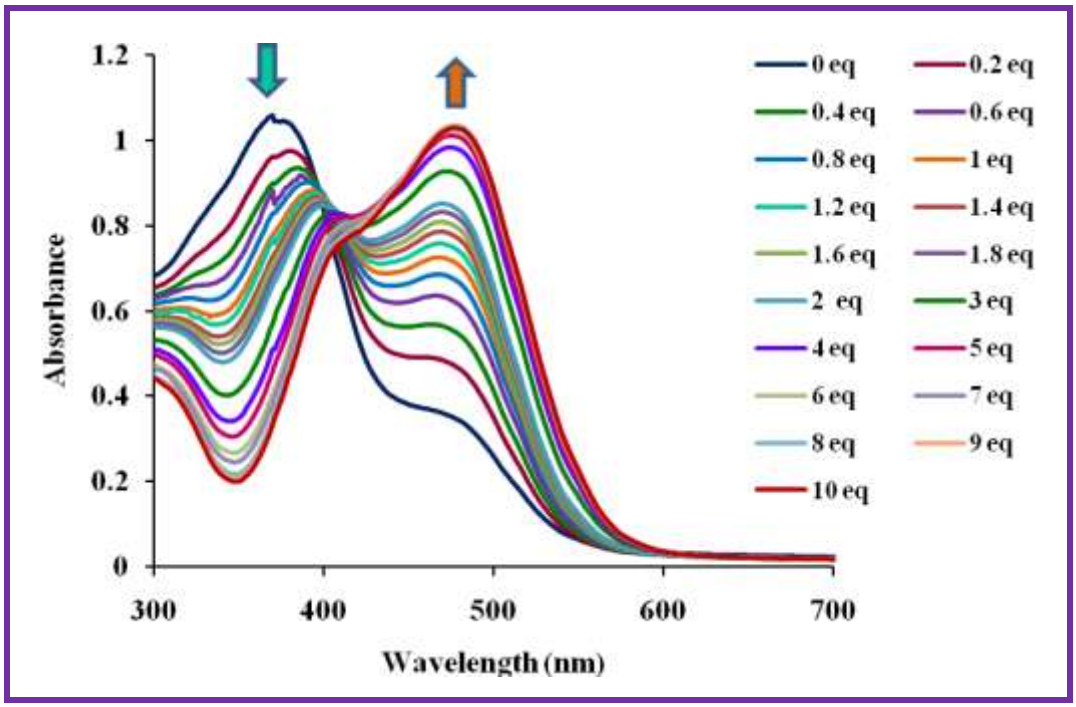

Figure S16. UV-Vis absorption spectra of receptor **1** (2×10^{-5} mol L^{-1}) in 9:1, DMSO-water upon addition of TBAF (0-10 equiv.).

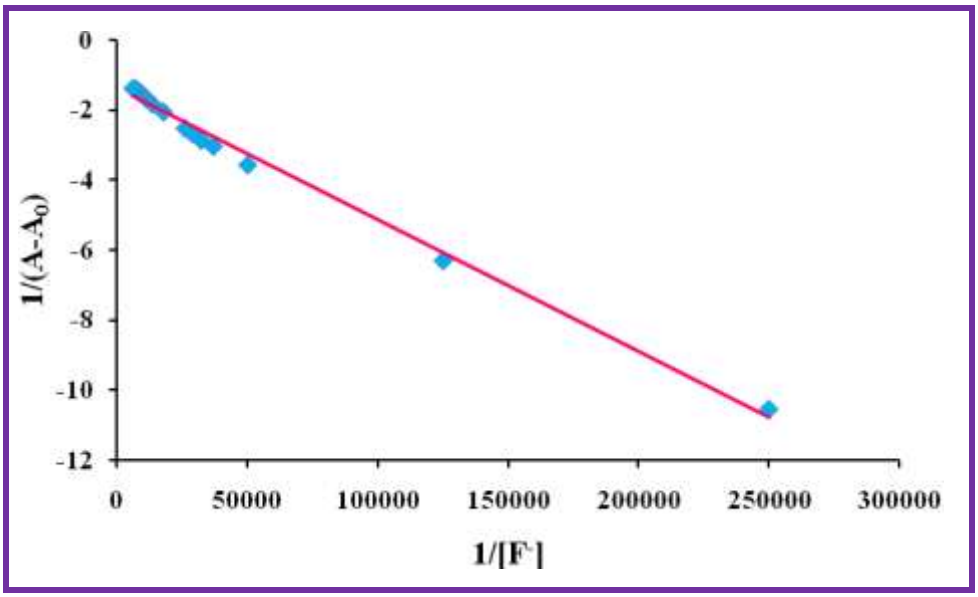

Figure S17. Benesi–Hildebrand plot of receptor **1** binding with F^- anion (in form of TBAF) associated with absorbance change at 369 nm in 9:1, DMSO-water.

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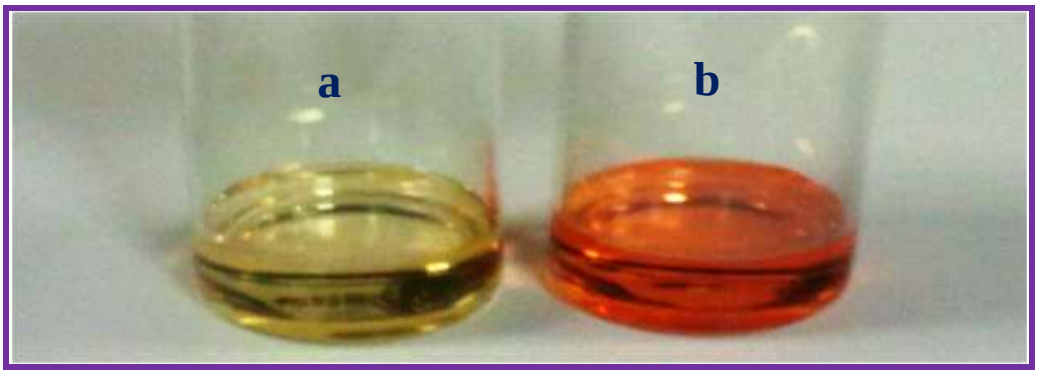
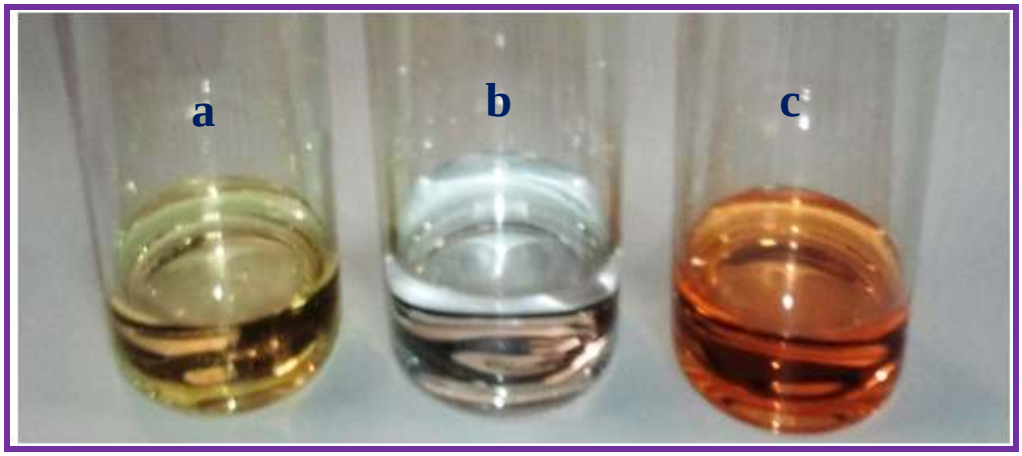
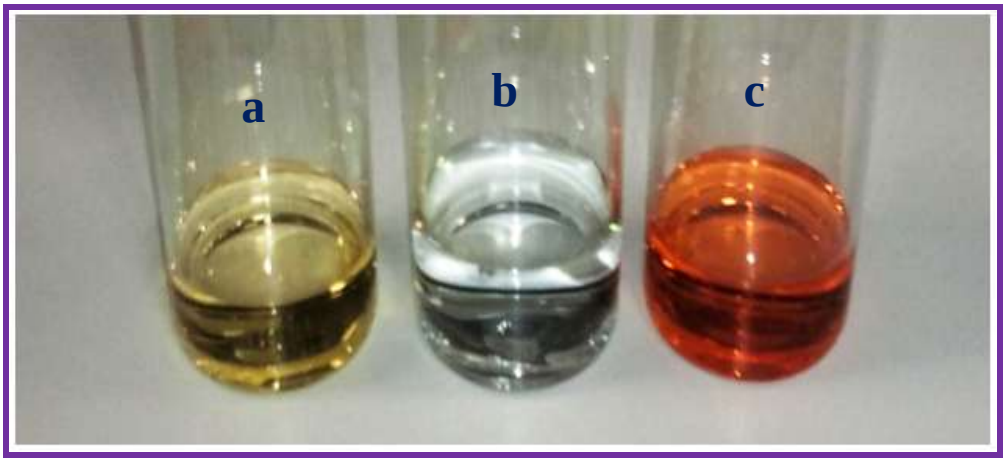


A: (a) **1**, (b) **1**+ one drop of NaF solution in water



B: (a) **1**, (b) sea water, (c) **1**+ one drop of sea water



C: (a) **1**, (b) commercial mouthwash, (c) **1**+ one drop of commercial mouthwash

Figure S18. Colour change after addition of one drop of A) NaF solution, B) sea water and C) commercial mouthwash.

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Preparation of sample containing toothpaste:

1 mg of commercially available toothpaste (Crest brand) was added to 1 ml water. After fully dissolve of toothpaste in water, the resultant foam was filtered and 0.25 ml filtrate was added to the receptor solution. The resultant solution consisted of 0.05 mg mL^{-1} toothpaste, 2×10^{-5} mol L^{-1} F^- ions (from standard solution of TBAF) and 2×10^{-5} mol L^{-1} receptor **1** in 4.5:0.5, DMSO-water. Then, the UV-Vis absorption spectrum of outcome solution was measured and compared to the toothpaste-free F^- solution. As it is shown, the signal from the F^- contaminated toothpaste solution (B) was stronger than that from the one without toothpaste (A), indicating the concentration of fluoride in solution (B) is higher than in (A). In this way receptor **1** can be applied in qualitative detection of fluoride in toothpaste.

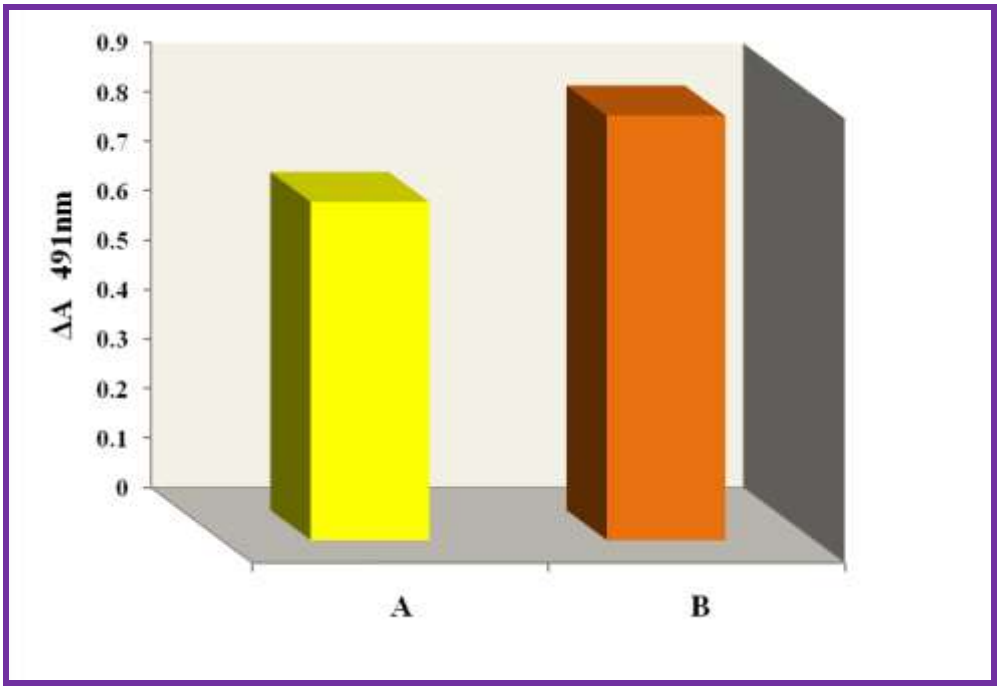

Figure S19. The proof of concept for fluoride detection in toothpaste A) **1**+ F^-; B) **1**+ F^- + toothpaste.

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Quantitative detection of fluoride in commercial mouthwash:

A set of known various standard solutions of NaF were prepared in standard flasks. Then, the UV-Vis absorption spectra were recorded and the absorbance at 467 nm was monitored to establish standard plot. The unknown sample was prepared by dilution of 10 µL of commercial mouthwash (Oral-B brand) to 5 mL and the electronic spectrum was measured. The concentration of fluoride was established by referring to the calibration graph.

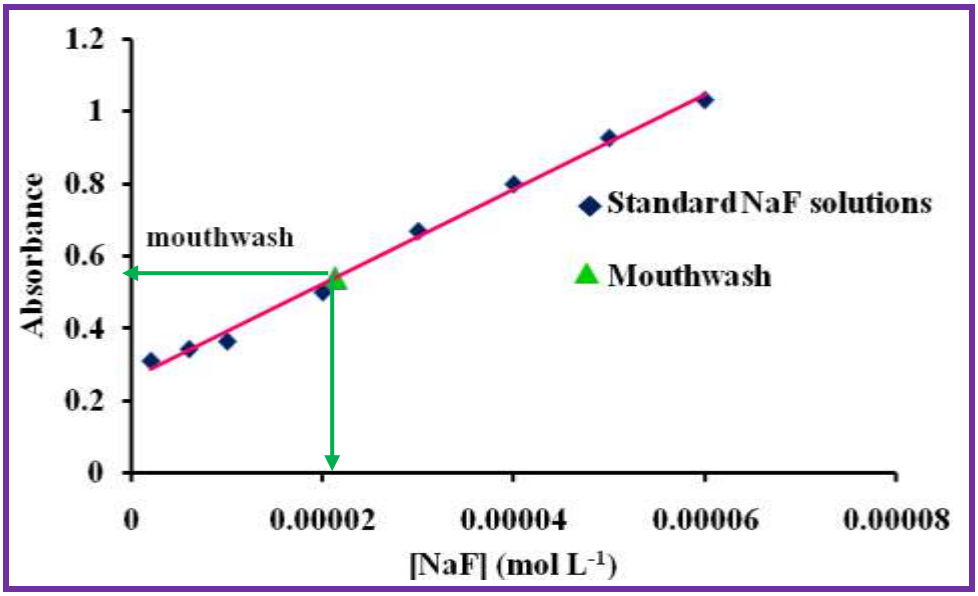

Figure S20. Calibration curve for determining concentration of fluoride anion in commercial mouthwash.

The value obtained from the standard plot was multiplied by the proper dilution factor to determine actual fluoride anion concentration in unknown sample. The value was 202.3 ppm, in accord with reported standard value.

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Phosphate interference study:

Phosphates enter waterways from human and animal wastes, phosphate-rich rocks, and wastes from laundries, cleaning, industrial processes and farm fertilizers. Phosphate is necessary for plant and animal growth. If too much phosphate is present, algae and water weeds grow widely, choke the waterway and use up large amounts of oxygen and in result many fish and aquatic organisms may die. The optimum concentration of phosphate for sea water is between 0.05 to 0.20 mg/l (ppm) and beyond this is toxic to aquatic life.

To investigate the interference effect, 0.25 ppm of $NaH_2PO_4^-$ was added to the receptor solution in DMSO-water (9/1, v/v, 0.1 mM HEPES buffer solution, pH 7.2). Neither any detectable colour, nor any UV-Vis spectra change was obtained (**Figure S21**). This exhibited that the recognition of fluoride in sea water was not interfered with phosphate.

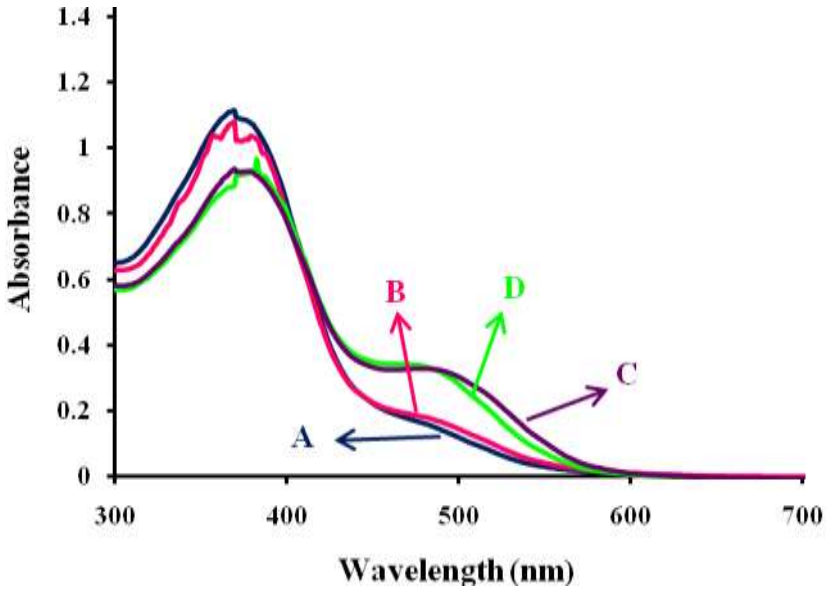

Figure S21

A) UV-Vis spectrum of receptor **1** before addition of anions

B) UV-Vis spectrum of receptor **1** in the presence of 0.25 ppm $NaH_2PO_4^-$

C) UV-Vis spectrum of receptor **1** in the presence of 0.1 ppm fluoride

D) UV-Vis spectrum of receptor **1** in the presence of 0.25 ppm $NaH_2PO_4^-$ and 0.1 ppm fluoride

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Determination of the pK_a value:

To determine the pK_a value of the phenolic group of **1**, the spectrophotometric pH titration was carried out (Initial pH of **1** is 8.77) in 9:1 DMSO-Water. The value was assigned as the maxima of the first derivative of the data shown in **Figure S22** (The inset shows the plot of the derivatives of the titrations).

(*J. Am. Chem. Soc.* ***2000***, *122, 6769-6770*)

The p*K*a was determined to be ~ 9.75 (on the basis of new band formed at 495 nm) indicating that **1** likely bound with fluoride through the formation of hydrogen bond complex (*Inorg. Chem.* ***2008***, *47, 5616-5624*).

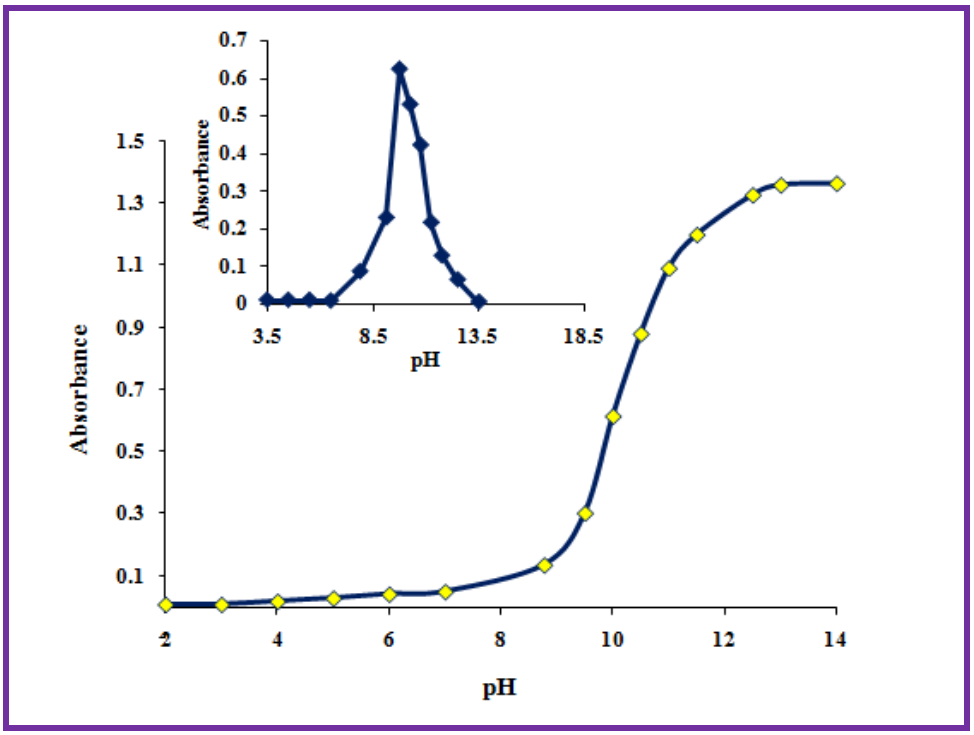

Figure S22

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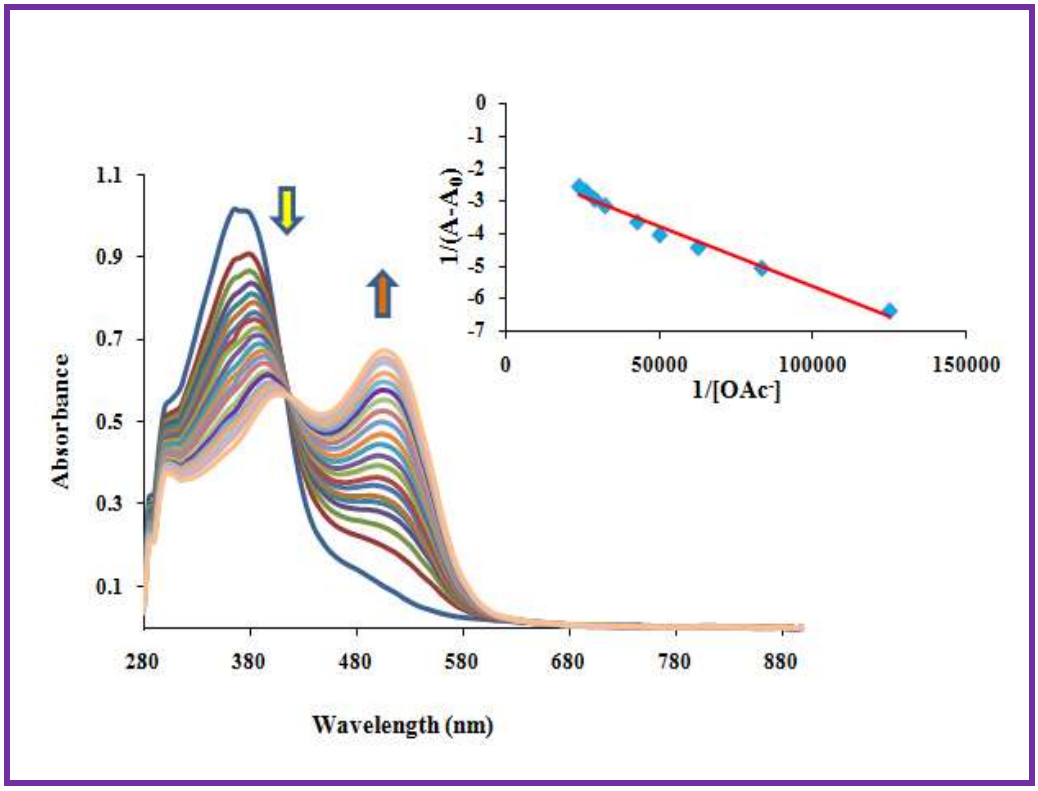

Figure S23. UV-Vis absorption spectra of receptor **1** (2×10^{-5} mol L^{-1}) in dry DMSO upon addition of AcO^- (0-10 equiv.). Inset showing the Benesi–Hildebrand plot of receptor **1** binding with AcO^- associated with absorbance change at 369 nm in DMSO.

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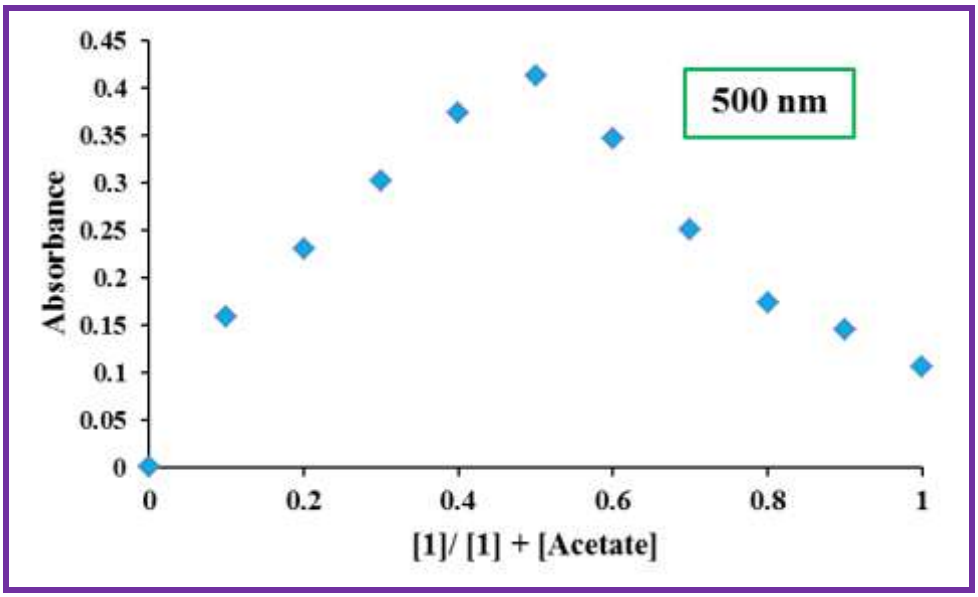

Figure S24. Job's plot for sensor **1** and acetate anion with a total concentration of 2.0×10^{-5} M in DMSO.

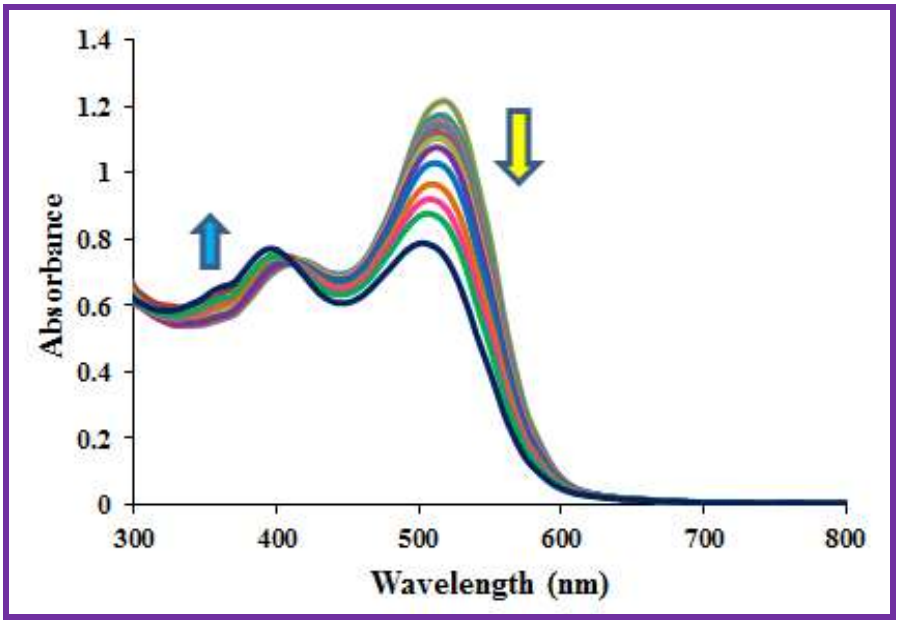

Figure S25. Changes in UV-Vis spectra of **1** +10 equiv AcO^- recorded in DMSO (2.0×10^{-5} M) after addition of 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 100, 120, 140, 180, 240 and 360 μL of CH_3OH.

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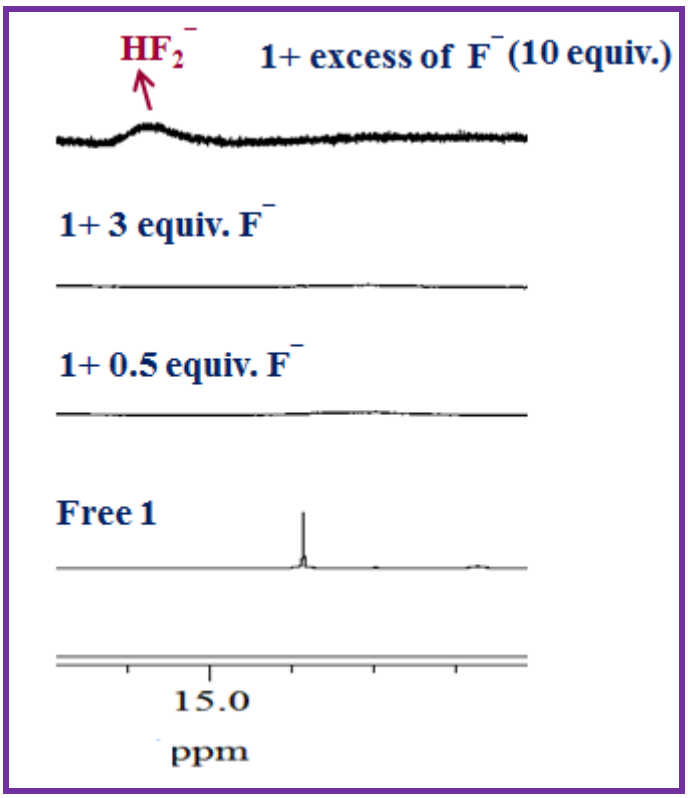

Figure S26. ^{1}H NMR spectra of receptor **1** in DMSO-d_6 (2×10^{-2} mol L^{-1}) in the absence and in the presence of different amounts of TBAF