Supplementary data

Fluorescence 'turn-on' sensor for F^- derived from Vitamin B_6 cofactor

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Experimental Section

Material and apparatus

Vitamin B_6 cofactor pyridoxal.HCl, 2-aminophenol and KOH for the synthesis of receptor **L** were obtained commercially from Acros Organic, India and were used without further purification. All the anions were used in the form of tetra-n-butylammonium (TBA) salts and were purchased from Spectro Chem Pvt. Ltd., India. All anions were stored in a vacuum desiccator containing self-indicating silica and dried fully before using. Analytical grade acetonitrile and methanol were used after distillation.

Melting point were measured on digital melting point apparatus VMP-DS "VEEGO" which was uncorrected. UV-Vis spectra were recorded on VARIAN CARY 50 Spectrophotometer with a quartz cuvette (path length = 1 cm). The fluorescence

spectra were recorded on a Perkin-Elmer LS55 luminescence spectrometer. ^{1}H NMR spectra were determined in DMSO-d_6 on BRUKER AVANCE II 400 MHz NMR using TMS as an internal standard.

General methods

Stock solution of the receptor (1.0 $\times 10^{-3}$ M) and anions (1.0 $\times 10^{-3}$ M) were prepared in acetonitrile. These solutions were used for all spectroscopic studies after appropriate dilution. For spectroscopic titrations, required amount of the receptor was taken directly into cuvette and spectra were recorded after successive addition of anion by using micropipette. The sample for ^{1}H NMR study was prepared by mixing both anion and receptor in an appropriate ratio. Then, the mixture was made soluble in DMSO-d_6 and spectrum was recorded on a Bruker Avance II 400 spectrometer by keeping TMS as an internal standard.

Computational methods

All theoretical calculations were carried out with the Gaussian 09W computer program using Gaussview 5.0.9 graphical interface.[1] Optimizations of the receptor **L** was carried out without symmetry constraints by applying B3LYP/6-31G(d,p) method in gas phase followed by the harmonic vibrational frequency was calculated using the same methods to ascertain the presence of a local minimum.

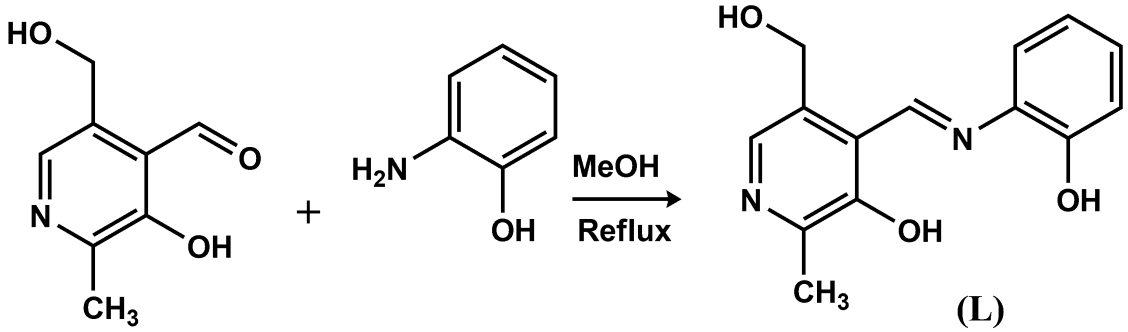
*Synthesis of **L***

Pyridoxal hydrochloride (0.5 gm, 0.0024 mol) was desalted by adding KOH (0.13 gm, 0.0024 mol) in methanolic medium (10 ml). After filtering KCl, 2-aminophenol (0.26 gm, 0.0024 mol) in 5 ml MeOH was added dropwise into the filtrate at room temperature. Then, the mixture was refluxed for two hours. A yellow coloured precipitate was obtained, which was filtered off, washed with cold ethanol followed by ether. The product was recrystallized to give yellow

crystals. Yield: 53%; M.P.: 208 °C; IR (KBr pellet, cm^{-1}): 3143.4, 3065.57, 3028.6, 2999.4, 2717.96, 1952.4, 1859, 1776.1, 1748.6, 1610.9, 1590.2, 1481.21, 1460.9, 1403.47, 1380.2, 1295.15, 1235.21, 1159.61, 1075.17, 1028.4, 732.82, 708.64, 651.80; ^{1}H NMR (300 MHz, DMSO-d_6, Me_4Si, δ, ppm): 14.69 (1H, s, -OH), 10.00 (1H, s, -CH=N), 9.24 (1H, s, -OH), 6.93 – 7.96 (5H, Ar-H), 5.40 (1H, t, -OH), 4.77 (2H, d, -CH_2-OH), 2.43 (3H, s, -CH_3), LC-MS for $C_{17}H_{13}NO_2$: calculated 258.27, found 259.1.

1. 1. M.J. Frisch et. al., Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT, 2009.

SCHEME AND FIGURES



Scheme S1. Synthesis of vitamin B_6 Schiff base analog **L**.

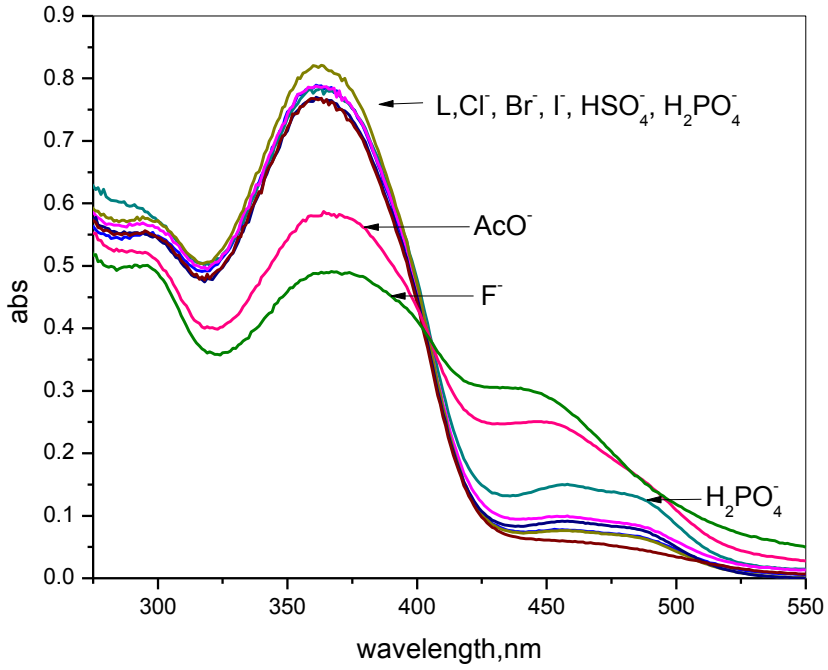


Fig. S1. UV-Vis spectra changes of sensor **L** (5.0×10^{-5} M) upon addition of one equivalent of different anions in DMSO.

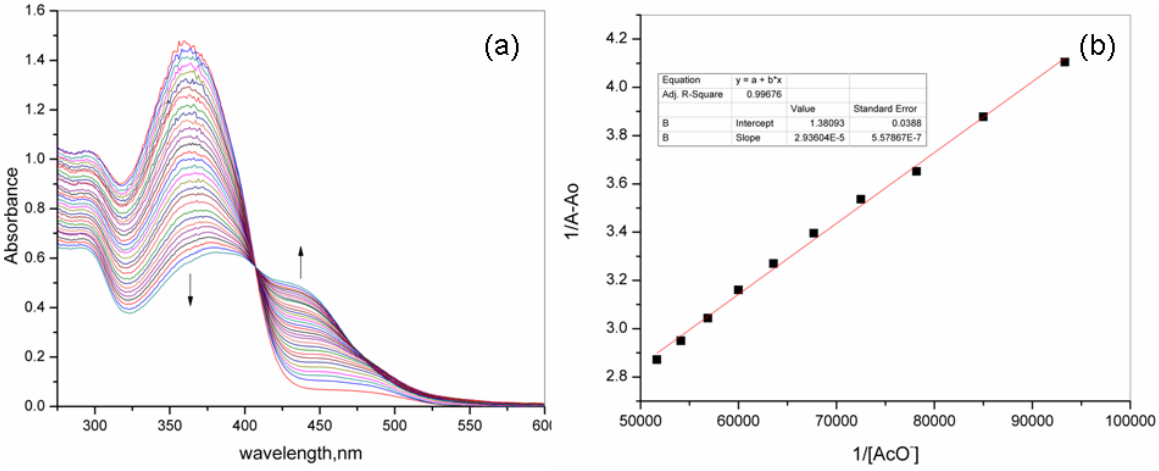


Fig. S2. Changes in the absorbance spectrum (a) of **L** (1.0×10^{-4} M) upon addition of incremental amounts of AcO^- in DMSO and (b) the B-H plot.

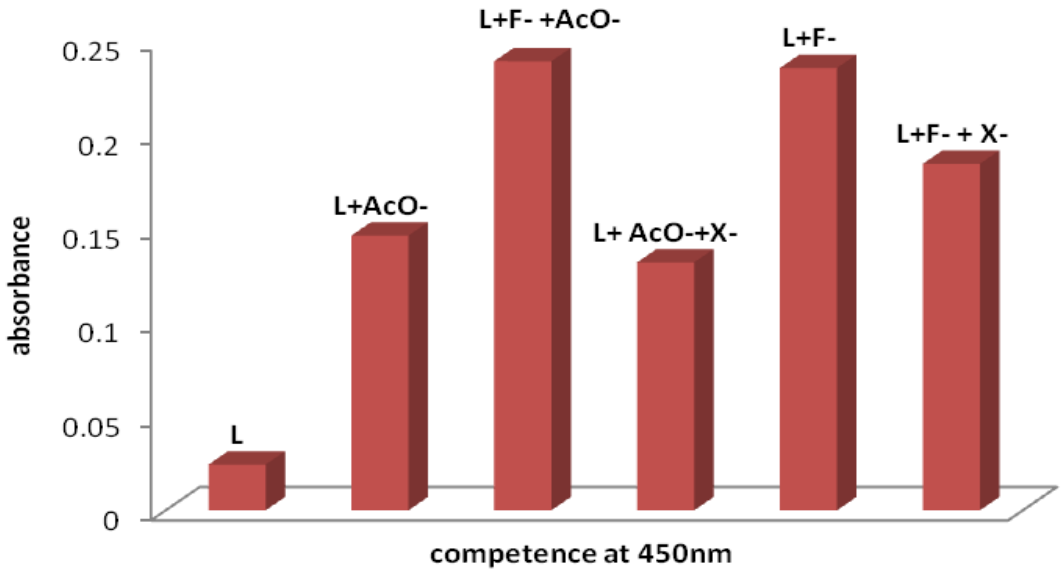


Fig. S3 Absorbance of **L** (4.0×10^{-5} M) at 450 nm under competitive environment in DMSO (X^- = Cl^-, Br^-, I^-, HSO_4^- and $H_2PO_4^-$).

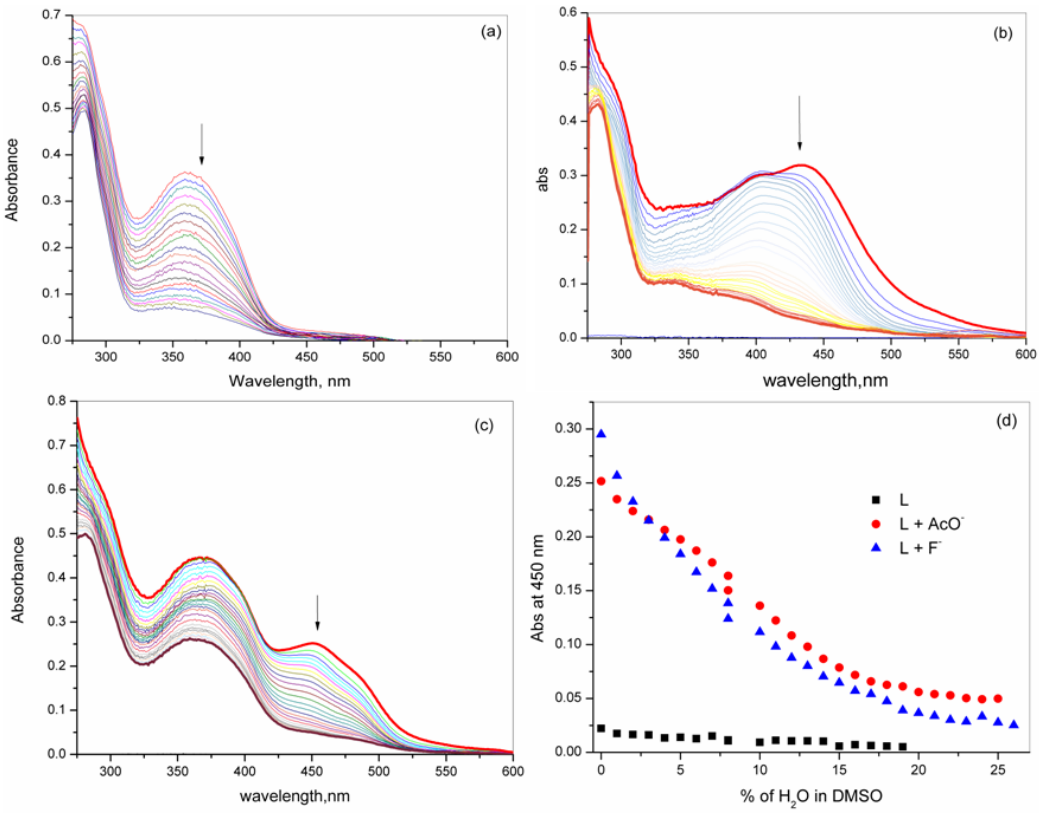


Fig. S4. Changes in the absorbance spectrum of (a) **L** (2.0×10^{-5} M) and in the presence of equimolar amount of (b) F^- and (c) AcO^- in DMSO upon addition of incremental amounts of water; (d) the absorbance at 450 nm with respect to the % of water in DMSO.

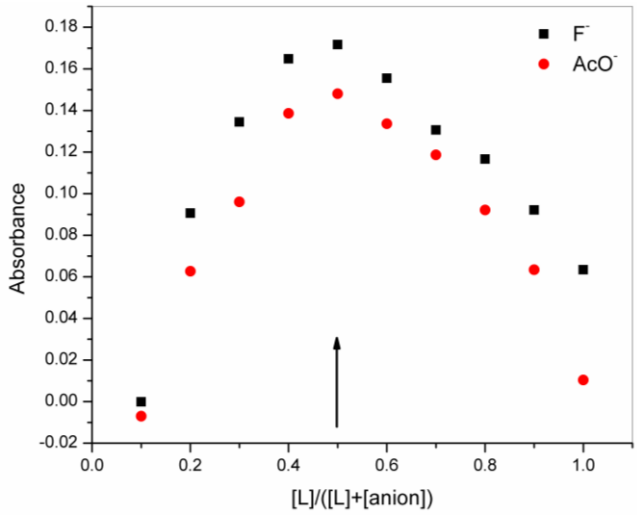


Fig. S5. The stoichiometry analysis for the complexation of **L** with anions (F^- and AcO^-) by Job's plot analysis.

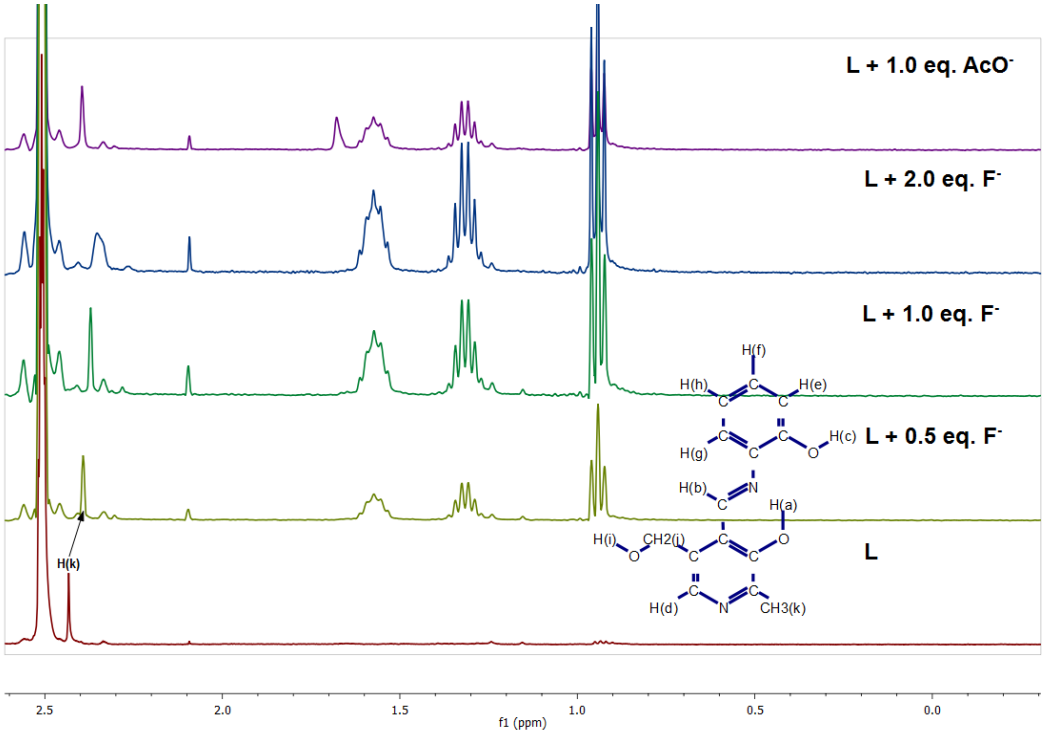


Fig. S6. ^{1}H NMR spectra (Upfield region) of **L** in absence and presence of different equivalents of TBA salts of fluoride and acetate in DMSO-d_6.

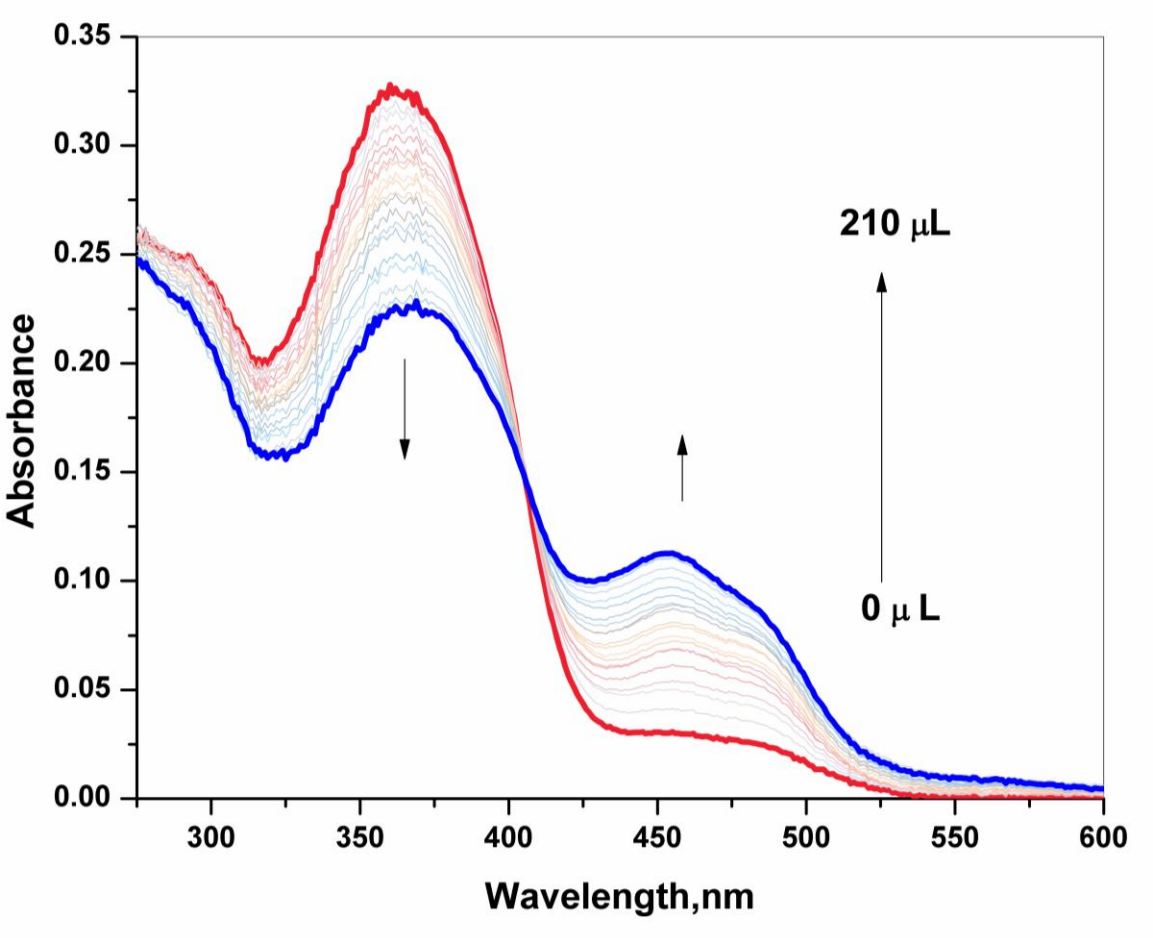


Fig. S7. UV-Vis absorbance spectra of **L** (1.0×10^{-5} M) upon successive addition of TBAOH (1.0×10^{-4} M) in DMSO.