

Electronic Supplementary Information

Dipyrrolyl-bis-sulfonamide chromophore based probe for anion recognition

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“This version of the Electronic Supplementary Information replaces a previous copy in which Figure S5 was incorrect.”

Contents

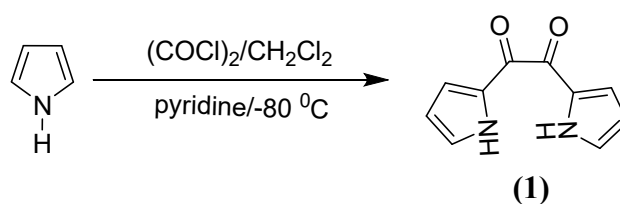
1. General Material and Methods
2. Synthetic protocol for 1, 2-Diamino-4, 5-bis (p-toluenesulfonamido) benzene
3. Synthesis of 2, 3-Dipyrrol-2-yl ethanedione (**2**)
4. Synthesis of 2, 3-dipyrrol-2-yl quinoxaline-6, 7-diyl bis (4-methyl benzene sulfonamide) (**3**)
5. **Fig. S1** FT-IR Spectrum of receptor **3**
6. **Fig. S2** ¹H NMR spectrum of receptor **3**
7. **Fig. S3** ¹³C - NMR spectrum of receptor **3**
8. **Fig. S4** HRMS spectrum of receptor **3**
9. **Fig. S5** Color changes of receptor **3** in CHCl₃ upon addition of tetrabutylammonium anions up to 5 equivalents under UV light ($\lambda_{\text{max}}=365$ nm).
10. **Fig.S6** Changes in absorption spectra of receptor **3** with an increasing amount of (A) H₂PO₄⁻ (B) AcO⁻.
11. **Fig. S7** Effect of various anion addition on the emission of **3** (5x10⁻⁵ M).

12. **Fig.S8** Effect of anion addition on the emission of **3** (5×10^{-5} M) with an increasing amount of (A) H_2PO_4^- (B) AcO^- (5×10^{-5} M).
13. **Fig.S9** Absorbance Intensity of solution **3** *versus* the concentration of F^- .
14. **Fig.S10** Absorbance Intensity of solution **3** *versus* the concentration of H_2PO_4^- .
15. **Fig.S11** Absorbance Intensity of solution **3** *versus* the concentration of AcO^- .

General Materials and methods:

All analytical reagent grade solvents were used without further purification. o-phenylene diamine, pyrrole, P-Toluenesulfonic acid, Tetra butyl ammonium fluoride (TBAF) were purchased from sigma Aldrich chemical company and used as such. ^1H and ^{13}C NMR spectra were taken on a Bruker 300 MHz spectrometer $\text{CDCl}_3/\text{DMSO-d}_6$ as solvent. IR spectra were obtained on a Perkin-Elmer Spectrum One FTIR spectrometer. Absorption spectra were recorded in a UV- Shimadzu UV-vis spectrophotometer. Fluorescence spectra were obtained in a Horiba FluroMax-4 spectrofluorometer. For absorption spectra, a stock solution of the fluoride ion (0.5×10^{-3} M) was prepared in chloroform. A stock solution of receptor **1** (0.5×10^{-4} M) was prepared in chloroform. In each titrations, 3.0ml of receptor (CHCl_3) was titrated with 0.2 eq. (10 μL)-2 eq. (100 μL) of anion in organic medium. Emission spectra were taken by using the same solution.

Synthesis of 2, 3-Dipyrrol-2-yl ethanedione (**1**)



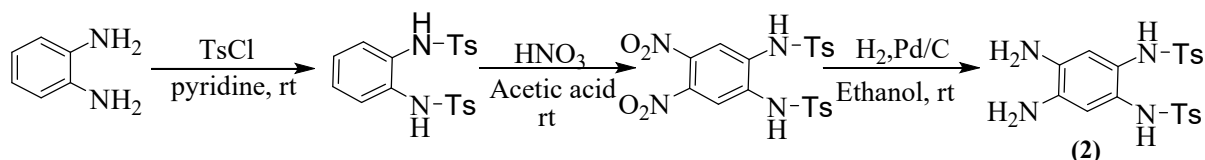
Oxalyl chloride (6.4 g, 0.05 mol) and dichloromethane (25 mL) were placed together under nitrogen atmosphere and stirred. Upon cooling to $-78\text{ }^\circ\text{C}$ in an acetone/ CO_2 bath, dry pyridine (10 g, 0.12 mol) was added, resulting in the formation of a yellow precipitate. To this cooled suspension was added a solution of freshly distilled pyrrole (6.7g, 0.1mol) in dichloromethane (25 mL) by use of cannula. Immediately, the reaction mixture was seen to turn from yellow to brown. The reaction was allowed to stir for an additional 15 min at $-60\text{ }^\circ\text{C}$, after which time hydrochloric acid (5 M, 100 mL) was added to quench the reaction. The biphasic system was then separated off and the organic phase was collected. The aqueous phase was extracted with

dichloromethane (3x30 mL), and the combined organic phase were washed with water (100 mL), dried over anhydrous sodium sulphate, filtered and evaporated to dryness. This afforded green precipitate which was purified by silica gel column chromatography (dichloromethane eluent) to afford product 2.43 gm (38%) yield as yellow powder:

$^1\text{H NMR}$: (300 MHz, DMSO d_6): δ 7.17 (m, 2H), 7.05 (m, 2H), 7.24 (d, $J = 8.0$ Hz, 4H), 6.26 (m, 2H); ESI-MS: m/z : calc for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2$, 189.05, found: 189 ($\text{M}+\text{H}$) $^+$.

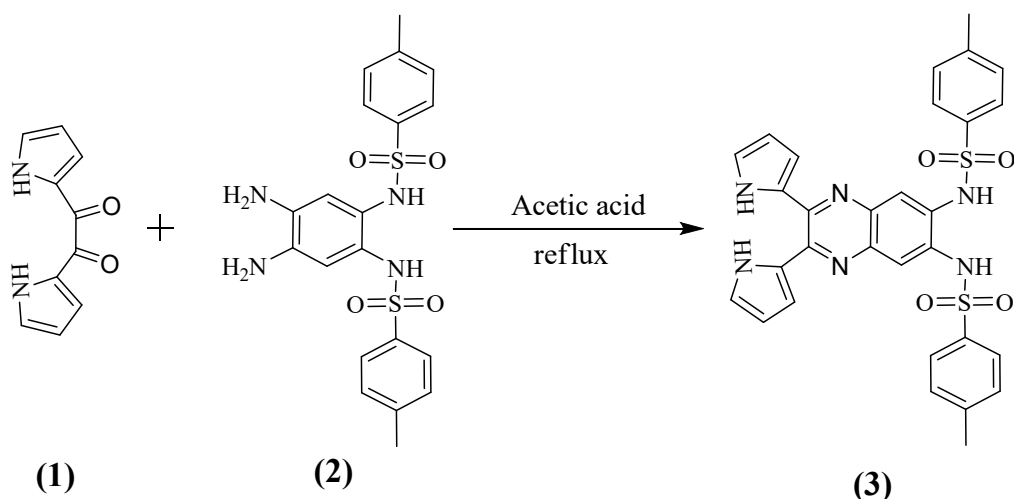
1, 2-Diamino-4, 5-bis (*p*-toluenesulfonamido) benzene (2)

This compound was synthesized by known literature procedure in three steps:



4, 5-dinitro-4, 5-bis (*p*-toluenesulfonamido) benzene (1.5 g, 1.97 mmol) and Pd/C (100 mg, 10%) were suspended in ethanol (85 mL). The resulting mixture was carried out at room temperature for 24 h in a hydrogen atmosphere. After completion of the reaction, the catalyst was filtered off and the residue washed with boiling ethanol. The solvent was evaporated under reduced pressure. After re-precipitation from methanol; product **2** was obtained as a yellowish solid in 90% (1.35 gm). decomp 209-212 $^\circ\text{C}$, FTIR Perkin Elmer (KBr) 3447, 3404, 2923, 2341, 1618, 1586, 1514, 1347-1324, 1156-1165 cm^{-1} ; $^1\text{H NMR}$ (DMSO- d_6 , 300 MHz) δ 8.38 (s, 2H), 7.56 (d, $J = 8.3$ Hz, 4H), 7.24 (d, $J = 8.0$ Hz, 4H), 6.24 (s, 2H), 4.15 (s, 4H), 2.38 (s, 6H); ESI-MS m/z calcd for $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_4\text{S}_2$ 446.1082, found 447.

2, 3-dipyrrol-2-yl quinoxaline-6, 7-diyl bis (4-methylbenzenesulfonamide) (3):



The diketone **(1)** (200 mg, 1.06 mmol) was dissolved in glacial acetic acid (50 ml) and to this was added a solution of **(2)** (4, 5-diamino-1, 2-phenylene) bis (4-methylbenzenesulfonamide) (948 mg 2.12 mmol) in acetic acid (40 mL) with stirring. The resultant mixture was then brought to reflux for 5 h in dark under an atmosphere of nitrogen. After this time the majority of acetic acid was removed under vacuum and the residue was taken up in a mixture of water (50 mL) and dichloromethane (30 mL) the organic phase was separated off and the aqueous phase was extracted with further dichloromethane (2x30 mL). The organic phase were combined and washed with saturated aqueous sodium bicarbonate solution (70 mL), water (50 mL) then brine (2x30 mL). After drying over anhydrous sodium sulphate, the solution was filtered and evaporated to dryness. The residue obtained was the purified using silica gel column chromatography as eluent (DCM: MeOH) to afford product (445 mg, 70%) of 2, 3-dipyrrol-2-yl quinoxaline-6, 7-diyl bis (4-methylbenzenesulfonamide).

FTIR Perkin Elmer (KBr): 3445, 3373, 3054, 2923, 2341, 1734, 1618, 1586, 1514, 1487, 1329, 1161. cm^{-1} ; $^1\text{H NMR}$: (300 MHz, CDCl_3 , TMS): δ 9.58 (s, 2H), 7.62 (d, 4H), 7.39 (s, 2H), 7.23 (d, 4H), 6.70(m, 2H), 6.89(m, 2H), 6.27(m, 2H), 4.68(s,2H), 2.33(s,6H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , TMS): 144.4, 143.9, 137.7, 135.1, 131.1, 129.7, 128.6, 127.6, 122.4, 121.5, 113.1, 110.0, 21.5; **ESI-MS**: m/z 598 (M^+), 599 ($\text{M}+\text{H}^+$), 616 ($\text{M}+\text{H}_2\text{O}^+$); **HRMS** m/z : calcd for $\text{C}_{30}\text{H}_{26}\text{N}_6\text{O}_4\text{S}_2$: 599.15448, found 599.15297

Supporting figures

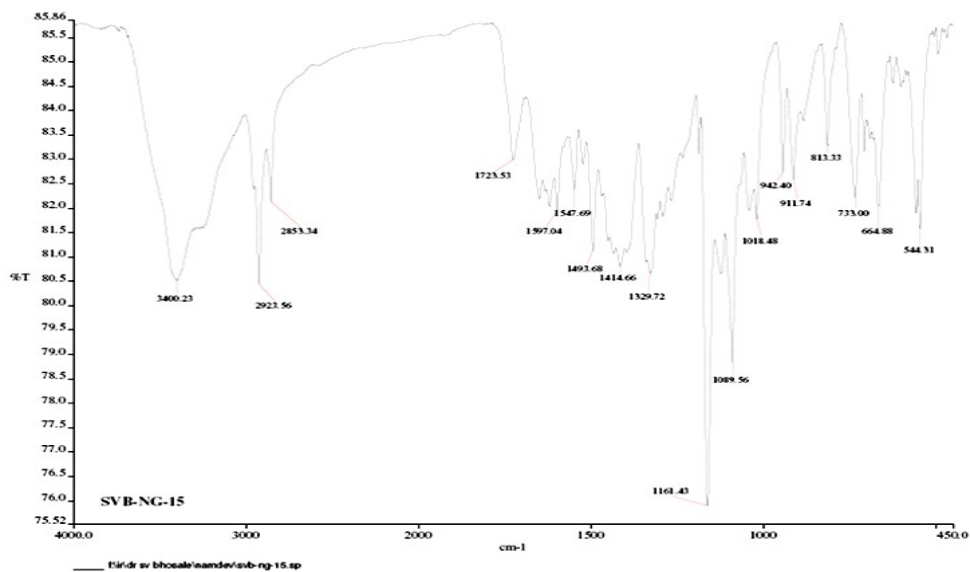


Fig. S1 FT-IR Spectrum of receptor 3

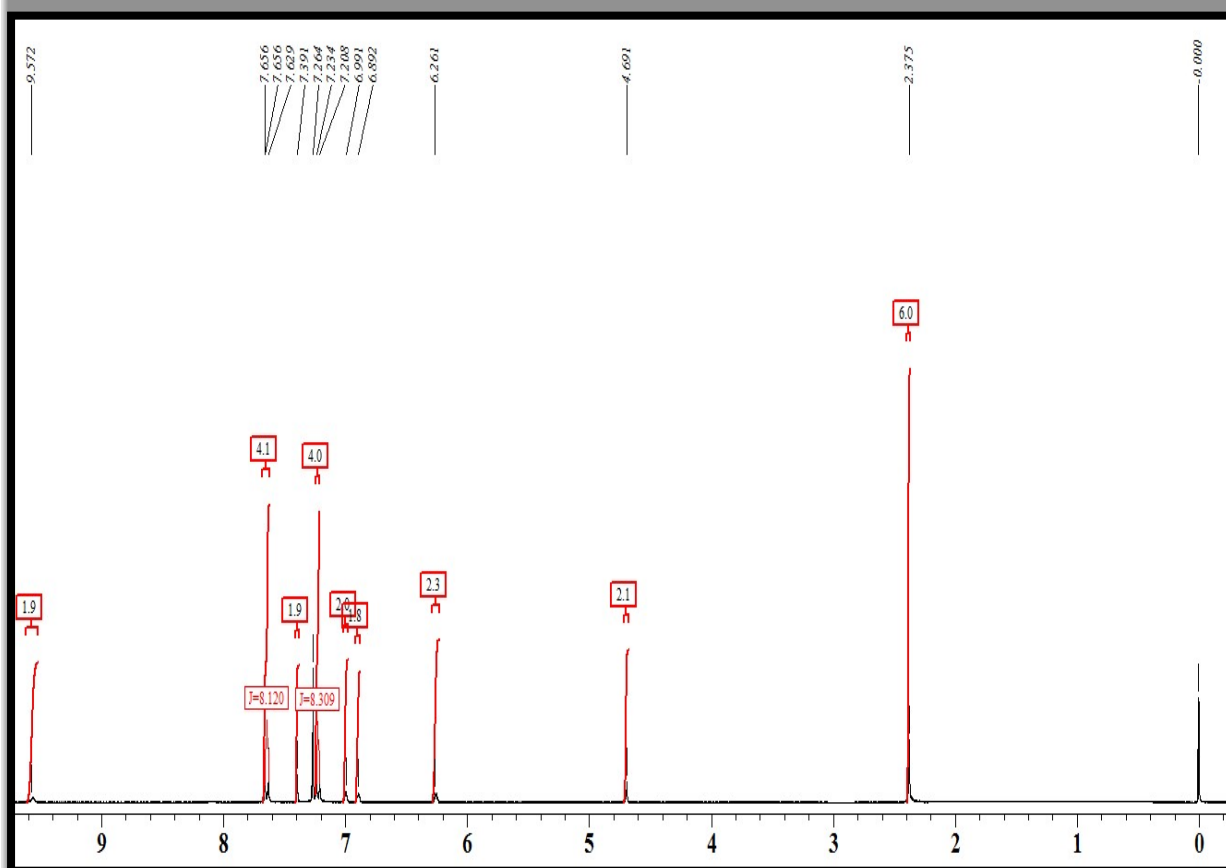


Fig. S2 ^1H NMR spectrum of receptor 3

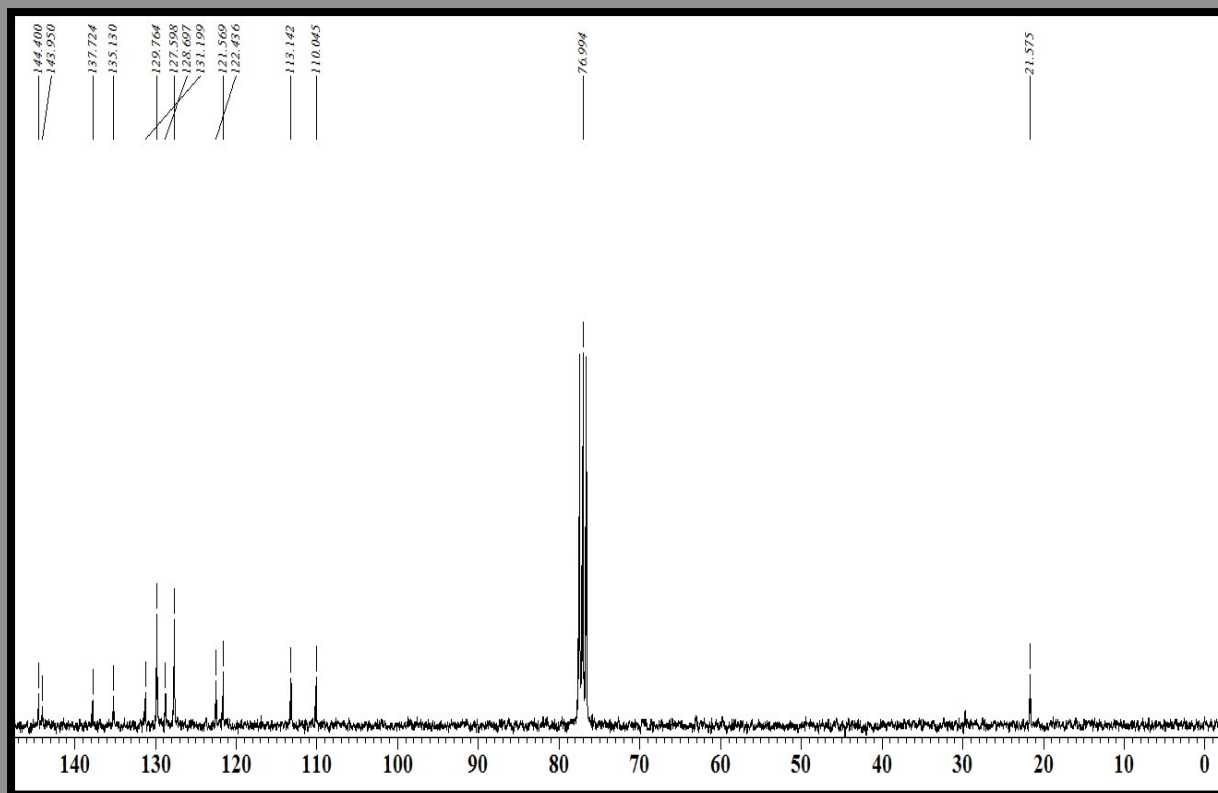


Fig. S3 ^{13}C - NMR spectrum of receptor 3

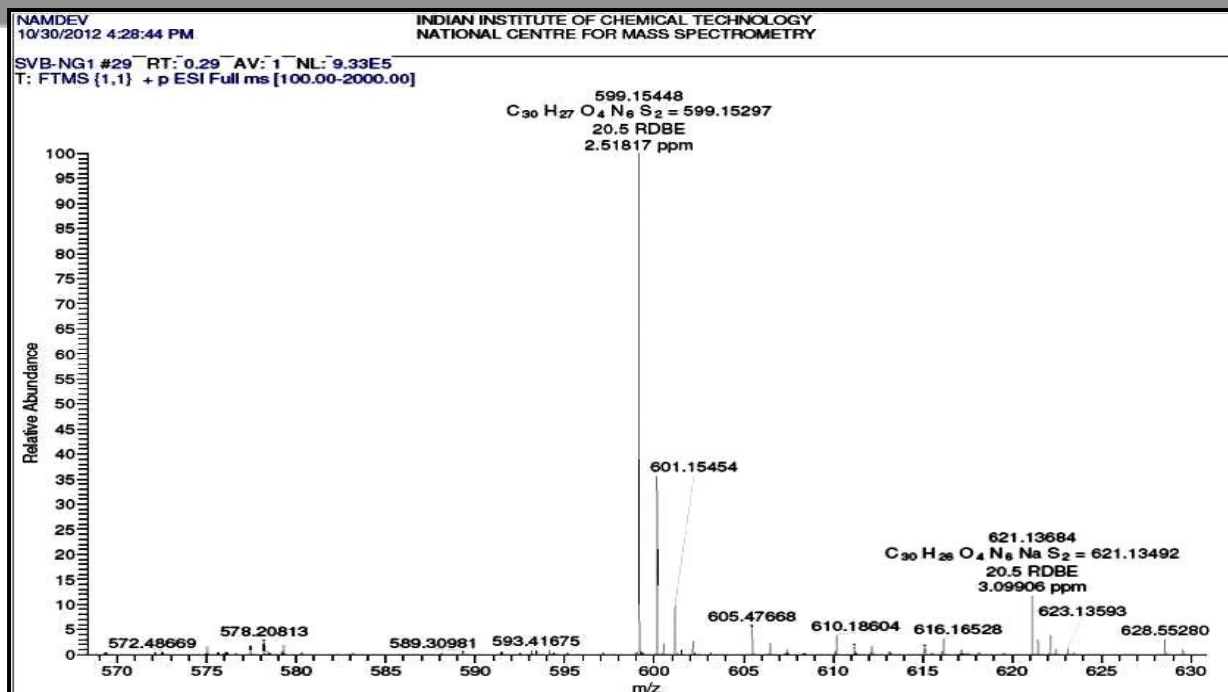


Fig. S4 HRMS spectrum of receptor 3

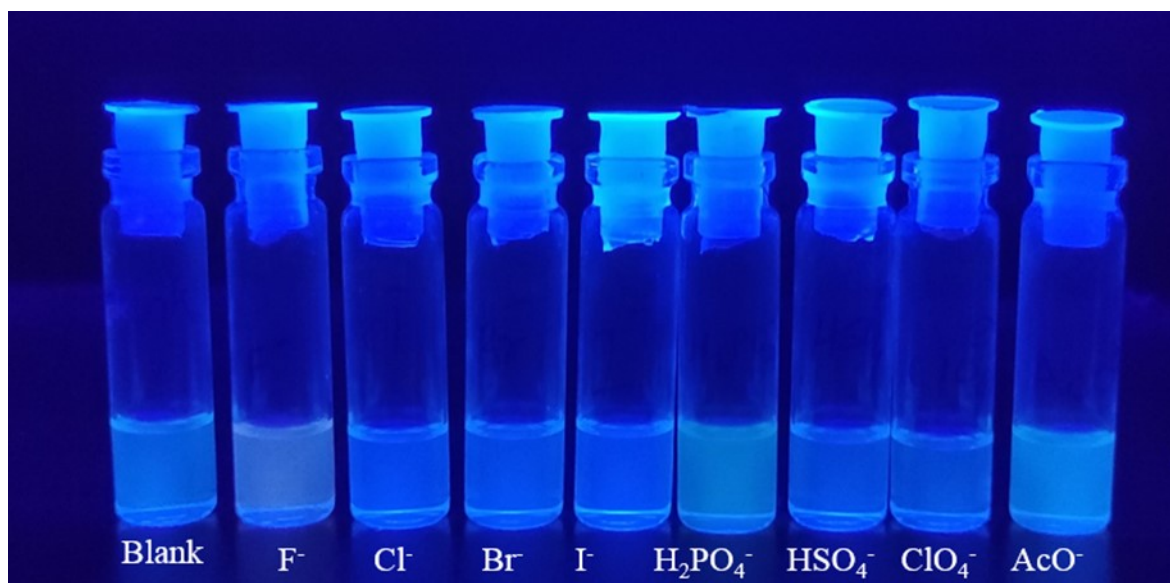


Fig. S5 Color changes of receptor **DPBS** (5×10^{-5} M) in CHCl_3 upon addition of 5 equivalents tetrabutylammonium anions (5×10^{-4} M) under UV light ($\lambda_{\text{max}}=365$ nm).

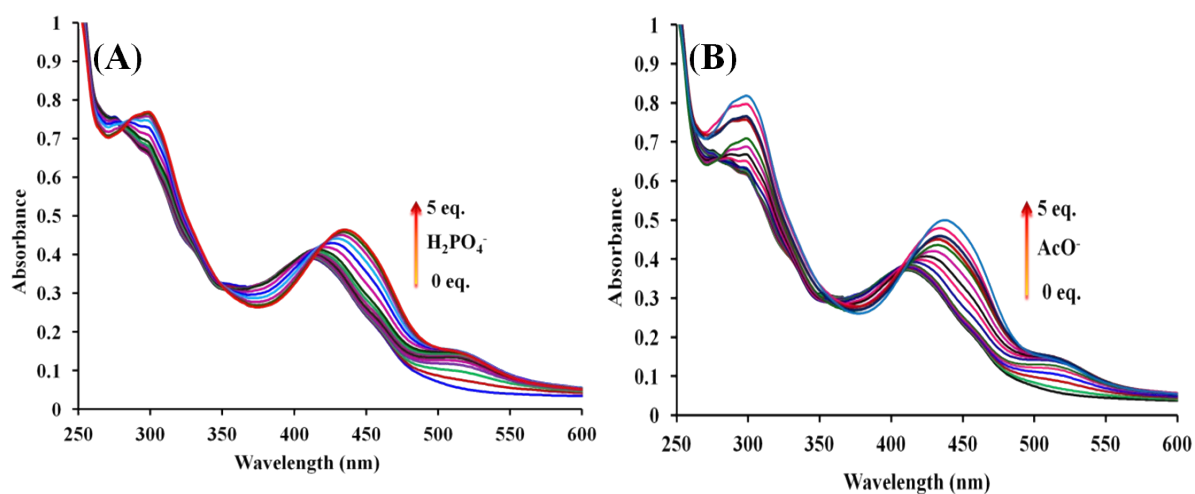


Fig. S6 Changes in absorption spectra of receptor **DPBS** (5×10^{-5} M) with an increasing amount of (A) H_2PO_4^- (B) AcO^- (5×10^{-4} M) respectively.

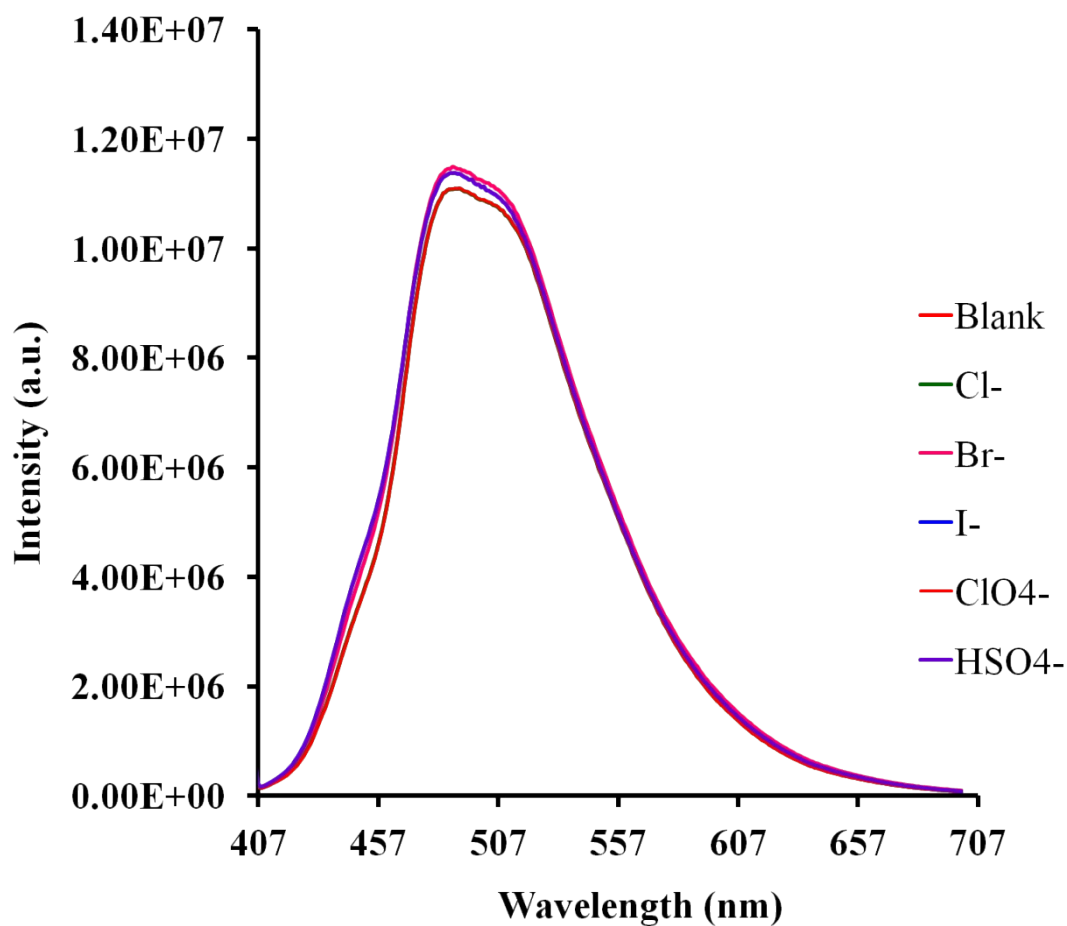


Fig.S7 Effect of various 5 equivalent anion addition (5×10^{-4} M) on the emission ($\lambda_{\text{ex}}=400$ nm) of DPBS (5×10^{-5} M).

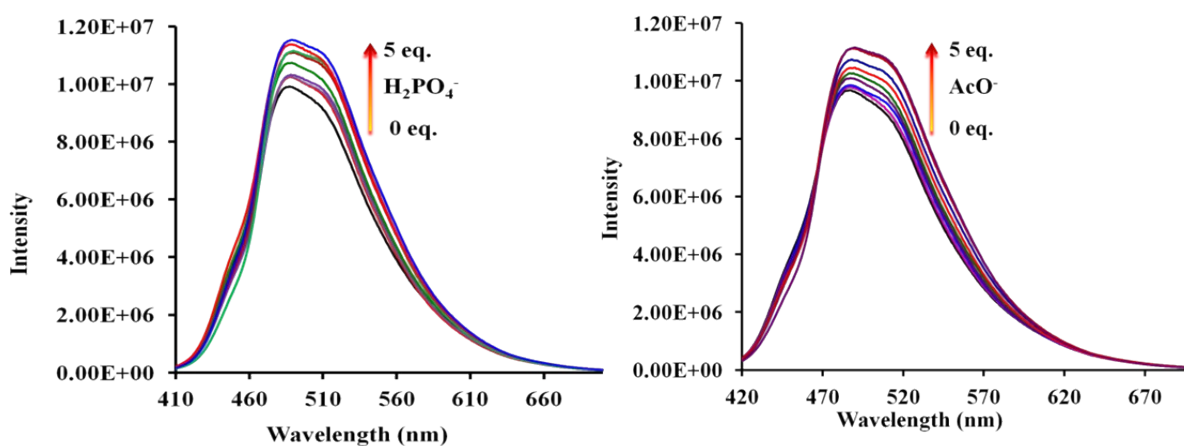


Fig. S8 Effect of anion addition on the emission ($\lambda_{\text{ex}}=400$ nm) of DPBS (5×10^{-5} M) with an increasing amount of (A) H_2PO_4^- (B) AcO^- (5×10^{-4} M) respectively.

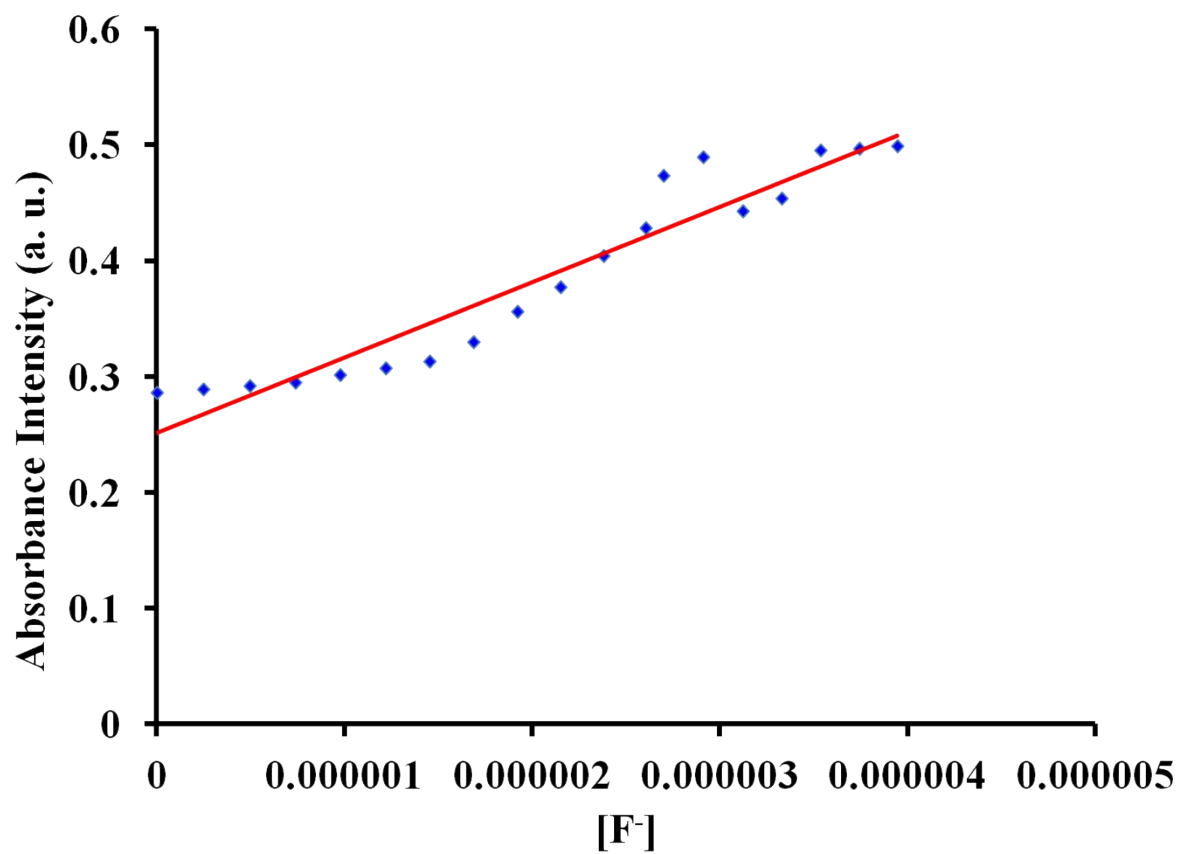


Fig.S9 Absorbance Intensity of solution DPBS (5×10^{-5} M) versus the concentration of F⁻.

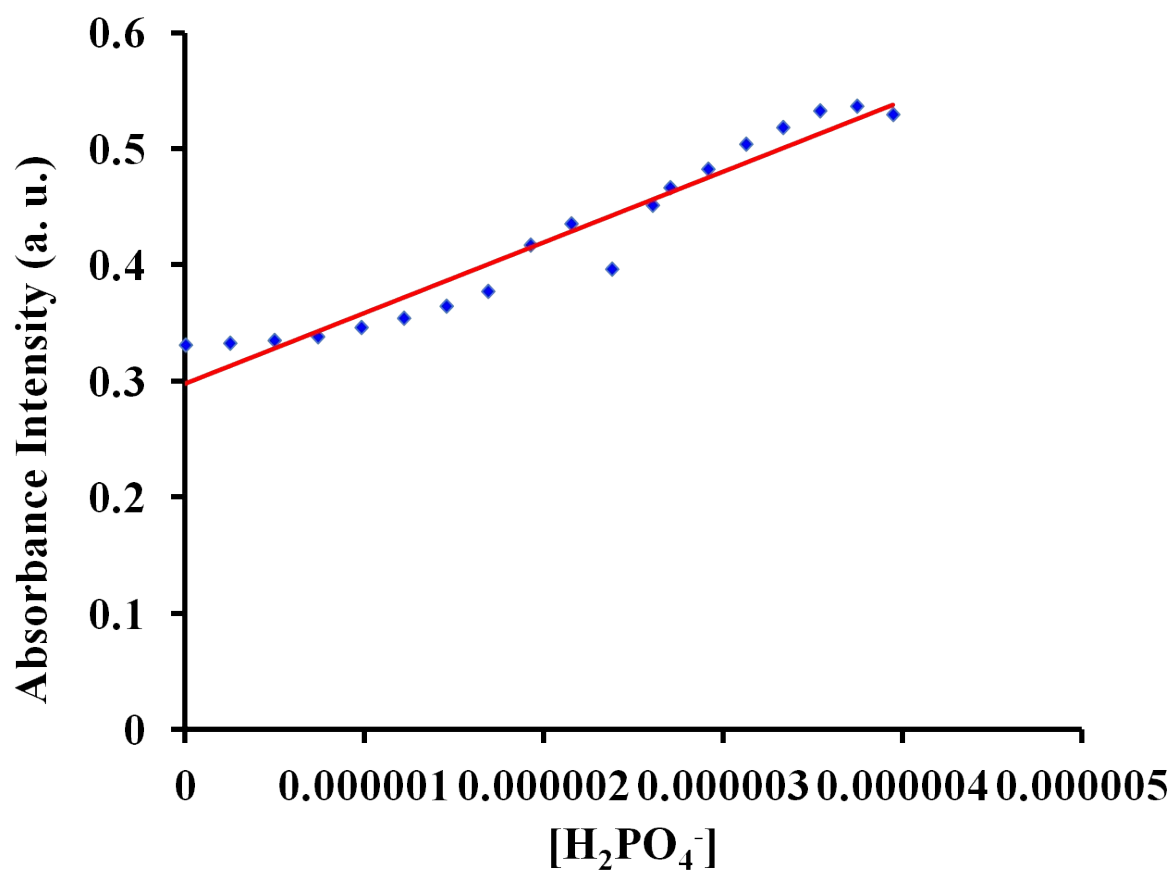


Fig.S10 Absorbance Intensity of solution DPBS (5×10^{-5} M) versus the concentration of H_2PO_4^- .

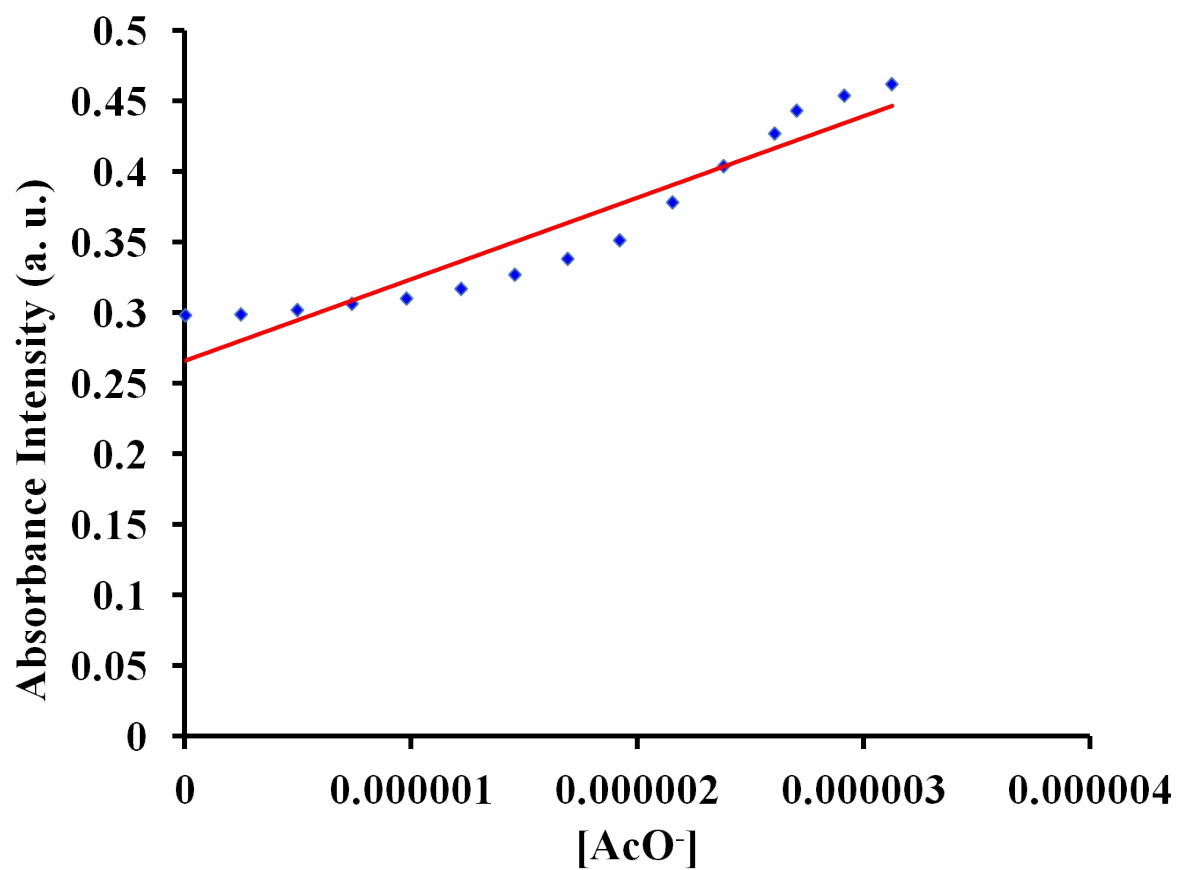


Fig.S11 Absorbance Intensity of solution **DPBS** (5×10^{-5} M) versus the concentration of AcO^- .