Supporting Information

Phosphonium and Ammonium Fluorescein for Selective Detection of HSO_4^- and CN^- Ions in Aqueous Medium

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EXPERIMENTAL METHOD

Materials and methods: Fluorescein dye, chloroform, NaOH and various anionic salts were purchased from Sigma-Aldrich, Avara and Alfa Aesar. Solutions of anion salts were prepared from their tetra-butylammonium salts. All reagents and solvents were used as received without further purification. Ultrapure Millipore water was used throughout the experiments. Infrared spectra were recorded on a Perkin-Elmer's Spectrum 65 FT-IR Spectrometer using KBr pellet. The Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker Avance 500 MHz FT-NMR spectrometer at room temperature in MeOH-d4 and DMSO-d6. Multiplicities are abbreviated as s = singlet, d = doublet, t = triplet, quart = quartet, quint = quintet, sext = sextet and m = multiplet. UV visible absorption spectra were recorded by using an analytical UV SPECTRO 2060+ UV-vis Spectrophotometer, and Fluorescence spectra were recorded on Jasco FP 6500 spectrophotometer.

Synthesis and characterization:

Synthesis and characterization of N-Boc-phenylalaninol (**5**): The phenyl alaninol (**4**) (1.0 g, 6.60 mmol) was dissolved in 10.0 mL methanol in a 50 mL round bottom flask and cooled to 0 °C. The triethylamine (1.74 mL, 13.2 mmol) and $(Boc)_2O$ (2.16 g, 9.9 mmol) were added to this solution. The reaction mixture was stirred at 0 °C to rt. for 4 h. The progress and completion of the reaction were determined by the TLC technique. On completion of the reaction, the hexane was added to precipitate out the product and to remove unreacted $(Boc)_2O$. The mixture was washed with hexane (2 x 15 mL) and ethyl acetate/hexane ratio (2:98) (2 x 10 mL) to produce a pure product **5** as a white solid (1.57 g, 95%) yield. R_f = 0.50, (8:2 hexane: ethyl acetate); ^{1}HNMR (500 MHz $CDCl_3$): δ 7.30 (t, 2H, *J* = 7.3 Hz), 7.22 (d, 3H, *J* = 7.8 Hz), 4.80 (s, 1H), 3.87 (s, 1H), 3.65 (dd, 1H, *J* =7.6 Hz), 3.55 (m, 1H), 2.83 (d, 2H, *J* =6.6 Hz), 1.41 (s, 9H).

Synthesis and characterization of N-Boc-OTs-L-phenylalaninol (**6**): N-Boc-L-phenylalaninol (**5**) (1.0 g, 3.97 mmol) was dissolved in 5.0 mL of dry DCM in a 50 mL round bottom flask. The RBF was then transferred to the ice bath, and the temperature of the solution was maintained at 0 °C. The triethylamine (2.2 mL, 15.88 mmol), DMAP (48 mg, 0.397 mmol) and *p*-toluenesulfonyl chloride (1.5 g, 7.94 mmol) were added to this solution. The reaction mixture was stirred at 0 °C to rt. for 4 h. The TLC techniques measured the progress and completion of the reaction. Once the reaction was completed, the water was added to the reaction mixture and allowed to stir for 5 min to dissolve the salt in water. The organic layer was collected after separating the DCM layer from water. The product was extracted in the organic layer and the solvent was evaporated in a rotary evaporator to obtain the crude product, which was purified through column chromatography having silica gel as the stationary phase and ethyl acetate: hexane as the mobile phase. The pure product **6** was obtained as a white solid yielding 75% as an isolated yield. R_f = 0.5 (hexane: ethyl acetate = 8:2); ^{1}HNMR (500 MHz, $CDCl_3$): δ/ppm 7.78 (d, 2 H, *J* = 8.0 Hz), 7.35 (d, 2 H, *J* = 8.2 Hz), 7.20 (m, 3 H), 7.70 (d, 2 H, *J* = 7.0 Hz), 4.77 (d, 1 H, *J* = 8.3 Hz), 4.00 (t, 1 H, *J* = 9.5 Hz), 3.84 (d, 1 H, *J* = 8.3 Hz), 2.83 (dd, 1 H, *J* = 6.9 Hz), 2.76 (q, 1 H, *J* = 7.16 Hz), 2.46 (s, 3 H), 1.38 (s, 9 H); ^{13}CNMR δ/ppm (125 MHz, $CDCl_3$): 155.0, 145.0, 136.6, 132.2, 130.0, 129.2, 128.6, 128.0, 126.7, 79.7, 70.0, 50.8, 37.1, 28.2 (x3), 21.7.

Synthesis and characterization of (S)-(3-phenyl-2-aminopropyl)-trimethylammonium (PTMA) tosylate (**8**): To N-Boc-*O*Ts-L-phenylalaninol (**6**) (250 mg, 0.61 mmol), 31-35% ethanolic solution of trimethylamine (4.0 mL) was added and the reaction mixture was allowed to stir at rt. to 50 °C. The reaction mixture was allowed to stir for 6 h. The progress of reactions was monitored by TLC and the completion of the reaction was found at rt. and 50 °C separately providing 48% and 65%, respectively. The excess of trimethylamine was evaporated in rotary evaporator providing the crude N-Boc protected trimethylammonium tosylate salt **(7)**. The 2.0 ml of 20% TFA solution in DCM was added to the crude residue **7** and allowed to stir for 10 min for Boc deprotection, and the excess TFA was evaporated in a rotary evaporator. The final product **8** was purified by washing the crude mixture with diethyl ether followed by an ethyl acetate-hexane mixture. The pure product (**8**) was collected as a yellowish semi-solid and the isolated yield was 30%. The synthesized compound, (S)-(3-phenyl-2-aminopropyl)-trimethylammonium (PTMA) tosylate **(8)** was further recrystallized in methanol. R_f = 0.2 (DCM: MeOH = 20:1); ^{1}HNMR (500 MHz, MeOH-d4): δ/ppm 7.67 (d, 2 H, *J* = 7.6 Hz), 7.27 (q, 2 H, *J* = 7.3 Hz), 7.20 (d, 5 H, *J* =7.5 Hz), 4.35 (t, 1 H, *J* =8.4 Hz), 4.21 (q, 1 H, *J* = 8.5 Hz), 4.10 (quint, 1 H, *J* = 5.63 Hz), 3.46 (s, 3 H), 3.27 (s, 3 H); 3.12 (s, 3 H), 2.84 (s, 1 H), 2.81 (t, 1 H, *J* = 6.7 Hz), 2.63 (d, 1H, J =14.0 Hz), 2.33 (s, 3 H); ^{13}CNMR δ/ppm

(125 MHz, MeOH-d4): 143.5, 142.0, 137.7, 131.3, 130.6, 130.5, 130.1 (x3), 128.0, 127.0 (x2), 70.6, 58.7, 54.7, 54.0, 45.5, 41.7, 21.3; Mass: Calculated for $[M]^+$ m/z = 193.17 found m/z: 193.14 for $[M]^+$

Synthesis and characterization of (S)-(3-phenyl-2-aminopropyl)-triphenylphosphonium (PTPP) *tosylate* (**10**): *N*-Boc-*O*Ts-L-phenylalaninol (**6**) (500 mg, 1.2 mmol) was dissolved in toluene (6 mL), and triphenylphosphine (644.62 mg, 2.46 mmol) was added to it reaction mixture and refluxed at 60 °C for 4 days under nitrogen atmosphere. The progress of the reactions was monitored by TLC. Once the reaction was completed, the excess solvent was evaporated in a rotary evaporator providing the crude N-Boc protected triphenylphosphonium tosylate salt (**9**). The 2.0 ml 20% TFA solution in DCM was added to the crude residue **9** and allowed to stir for 10 min for Boc deprotection. The TFA and excess solvent were evaporated in a rotary evaporator. The final product **10** was purified by washing the crude mixture with diethyl ether followed by an ethyl acetate-hexane mixture. The pure product (S)-(3-phenyl-2-aminopropyl)-triphenylphosphonium (PTPP) tosylate (**10**) was obtained as a white solid and the isolated yield was 30%. R_f = 0.3 (7:3 hexane: ethyl acetate); FTIR (KBr): υ_{max}/cm^{-1}: 3400 (NH_2 stretching) 3118 (aromatic CH stretching), 2936, 2841 (C-H stretching of L-phenylalaninol) 1223 (C-N stretching); Mass: Calculated for $[M]^+$ m/z = 396.1876 found m/z: 396.2000 for $[M]^+$; ^{1}HNMR (500 MHz, DMSO-d6): δ/ppm 8.21 (br s, 4 H), 7.74 (d, 3 H, *J* = 7.6 Hz), 7.32 (br t, 6 H, *J* = 8.0 Hz), 7.24 (m, 5 H), 7.11(br d, 3 H , *J* = 7.7 Hz), 7.03 (m, 3 H), 4.08 (dd, 1 H, J = 2.8, 10.7 Hz) 3.82 (dd, 1 H, *J* = 4.5, 10.5 Hz), 3.67 (m, 1 H), 3.42 (s, 2 H), 2.89 (dd, 1 H, *J* = 5.7, 12.8 Hz) 2.74 (dd, 1 H, *J* = 9.3, 12.8 Hz), 2.28 (s, 3 H)..

Synthesis and characterization of fluorescein-L-3-phenyl-2-aminopropyl trimethylammonium (FPTMA) tosylate ***(1):***

(A) Mechanochemical method: Fluorescein monoaldehyde (**11**) (200 mg, 0.55 mmol) was taken in a clean and dry mortar, and (S)-(3-phenyl-2-aminopropyl)-trimethylammonium (PTMA) tosylate (**8**) (354 mg, 0.50 mmol) was added to it followed by a few drops of methanol. The reaction mixture was ground well with a pestle for 30 min, and the progress of the reaction was monitored by the TLC technique. The obtained crude was purified by washing with DCM followed by DCM/MeOH mixture in 50:1 ratio, and the isolated yield was found to be 60% of FPTMATs (**1**).

(B) Solution-based method: To a solution of fluorescein monoaldehyde (2) (100 mg, 0.28 mmol) in methanol (20 mL), acetic acid in a catalytical amount to maintain pH 6.5 and (S)-(3-phenyl-2-aminopropyl)-trimethylammonium (PTMA) tosylate (**8**) (177 mg, 0.25 mmol) was added. The mixture was stirred for 24 h at rt. The completion of the reaction was confirmed using thin-layer chromatography. The obtained crude mixture was purified by washing with DCM followed by DCM/MeOH mixture in 50:1 ratio, the isolated yield was found to be 45% for FPTMATs (**1**). R_f = 0.2 (DCM: MeOH = 10:1); 1HNMR (500 MHz, MeOH-d4): δ/ppm 8.50 (d, 1 H, J = 3.26 Hz), 7.92 (d, 1H, J = 7.6 Hz), 7. 71 -7.60 (m, 4 H), 7.22 (t, 2 H, J = 6.9 Hz), 7.14-7.01 (m, 7 H), 6.63 (m, 1 H), 6.47 (m, 4 H), 4.30 (s, 1 H), 3.98 (q, 1 H, J = 9.0 Hz), 3.72 (d, 1 H, J = 13.5 Hz), 3.10 (s, 9 H), 3.07 (m, 1H), 2.76 (m, 1 H), 2.27 (s, 3 H); ^{13}CNMR δ/ppm (125 MHz, MeOH-d4): 171.5, 163.7, 163.2, 153.4, 152.8, 142.7, 142.0, 137.0, 136.3, 134.0, 131.3,131.1, 130.1, 129.8 (x2), 129.7, 129.6, 128.3, 126.9, 126.3 (x2), 125.5, 125.3, 119.5, 116.7, 115.3, 115.0, 111.2, 109.8, 107.4, 103.8, 71.2, 65.3, 54.7 (x3), 42.3, 35.2, 30.6, 21.2; FTIR (KBr): υ_{max}/cm^{-1} 3706 (O-H stretching), 3046 (O-H stretching and aromatic CH stretching), 2961, 2926, 2879, 2840 (aliphatic C-H stretching, 1765 (C=O stretching for lactone), 1646 (C=N stretching of amine), 1229 (C-N stretching), 1466 (C-H stretching for CH_3); Mass: Calculated for $[M]^+$ m/z = 535.22, Found m/z = 535.17 for $[M]^+$. Molecular formulae $C_{40}H_{38}N_2O_8S$

Synthesis of fluorescein-L-3-phenyl-2-aminopropyl triphenylphosphonium (FPTPP) tosylate (**2**)*:*

(A) Mechanochemical method: Fluorescein monoaldehyde (**11**, FMA) (200 mg, 0.55 mmol) was taken in clean and dry mortar. The (S)-(3-phenyl-2-aminopropyl)-triphenylphosphonium (PTPP) tosylate (**10**) (455 mg, 0.5 mmol) was added to it followed by a few drops of methanol. The reaction mixture was ground well with a pestle for 30 min, and the progress of the reaction was monitored by the TLC technique. The crude mixture was purified by washing with hexane followed by DCM/MeOH mixture in 50:1 ratio, the isolated yield was found to be 55% for FPTPPTs (**2**).

(B) Solution-based method**:** To a solution of fluorescein monoaldehyde (**11**, FMA) (100 mg, 0.28 mmol) in methanol (20 mL), acetic acid in a catalytic amount to maintain pH 6.5 and (S)-(3-phenyl-2-aminopropyl)-triphenylphosphonium (PTPP) tosylate (**10**) (227 mg, 0.25 mmol) was added. The mixture was stirred for 48 h at rt. The completion of the reaction was confirmed using thin-layer chromatography. The crude material was purified by washing with hexane followed by DCM/MeOH mixture in 50:1 ratio, and the isolated yield was found to be 35% for FPTPPTs (**2**). R_f = 0. 7 (DCM: MeOH = 20:1); ^{1}HNMR (500 MHz, DMSO-d6): δ/ppm 14.36 (d, 1 H, *J* = 9.2 Hz), 10.23 (s, 1 H), 8.83 (d, 1 H , *J* = 8.0 Hz), 8.01 (d, 1 H, *J* = 7.4 Hz), 7.80 (m, 2 H), 7.72 (m, 4 H), 7.47 (d, 1 H, *J* =7.5 Hz), 7.28 (m, 10 H), 7.21 (m, 6 H), 7.11 (d, 1 H, *J* = 7.5 Hz), 6.75 (s, 1 H), 6.66 (d, 1 H, *J* = 8.8 Hz), 6.58 (m, 5 H), 4.35 (t, 1 H, *J* = 9.5 Hz), 4.26 (d, 1 H, *J* = 9.6 Hz), 4.09 (s, 1 H), 3.03 (d, 1 H, *J* = 12.3 Hz), 2.91 (d, 1 H, *J* = 8.9 Hz), 2.29 (s,

3 H); ^{13}CNMR (125 MHz, DMSO-d6): δ/ppm 168.7, 165.4, 161.4, 159.5, 151.0, 150.3, 145.5 (x2), 145.0, 137.8, 134.6, 133.4, 132.1, 132.0 130.3-130.0 (x3), 129.4, 129.3, 129.0, 128.7-128.1 (x12), 127.5, 127.4, 126.6, 126.4, 126.1, 125.5 (x3), 124.0, 119.7, 114.4, 113.3, 109.4, 107.1, 105.2, 102.5, 102.0, 94.1, 39.5, 39.7, 39.9, 21.1; FTIR (KBr): υ_{max}/cm^{-1} 3073 O-H stretching), 3035 (O-H stretching and aromatic CH stretching), 2965, 2916, 2868, 2840 (aliphatic C-H stretching), 1761 (C=O stretching for lactone), 1644 (C=N stretching of amine), 1221 (C-N stretching); Mass: Calculated $[M]^+$ m/z = 738.24, Found m/z = 738.35 for $[M]^+$ Molecular formulae: $C_{55}H_{44}NO_8PS$

Table S1. Synthesis of anionic receptors through MC and SBS method at room temperature

method	Product (yield)	reactants	mmol	wt. (mg)	time	purification method
MC	FPTMATs (60%)	FMA	0.55	200	30 min	DCM and DCM: MeOH (50:1)
		PTMATs	0.50	353.68		
		MeOH	-------	Few drops		
SBS	FPTMATs (45%)	FMA	0.275	100	48 h	DCM and DCM: MeOH (50:1)
		PTMATs	0.25	176.84		
		MeOH	------	20 mL		
		AcOH (Cat.)				
MC	FPTPPTs (55%)	FMA	0.55	200	30 min	Hexane and DCM: MeOH (50:1)
		PTPPTs	0.50	455.29		
		MeOH	-----	Few drops		
SBS	FPTPPTs (35%)	FMA	0.275	100	48 h	Hexane and DCM: MeOH (50:1)
		PTPPTs	0.25	227.64		
		MeOH	--------	20 mL		
		AcOH (Cat.)				

Solution preparation for solubility, solvent effect and pH effect study:

Anionic receptors FPTMATs **(1)** (7.07 mg, 10.0 mmol) and FPTPPTs **(2)** (9.10 mg, 10.0 mmol) were dissolved in 1.0 mL methanol and DMSO respectively to prepare the 1 x 10^{-2} M stock solution. The 10.0 µL solution of FPTMATs **(1)** and FPTPPTs **(2)** were taken out from 1 x 10^{-2} M stock solution and diluted with 2.0 mL of various solvents to prepare the final 50 x 10^{-6} M concentration. The UV-vis spectra were measured at room temperature without giving any incubation time. For the pH study, 5.0 µL solution was taken out from 1 x 10^{-2} M stock solution and diluted with 2.0 mL of various solvents to prepare the final 20 x 10^{-6} M concentration. The UV-vis spectra were recorded at room temperature after incubating samples for 1 hour.

Solution preparation for absorbance study and UV-vis measurements:

From the 1 x 10^{-2} M stock solutions of FPTMATs (**1**) and FPTPPTs (**2**), the 500.0 µL solution was taken out and diluted with 50.0 mL 95:5 water-methanol to prepare the final 100.0 µM. The 1 x 10^{-2} M stock solution of all anions was made from their tetrabutylammonium salts by dissolving in water. The 75.0 µM stock solutions of ions were taken out and diluted up to 1.5 mL with water-methanol (95:5) to prepare 5 x10^{-4} M concentration. To perform the study of ion selectivity, 1.5 mL anion salts solution was added to 1.5 mL of FPTMATs (**1**) and FPTPPTs (**2**) solution to prepare 5:1 (ions: receptor) ratio for scanning of various anions. The UV-vis spectra were noted at room temperature without giving any incubation time.

The experiment and solution preparation for anion scanning by FPTMATs (**1**) in water and at pH 7.4 was also performed and prepared in the same manner.

The UV-visible titration of FPTMATs (**1**) and FPTPPTs (**2**) to determine LOD for strongly interacting anions HSO_4^- ion and CN^- ion respectively was performed in 95:5 water-methanol. A stock solution of HSO_4^- and CN^- ion in 10^{-2} M, 10^{-3} M and 10^{-4} M were prepared in water. The calculated amount of HSO_4^- ion solution was added to 50.0 µM FPTMATs (**1**) in 95:5 water-methanol

solution to make a final concentration of HSO_4^- ion from 0.01 eq. to 10.0 eq. ($0.5x10^{-6}$ M to $5x10^{-4}$ M) and UV-visible absorption spectra were recorded. Similarly, the incremental amount of CN^- ion was added to FPTPPTs (**2**) of known concentrations from 0.01 eq. to 50.0 eq. (0.5×10^{-6} M and 5×10^{-3} M) and the UV-visible absorption spectra were recorded by mixing well the solution and without giving any time for incubation.

Solution preparation for fluorescence measurements: From the 1×10^{-2} M stock solutions of FPTMATs **(1)** and FPTPPTs **(2),** the 100.0 µL solution was taken out and diluted with 50.0 mL 95:5 water-methanol to prepare the final 20.0 µM concentration. From 1×10^{-2} M solution of anions of their tetra butyl ammonium salts in water solution, the 30.0 µM anionic solutions were taken out and diluted with 1.5 mL 95:5 (v/v) water-methanol solution to prepare the final concentration 2×10^{-4} M (200.0 µM). To perform the ion selectivity study, the 1.5 mL 200.0 µM anion solution was added to 1.5 mL of FPTMATs (**1**) and FPTPPTs (**2**) in 95:5 water-methanol solutions separately. The emission spectra were obtained by mixing well the solutions at room temperature without giving any incubation time. The emission spectra were recorded at λ_{ex} = 460 nm with slit width = 3.0 nm and instrument sensitivity low.

The fluorometric titration of FPTMATs **(1)** and FPTPPTs (**2**) was performed in 95:5 water-methanol to determine LOD for the strongly interacting anions HSO_4^- ion and CN^- ion, respectively. A stock solution of HSO_4^- ion and CN^- ion in 10^{-2} M, 10^{-3} M and 10^{-4} M were prepared in water. The calculated amount of HSO_4^- ion solution was added to 10.0 µM FPTMATs (**1**) in 95:5 water-methanol solution to make the final concentration of HSO_4^- ion ranging from 0.1 eq. to 10.0 eq. ($1x10^{-6}$ M to $1x10^{-4}$ M) and the fluorescence spectra were recorded at λ_{ex} = 460 nm with slit width = 3.0 nm and instrument sensitivity low. Similarly, the incremental amount of CN^- ion was added to FPTPPTs **(2)** of known concentrations ranging from 0.1 eq. to 10.0 eq. (1×10^{-6} M and 1×10^{-4} M) and the fluorescence spectra were recorded by mixing well the solution and without giving any time for incubation at λ_{ex} = 460 nm with slit width 3.0 nm and instrument sensitivity low in water/methanol (95:5 v/v).

Preparation of solution for Job plot measurements: The same concentration of anionic receptor FPTMATs **(1)** and HSO_4^- ion as 100×10^{-6} M was prepared in water/methanol (95:5 v/v). The different volumes ranging from 0.3 mL to 3.0 mL of receptor FPTMATs (**1**) were transferred into vials and were made up with the equal concentration of HSO_4^- ion to prepare a total volume of 3.0 mL and mole fraction ratio of HSO_4^- ion from 0 to 0.9. The UV-visible spectra were recorded at room temperature without giving any incubation time.

Job's plot for FPTPPTs (**2**) and CN^- ion was also performed at the same concentration and with the same method in water/methanol (95:5 v/v).

Preparation of solution for Mass spectroscopic study: The ESI-MS, a soft ionization technique ascertained the complex formation of the FPTMATs (**1**) and FPTPPTs (**2**) with HSO_4^- ion and CN^- ion. The compounds were dissolved in methanol (10.0 mL), and an excess amount (10-fold) of the tetrabutylammonium salt of HSO_4^- ion and CN^- ion were added into the solutions of FPTMATs (**1**) and FPTPPTs (**2**), respectively. The reaction mixtures were shaken well, and the solutions were analysed by LC-MS (ESI-MS) instrument. The mass data obtained are as follows. For FPTMATs-HSO_4^- complex, the MS (m/z): found 731.2254 for [FPTMATs+$2HSO_4^-$], calculated 731.1581; For FPTPPTs-CN^- ion MS (m/z): found 765.2441for [FPTPPTs+$CN^- + H^+$], calculated 765.2513.

Preparation of solution for FTIR spectroscopic study: The complex formation of the FPTMATs (**1**) and FPTPPTs (**2**) with HSO_4^- ion and CN^- ion were determined by FTIR technique. The compounds were dissolved in methanol (10.0 mL), and an excess amount (5 fold) of the tetrabutylammonium salt of HSO_4^- and CN^- ion were added into the solutions, respectively. The reaction mixtures were shaken well and dried in a vacuum oven for 24 h, and the FTIR spectrum was recorded on KBr pellet. The FTIR data obtained are as follows. For FPTMATs-HSO_4^- complex: ν cm^{-1} 3698, 3300, 2960, 2870 and 1400; For FPTPPTs-CN^- complex: ν cm^{-1} 3681, 3336, 2967, 2873, 2271, 1470.

Preparation of solution for ^{1}HNMR titration of the FPTMATs (1) and FPTPPTs (2) with HSO_4^- and CN^- ion:

The anionic receptors FPTMATs **(1)** (17.65 mg) and FPTPPTs **(2) (**22.75 mg**)** were dissolved in 0.5 mL MeOH-d4 and DMSO-d6, respectively to prepare 50.0 mmol receptor solution. 10.5 mL stock solution of $TBAHSO_4$ and TBACN were made in MeOH-d4 and DMSO-d6. The calculated amount of HSO_4^- ion was added to 50.0 mmol FPTMATs **(1)** solution to prepare an equivalent concentration ratio of 0.5, 1.0, 2.0 and 3.0 in MeOH-d4. ^{1}HNMR spectra were recorded at room temperature after mixing well the solution**.** ^{1}HNMR titration of FPTPPTs (2) with CN^- ion was also performed at the same experimental condition in DMSO-d6.

Preparation of solution for HSO_4^- ion and CN^- ion detection at different pH:

From the prepared stock solution of FPTMATs **(1)** and FPTPPTs (**2**) in the concentration of 1 x 10^{-2} M, 50.0 µL solution was taken out and diluted with 10.0 mL 10.0 mM Tris-HCl buffer with the respective pH solution to prepare 50.0 µM concentrations. The 1.5 mL FPTMATs (**1**) and FPTPPTs (**2**) solution were taken out and diluted with the same pH solution and incubated for 1hr, and the UV-vis spectra were recorded. From the 1 x 10^{-2} M stock solution of HSO_4^- and CN^- ion, the 250.0 µL solution was taken out and diluted with 10.0 mL with the respective pH solution to prepare the final concentration of 250.0 µM. The 1.5 mL of HSO_4^- ion solution was added to 1.5 mL 50.0 µL FPTMATs **(1)** solution. The UV-vis spectra were obtained at room temperature without giving any incubation time to study the detection of HSO_4^- ion at different pH. Similarly, 1.5 mL of CN^- ion solution was added to 1.5 mL 50.0 µL FPTPPTs **(1)** solution and the UV-vis spectra were measured at room temperature without giving any incubation time to study the detection of CN^- ion at different pH.

Preparation of paper strips of FPTPPTs:

Cellulose-based filter paper (Whatman filter paper) was cut into a square and immersed in a solvent solution of FPTPPTs **(1)**. After 5 minutes, the filter paper was removed from the solution and air-dried. The paper- strip containing FPTPPTs **(1)** was exposed to an aqueous solution of CN^- ion. After the paper strip was removed from the aqueous solution of CN^- ion the changes in the colour of the strip were recorded with daylight, UV light and fluorescent lamp.

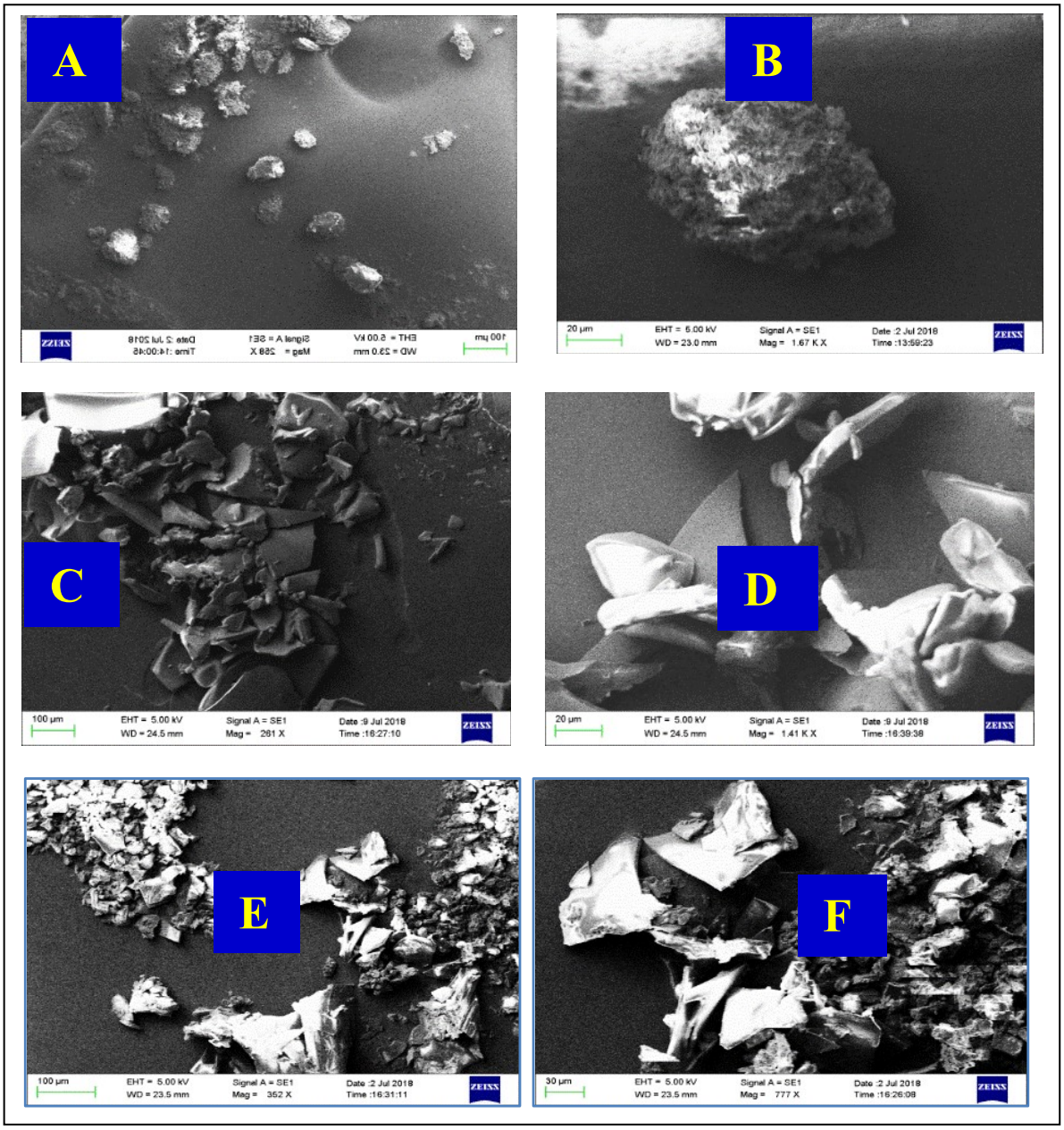


Figure S1. SEM images of FMA and anionic receptors at 100 µm and 20 µm scales: FMA **(A–B),** FPTMATs **(C–D),** and FPTPPTs **(E–F)**

Table S2. UV-vissorption data of FPTMATs in different solvents						
Sr. No.	Solvents		Polarity of solvents	Solubility	λ_{max} (nm) visible region	λ_{max} (nm) UV region
1.	polar protic	Methanol	5.1	Soluble	490	280
2.		Ethanol	5.2	Partially insoluble	490	280
3.		Water	9.0	Soluble	460	310
4.	nonpolar aprotic	Toluene	2.4	Insoluble	495	285
5.	polar aprotic	THF	4.0	Soluble	510	270
6.		Chloroform	4.1	Insoluble	475	285
7.		Acetonitrile (ACN)	5.8	Partially insoluble	495	280
8.		Dimethyl formamide	6.4	Highly soluble	510	280
9.		Dimethyl sulfoxide	7.2	Highly soluble	520	280

Table S3. The UV-vis absorption data of FPTPPTs in different solvents				
Sr. No.	**Solvent (L4)**	**Polarity of solvents**	**Solubility**	**Observed λ_{max} (nm) In visible region**
1.	THF	4.0	Soluble	480
2.	Toluene	2.4	Partially	485
3.	Chloroform	4.1	Partially	475
4.	Methanol	5.1	Soluble	470
5.	Ethanol	5.2	Partially insoluble	475
6.	Acetonitrile	5.8	Partially insoluble	475
7.	Dimethyl formamide	6.4	Highly soluble	515
8.	Dimethyl sulfoxide	7.2	Highly soluble	480
9.	Water	9.0	Partially	480

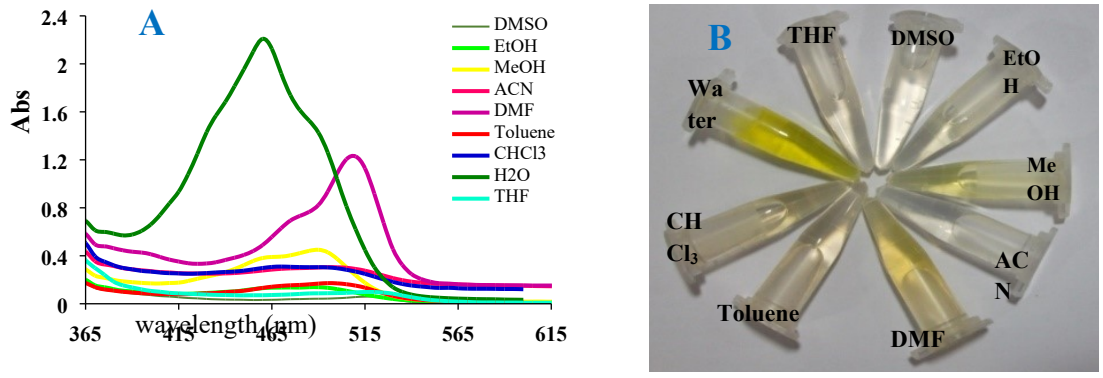


Figure S2. (A) UV-vis absorbance spectra and **(B)** the colour of FPTMATs (50.0 µM) in various protic-aprotic organic and aqueous solvents

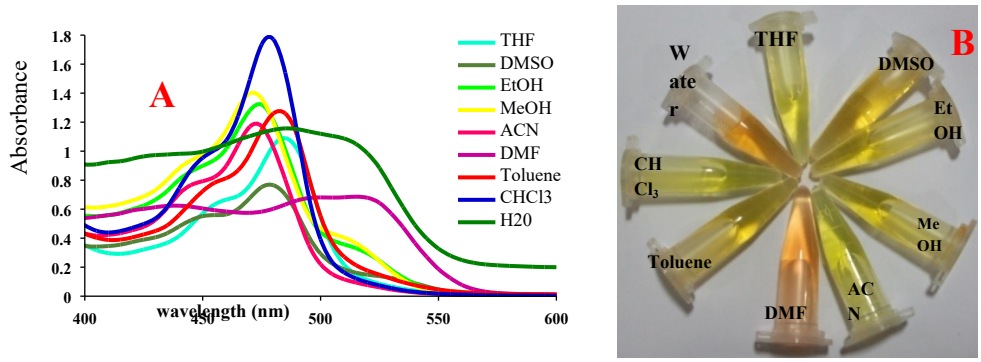


Figure S3. (A) UV-vis absorbance spectra of receptor FPTPPTs (50.0 µM) in various protic-aprotic organic and aqueous solvents. **(B)** FPTPPTs color appearance at 50.0 µM in various protic-aprotic organic and aqueous solvents.

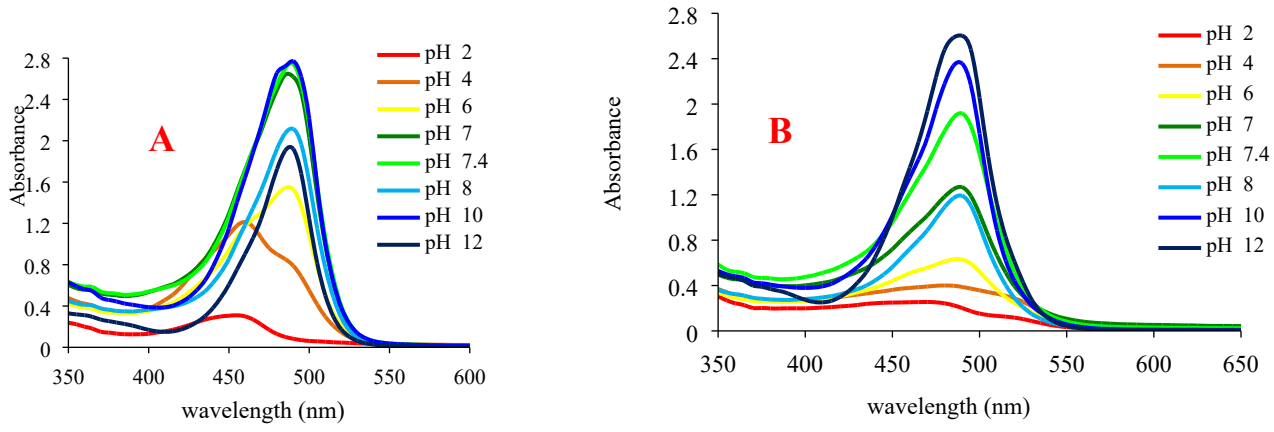
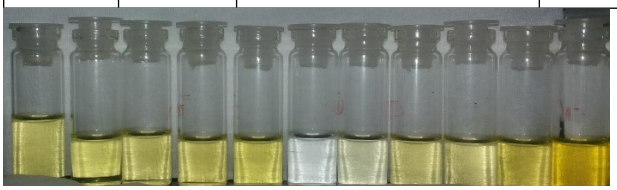


Figure S4. (A) UV-vis absorbance spectra of anionic receptor FPTMATs (25.0 µM) and **(B)** FPTPPTs (25.0 µM) at different pH in 10.0 mM Tris-HCl buffer

Table S4. UV-vis λ_{max} at different pH for FPTMATs **(1)** and FPTPPTs **(2)**			
Sr. No.	pH	λ_{max} in nm (FPTMATs)	λ_{max} in nm (FPTPPTs)
1.	pH 2	455	470
2.	pH 4	455	480
3.	pH 6	485	485
4.	pH 7	485	490
5.	pH 7.4	490	490
6.	pH 8	490	490
7.	pH 10	490	490
8.	pH 12	490	490



FPTMA F^- Cl^- Br^- I^- HSO_4^- HPO_4^{-2} ClO_4^- NO_3^- AcO^- CN^-

Figure S5. The appearance of colour of 50.0 µM anionic receptor FPTMATs upon the addition of a series of 250.0 µM anions each separately in the mixture of water and methanol (95: 5)

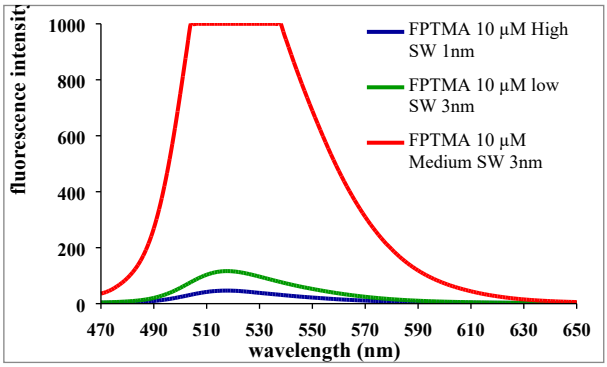


Figure S6. Fluorescence intensity of FPTMATs (**1**) at different instrument sensitivity and slit width, λ_{ex} at 460 nm in water/methanol (95: 5 v/v)

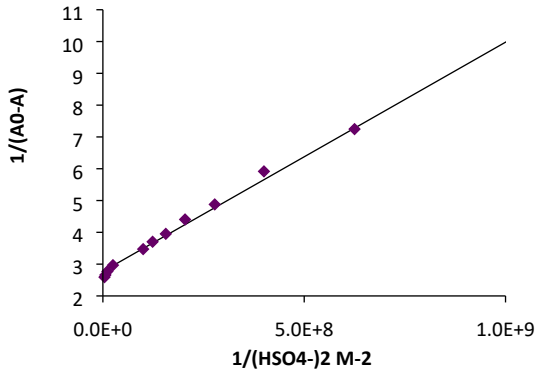


Figure S7. Benesi-Hildebrand plot (absorbance at 460 nm) of FPTMATs (**1**) with 1:2 stoichiometry for the complex formation between FPTMATs (**1**) and HSO_4^- ion in 95:5 water/methanol mixture

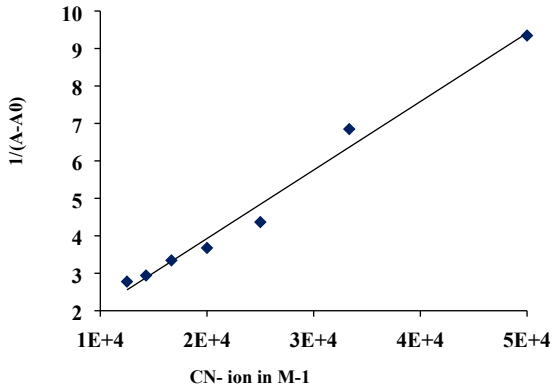


Figure S8. Benesi-Hildebrand plot (absorbance at 485 nm) of FPTPPTs (**2**) with 1:1 stoichiometry for complex formation between FPTPPTs (**2**) and CN^- ion in water/methanol (95: 5 v/v)

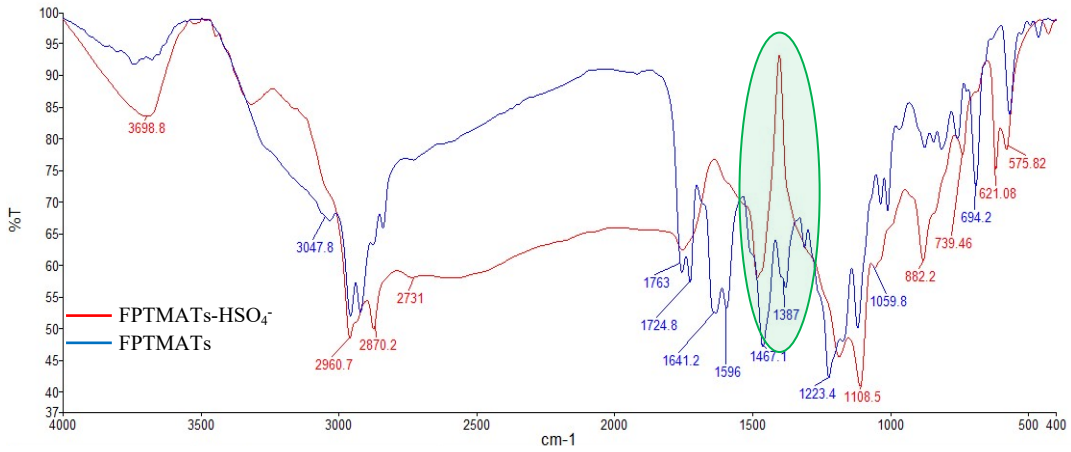


Figure S9. FTIR spectrum of FPTMATs–$(HSO_4^-)_2$ complex

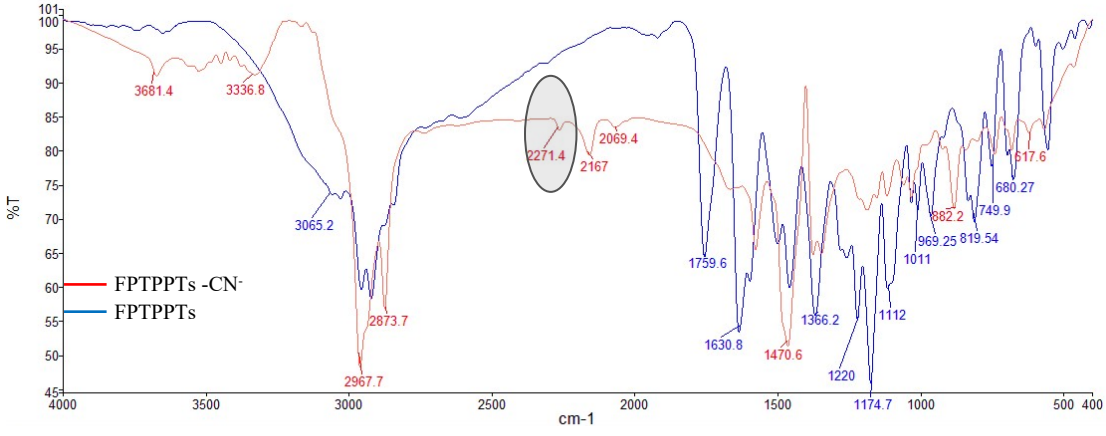


Figure S10. FTIR spectrum of FPTPPTs–CN^- complex

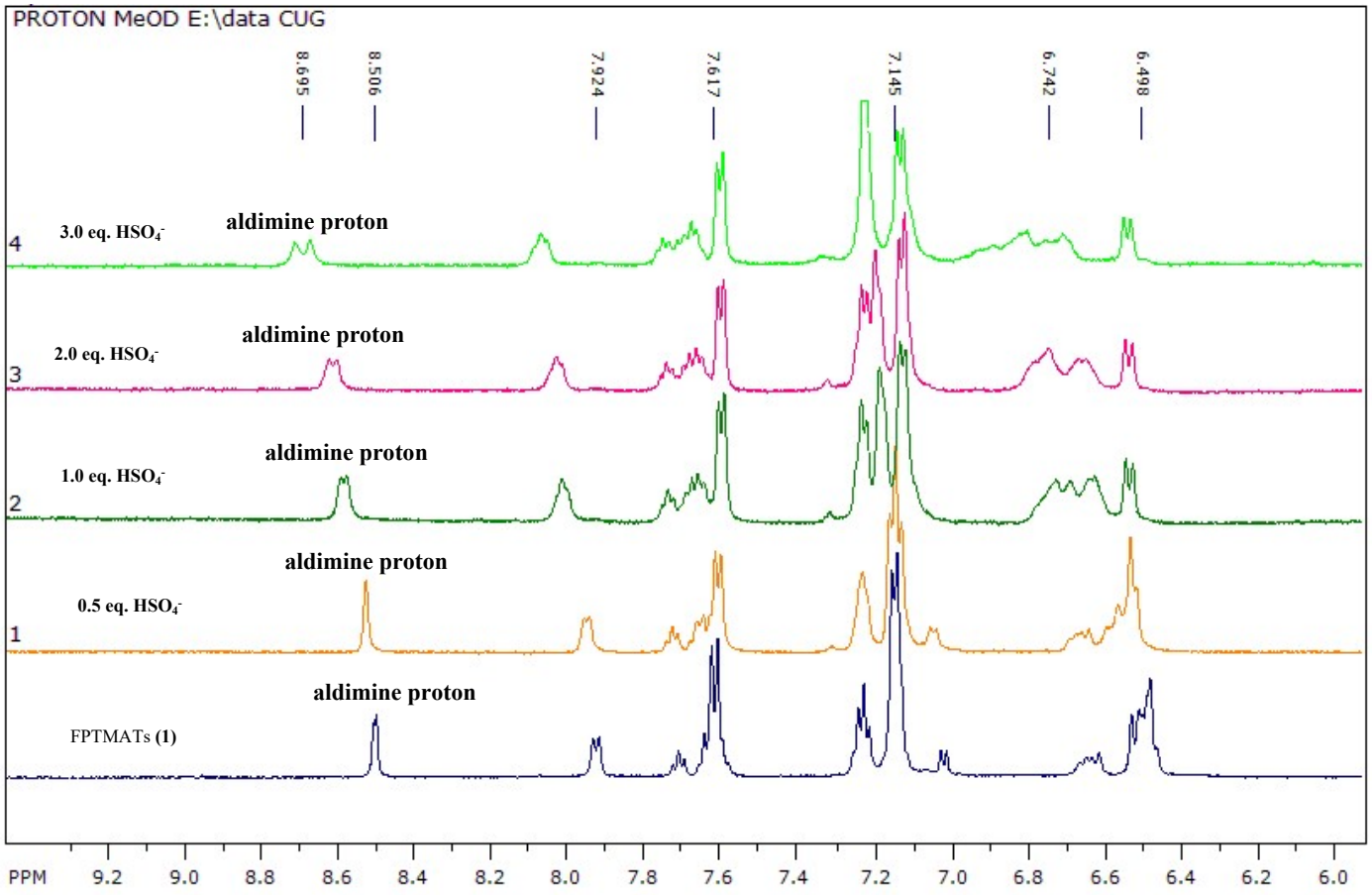


Figure S11. ^{1}HNMR titration spectrum of FPTMATs–HSO_4^- in MeOH-d4

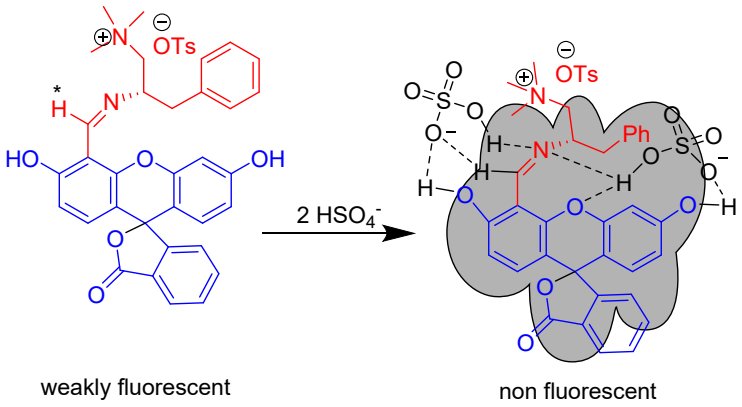


Figure S12. Proposed binding mechanism for HSO_4^- ion with FPTMATs

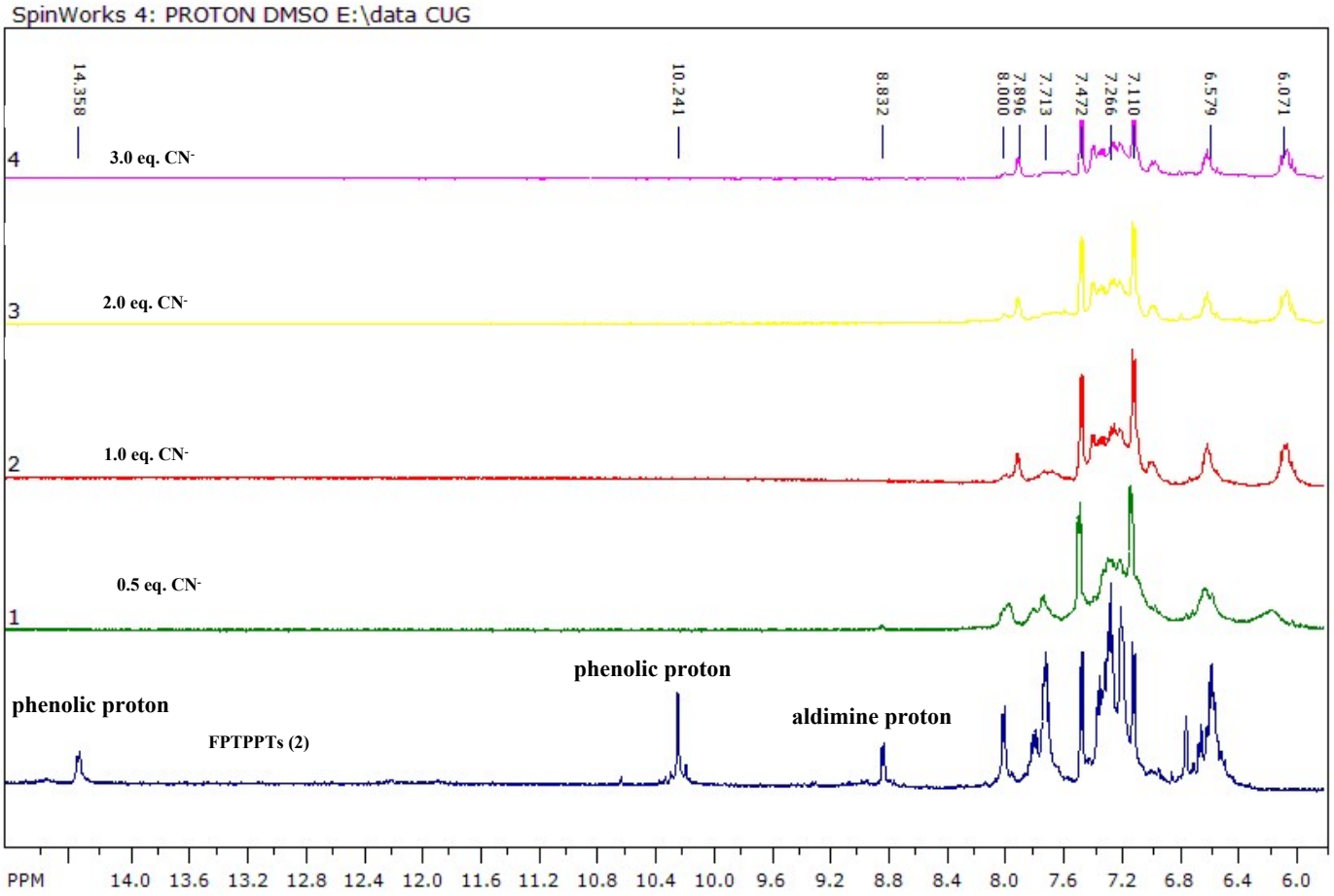


Figure S13. ^{1}HNMR titration spectrum of FPTPPTs–CN^- complex in DMSO-d6

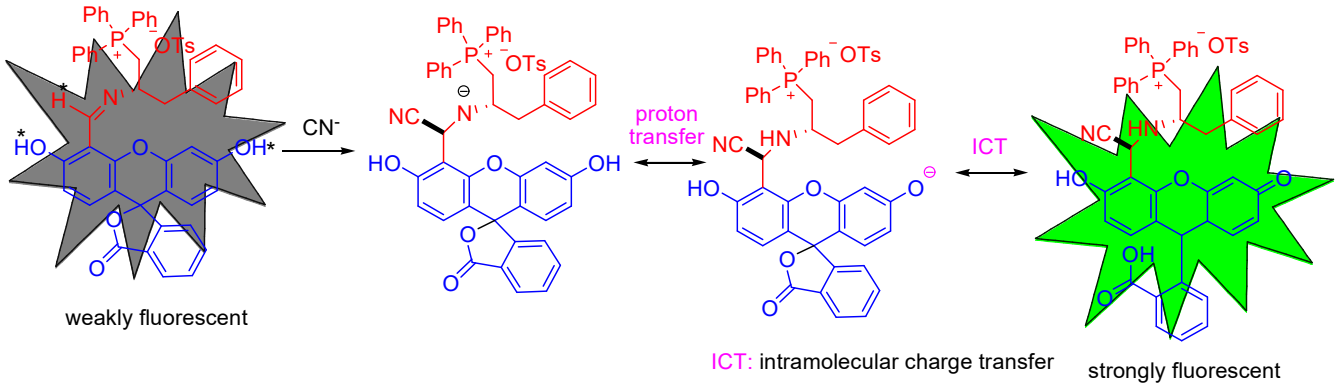


Figure S14. Plausible reaction pathway upon addition of cyanide ion in FPTPPTs solution

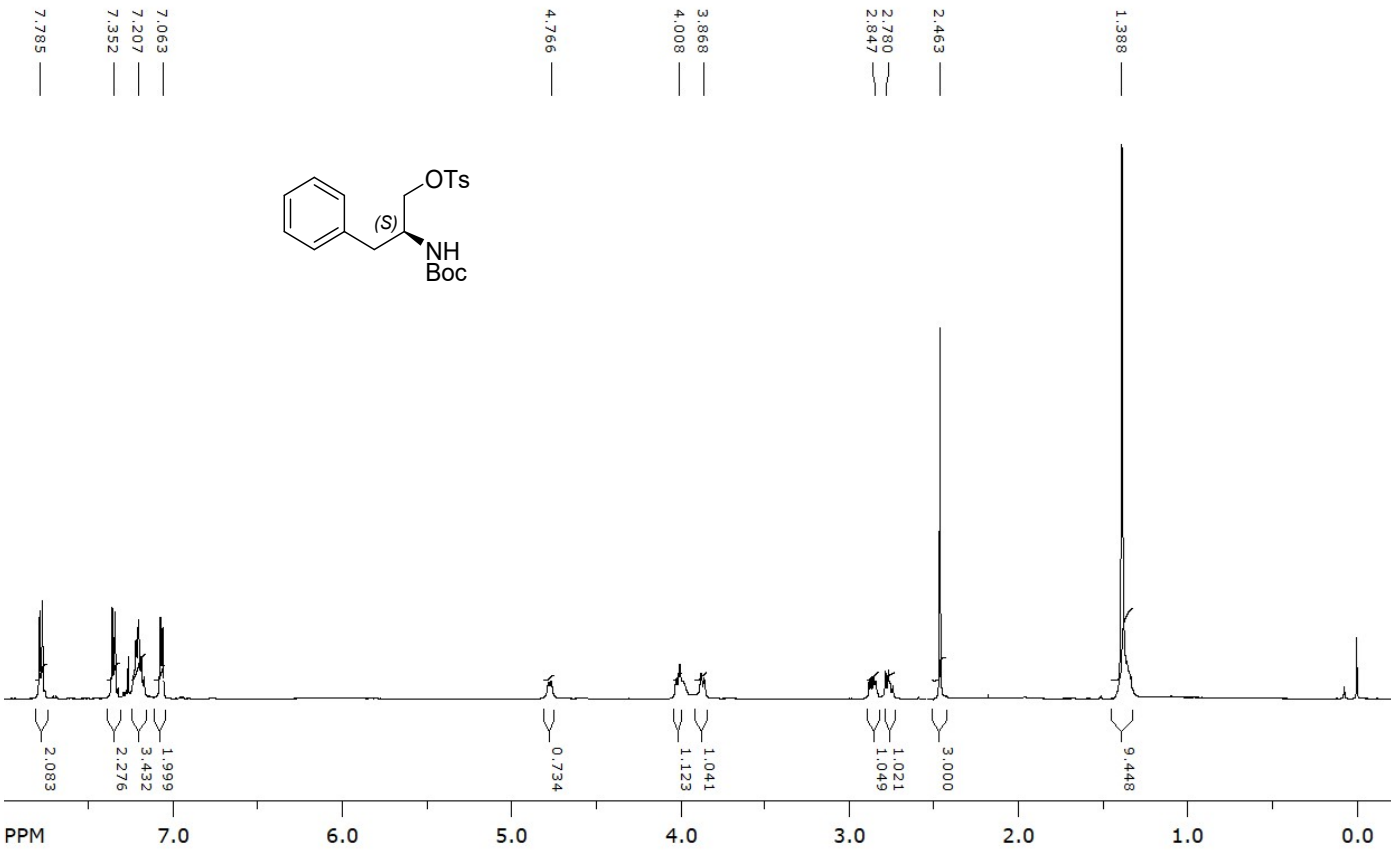


Figure S15. [1]HNMR spectrum of compound **6** in $CDCl_3$ at 500 MHz

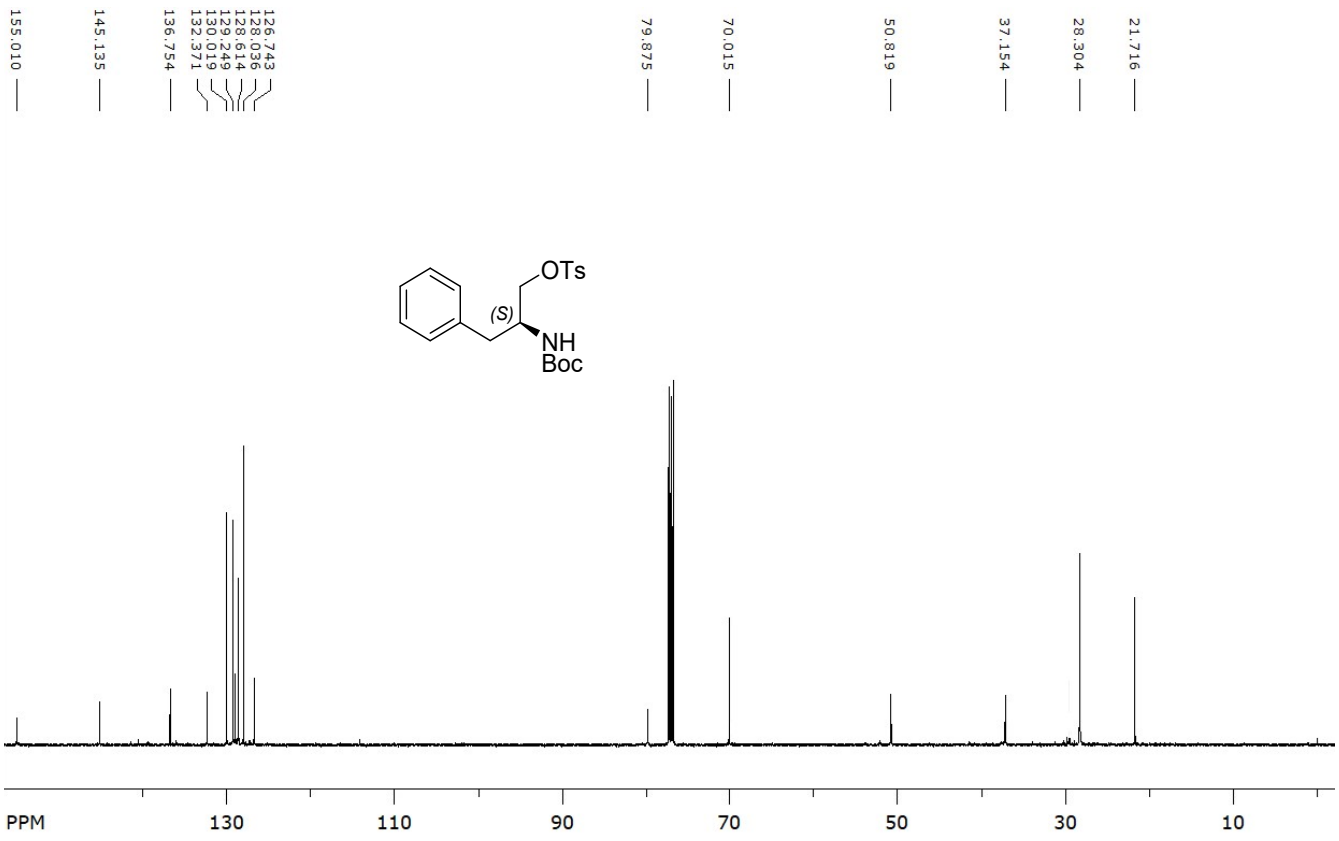


Figure S16. [13]CNMR spectrum of compound **6** in $CDCl_3$ at 125 MHz

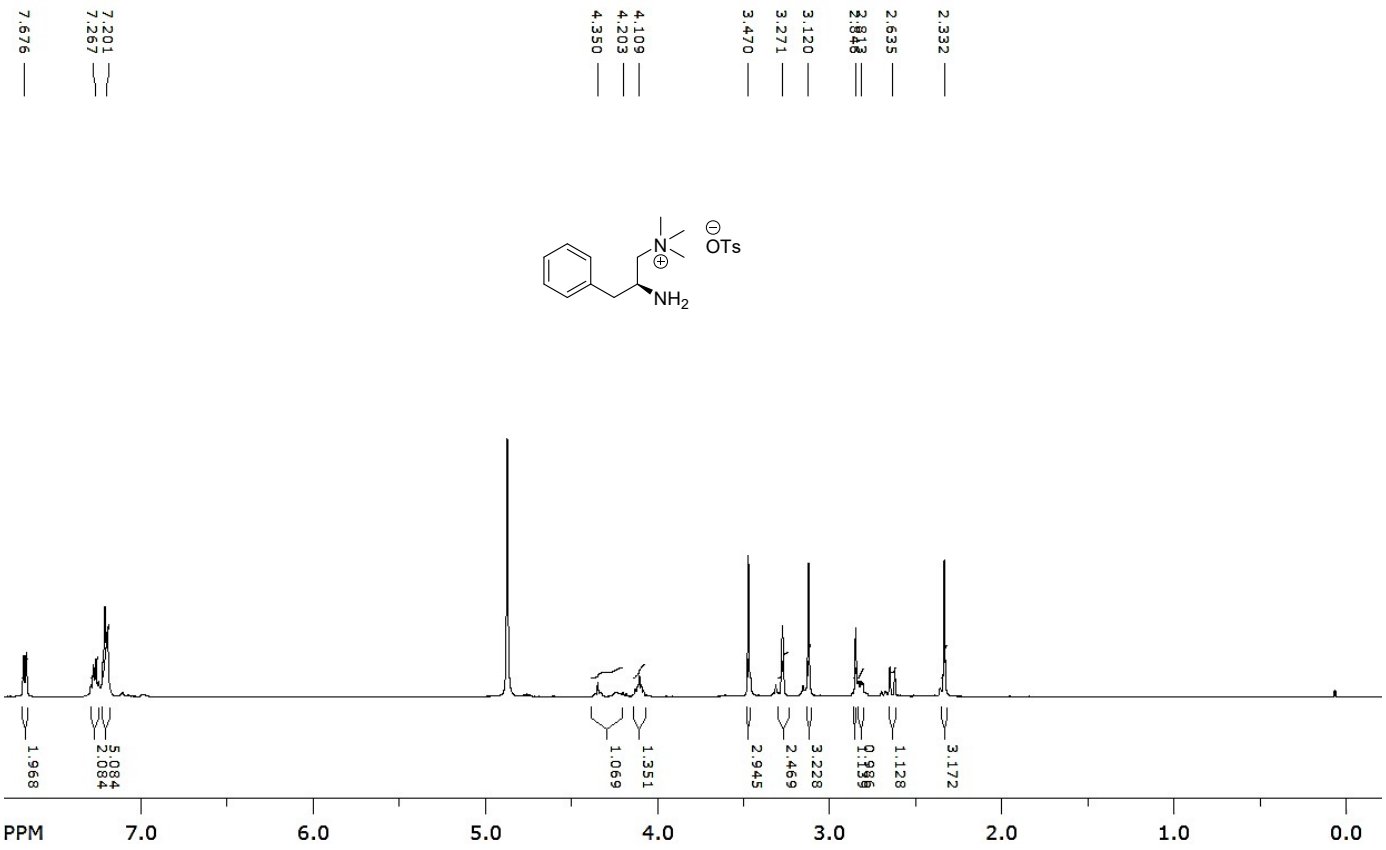


Figure S17. [1] HNMR spectrum of compound **8** in MeOH-d4 at 500 MHz

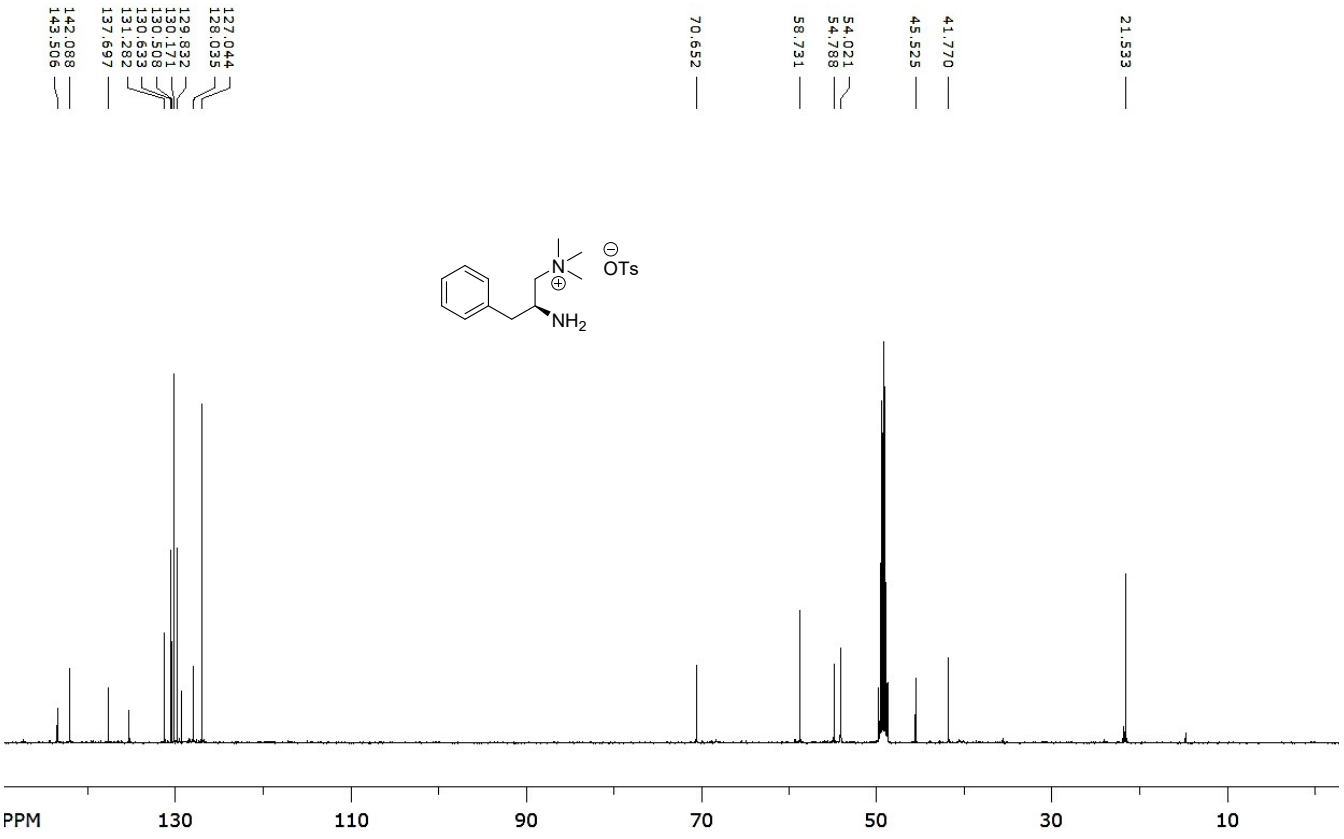


Figure S18. [13] CNMR spectrum of compound **8** in MeOH-d4 at 125 MHz

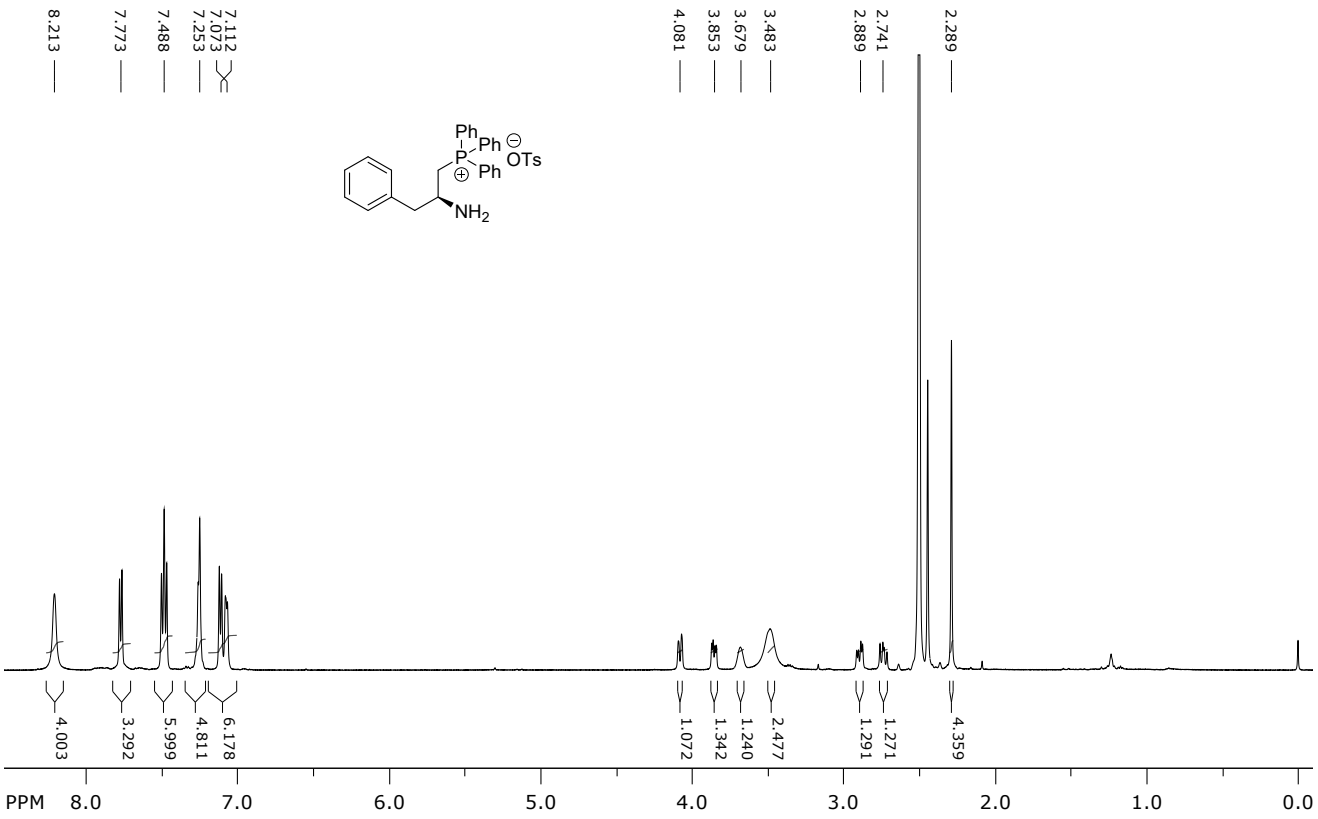


Figure S19. [1] HNMR spectrum of compound **10** in DMSO-d6 at 500 MHz

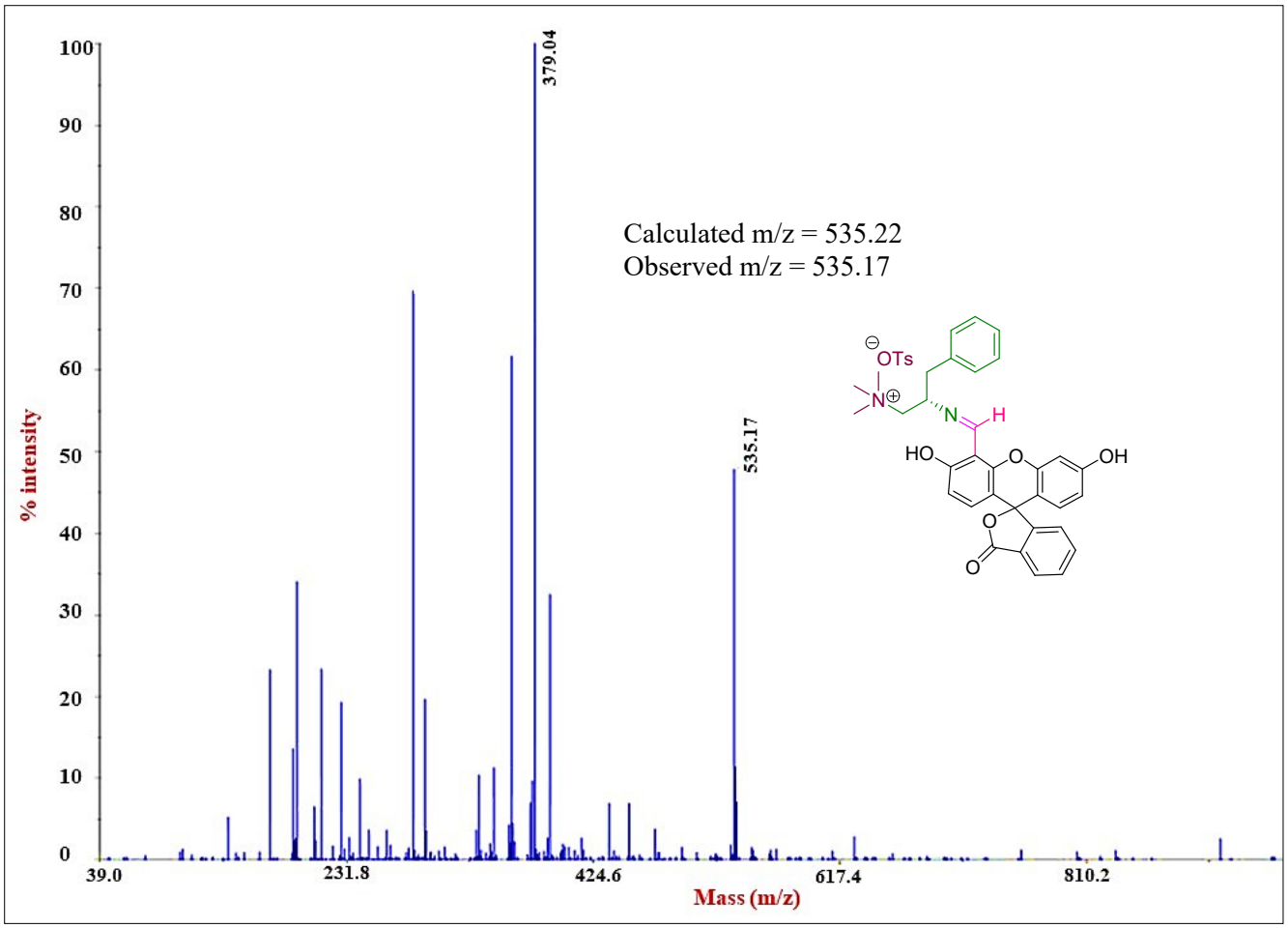


Figure S20. MALDI-TOF MASS spectra anionic receptor FPTMATs **(1)**

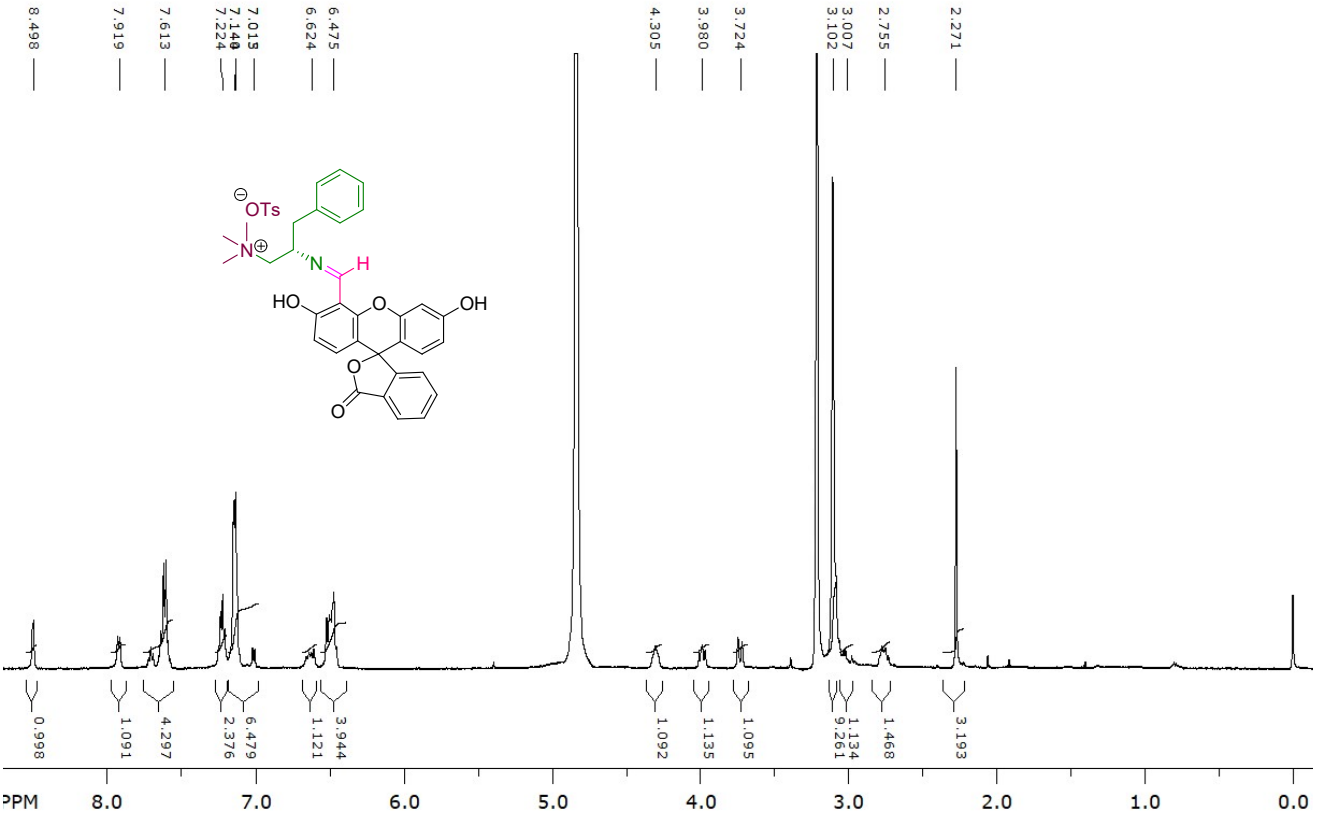


Figure S21. [1]HNMR spectra of anionic receptor FPTMATs (**1**) in MeOH-d4 at 500 MHz

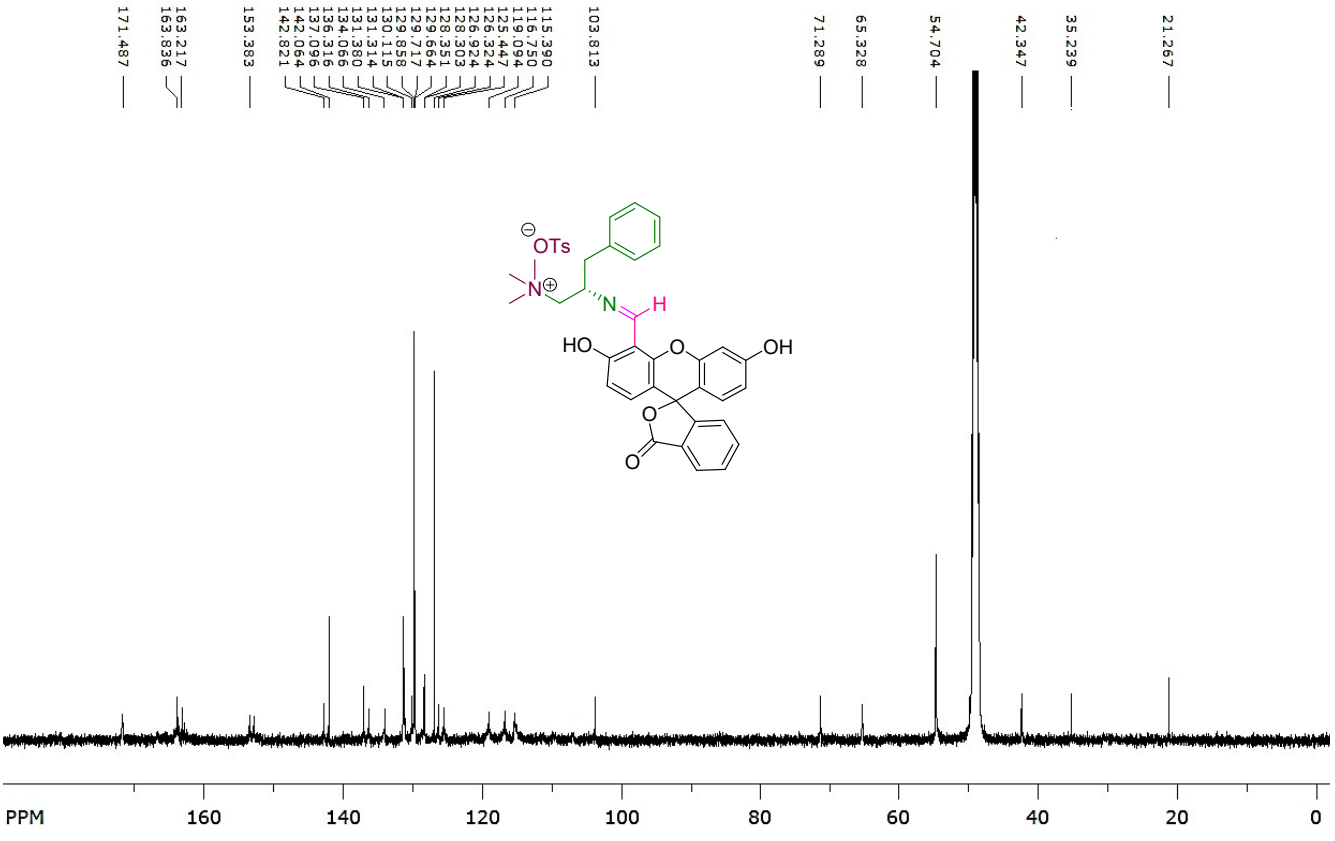


Figure S22. [13]CNMR spectra of anionic receptor FPTMATs (**1**) in MeOH-d4 at 125 MHz

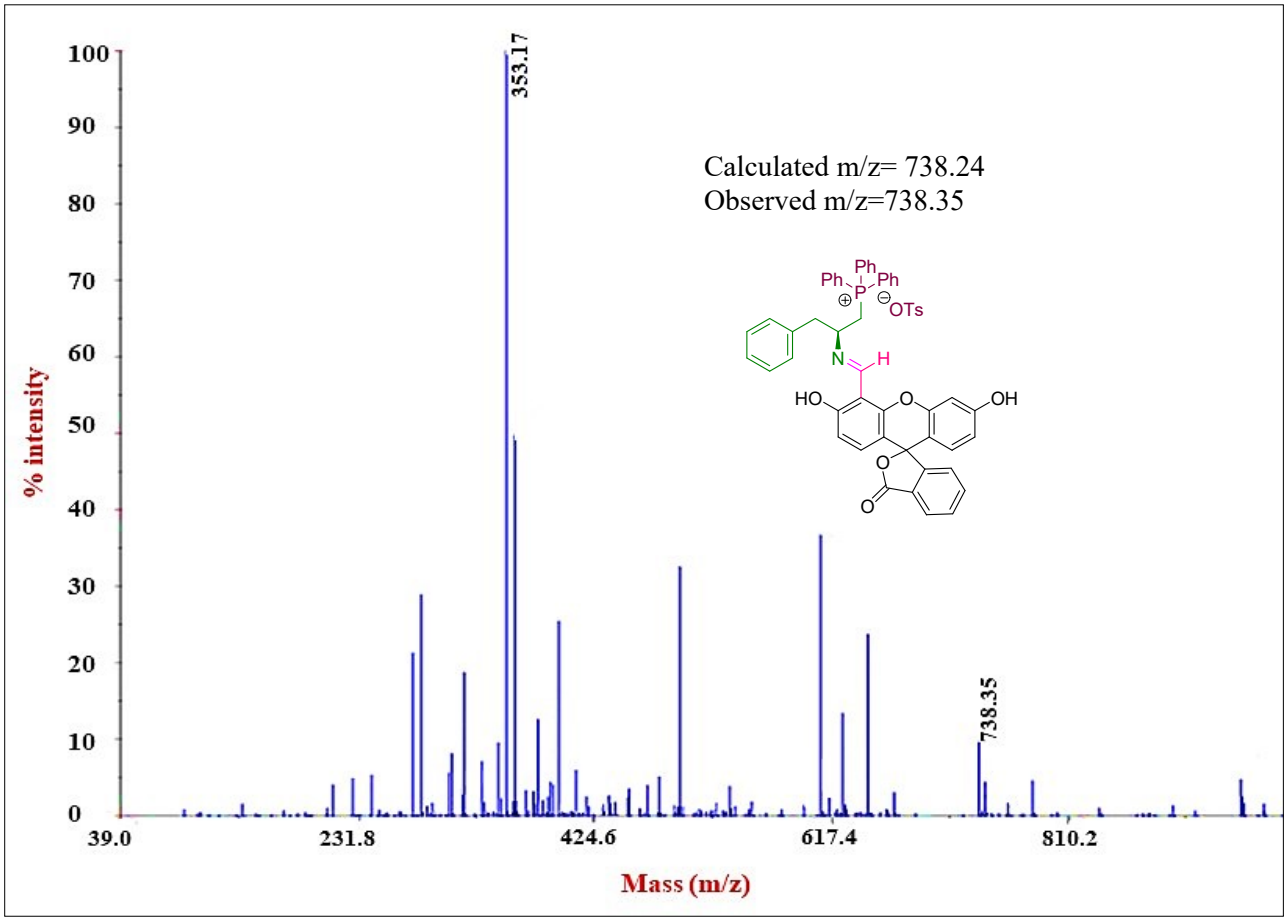


Figure S23. MALDI-TOF Mass spectra of anionic receptor FPTPPTs **(2)**

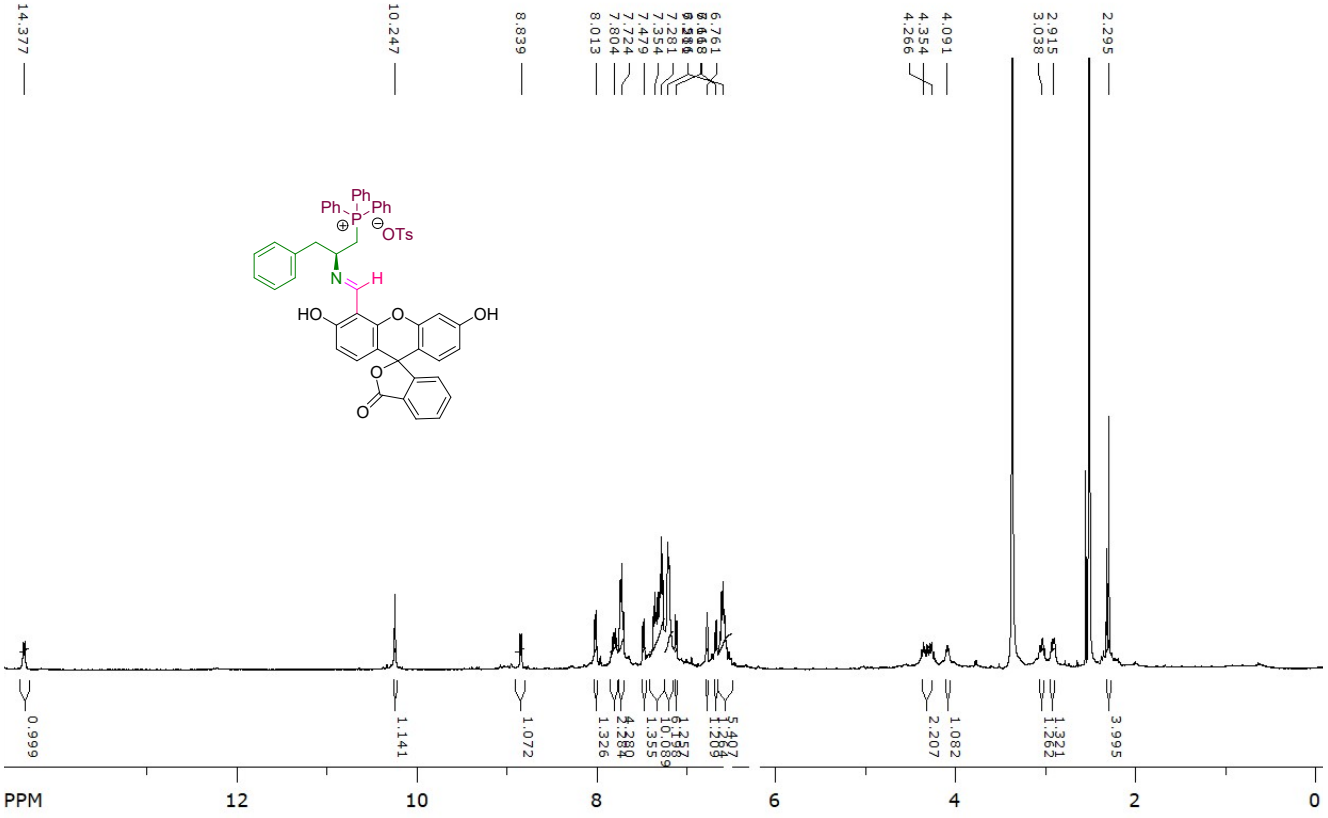


Figure S24. [1]HNMR spectra of anionic receptor FPTPPTs (**2**) in DMSO-d6 at 500 MHz

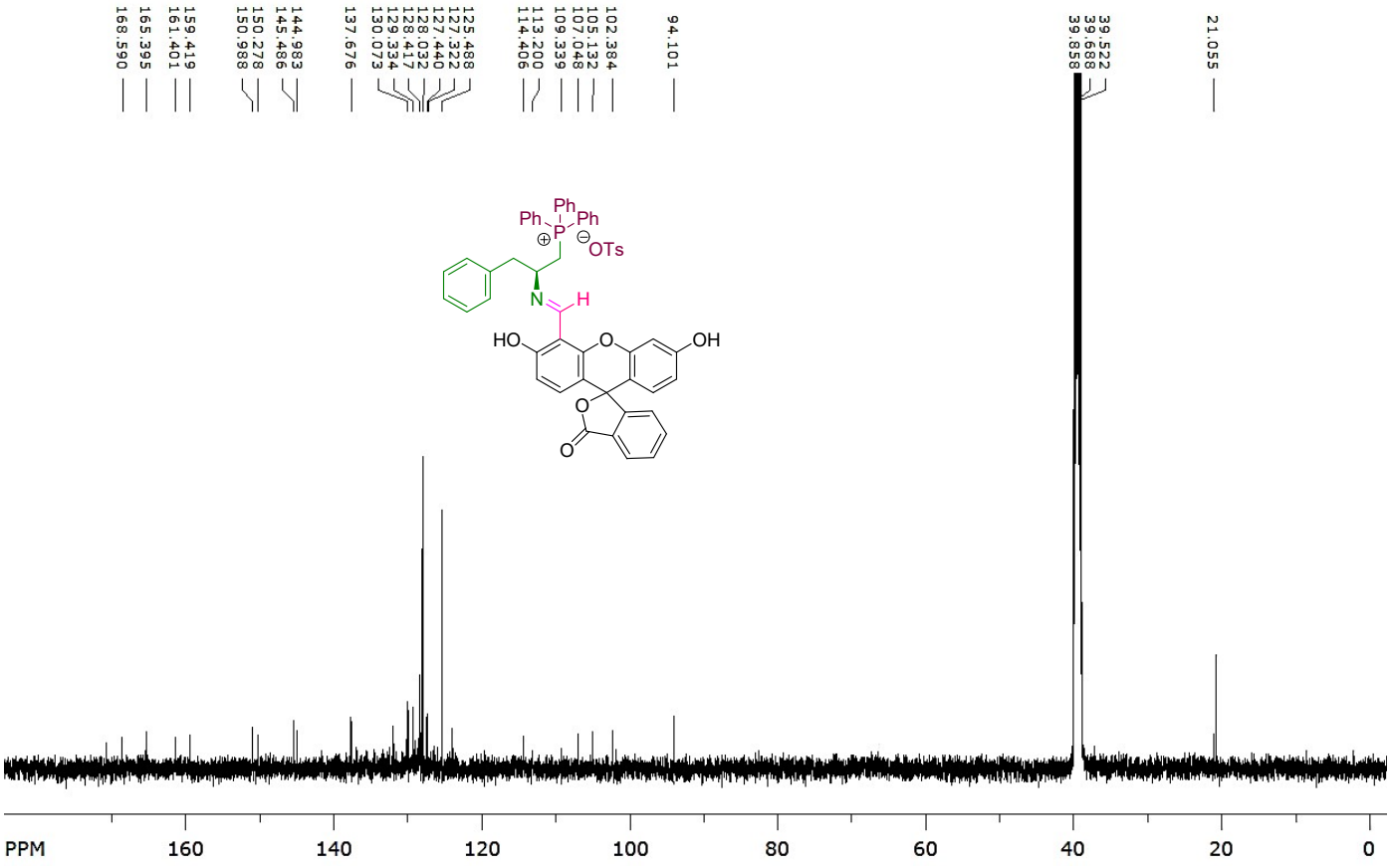


Figure S25. [13]CNMR spectra of anionic receptor FPTPPTs (**2**) in DMSO-d6 at 125 MHz

Table S5. Comparison of the sensing performance of FPTMATs (**1**) and FPTPPTs (**2**) with related reported chemosensors for HSO_4^- and CN^- detection

Sensor / Receptor	Analyte	Medium / Solvent system	Detection Mode	Limit of Detection (LOD)/ Key Performance	Reference
FPTMATs **(1)**	HSO_4^-	MeOH/H_2O (5%)	"Turn-off" fluorescence (H-bonding & electrostatic interaction)	3.13 nM	*This work*
FPTPPTs **(2)**	CN^-	MeOH/H_2O (5%)	"Turn-on" fluorescence (nucleophilic addition & ICT)	51.17 nM	*This work*
Amine-substituted heptamethine cyanine dye	CN^-	Aqueous solution (water)	Near-infrared fluorescence turn-on, highly selective enhancement with CN^-	LOD = 5 mM; but *"highly selective fluorescence enhancement"* and demonstrated for bioimaging in cells.	Ref 1
Tetrasubstituted imidazole core chemodosimeter with ESIPT	CN^-	HEPES buffer : DMF (2:8, v/v)	Fluorescent "chemodosimeter" (reaction-based); CN^- perturbs ESIPT leading to strong fluorescence response	high selectivity for CN^- over other anions; works in solution and on test paper strips LOD = 0.59 μM	Ref 2 .
dicyanovinyl-phenanthridine	CN^-	Acetonitrile (CH_3CN)	"Turn-off" fluorescence via nucleophilic addition	LOD = 39.3 nM; binding constant $K_a \approx 5.22 \times 10^6\ M^{-1}$	Ref 3
BID (benzothiazole-indene-dione)	CN^-	Mixed (e.g., ACN/H_2O)	Turn-on fluorescence via nucleophilic addition (disruption of ICT)	LOD = 5.97 nM, pH range 6.0–12.0, high selectivity; real water-samples + live cells demonstrated	Ref 4
PDBT (benzothiazole-phenylene diacetonitrile)	CN^-		Colorimetric + fluorescence, via nucleophilic addition disrupting conjugation / ICT	Bright brown color upon CN^- addition, good sensitivity; LOD 0.62 μM.)	Ref 5
AIE-type	CN^-	Water / Mixed (pH 4–11)	Turn-on fluorescent (aggregation-induced emission)	LOD (fluorescence) = 68 nM, also colorimetric; tested in real water samples with good recovery	Ref 6
Sensor 1 (phenothiazine-benzofuran)	CN^-	Biological / aqueous environment (cells)	Fluorescence quenching (turn-off) via nucleophilic attack and ICT disruption	Detection limit = **2.0×10^{-6} M**; binding constant = ~$5.943 \times 10^3\ M^{-1}$; demonstrated in live cells and zebrafish	Ref 7
Indolium-based probe (tetramethylindolium + benzothiophene)	CN^-	(Solvent as per the paper)	Fluorescence quenching (turn-off) via nucleophilic attack on quaternary amine salt	Fast response; quenching upon CN^- addition (exact LOD 1.53×10^{-6}M)	Ref 8
triphenylamine + dicyanovinyl	CN^-	Likely organic (as in the paper)	NIR "on–off" fluorescence + colorimetric, nucleophilic attack blocks ICT	LOD = 0.46 nM	Ref 9
Electron-deficient tripodal amide receptor	CN^-	Acetonitrile (cassette prepared)	Turn-on fluorescence & colorimetric via nucleophilic addition	LOD = $1x10^{-7}$ M; strong fluorescence enhancement; color change from colorless to yellowish-brown	Ref 10
Benzimidazole-based (L_1H / L_2H)	HSO_4^-	Ethanol / H_2O (HEPES buffer, 1:5 v/v)	Fluorescence turn-on (H-bonding / deprotonation)	LOD = ~18.08 nM (L_1H), ~14.11 nM (L_2H)	Ref 11
Non-cyclic dipodalamine phenol receptor (L)	HSO_4^-	Aqueous (or water-rich) medium	Absorbance red-shift + Fluorescence change	LOD = 0.25 mM	Ref 12
Coumarin-based derivative	HSO_4^-	Aqueous solution	"Turn-on" fluorescence	(from abstract) highly selective and sensitive turn-on for HSO_4^- LOD = 3.75×10^{-6} M	Ref 13

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