Coumarin functionalized thiocarbonohydrazones as a new class of chromofluorescent receptors for selective detection of fluoride ion†

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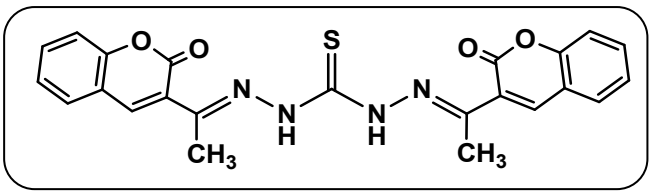
Electronic Supplementary Information (ESI†)

Contents

1. Synthesis procedure of receptors 4 and 5

A hot solution of thiocarbonohydrazide (0.28 gm, 2.64 mmol) in water (5 mL) was added slowly in dropwise manner over 15 minutes to the acetyl-coumarin derivative **1** (1.0 gm, 5.31 mmol) or **2** (1.26 gm, 5.29 mmol) dissolved in 30 mL ethanol under hot (50 ℃) condition. Initially the solution looked turbid and solution became clear after complete addition of thiocarbonohydrazide. Then the solution was allowed to reflux for 6 h with stirring till complete precipitation if formed. The precipitate was cooled, filtered and washed with boiling water followed by hot ethanol to get a solid powder **4** (light orange colour) or **5** (yellowish colour) which was then dried in vacuum to obtain the pure product in quantitative yields (**4** = 82 %, **5** = 80 %).

2. Bis(3-acetyl-2*H*-chromen-2-one)thiocarbonohydrazone (4)



M.P. = 215 ℃. ^{1}H NMR (400 MHz, *DMSO-d_6*) δ (ppm) = 2.21 (6H, s, CH_3), 7.37-7.43 (4H, m, Ar-H), 7.62-7.66 (2H, m, Ar-H), 7.74 (2H, d, *J* = 8.0 Hz, Ar-H), 8.47 (2H, s, =CH-Ar), 9.76 (1H, s, -NH, D_2O exchangeable), 10.41 (1H, s, NH, D_2O exchangeable). ^{13}C NMR (100 MHz, *DMSO-d_6*) δ (ppm) = 11.2, 114.7, 116.5, 119.2, 124.8, 129.2, 140.4, 140.5, 158.6, 160.4, 162.8, 174.4. FT-IR (KBr) ν (cm^{-1}) = 3270, 2937, 1715, 1601 (>C=N-), 1532, 1505, 1427, 1375, 1240 (>C=S), 1152, 1125, 1098, 1008, 978, 850. UV-vis. (DMSO, 20 μM) = λ_{max} (nm) 342 (n-π*). Fluorescence emission at λ_{ex} 360 nm (DMSO, 10 μM) = 437 nm.

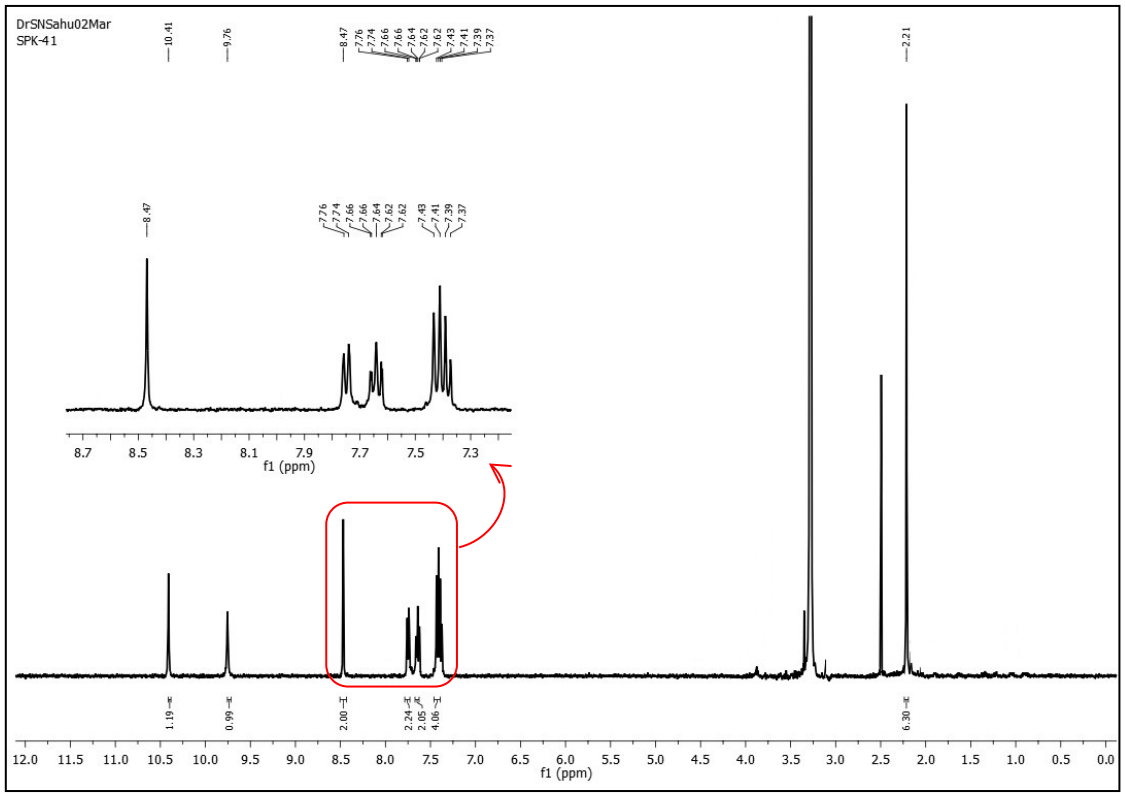


Figure S1: ^{1}H NMR spectrum of **4** in DMSO-d_6.

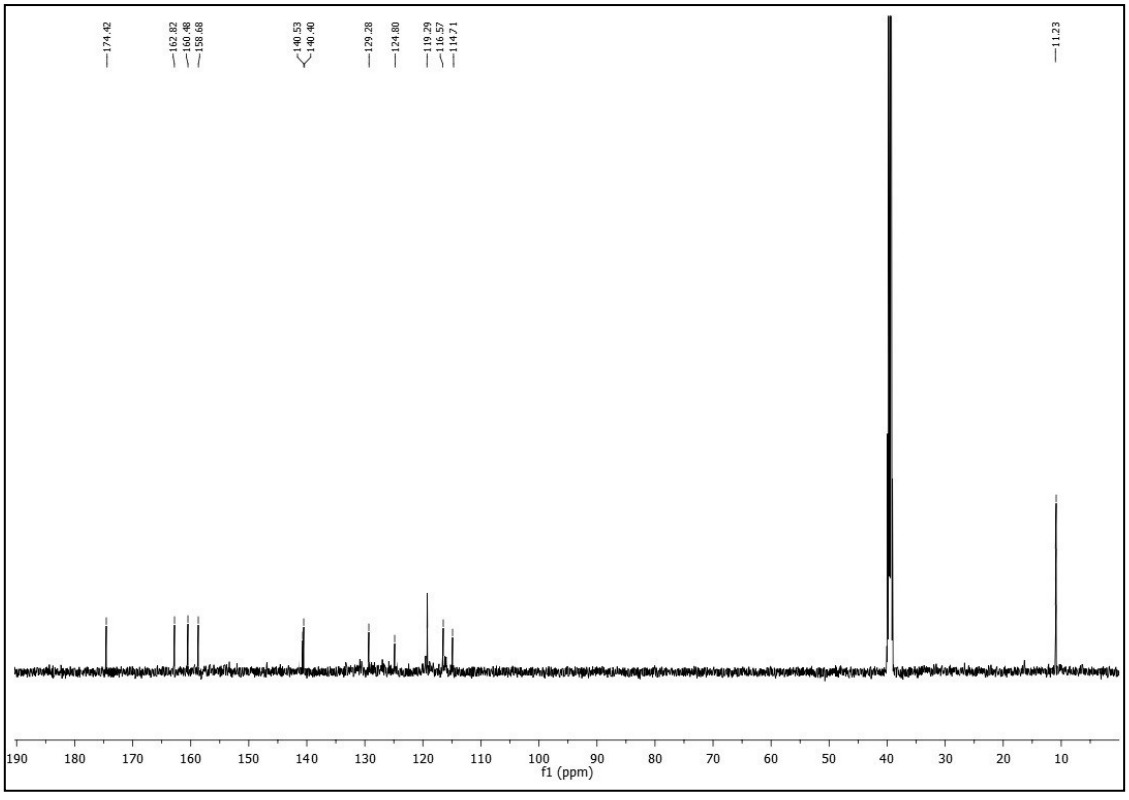


Figure S2: ^{13}C NMR spectrum of **4** in DMSO-d_6.

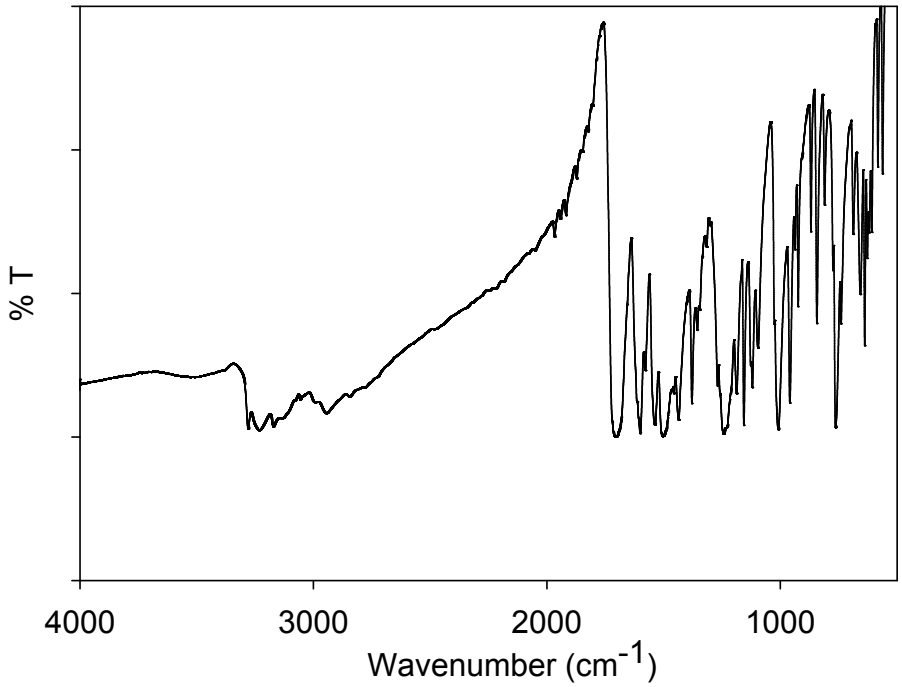
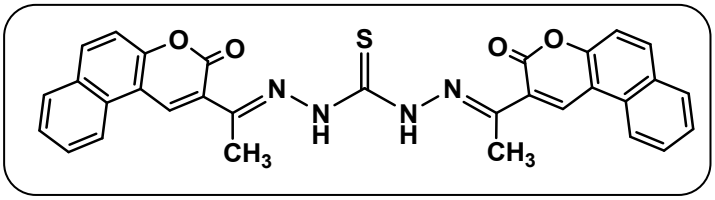


Figure S3: FT-IR spectrum of **4**.

3. Bis[2-acetyl-3*H*-benzo[*f*]chromen-3-one]thiocarbonohydrazone (5)



M.P. = 221 ℃. ^{1}H NMR (400 MHz, *DMSO-d_6*) δ (ppm) = 2.27 (6H, s, CH_3), 7.58-7.66 (4H, m, Ar-H), 7.76 (2H, m, Ar-H), 8.05 (2H, d, *J* = 8.0 Hz, Ar-H), 8.20 (2H, d, *J* = 8.0 Hz, Ar-H), 8.68 (2H, d, *J* = 8.0 Hz, Ar-H), 9.12 (2H, s, =CH-Ar), 9.97 (1H, s, -NH, D_2O exchangeable), 10.40 (1H, s, NH, D_2O exchangeable). ^{13}C NMR (100 MHz, *DMSO-d_6*) δ (ppm) = 12.6, 112.3, 116.4, 122.3, 122.9, 126.5, 129.1, 129.3, 129.8, 136.2, 142.4, 155.3, 158.4, 179.0. FT-IR (KBr) ν (cm^{-1}) = 3225, 3005, 1725, 1675, 1599 (>C=N-), 1552, 1510, 1453, 1390, 1353, 1246 (>C=S), 1210, 1097, 1024, 975, 825. UV-vis. (DMSO, 20 μM) = λ_{max} (nm) 379 (n-π*). Fluorescence emission at λ_{ex} 360 nm (DMSO, 10 μM) = 455 nm.

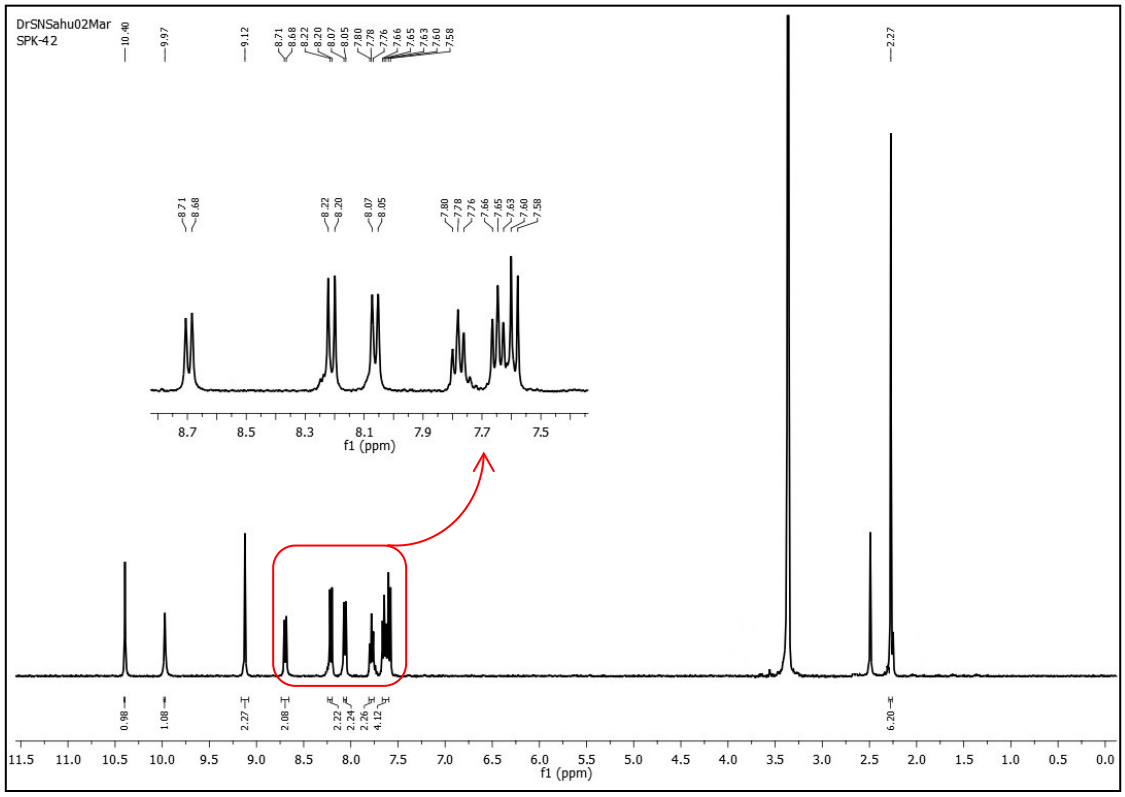


Figure S4: ^{1}H NMR spectrum of **5** in DMSO-d_6.

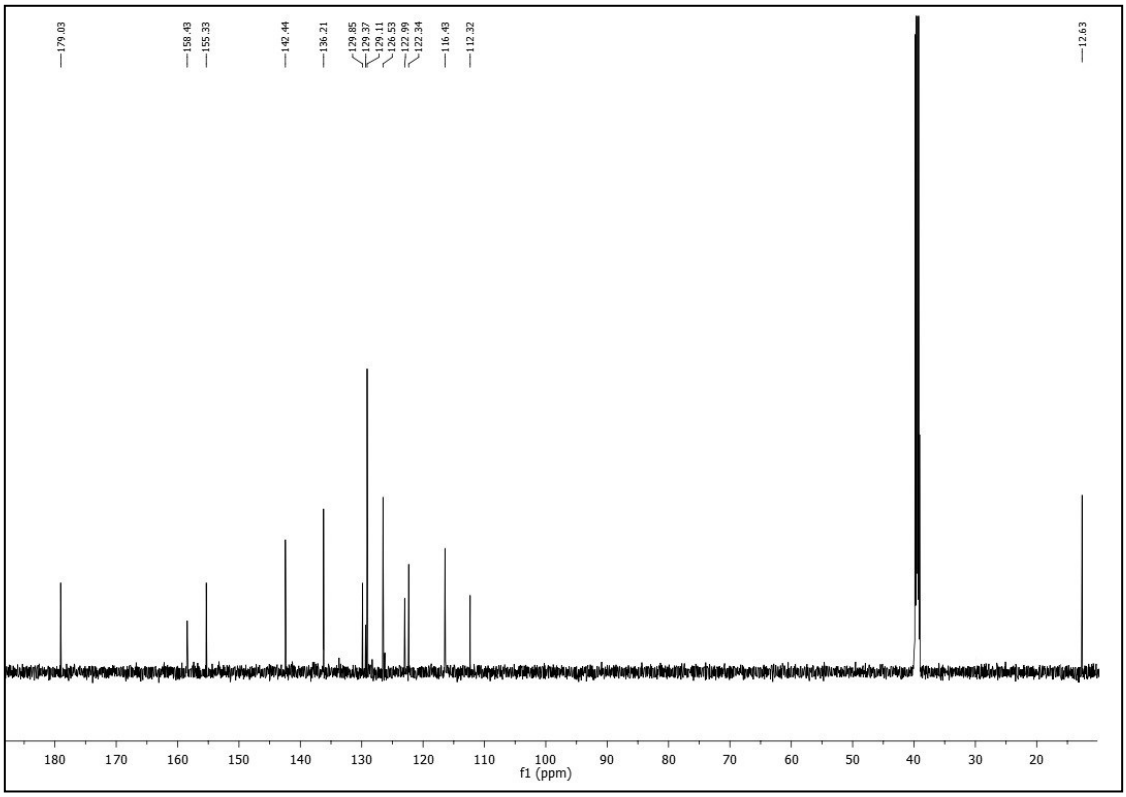


Figure S5: ^{13}C NMR spectrum of **5** in DMSO-d_6.

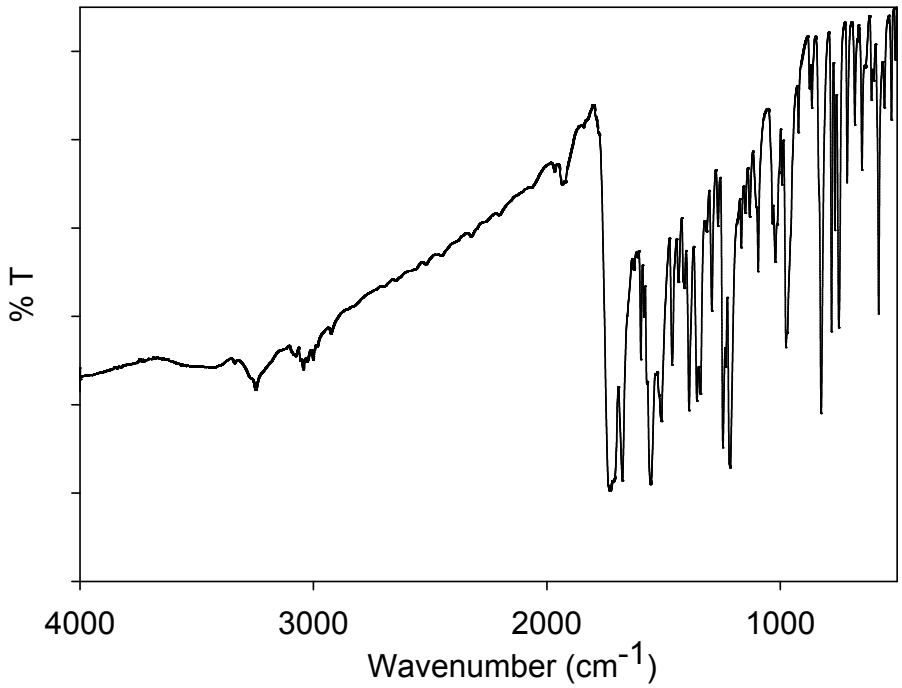


Figure S6: FT-IR spectrum of **5**.

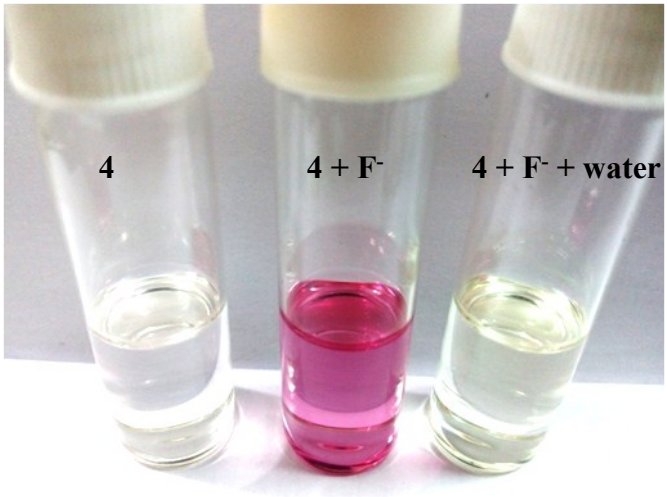


Figure S7: Colour changes observed by addition of few drops of water to receptor **4**+ F^- complex solution

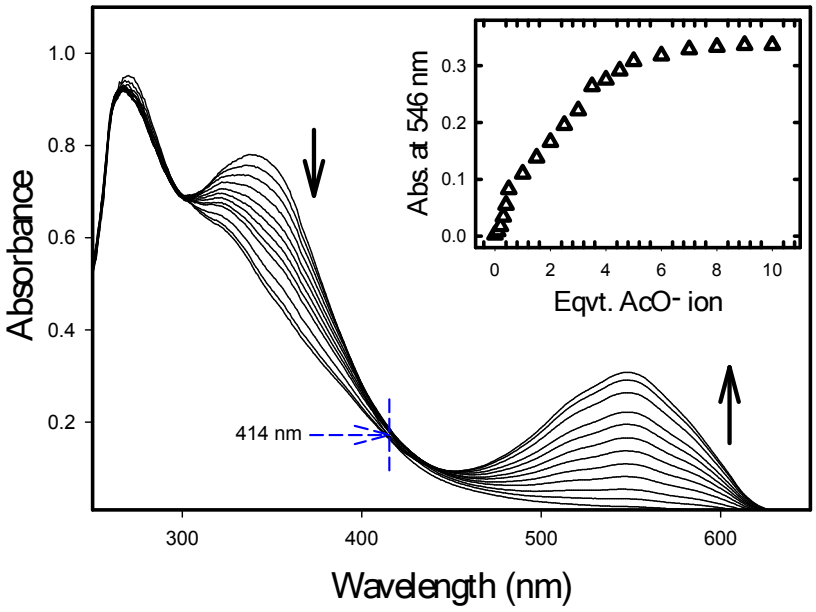


Figure S8: UV-visible titration spectra of **4** (20 μM) with 0–10 equiv. of acetate ion (TBA salt) in DMSO. Inset shows the change in absorbance at 546 nm with the addition of various equiv. of AcO^- ions.

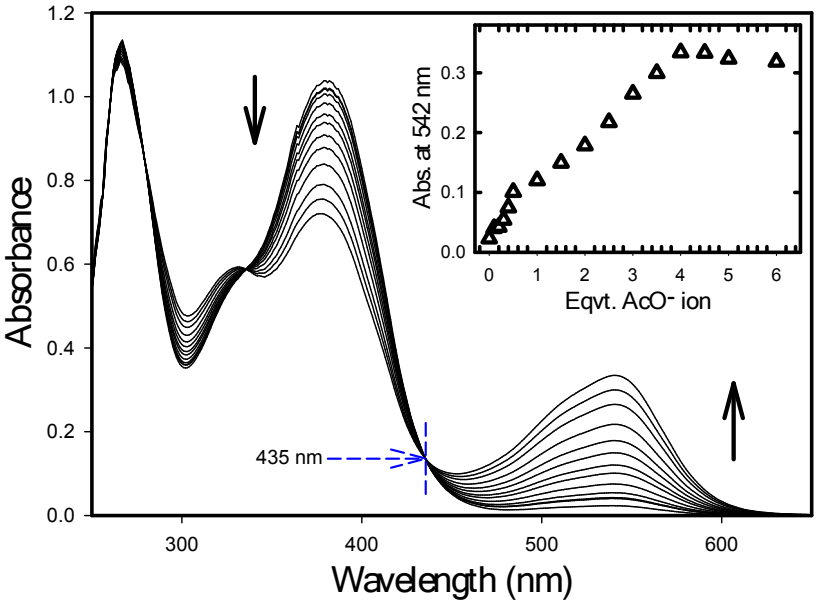


Figure S9: UV-visible titration spectra of **5** (20 μM) with 0–6 equiv. of acetate ion (TBA salt) in DMSO. Inset shows the change in absorbance at 542 nm with the addition of various equiv. of AcO^- ions.

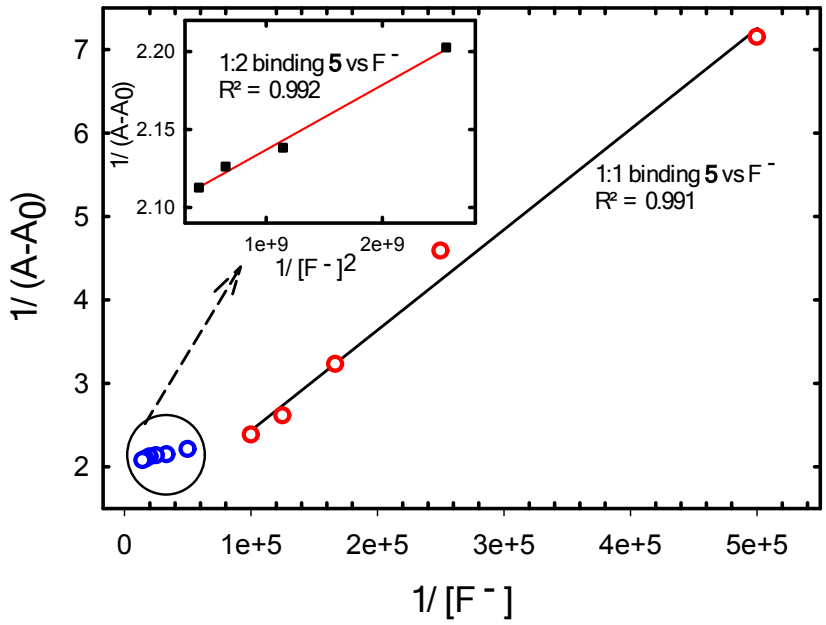


Figure S10: Benesi-Hildebrand (B-H) plot of $1/(A-A_0)$ at 542 nm vs $1/[F^-]$ indicating 1:1 binding between **5** and F^- ion. Inset shows the B-H plot of $1/(A-A_0)$ at 542 nm vs $1/[F^-]^2$ indicating 1:2 binding between **5** and F^- ion.

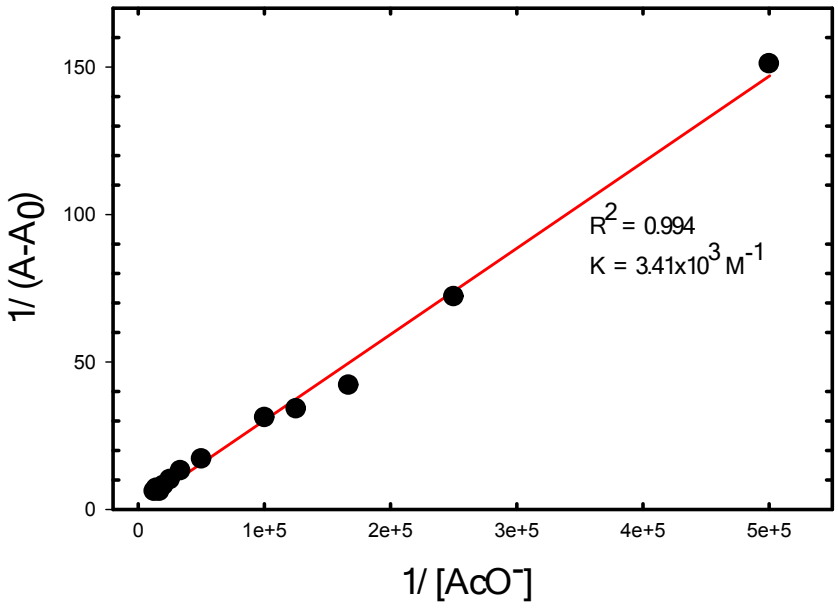


Figure S11: Benesi-Hildebrand plot of **4** with acetate ions indicating 1:1 binding stoichiometry.

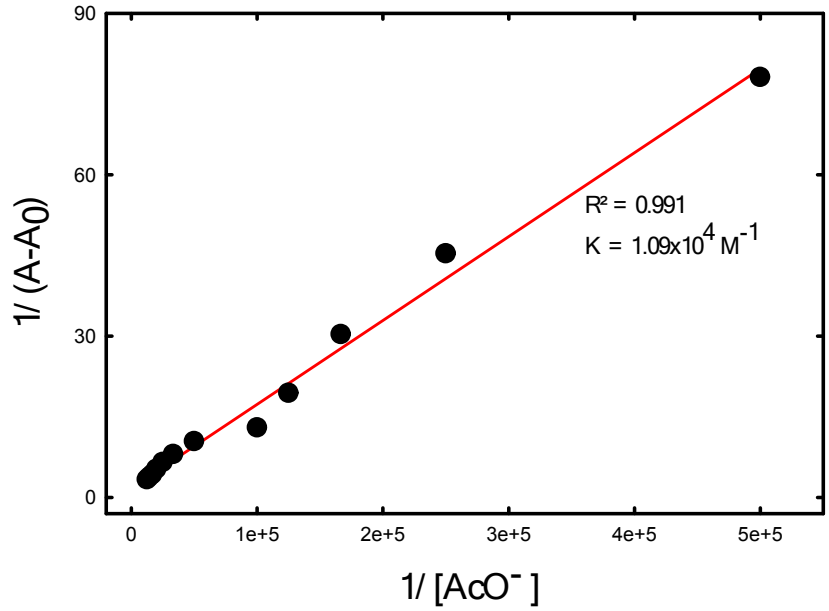


Figure S12: Benesi-Hildebrand plot of 5 with acetate ions indicating 1:1 binding stoichiometry.

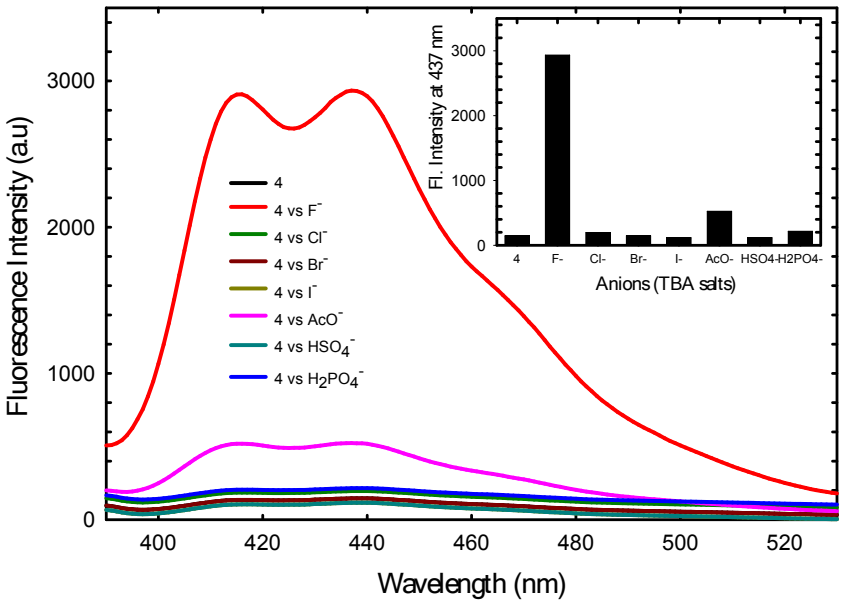


Figure S13: Emission spectra of **4** (10 μM) upon addition of 10 equiv. of F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^- and AcO^- ions (as tetrabutylammonium salts) in DMSO, λ_{ex} = 360 nm. Inset shows the emission intensity at 437 nm vs. various anions

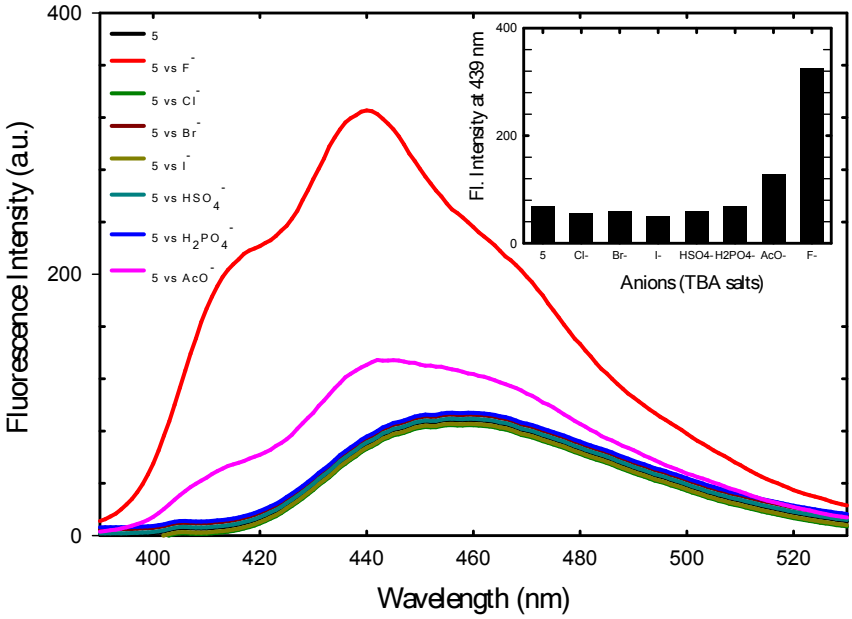


Figure S14: Emission spectra of **5** (10 μM) upon addition of 10 equiv. of F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^- and AcO^- ions (as tetrabutylammonium salts) in DMSO, λ_{ex} = 360 nm. Inset shows the emission intensity at 439 nm vs. various anions

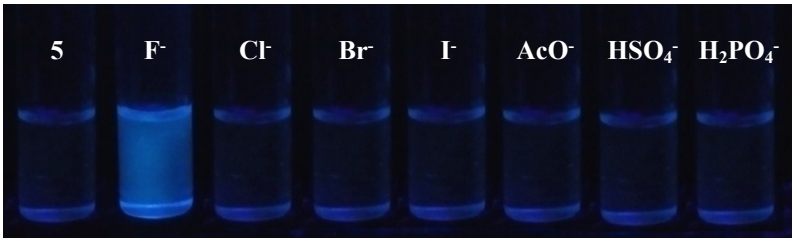


Figure S15: Fluorescent "turn on" behaviour of **5** for fluoride ion over other anions in DMSO solution (10μM) with the addition of 5 equivalents of various anions (as TBA salts) under UV light (365 nm).

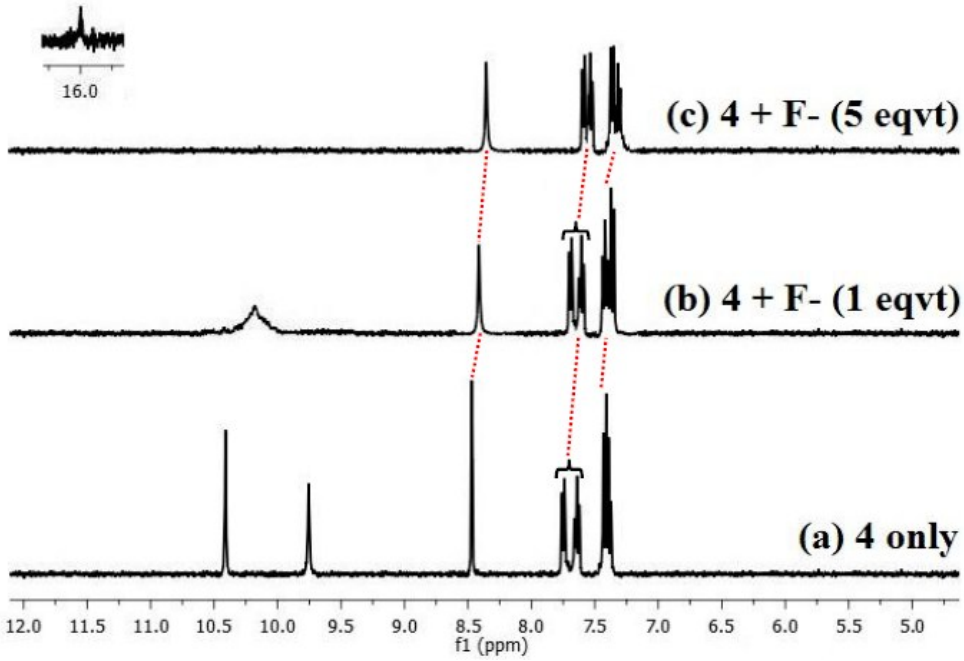


Figure S16: Partial ^{1}H NMR spectra (400 MHz and 298 K) of receptor **4** (10 mM) upon addition of various equivalents of TBAF (40 mM) in DMSO-d_6.

Cartesian coordinates of receptor 4

ATOM	1	C	-1.530	-5.950	-5.883	ATOM	26	C	1.621	2.185	1.782
ATOM	2	C	-1.243	-4.984	-4.936	ATOM	27	C	1.767	1.449	3.093
ATOM	3	C	-1.900	-4.998	-3.690	ATOM	28	H	0.823	1.443	3.648
ATOM	4	C	-2.840	-6.004	-3.442	ATOM	29	H	2.063	0.413	2.918
ATOM	5	C	-3.136	-6.982	-4.386	ATOM	30	H	2.526	1.894	3.731
ATOM	6	C	-2.477	-6.946	-5.606	ATOM	31	C	1.936	3.629	1.750
ATOM	7	H	-0.941	-3.257	-2.834	ATOM	32	C	2.033	4.373	0.479
ATOM	8	H	-1.033	-5.932	-6.844	ATOM	33	C	2.468	6.410	1.746
ATOM	9	H	-0.510	-4.211	-5.134	ATOM	34	N	-0.570	-1.376	0.125
ATOM	10	C	-1.667	-4.043	-2.660	ATOM	35	H	-1.007	-1.291	1.034
ATOM	11	H	-3.860	-7.752	-4.156	ATOM	36	N	0.746	0.323	0.843
ATOM	12	H	-2.704	-7.695	-6.354	ATOM	37	H	0.478	-0.012	1.765
ATOM	13	C	-3.280	-5.155	-1.209	ATOM	38	O	2.245	5.747	0.575
ATOM	14	C	-2.308	-4.084	-1.453	ATOM	39	O	1.951	3.933	-0.643
ATOM	15	O	-3.497	-6.040	-2.246	ATOM	40	C	2.472	5.703	2.953
ATOM	16	O	-3.923	-5.366	-0.197	ATOM	41	C	2.748	6.401	4.142
ATOM	17	C	-1.993	-3.066	-0.417	ATOM	42	C	3.011	7.756	4.106
ATOM	18	C	-2.787	-2.897	0.849	ATOM	43	H	2.757	5.859	5.080
ATOM	19	H	-2.856	-1.845	1.132	ATOM	44	H	3.239	8.289	5.020
ATOM	20	H	-3.790	-3.290	0.748	ATOM	45	C	2.177	4.307	2.910
ATOM	21	H	-2.302	-3.437	1.670	ATOM	46	H	2.121	3.790	3.859
ATOM	22	N	-0.989	-2.332	-0.734	ATOM	47	C	2.711	7.778	1.699
ATOM	23	C	0.335	-0.421	-0.236	ATOM	48	H	2.686	8.297	0.750
ATOM	24	S	0.889	-0.171	-1.802	ATOM	49	C	2.985	8.443	2.884
ATOM	25	N	1.171	1.611	0.711	ATOM	50	H	3.184	9.507	2.861

Cartesian coordinates of receptor 4+F^-

ATOM	1	C	-2.165	-6.339	-5.876
ATOM	2	C	-1.630	-5.380	-5.090
ATOM	3	C	-2.044	-5.264	-3.758
ATOM	4	C	-2.932	-6.162	-3.237
ATOM	5	C	-3.492	-7.101	-4.045
ATOM	6	C	-3.128	-7.204	-5.348
ATOM	7	H	-0.742	-3.462	-3.279
ATOM	8	H	-1.856	-6.434	-6.896
ATOM	9	H	-0.897	-4.708	-5.485
ATOM	10	C	-1.503	-4.112	-2.902
ATOM	11	H	-4.224	-7.772	-3.647
ATOM	12	H	-3.576	-7.949	-5.971
ATOM	13	C	-3.048	-4.931	-1.148
ATOM	14	C	-2.019	-3.925	-1.677
ATOM	15	O	-3.291	-6.166	-1.839
ATOM	16	O	-3.679	-4.676	-0.089
ATOM	17	C	-1.594	-2.715	-0.824
ATOM	18	C	-2.200	-2.510	0.577
ATOM	19	H	-2.237	-1.464	0.800
ATOM	20	H	-3.190	-2.915	0.600
ATOM	21	H	-1.594	-3.009	1.304
ATOM	22	N	-0.728	-1.871	-1.284
ATOM	23	C	1.079	-0.361	-0.697
ATOM	24	S	1.857	-0.481	-2.052
ATOM	25	N	1.866	1.521	0.642
ATOM	26	C	1.731	2.141	1.769
ATOM	27	C	1.369	1.353	3.042
ATOM	28	H	0.305	1.309	3.144
ATOM	29	H	1.762	0.360	2.971
ATOM	30	H	1.789	1.843	3.896
ATOM	31	C	1.933	3.666	1.839
ATOM	32	C	2.301	4.464	0.581
ATOM	33	C	2.411	6.499	1.898
ATOM	34	N	-0.340	-0.772	-0.508
ATOM	35	H	-0.322	-0.963	0.466
ATOM	36	N	1.683	0.135	0.578
ATOM	37	H	0.984	-0.166	1.211
ATOM	38	F	-0.003	-0.839	1.722
ATOM	39	O	2.283	5.900	0.591
ATOM	40	O	2.610	3.852	-0.474
ATOM	41	C	2.127	5.818	3.044
ATOM	42	C	2.144	6.482	4.278
ATOM	43	C	2.512	7.783	4.344
ATOM	44	H	1.871	5.958	5.171
ATOM	45	H	2.527	8.288	5.287
ATOM	46	C	1.801	4.320	3.003
ATOM	47	H	1.491	3.804	3.888
ATOM	48	C	2.826	7.837	1.979
ATOM	49	H	3.099	8.364	1.090
ATOM	50	C	2.877	8.466	3.178
ATOM	51	H	3.193	9.487	3.233

4. Procedure for Job's plot experiment:

A series of solutions containing receptor **4** or **5** and tetrabutylammonium fluoride were prepared such that the sum of the total concentration of receptor **4** or **5** and fluoride ion remained constant (100 μM). The mole fraction of receptor (X_R) was varied from 0.1 to 1.0. The corrected absorbance ($[A-A_0] / [A_0]$) at 546 nm and 542 nm for receptor **4** and **5** respectively were plotted against the molar fraction of the receptor solution. The value of mole fraction of receptor at maximum absorption (X_{max}) was obtained from the plot and the stoichiometry ratio (n) of the receptor-fluoride ion complex ($R:F_n$) at equilibrium was calculated from the relationship, $n= X_{max}/(1- X_{max})$.

5. General method for ^{1}H NMR titrations experiments.

A 10 mM solution of receptor **4** was prepared in DMSO-d_6. To a 0.5 ml of receptor solution, various equivalents of tetrabutylammonium fluoride (40 mM in DMSO-d_6) were added to an NMR tube and the spectra were recorded.