Supporting Information

A fluorescent chemosensor for detection of perchlorate ions in water

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Content

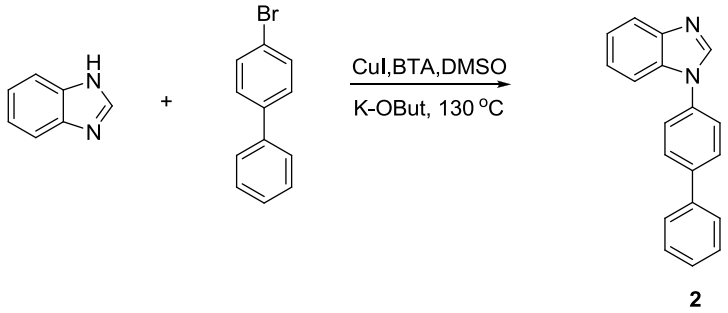
1. Experimental Details

1.1 General Remarks: All chemicals were obtained from common suppliers (Aldrich, Across, SDFCL, Spectrochem etc.) and used without further purification. 1-(4-bipenyl)benzimidazole (2) was synthesized by CuI, benzotriazole catalyzed N-arylation of benzimidazole with 4-bromobiphenyl as reported in literature[1]. ^{1}H and ^{13}C NMR spectra were recorded on Brucker-400 and JEOL-300 instruments using the resonance of solvents having TMS as internal standard. Shifts are given in ppm; coupling constants in Hz. UV-Vis studies of compounds were

performed on Shimadzu-2450 and fluorescence studies were carried out on BH-CHRONOS spectrophotometers.

Experimental section.

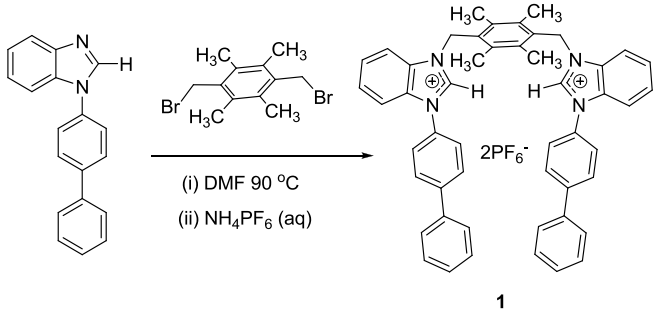
Synthesis of compound 2.



Scheme 1. Synthesis of **2**

4-Bromobiphenyl (3.5 g, 15.2 mmol), CuI (120 mg, 0.6 mmol) and benzotriazole (150 mg, 1.2 mmol) were dissolved in DMSO (8 ml). Benzimidazole (1.5 g, 12.7 mmol) and K-OBu^t (1.7 g, 15.2 mmol) were added under N_2 and resulting solution was heated at 130 ^oC for 24h. The reaction mixture was cooled to room temperature and aqueous solution of EDTA (1.2 mmol) was added. The reaction mixture was extracted with ethyl acetate (3 × 30 ml). The solvent was distilled off, and the residue on column chromatography with hexane-chloroform (9:1) mixture as eluent gave pure compound **2**, white solid (2.4 g). Yield 70 %; M**.** pt. 185 ^oC; Lit mp 185-190 ^oC; **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.34 - 7.39 (m, 2H, ArH), 7.42 (d, 1H, *J* = 7.2 Hz, ArH), 7.49 (t, 2H, *J* = 7.2 Hz, ArH), 7.58 - 7.66 (m, 5H, ArH), 7.79 (d, 2H, *J* = 8.4 Hz, ArH), 7.89 - 7.92 (m, 1H, ArH), 8.16 (s, 1H, Bim C2-H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 110.9, 121.1, 123.3, 124.2, 124.7, 127.5, 128.3, 129.1, 129.4, 134.2, 135.9, 140.2, 141.5, 142.7, 144.5. CHN analysis: Found C, 84.44; H, 5.28; N, 10.38 %; $C_{19}H_{14}N_2$ requires C, 84.42; H, 5.22; N, 10.36 %.

Synthesis of chemosensor 1.



Scheme 2. Synthesis of **chemosensor - 1**

The solution of 1-(4-bipenyl)benzimidazole (270 mg, 1 mmol) and 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (160 mg, 0.5 mmol) was heated in DMF (2 ml) at 100 ^oC under N_2 for 8 h. After completion of the reaction, the solvent was removed under vacuum. The crude

residue was dissolved in methanol and was filtered to remove suspended impurities. To this filtrate, aqueous solution of NH_4PH_6 (163 mg, 1 mmol) was added drop wise with continuous stirring and stirring was continued for 7-8 h. The white solid separated was filtered and was crystallized from acetonitrile - isopropanol (8:2) mixture to get **1** as white crystalline solid (440 mg). Yield 89 %; M. pt. 258 ^oC; **^{1}H NMR** (DMSO-d_6, 400 MHz): δ 2.37 (s, 12H, 4 x CH_3), 5.93 (s, 4H, 2 x CH_2), 7.46-7.52 (m, 6H, ArH), 7.71 (d, 4H, *J* = 8.0 Hz, ArH), 7.79 - 7.91 (m, 10H, ArH), 7.98 (d, 4H, *J* = 8.4 Hz, ArH), 8.36 (d, 2H, *J* = 8.0 Hz, ArH), 9.38 (s, 2H, ArH); **^{13}C NMR** (DMSO d_6 400 MHz): δ 16.6, 46.6, 113.7, 114.2, 126.5, 126.6, 127.2, 127.8, 128.1, 128.3, 129.2, 129.6, 131.6, 131.9, 132.1, 135.8, 138.4, 140.8, 142.3. HRMS *m/z* (TOF MS ES$^+$) calculated for $C_{50}H_{44}N_4PF_6^+$ [M^+], 845.3202; found 845.3196. CHN analysis: Found C, 59.58; H, 4.68; N, 5.87 %; $C_{50}H_{44}F_{12}N_4P_2$ requires C, 60.61; H, 4.48; N, 5.65 %.

2. Spectra of 2 and chemosensor 1

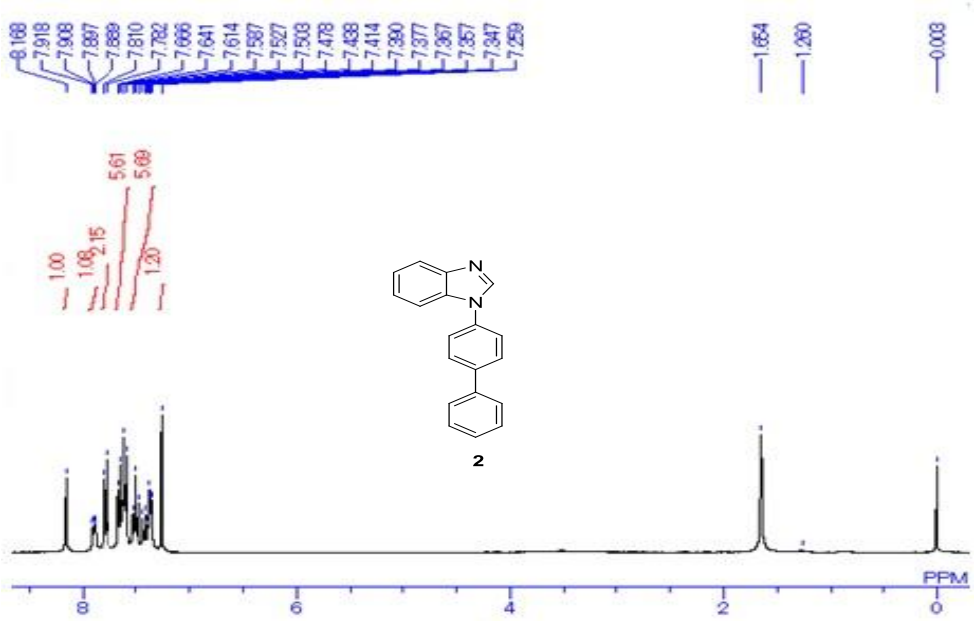


Figure S1. ^{1}H NMR spectrum of **2**.

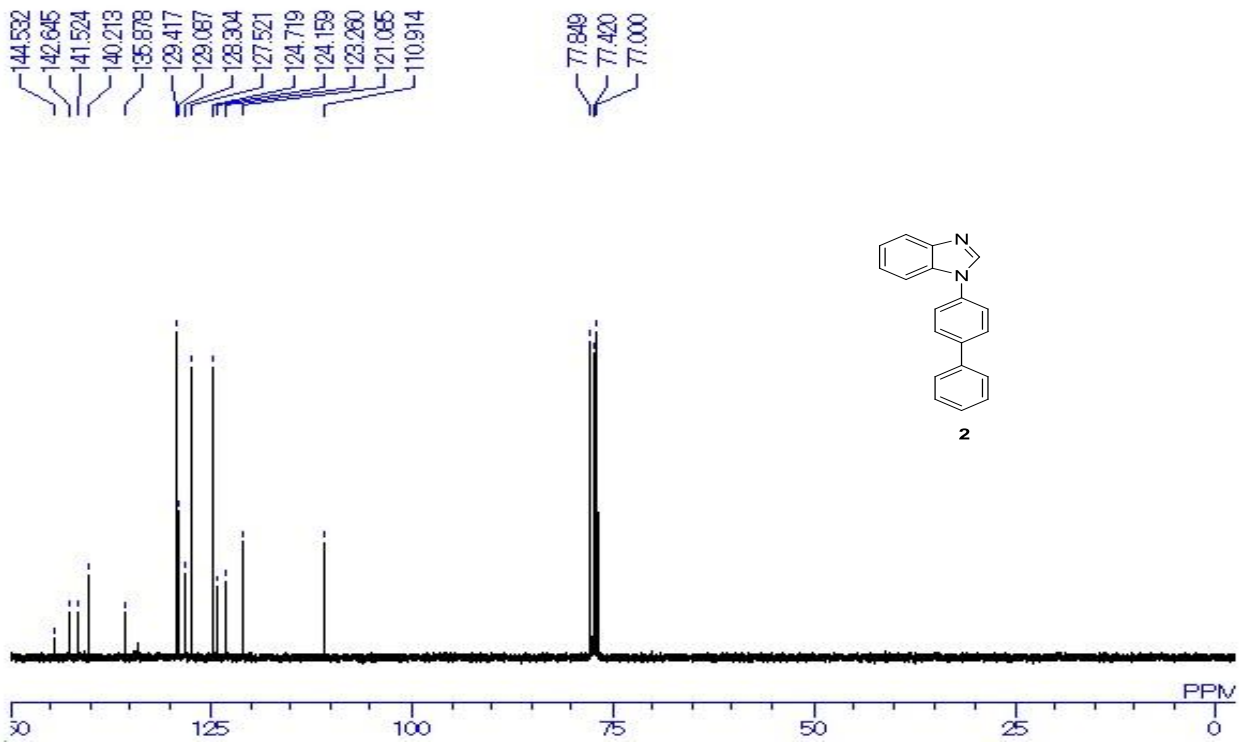


Figure S2. ^{13}C NMR spectrum of **2**.

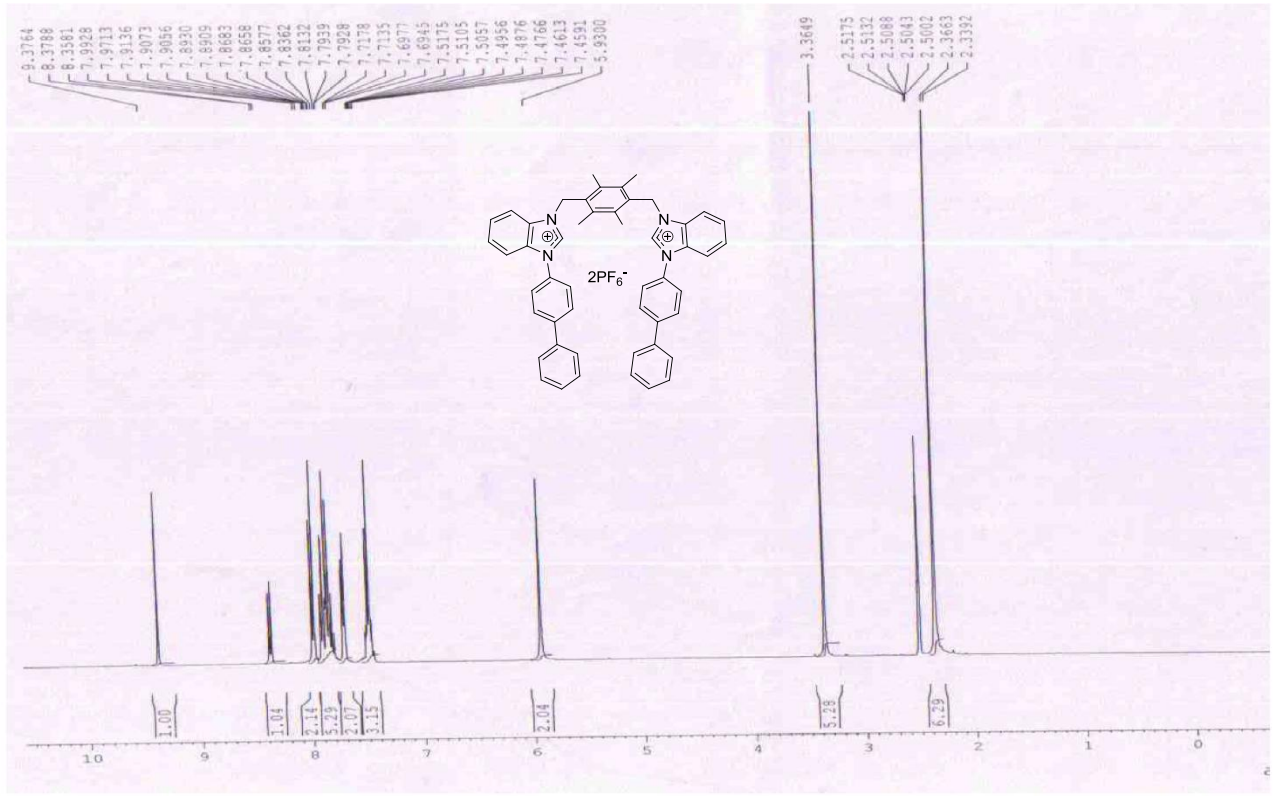


Figure S3. ^{1}H NMR spectrum of chemosensor **1**

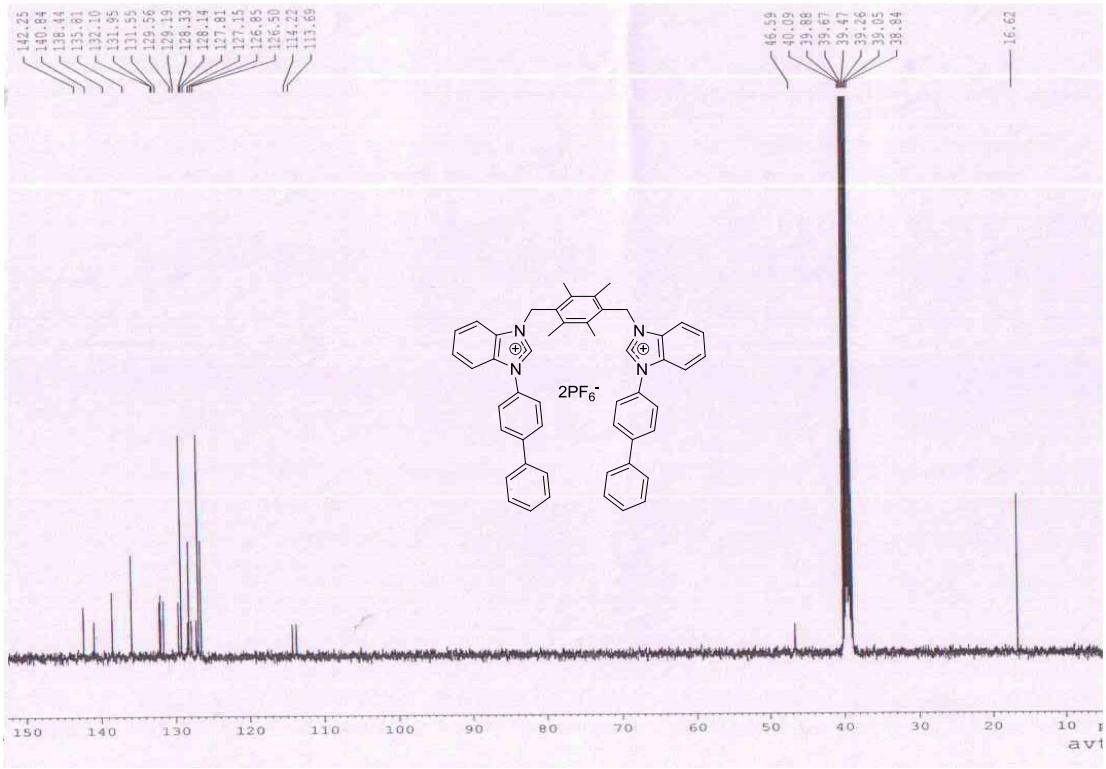


Figure S4. ^{13}C NMR spectrum of chemosensor **1**

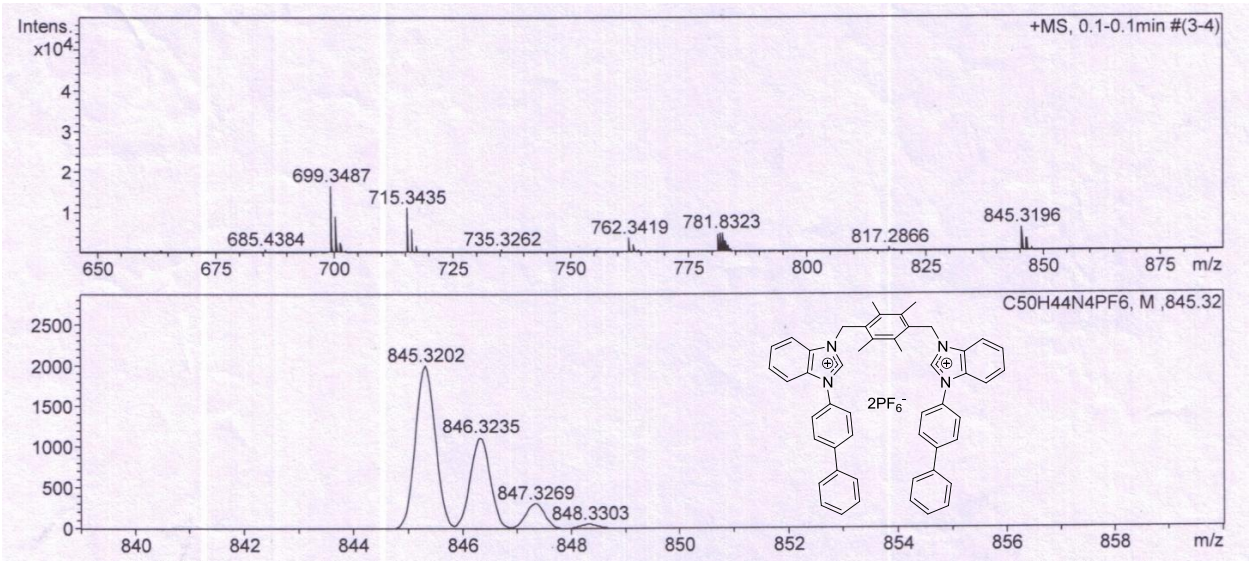


Figure S5. HRMS of chemosensor **1**

3. UV-Vis and Fluorescence studies of chemosensor 1

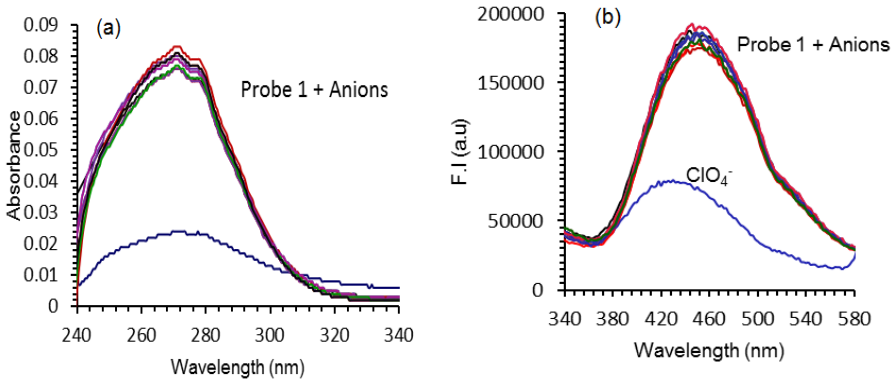


Figure S6. Effect of different anions on (a) the absorption (b) fluorescence spectrum (λ_{ex} 290 nm) of chemosensor **1** (2 µM) in HEPES buffer, pH 7.4 (2% DMSO).

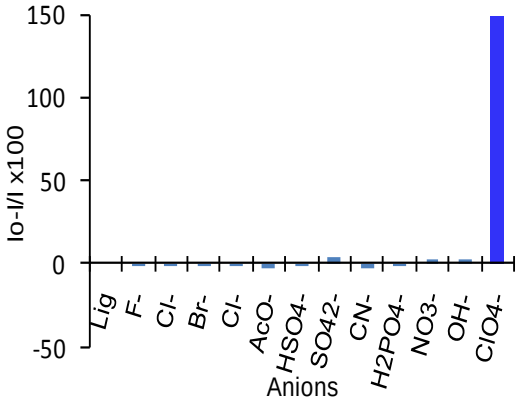


Figure S7. The bar diagram showing difference in I_o/I ×100 values (λ_{ex} 290 nm) on addition of different anions to the solution of chemosensor **1** (2 µM) in HEPES buffer, pH 7.4 (2% DMSO).

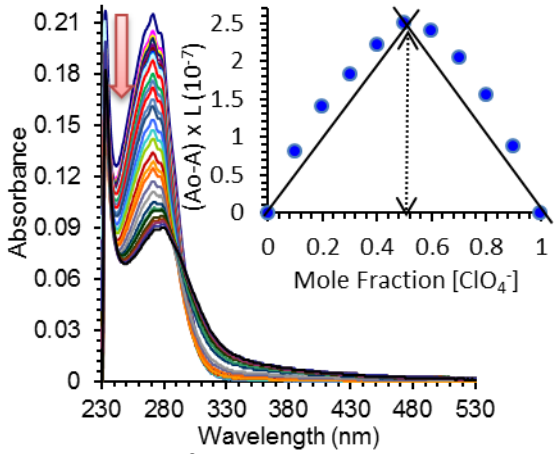


Figure S8. Effect of gradual addition of $NaClO_4$ on the absorption of chemosensor **1** [5 µM, HEPES buffer, pH 7.4 (2% DMSO)]; logβ = 4.24 ± 0.05. Inset shows Job's plot showing the inflexion point near to 0.5 indicative of the existence of 1:1 stoichiometric (**1**:ClO_4^-).

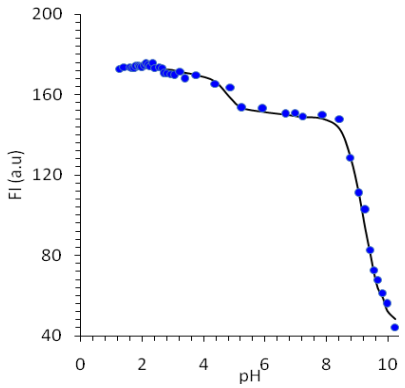


Figure S9: Effect of pH on the fluorescence of chemosensor **1**.

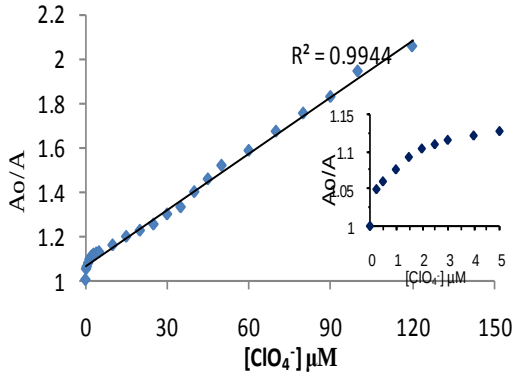


Figure S10. Absorption response A_o/A (270 nm) of chemosensor **1** in HEPES buffer, pH 7.4 (2% DMSO) on addition of perchlorate ions.

4. HRMS and 1 HNMR analysis of 1 + ClO_4^- complex

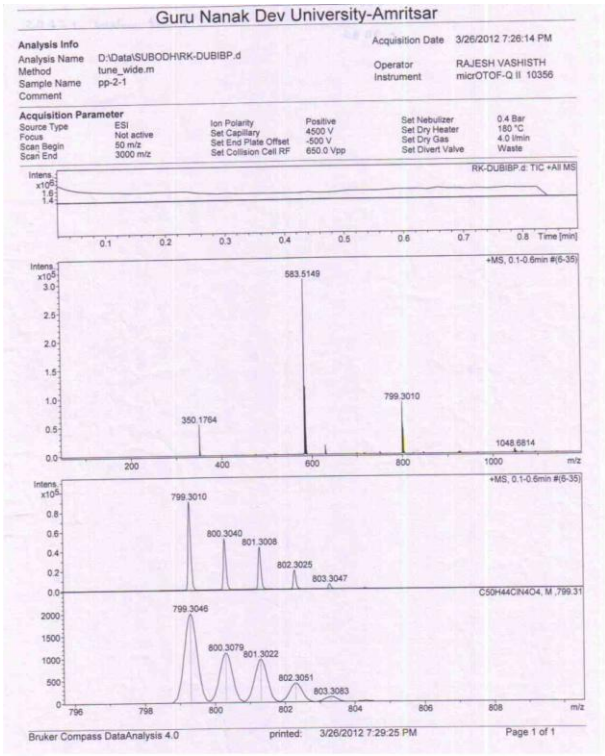


Figure S11. HRMS of chemosensor **1** as PF_6^- counter anions + 10 equiv. ClO_4^- shows formation of complex (1:1) with ClO_4^-

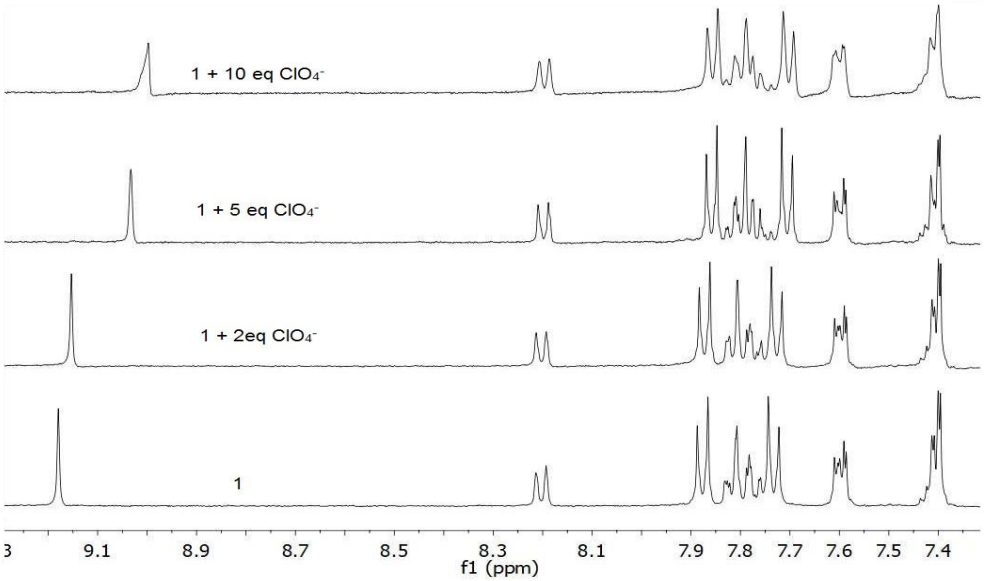


Figure S12. ^1H NMR titration of chemosensor 1 with ClO_4^- in DMSO + Water (3:1).

5. Evaluation of Thermodynamic parameters:

To evaluate thermodynamic parameters i.e. enthalpy and entropy, the association constant (log *K*) values at three different temperature i.e. at 288 K, 298 K and 308 K were determined using UV-Vis titrations of chemosensor **1** with sodium perchlorate. The log K values were converted to ΔG using equation -RT lnK. The Van't Hoff plot of ΔG against temperature provides ΔH and TΔS values.

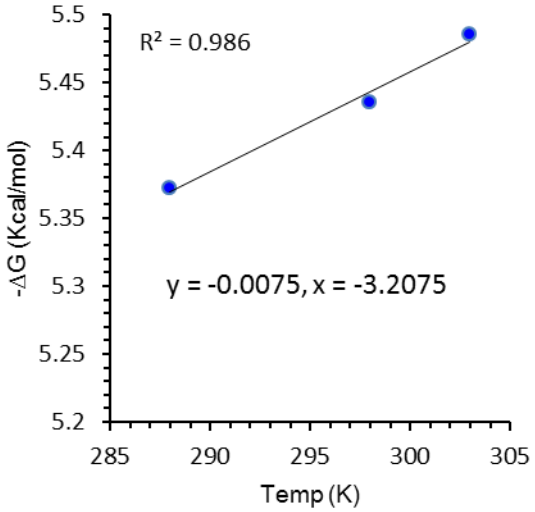


Figure S13. Free energy vs. temperature plots of **chemosensor -1** against ClO_4^- ions.

6. X-ray crystal structure of chemosensor 1 (ccdc no 888486)

Table S1. Crystal data and structure refinement for chemosensor 1

Identification code	shelxl	
Empirical formula	C50 H44 F12 N4 P2, CH_3CN	
Formula weight	1031.91	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 24.481(2) Å	α= 90°
	b = 8.9613(5) Å	β= 108.336(2)°
	c = 23.769(2) Å	γ = 90°
Volume	4949.8(6) $Å^3$	
Z	4	
Density (calculated)	1.385 Mg/m^3	
Absorption coefficient	0.175 mm^{-1}	
F(000)	2128	
Crystal size	0.24 x 0.12 x 0.10 mm^3	
Theta range for data collection	1.74 to 25.01°.	
Index ranges	-29<=h<=29, -10<=k<=7, -28<=l<=28	
Reflections collected	33031	
Independent reflections	8713 [R(int) = 0.0788]	
Completeness to theta = 25.01°	99.9 %	
Absorption correction	multi-scans	
Max. and min. transmission	0.74520 and 0.6674	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8713 / 12 / 665	
Goodness-of-fit on F^2	0.971	
Final R indices [I>2sigma(I)]	R1 = 0.0730, wR2 = 0.1870	
R indices (all data)	R1 = 0.2041, wR2 = 0.2554	
Largest diff. peak and hole	0.346 and -0.420 $e.Å^{-3}$	

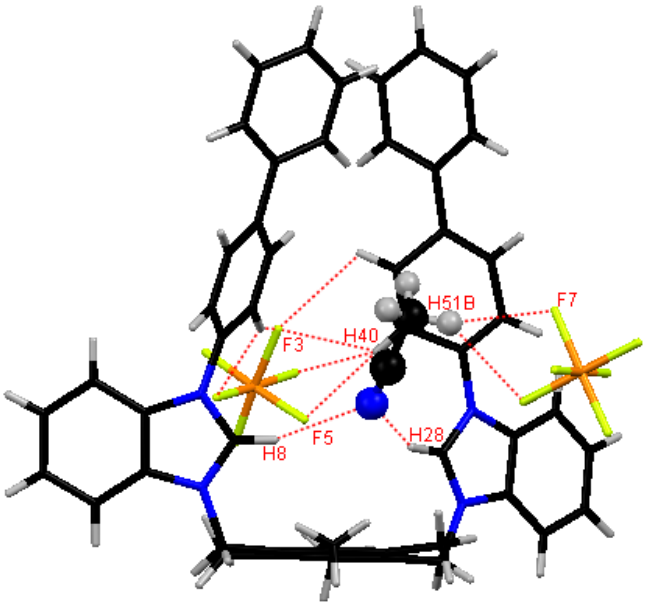


Figure S14. H-bonding interactions between the chemosensor **1** and acetonitrile (solvent) and PF_6^- anions

Table S2- important H-bonds in the chemosensor 1

X-H…Y	X…Y(Å)	H…Y(Å)	∠X-H…Y(°)
C7-H7A...F10	3.287(8)	2.48	141
C7-H7A...F12	3.070(7)	2.87	92
C7-H7B...F12	3.070(7)	2.51	117
C8-H8...N5	3.288(10)	2.40	159
C13-H13...F7	3.663(9)	2.89	140
C16-H16 ...F1	3.398(11)	2.61	143
C16-H16 ...F3	3.247(7)	2.40	151
C28-H28...F5	3.387(8)	2.94	111
C28 -H28 ...N5	3.433(10)	2.60	149
C47-H47A ...N1	3.630(7)	2.99	125
C48-H48B ...N4	3.492(7)	2.83	127
C49 -H49B...N4	3.416(8)	2.74	128
C49-H49C...F4	3.624(7)	2.68	166
C49 -H49C...F5	3.369(10)	2.79	120
C50-H50B...F1	3.674(12)	2.85	145
C50-H50B ...N1	3.305(8)	2.85	110
C39 -H39...F3	3.084(18)	2.59	113
C40-H40...F3	2.949(15)	2.34	122
C40-H40 ...F5	3.171(19)	2.31	153
C40-H40...F6	3.420(17)	2.58	151

C20-H20...F2[a]	3.799(9)	2.95	153
C47-H47A...F6[a]	3.616(8)	2.69	160
C24-H24...F2[b]	3.341(11)	2.64	132
C25-H25...F3[b]	3.352(9)	2.58	140
C48-H48B...F11[c]	3.803(6)	2.91	156
C27-H27A...F12[c]	3.404(5)	2.50	155
C31-H31...F11[d]	3.337(7)	2.49	151
C30-H30...F10[d]	3.329(8)	2.52	145
C32-H32...F9[e]	3.321(6)	2.62	133
C49-H49A...F12[f]	3.282(7)	2.86	108
C49-H49A...F9[f]	3.612(8)	2.86	136
C51-H51B...F7[g]	3.374(10)	2.53	146
C51-H51B...F8[g]	3.350(10)	2.66	129
C51-H51B...F10[g]	3.796(10)	2.86	164
C36-H36...F9[g]	3.640(25)	2.84	144

(a) x,+y-1,+z (b) -x,+y-1/2,-z+1/2 (c) -x+1,+y+1/2,-z+1/2
(d) x,-y+1/2+1,+z+1/2 (e) -x+1,+y+1/2+1,-z+1/2 (f) x,+y+1,+z
(g) x,-y+1/2,+z+1/2