

Electronic Supplementary Information

Remarkably Selective Non-Linear Allosteric Regulation of Anion Binding by Tetracationic Calix[4]pyrrole Homodimer

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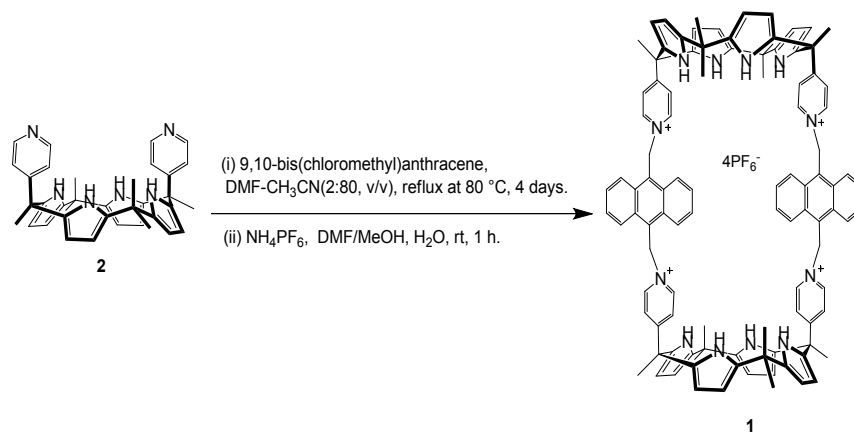
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General information and instrumentations

^1H NMR spectra were recorded on 400 and 300 MHz Bruker NMR spectrometer using TMS as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; br s, broad singlet; d, doublet; t, triplet; m, multiplet. ^{13}C NMR spectra were proton decoupled and recorded on a 100 MHz Bruker spectrometer using TMS as the internal standard. Pyrrole was distilled at atmospheric pressure from CaH_2 . Fluorescence spectra were recorded using Scinco FS-2 fluorescence spectrophotometer. Absorption spectra were recorded on Varian Cary 100 Conc UV-vis spectrophotometer. Isothermal titrations (ITC) were performed on VP-ITC microcalorimeter. All titrations were performed using HPLC grade CH_3CN purchased from Aldrich. All other chemicals and solvents were purchased from commercial sources and were used as such, unless otherwise mentioned.

Experimental Section

Synthetic Scheme. Synthesis of **1**.



Synthetic procedures

Synthesis of compound **1**

To a stirred solution of 9,10-bis(chloromethyl)anthracene (0.035 g, 0.127 mmol) in dry DMF (2 mL) was added compound **2** (0.071 g, 0.127 mmol) dissolved in dry CH_3CN (80 mL). The reaction mixture was refluxed for 4 days under nitrogen atmosphere. The reaction mixture

wasthen cooled to room temperature and the yellow precipitate was filtered. The precipitate was washed with ethylacetate several times to give tetrachloride salt of **1** (0.033 g, yield 31%). The tetrachloride salt (0.030 g, 18.1 μmol) without characterization was next dissolved in 5 mL hot DMF-CH₃OH (1:4, v/v) and NH₄PF₆ (0.295 g, 1.81 mmol) was added to it in one portion. After stirring for 30 min, water was added and stirred for additional 30 min at room temperature. The precipitate was filtered, washed with water and dried to give pure **1** (0.028g, 75%). ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.96 (s, 8H, NH), 9.07 - 9.05 (m, 16H), 7.80-7.77 (m, 8H), 7.14 (d, 8H, *J* = 6.9 Hz), 7.09 (s, 8H), 5.77 (t, 8H, *J* = 2.7 Hz) 5.50 (t, 8H, *J* = 2.7 Hz), 1.83 (s, 12H), 1.46 (s, 12H), 0.85 (s, 12H). ¹³C NMR (100 MHz, CD₃CN) δ 171.5, 143.5, 141.0, 135.0, 130.6, 129.5, 127.9, 127.8, 125.0, 104.0, 101.3, 54.5, 45.2, 34.0, 30.5, 26.0, 25.3; MALDI-TOF *m/z* calcd for C₁₀₄H₁₀₀F₂₄N₁₂P₄ (M) 2096.6761, (M - PF₆) 1951.7114, (M - 2PF₆) 1806.7467, (M - 3PF₆) 1661.7819, (M - 4PF₆) 1516.8172, found for (M - PF₆) 1951.3692, (M - 2PF₆) 1805.5494, (M - 3PF₆) 1661.7461(M - 4PF₆) 1516.0107.

General procedure for Uv-visible and Fluorescence titrations

Stock solutions of the host **1** (17.5 μM) and anionic guests (in mM range) were prepared in HPLC grade CH₃CN and 2 mL of the host solution was taken in the cuvette for each titration. For fluorescence, the solution was irradiated at $\lambda_{\text{ex}} = 370$ nm. Upon the addition of guest anions, the change in absorbance or emission of the host was noticed.

Procedure for Job's plot for the determination of stoichiometry

The stoichiometry was determined by the continuous variation method. Solutions of host and guest of equal concentrations (17.5 μM) were prepared in HPLC grade CH₃CN. Then host and guest solutions were mixed in different proportions maintaining a total volume of 3 mL of the mixture. The related compositions for host:guest (v/v) were 3:0, 2.8:0.2; 2.5:0.5, 2.2:0.8, 2:1, 1.8:1.2, 1.5:1.5, 1:2, 0.8:2.2, 0.5:2.5, 0.2:2.8. All the prepared solutions were kept for 1 h with occasional shaking at room temperature. Then absorbance of the solutions of different compositions was recorded. The concentration of the complex i.e., [HG] was calculated using the equation $[\text{HG}] = \Delta A/A_0 \times [\text{H}]$ where $\Delta A/A_0$ indicate the relative absorbances, [H] Corresponds the concentration of pure host. Mole fraction of the host (X_{H}) was plotted against concentration of the complex [HG]. In the plot, the mole fraction of the host at which the concentration of the host-guest complex concentration [HG] is maximum, gives the stoichiometry of the complex.

Procedure for isothermal titration experiments

Isothermal titration Calorimetry (ITC) experiment was performed by stepwise injection of 6 μ l of macrotricyclic **1** ($c = 1.35$ mM) in CH_3CN to the solution of TBAF ($c = 0.127$ mM) in CH_3CN at 298K. The ITC data were fitted to theoretical isotherm from the two sets of sites binding model provided in the Microcal ITC data analysis software.

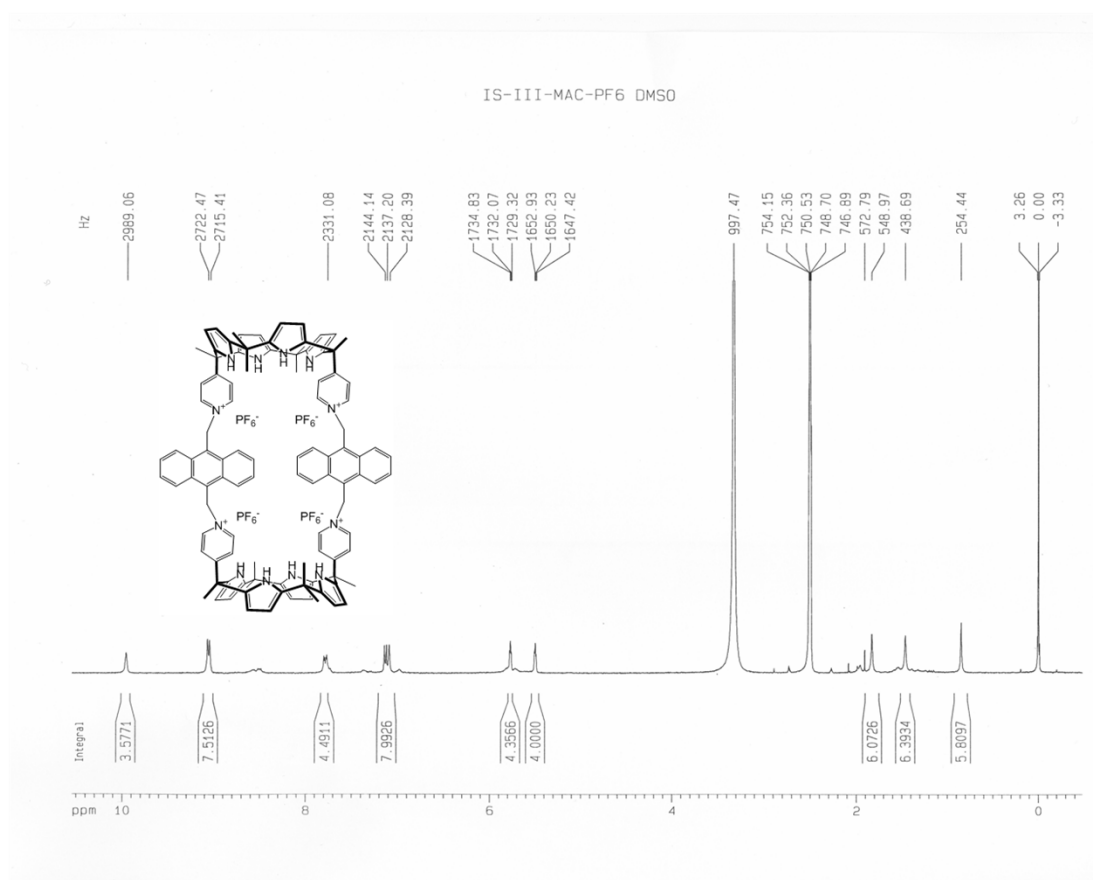


Figure S1. ^1H NMR spectrum of **1** in $\text{DMSO-}d_6$.

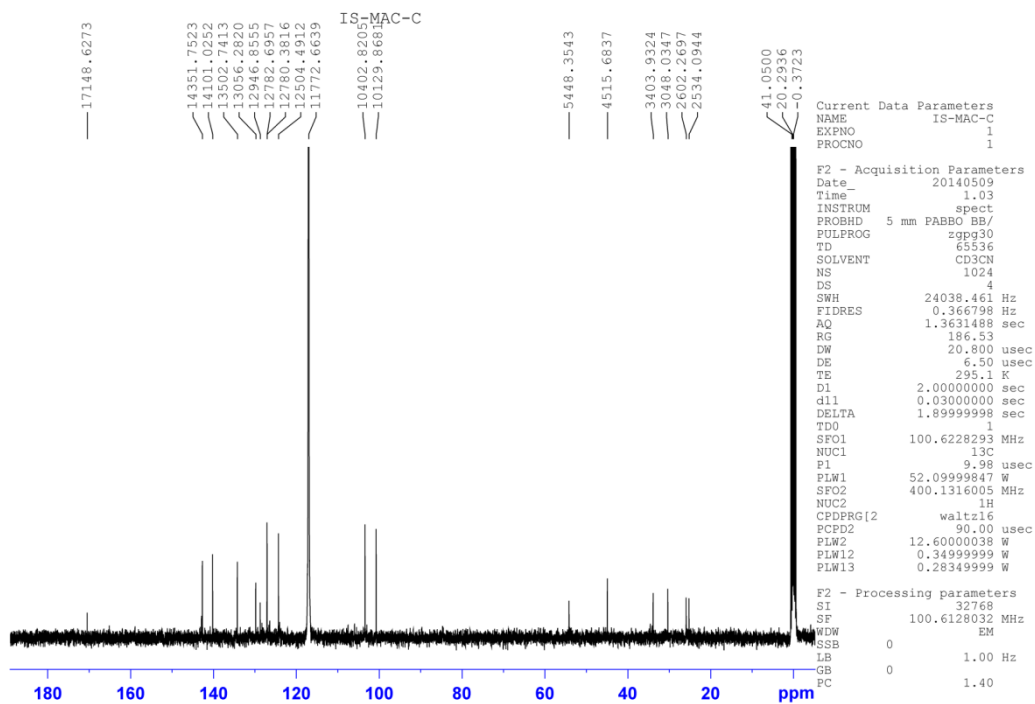
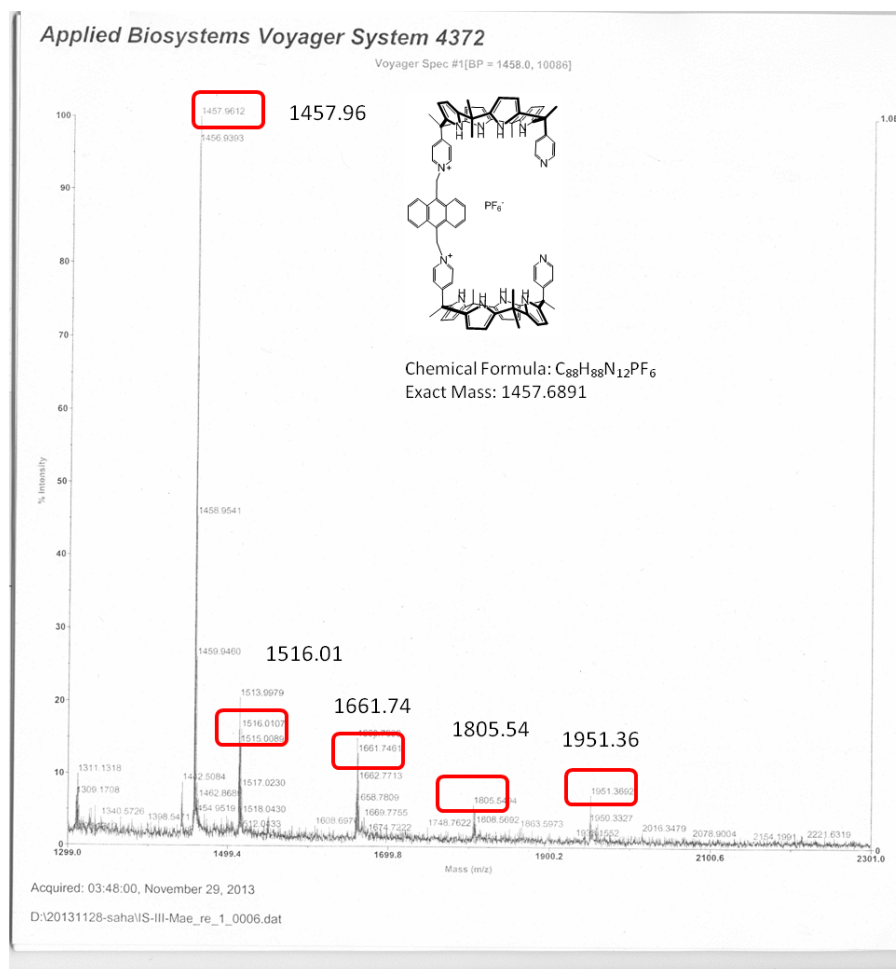


Figure S2. ^{13}C NMR spectrum of **1** in CD_3CN .



$$M^{4+} + 4 PF_6^- = 2097.84$$

$$M^{4+} + 3 PF_6^- = 1951.71$$

$$M^{4+} - H + 2 PF_6^- = 1805.74$$

$$M^{4+} + PF_6^- = 1661.78$$

$$M^{4+} = 1516.81$$

Figure S3.MALDI-TOF spectrum of 1.

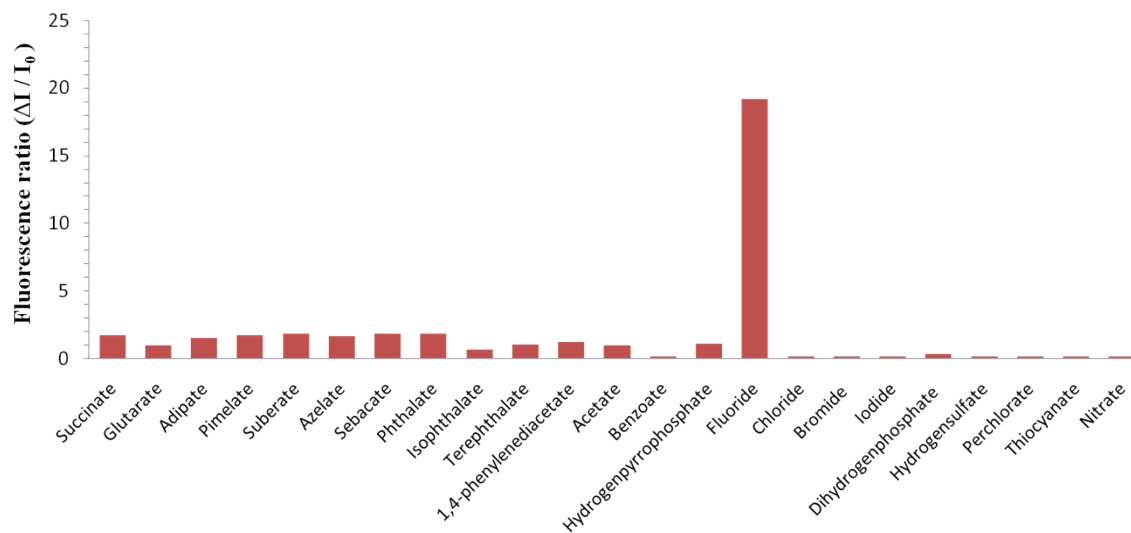


Figure S4. Change in fluorescence ratios ($\Delta I/I_0$) of **1** (17.2 μM) upon addition of 50.0 equivalents of various anions, measured at 421 nm.

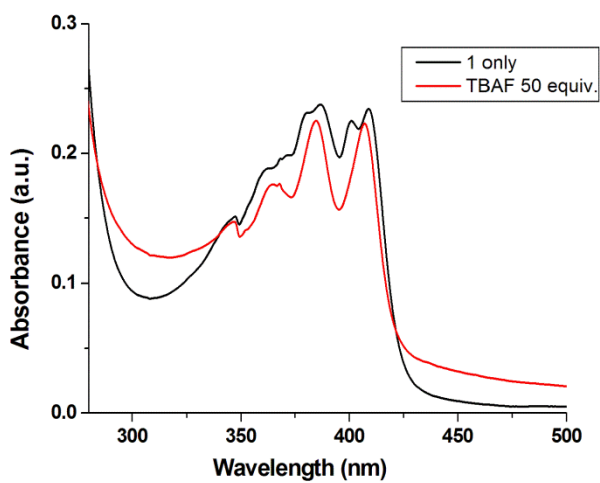


Figure S5. Change in absorbance of **1**(17.2 μM) upon addition of 50.0 equivalents of TBAF.

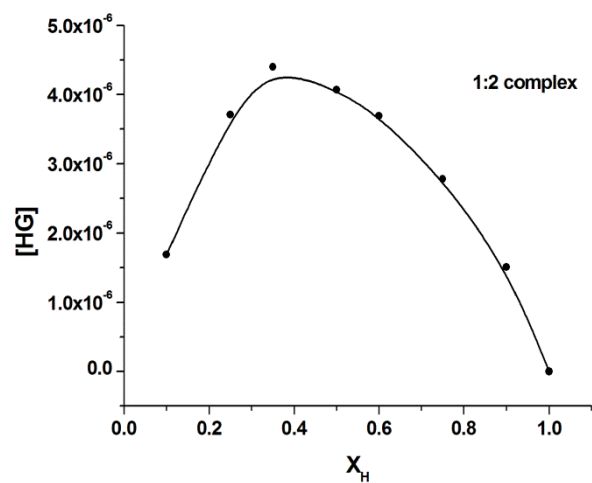


Figure S6. Job plot obtained from UV-vis titration of **1** with TBAF.

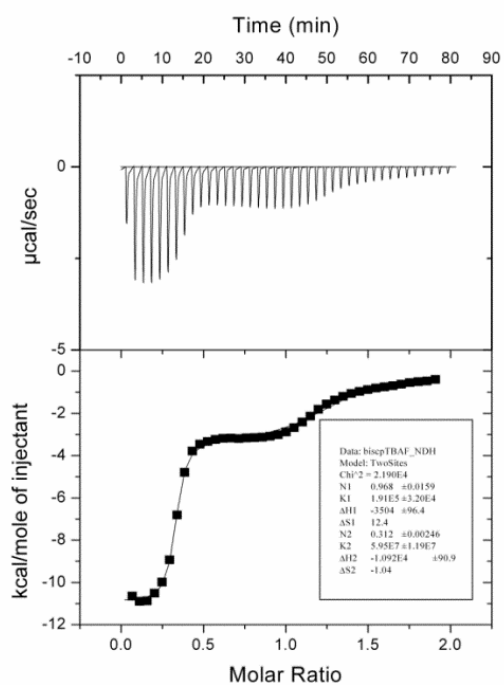


Figure S7. ITC plots showing titration of receptor **1** (initial concentrations: 1.35 mM) with [TBAF.3H₂O] (10.127 mM) at 298 K.

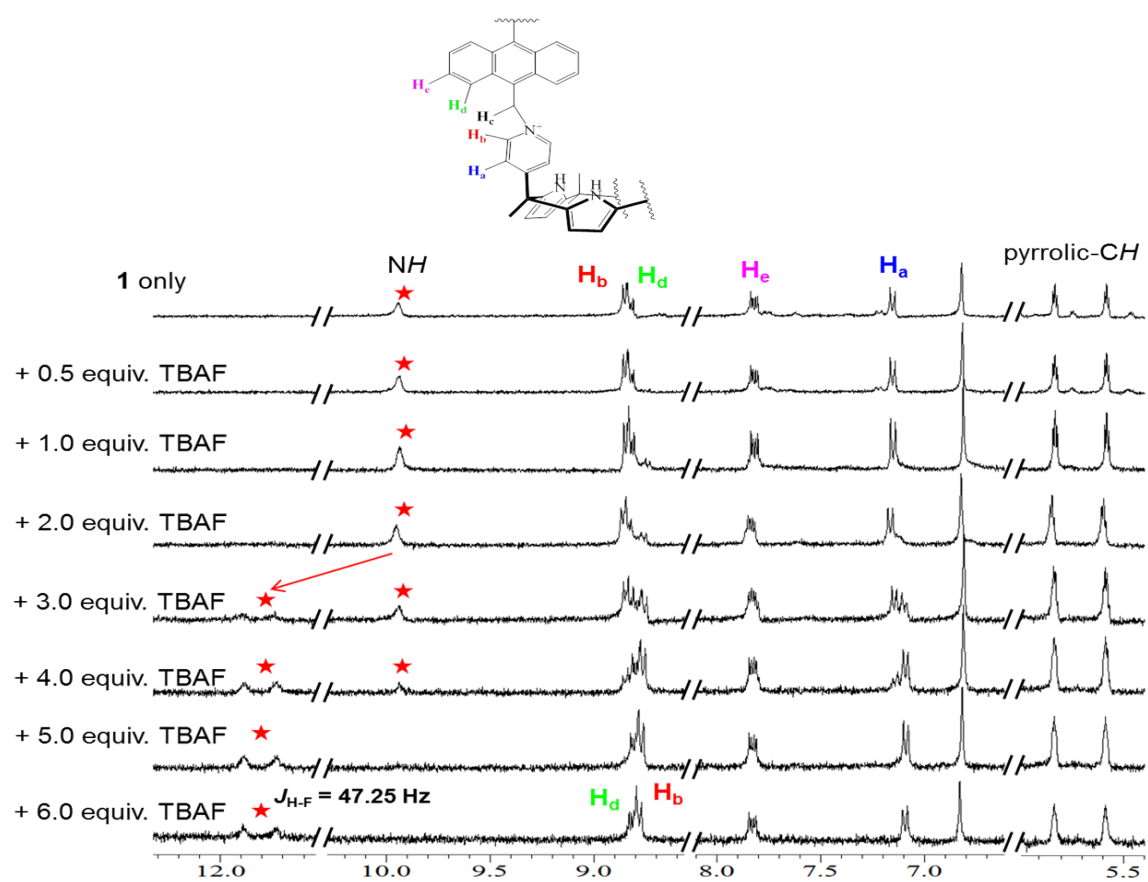


Figure S8. Partial ^1H NMR spectra recorded during the titration of receptor **1** ($c = 0.95$ mM) with TBAF in CD_3CN (downfield region).

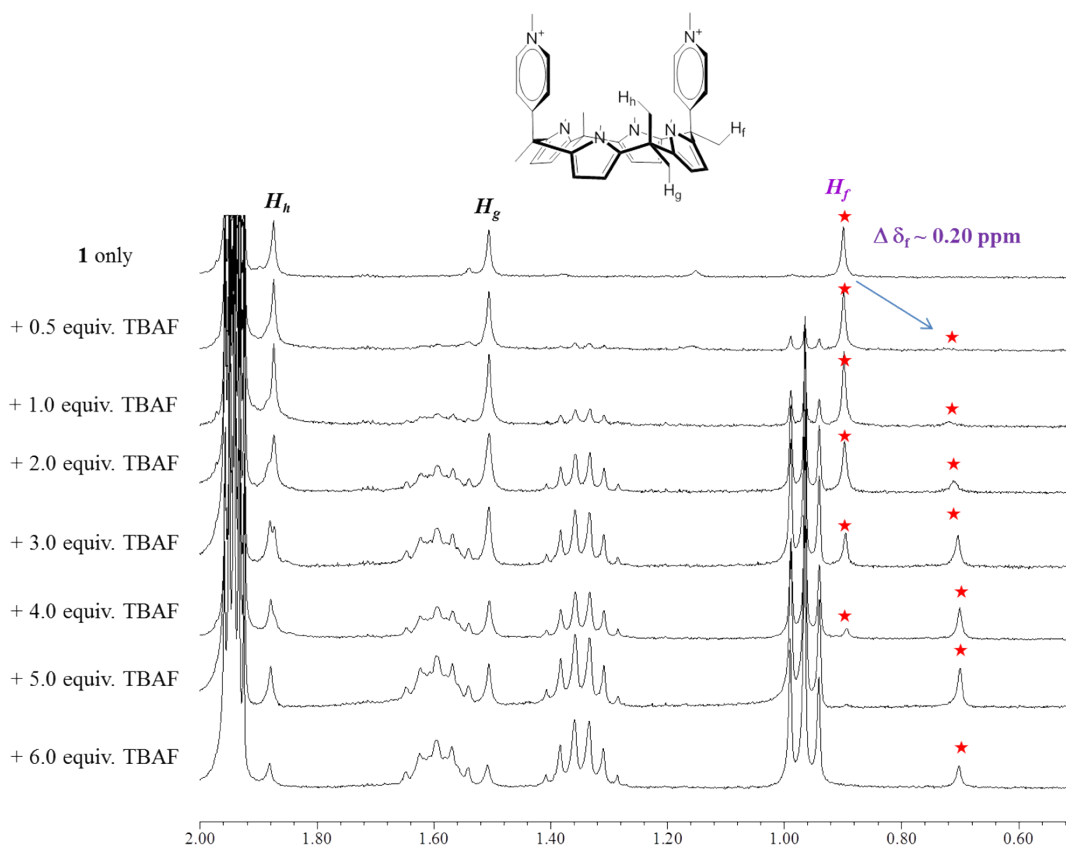


Figure S9. Partial ^1H NMR spectra recorded during the titration of receptor **1** (0.95mM) with TBAF in CD_3CN (Upfield region).

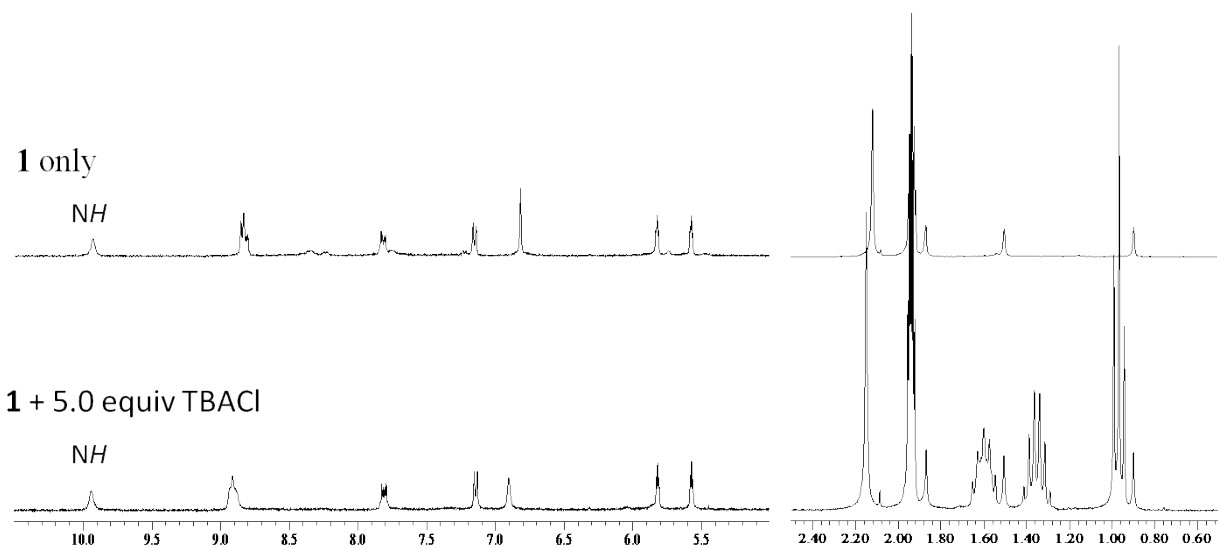


Figure S10. Partial ^1H NMR spectra of receptor **1** (0.95 mM) in absence and presence of 5.0 equivalents of TBACl in CD_3CN .

Table 1 Thermodynamic data for the interaction of 1 with TBAF in acetonitrile at 298K as determined by isothermal titration calorimetry (ITC).

n_1	ΔH_1	$T\Delta S_1$	ΔG_1	$K_1 (M^{-1})$	K_2/K_1	$\Delta\Delta G_{12}$
0.96	-3.50 ± 0.09	+3.69	-7.19	(1.91 ± 0.32) $\times 10^5$	~311	-3.73
n_2	ΔH_2	$T\Delta S_2$	ΔG_2	$K_2 (M^{-1})$		
0.31	-10.92 ± 0.09	-0.30	-10.61	(5.95 ± 1.91) $\times 10^7$		

