Supporting information of

A fluoride selective water-soluble anion receptor based on 1,2-Phenylenediacetic acid and calcium ion dimer.

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Contents

1. General information

Absorption spectra were recorded using biochrom Libra S70 spectrophotometer (Biochrom Ltd, England). NMR spectra were recorded using a BRUKER spectrometer operated at 500 MHz. ESI-MS spectrum was obtained using ESI Q-TOF Mass Spectrometer (Model : compact / Company : Bruker) at Sogang University. All measurements were carried out at room temperature (298 K). Calcium fluoride, tetrabutylammonium fluoride, calcium chloride, calcium bromide, and calcium iodide were purchased from Sigma Aldrich Chemical Co., Inc., and used as received.

2. Determination of association constants

We calculated association constants using non-linear regression method. Validity of the quantity of binding affinity is verified in regression coefficient by least square method. (Thordarson, P. *Chem. Soc. Rev.,* **2011**, 40, 1305–1323.)

a. UV-vis Spectroscopy

$$\Delta A = \frac{1 + aK_a + xK_a - \sqrt{-4axK_a^2 + (-1 - aK_a - xK_a)^2}}{2K_a}\Delta\varepsilon$$

where ΔA (measured change in absorbance relative to the initial solution) is the y variable; x is concentration of anion added; a is the initial concentration of receptor (held constant over the course of titration); $\Delta\varepsilon$ is the extinction coefficient difference between the free receptor and receptor-guest complex; K_a is the binding affinity of the receptor for the guest in question.

b. NMR Spectroscopy

$$\Delta\delta = \frac{1 + aK_a + xK_a - \sqrt{-4axK_a^2 + (-1 - aK_a - xK_a)^2}}{2aK_a}\delta_{\Delta HG}$$

where $\Delta\delta$ (measured change in chemical shift relative to the initial solution) is the y variable; x is concentration of anion added; a is the initial concentration of receptor (held constant over the course of titration); $\delta_{\Delta HG}$ is the difference of chemical shift between the free receptor and receptor-guest complex; K_a is the binding affinity of the receptor for the guest in question.

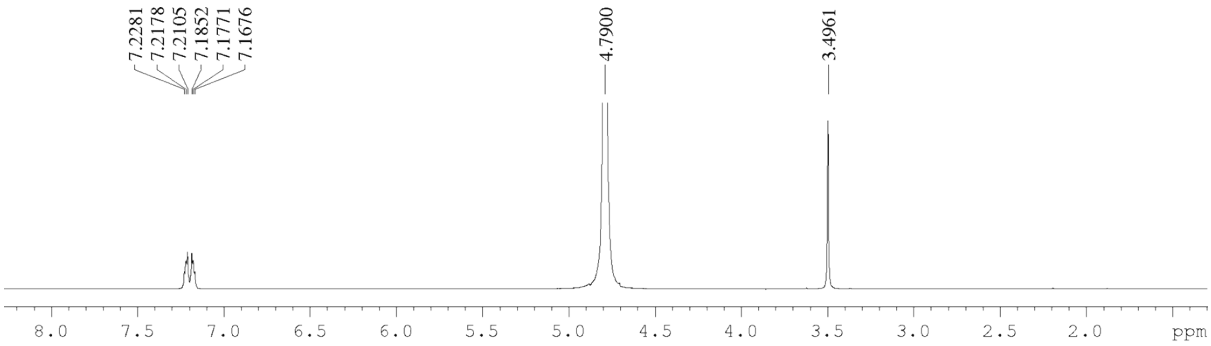

Figure S1. ^{1}H NMR spectrum of receptor **1**.

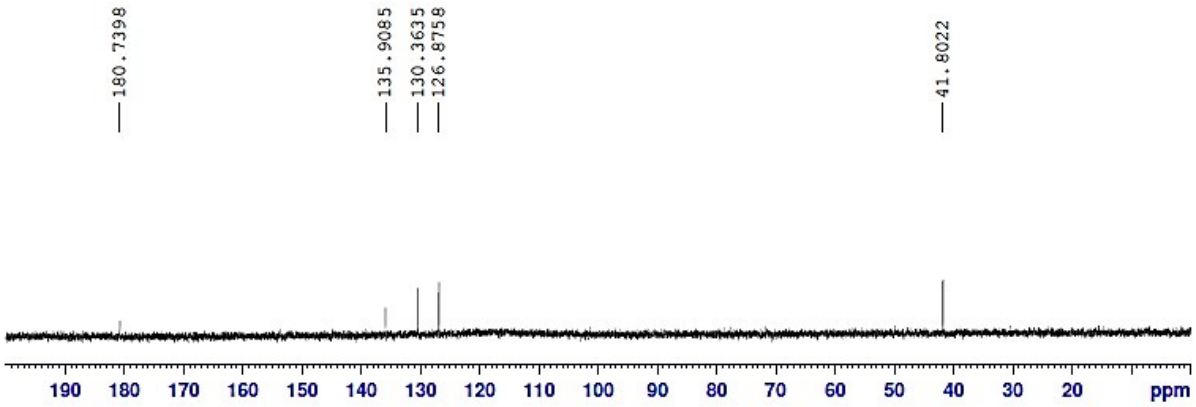

Figure S2. ^{13}C NMR spectrum of receptor **1**.

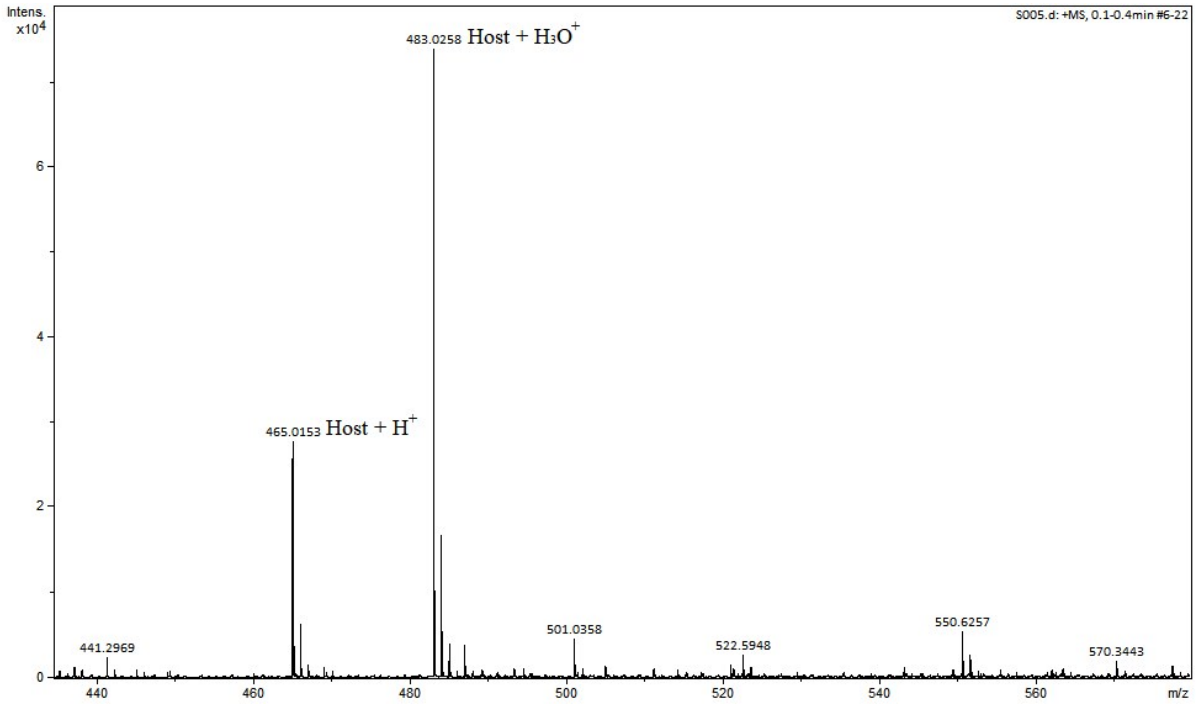

Figure S3. ESI-MS spectrum of receptor **1**.

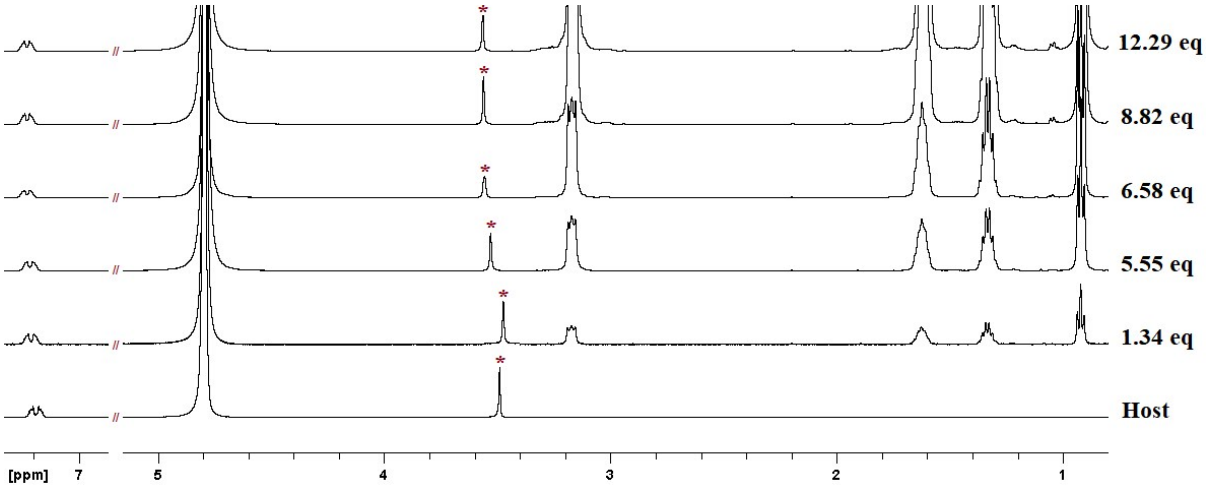

Figure S4. ^{1}H NMR spectra of 2 mM of receptor **1** increasing amounts of tetrabutylammonium fluoride in 100 % D_2O

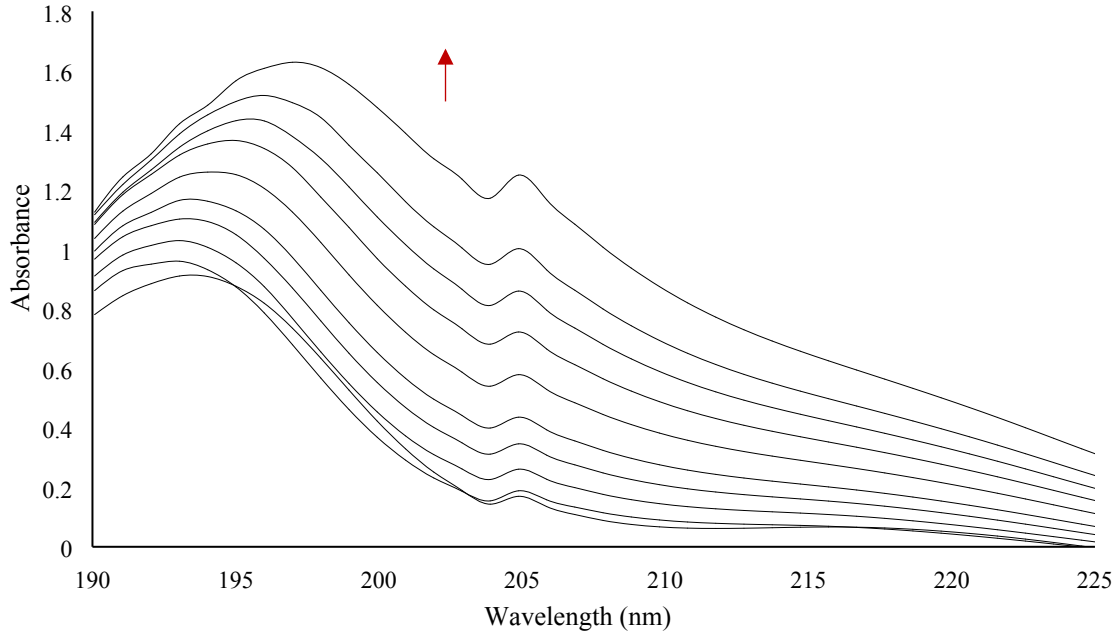

Figure S5. Family of UV-vis spectra recorded over the course of titration of 20 μM D_2O solution of the receptor **1** with the standard solution tetrabutylammonium fluoride

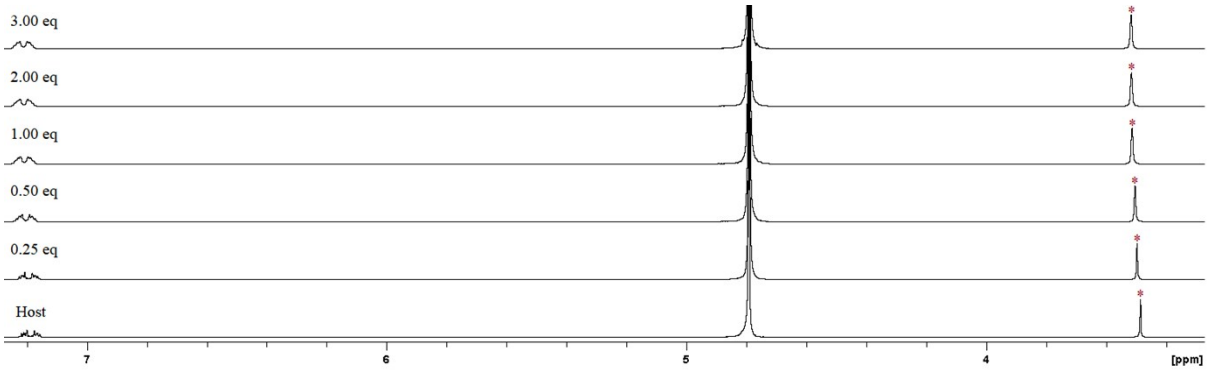

Figure S6. ^{1}H NMR spectra of 2 mM of receptor **1** increasing amounts of sodium fluoride in 100 % D_2O

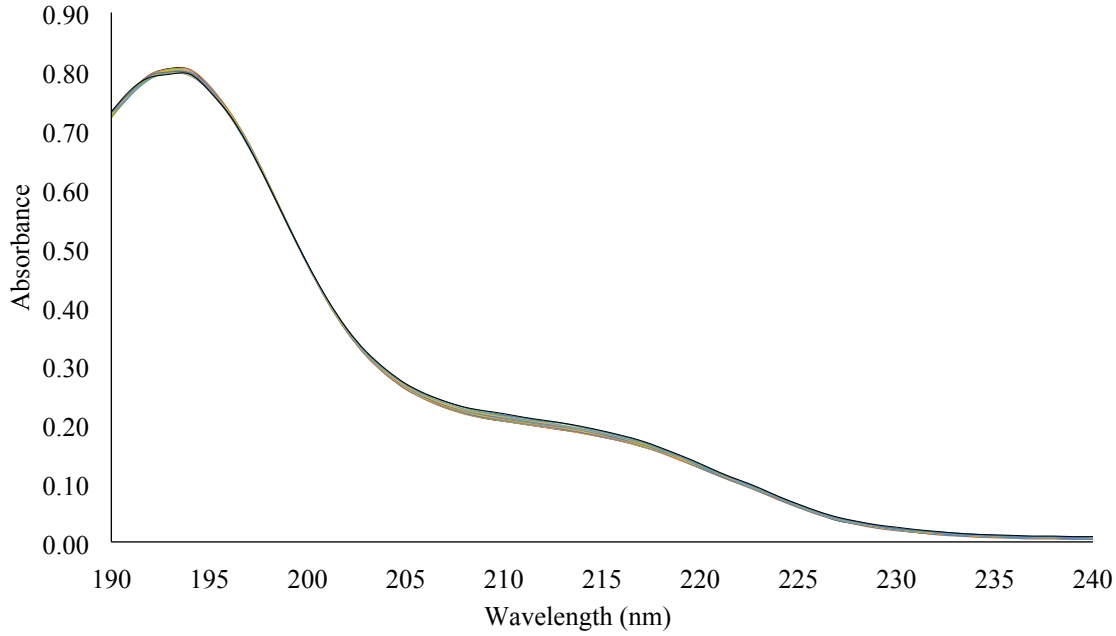

Figure S7. Family of UV-vis spectra recorded over the course of titration of 20 μM D_2O solution of the receptor **1** with the standard solution sodium fluoride

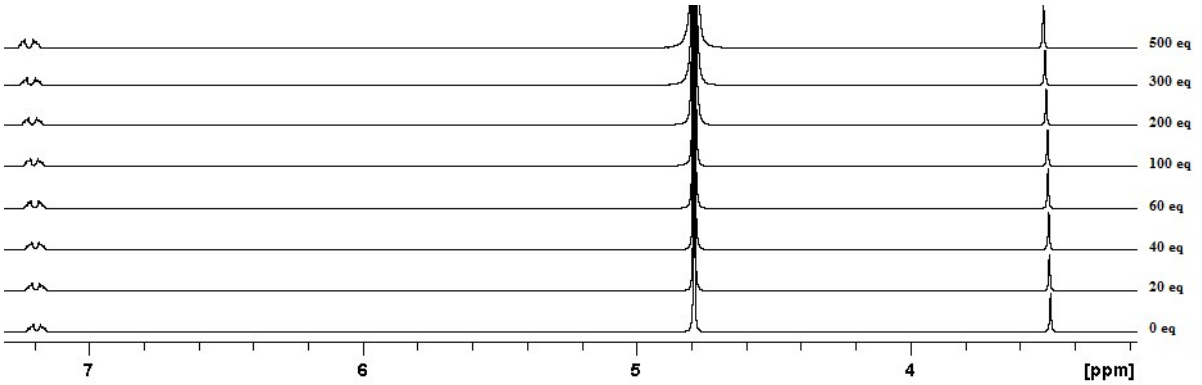

Figure S8. ^{1}H NMR spectra of 2 mM of receptor **1** amounts of $CaCl_2$ in 100 % D_2O

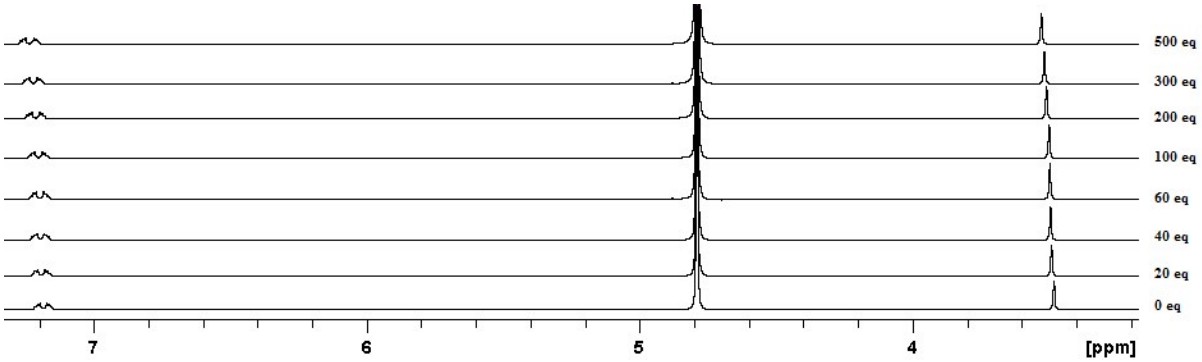

Figure S9. ^{1}H NMR spectra of 2 mM of receptor **1** increasing amounts of $CaBr_2$ in D_2O

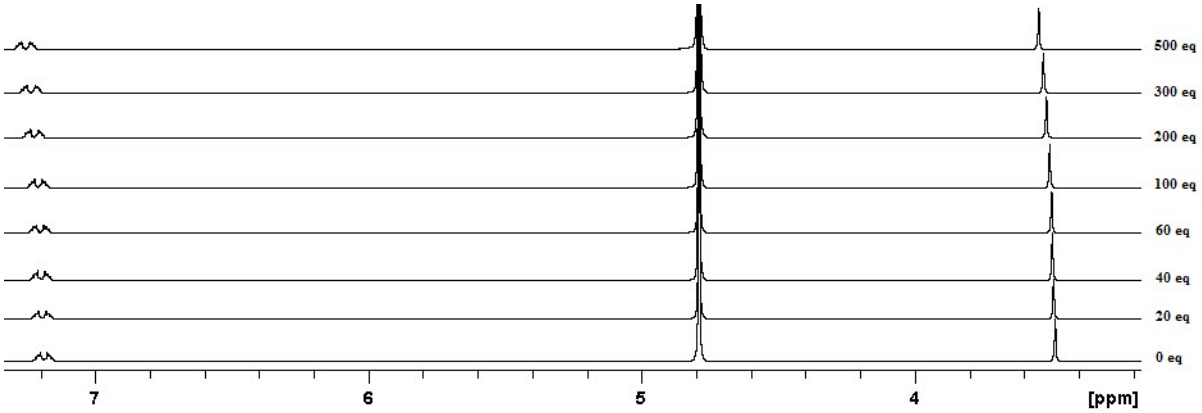

Figure S10. ^{1}H NMR spectra of 2 mM of receptor **1** increasing amounts of CaI_2 in D_2O

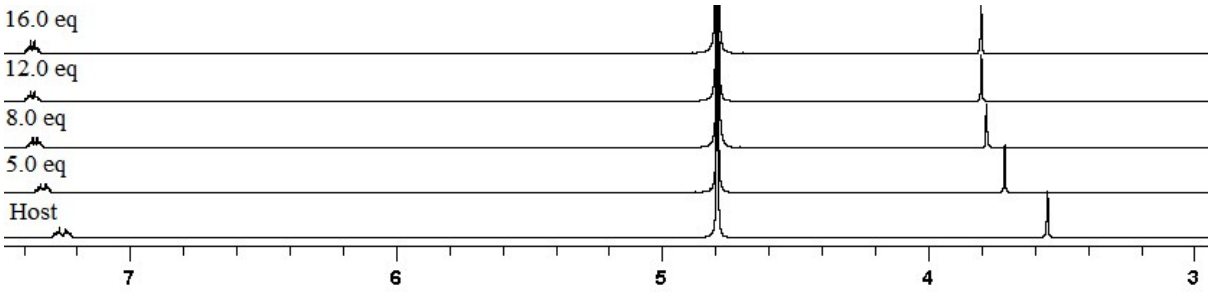

Figure S11. ^{1}H NMR spectra of 2 mM of receptor **1** increasing amounts of monocalcium phosphate in D_2O

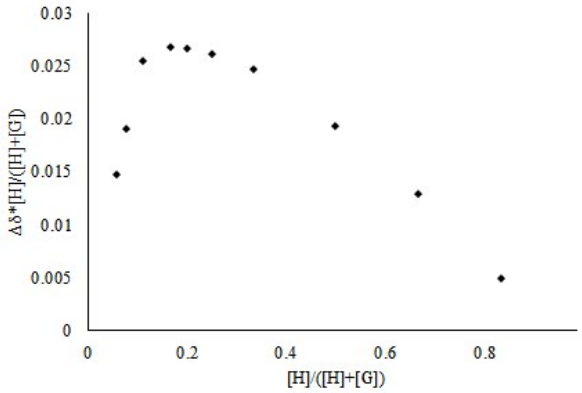

Figure S12. Job′s plot of receptor **1** with dihydrogen phosphate obtained by ^{1}H NMR in D_2O.

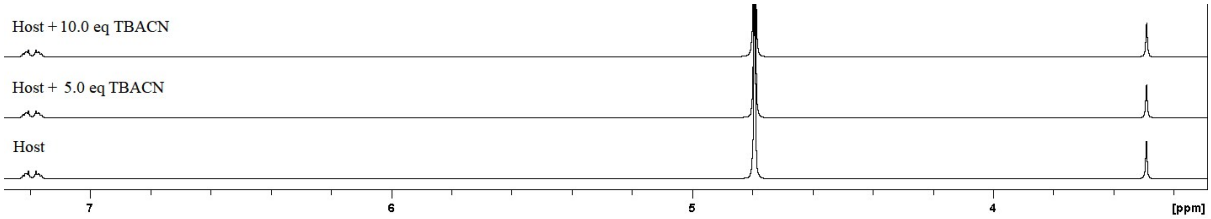

Figure S13. ^{1}H NMR spectra of 2 mM of receptor **1** increasing amounts of tetrabutylammonium cyanide in D_2O

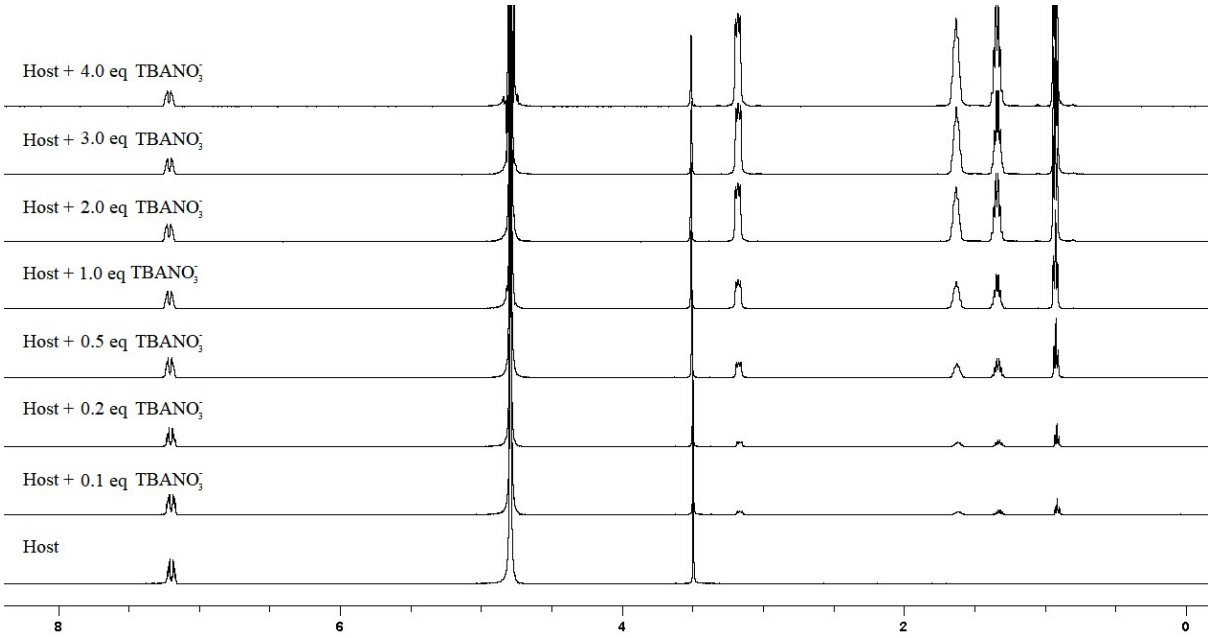

Figure S14. ^{1}H NMR spectra of 2 mM of receptor **1** increasing amounts of tetrabutylammonium nitrate in D_2O

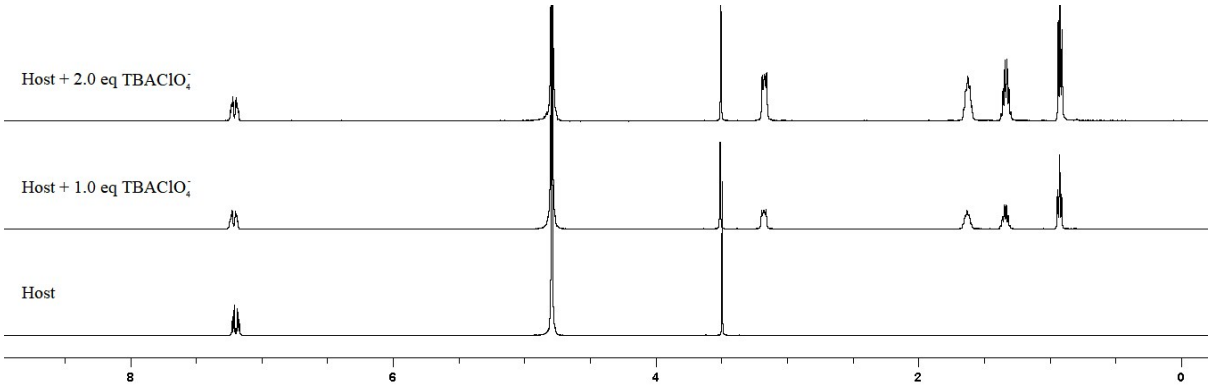

Figure S15. ^{1}H NMR spectra of 2 mM of receptor **1** increasing amounts of tetrabutylammonium perchlorate in D_2O

3. Detailed structural information of complexes including atomic charges obtained from electronic structure calculations (F^-, Cl^-, and Br^- complex respectively). The assigned atomic charges are based on Mulliken population analysis.

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42	C	2.0450	-0.1030	-1.6580	C	0	-0.318000
43	O	0.7940	-0.2180	-1.8610	O	0	-0.295000
44	O	2.5960	1.0160	-1.4910	O	0	-0.356000
45	Ca	0.3450	1.6360	-0.4370	Ca	0	1.138000
46	Ca	-0.3960	-1.2140	2.1430	Ca	0	1.290000
47	Br	0.5890	4.5120	0.0840	Br	0	-0.864000

@<TRIPOS>SUBSTRUCTURE

1 **** 1 TEMP 0 **** **** 0 ROOT