Dual sensing by simple heteroditopic salt receptors containing an anthraquinone unit

by
Marcin Karbarz, Jan Romański*
Faculty of Chemistry, University of Warsaw, Pasteura 1, PL 02-093 Warsaw, Poland

TABLE OF CONTENTS

GENERAL INFORMATION

Unless specifically indicated, all other chemicals and reagents used in this study were purchased from commercial sources and used as received. Purification of products was performed using column chromatography on silica gel (Merck Kieselgel 60, 230-400 mesh) with mixtures of chloroform/methanol. Thin-layer chromatography (TLC) was performed on silica gel plates (Merck Kieselgel 60 F254).

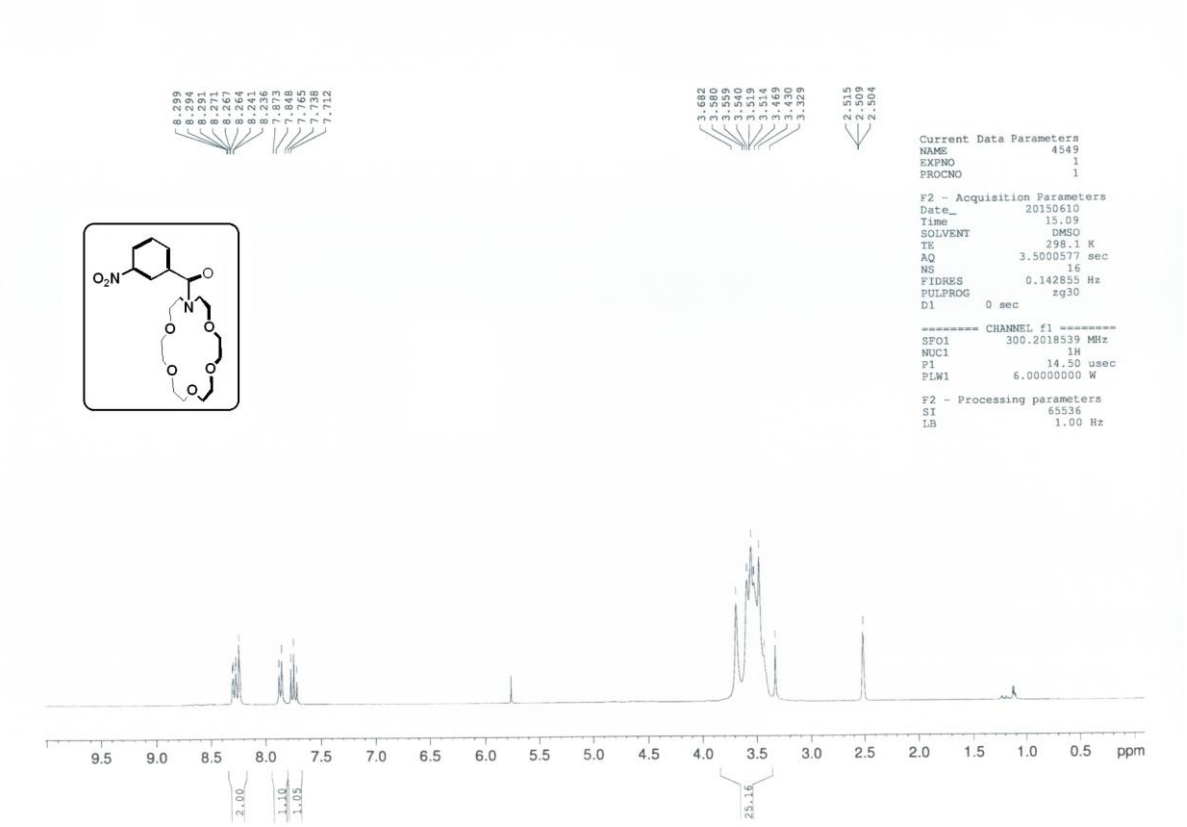
^{1}H and ^{13}C NMR spectra used in the characterization of products were recorded on Bruker 300 spectrometer using a residual protonated solvent as internal standard.

High resolution mass spectra (HRMS) were measured on a Quattro LC Micromass unit using ESI technique.

UV-vis analyses were performed using Thermo Spectronic Unicam UV500 Spectrophotometer.

The X-ray measurement of receptor **2** was performed at 100(2) K on a Bruker D8 Venture Photon100 diffractometer equipped with a TRIUMPH monochromator and a MoKα fine focus sealed tube (λ = 0.71073 Å).

Fig. S1 and S2: ^{1}H and ^{13}C NMR of compound **4a**



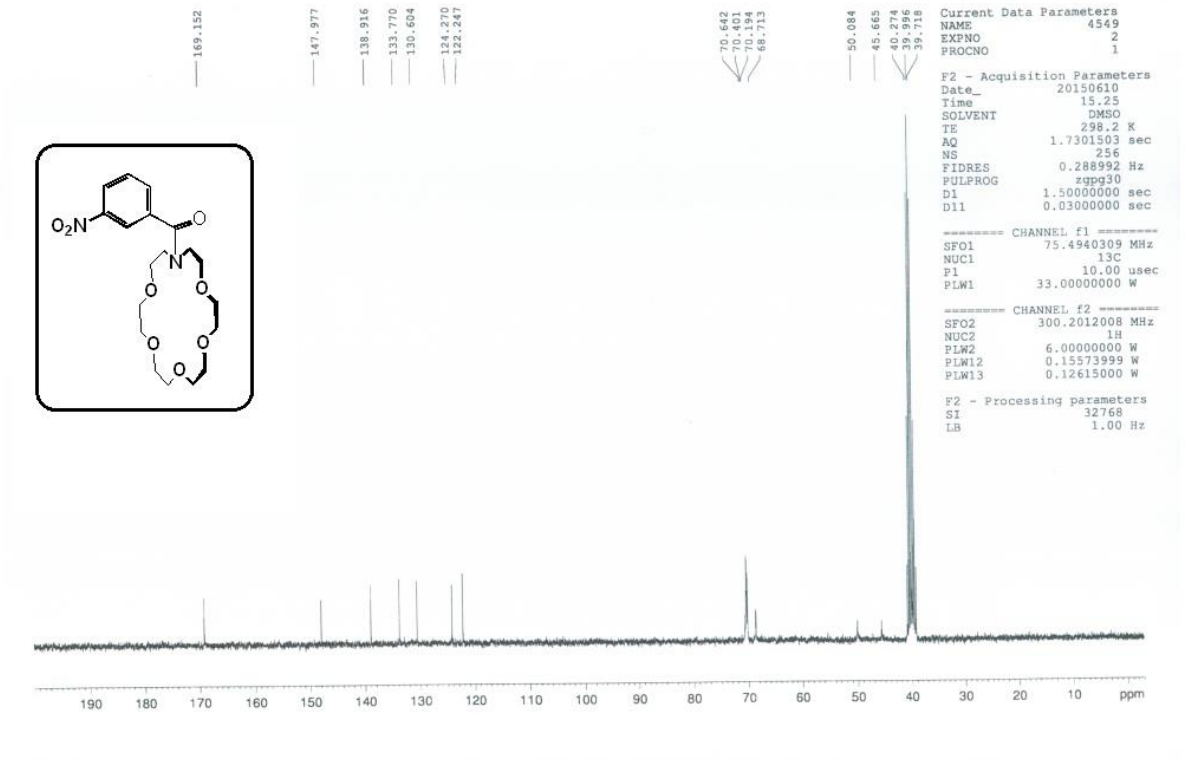
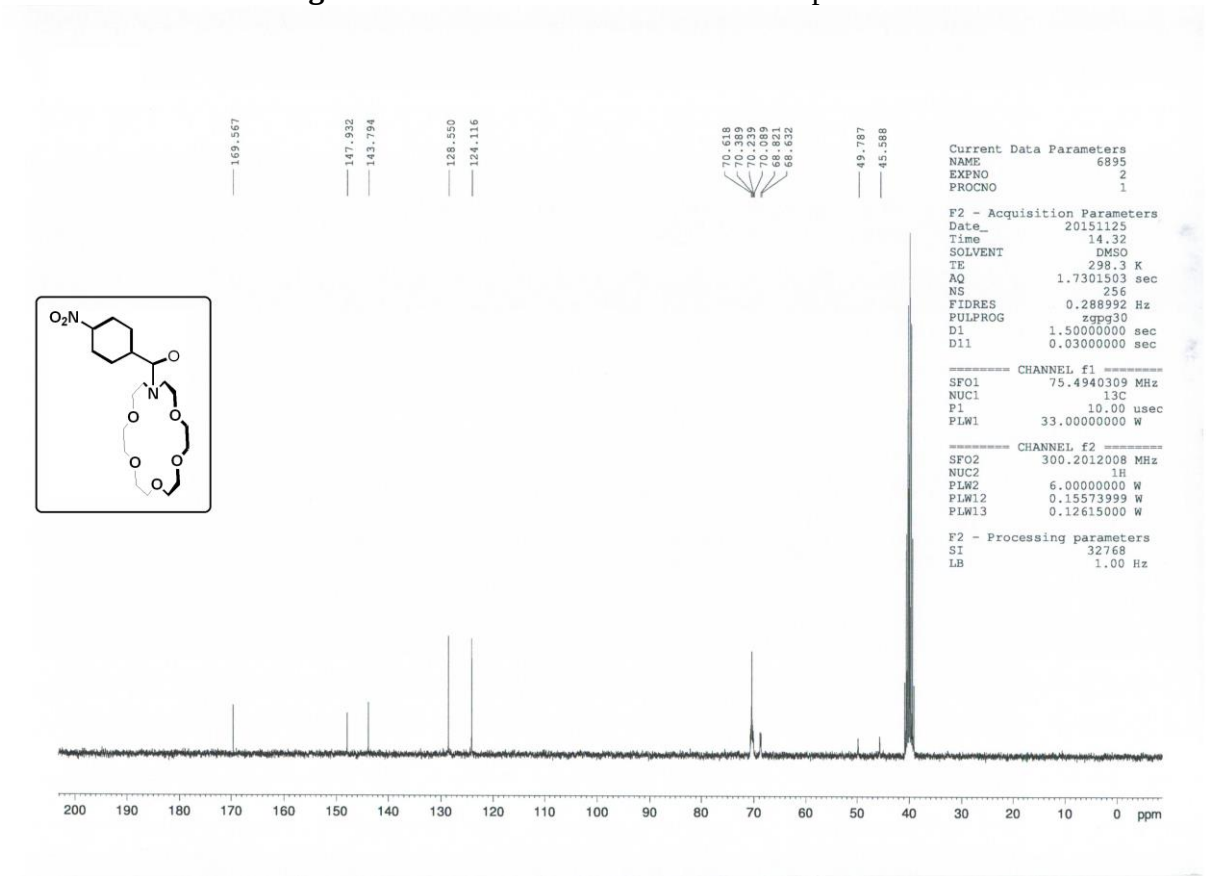


Fig. S3 and S4: ^{1}H and ^{13}C NMR of compound **4b**



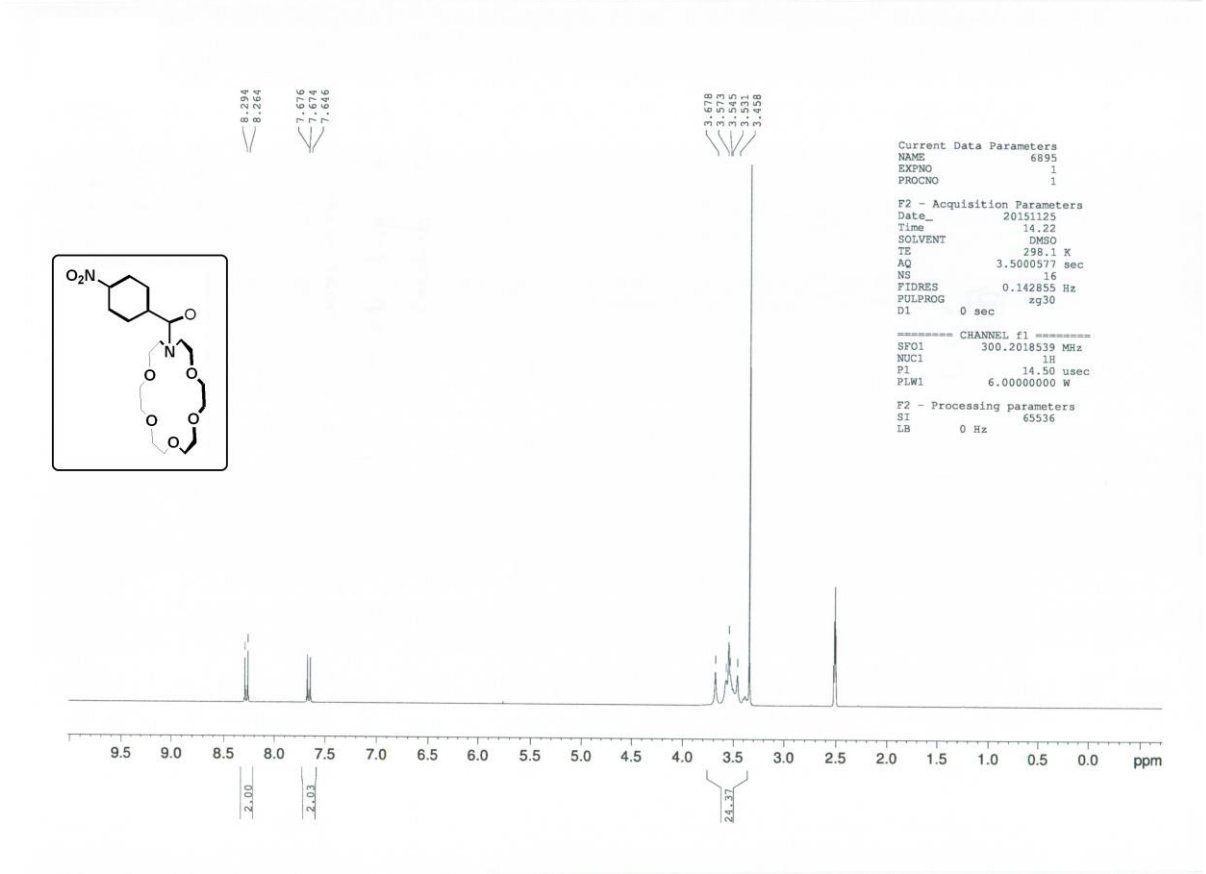


Fig. S5 and S6: ^{1}H and ^{13}C NMR of compound **6.**

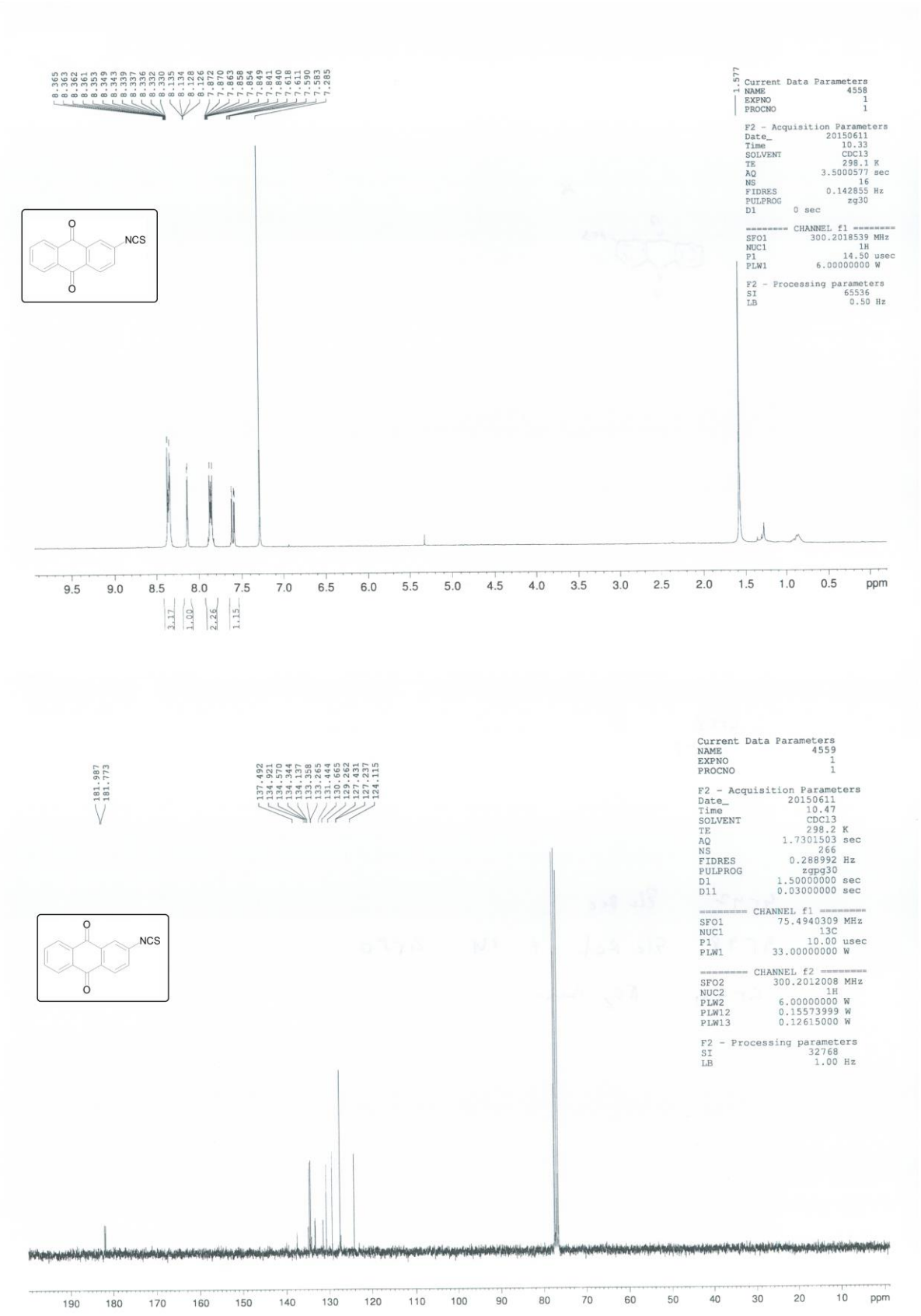
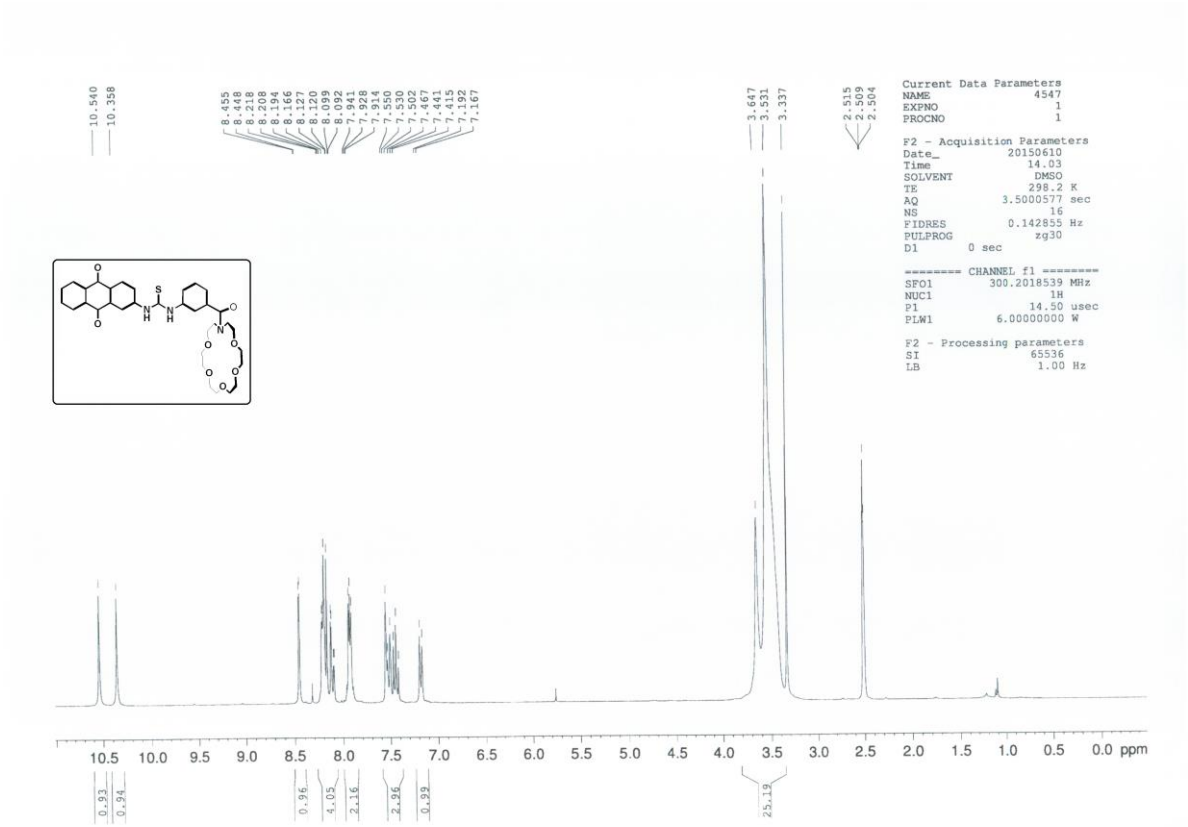


Fig. S7 and S8: ^{1}H and ^{13}C NMR of receptor **1.**



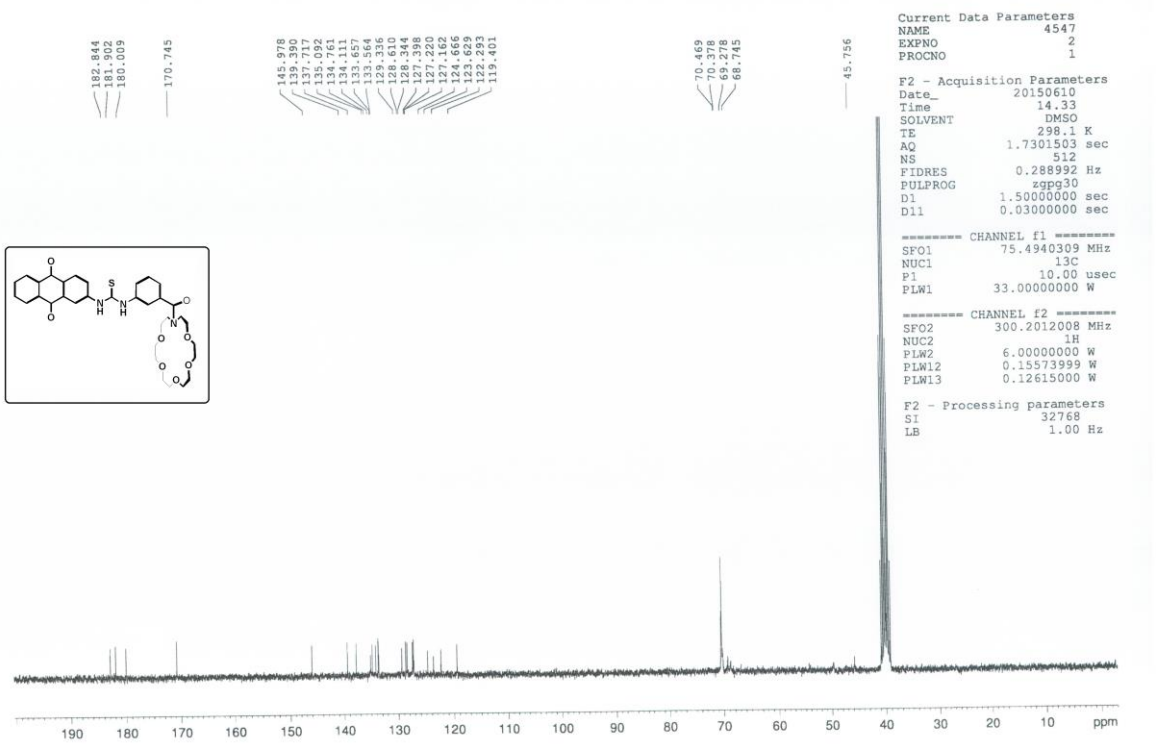


Fig. S9 ^{1}H-^{1}H ROESY of receptor **1** pretreated with Na^{+}. (Assignment of thiourea protons)

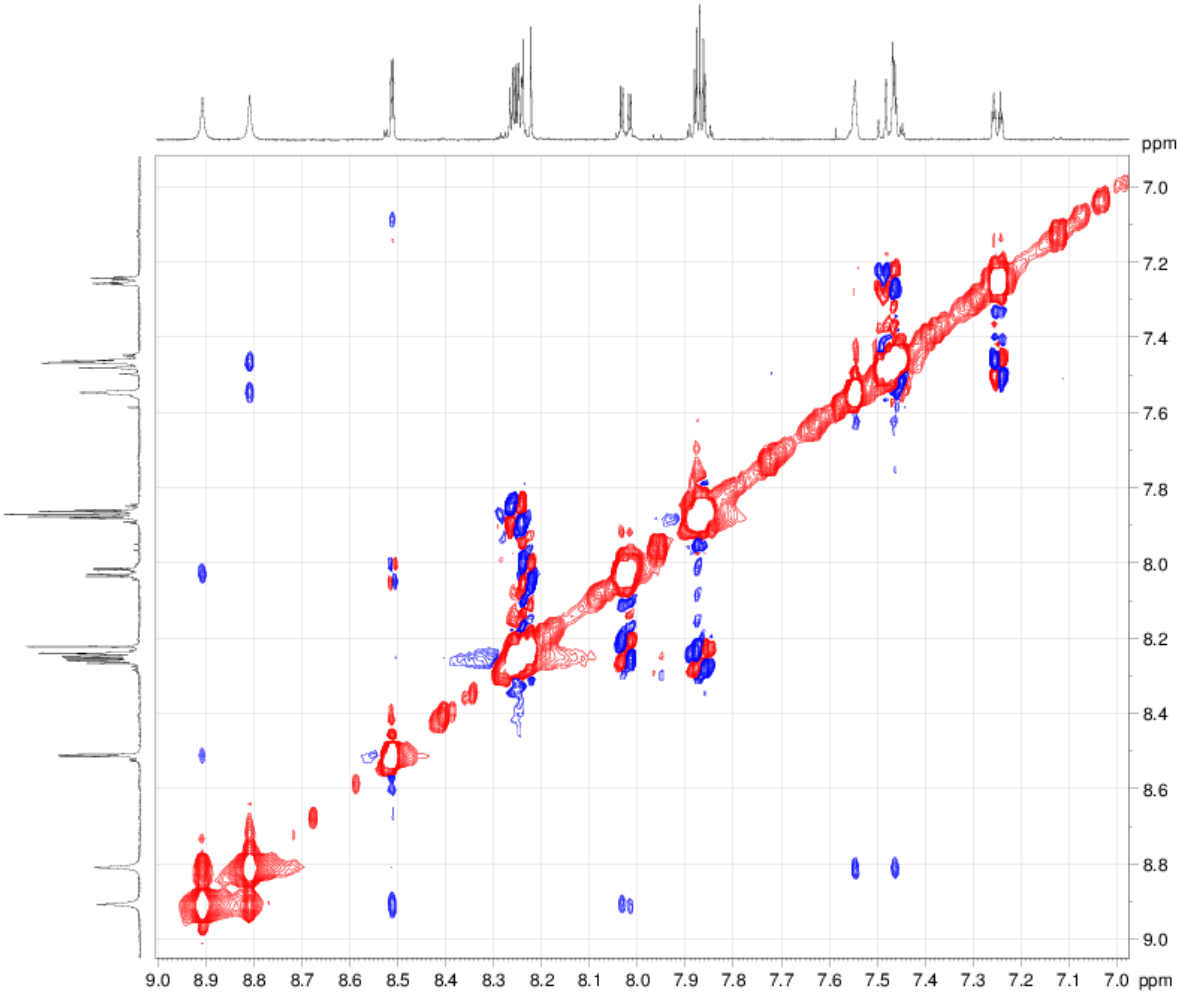
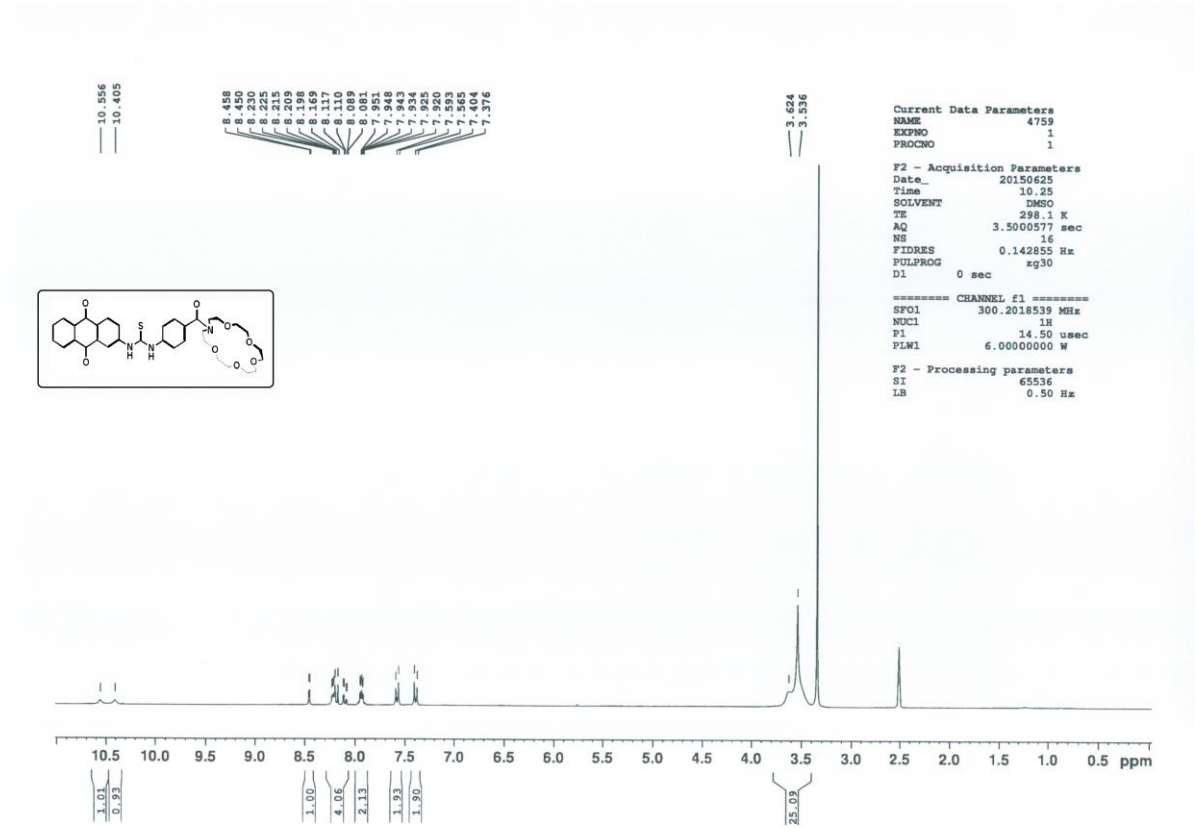


Fig. S10 and S11: ^{1}H and ^{13}C NMR of receptor **2.**



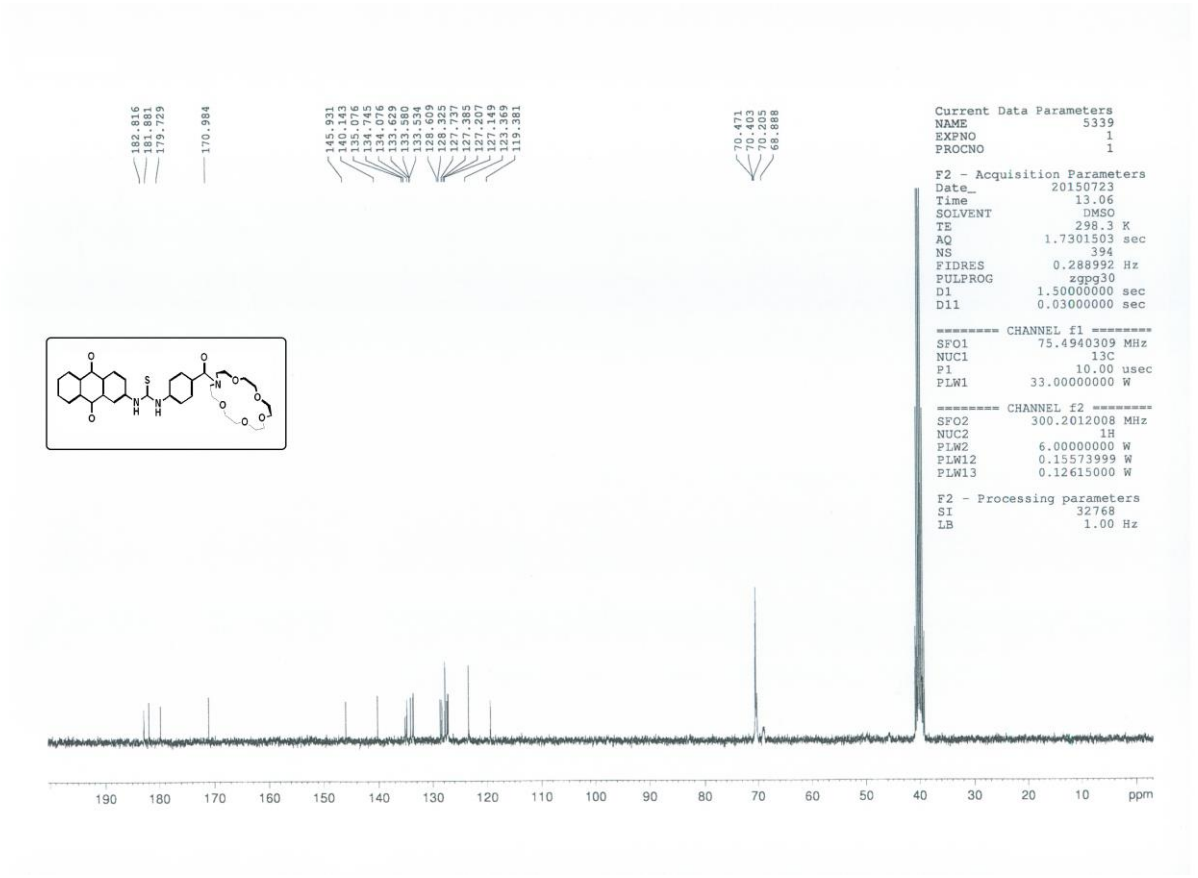
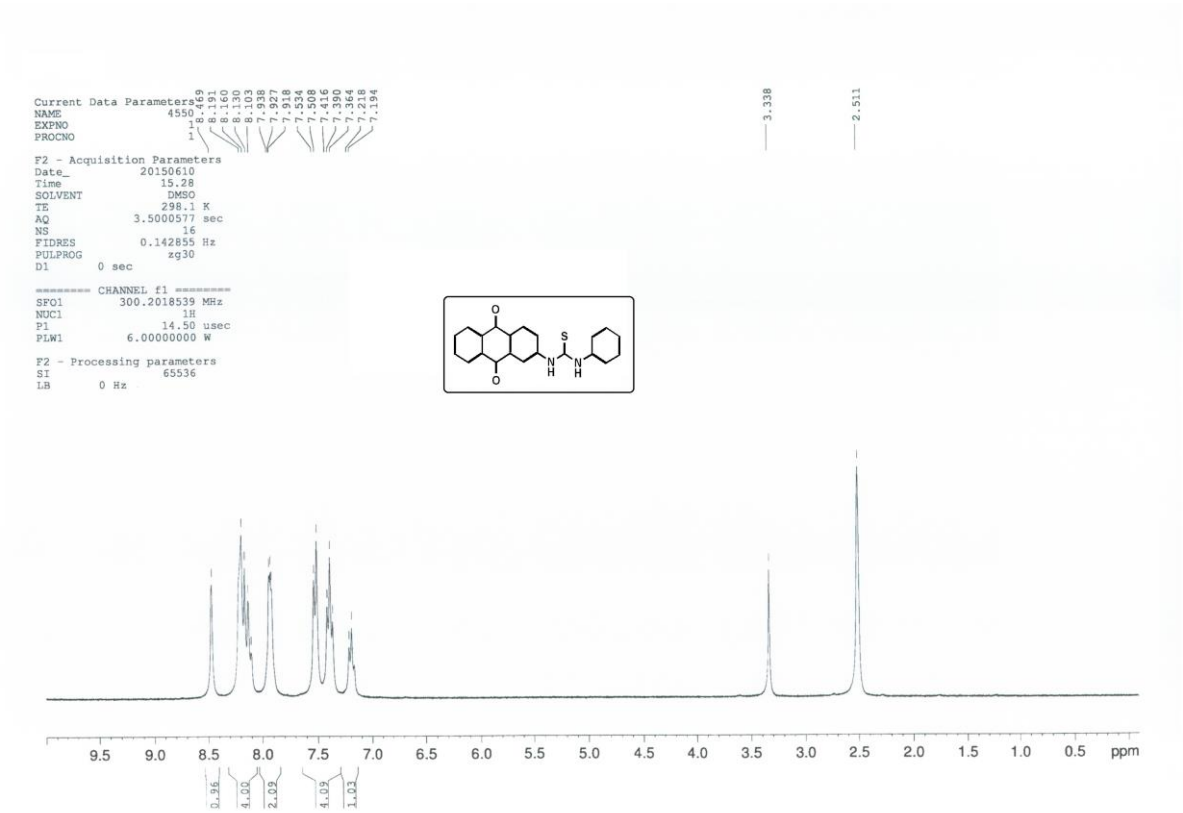


Fig. S12 and S13: ^{1}H and ^{13}C NMR of receptor **3.**



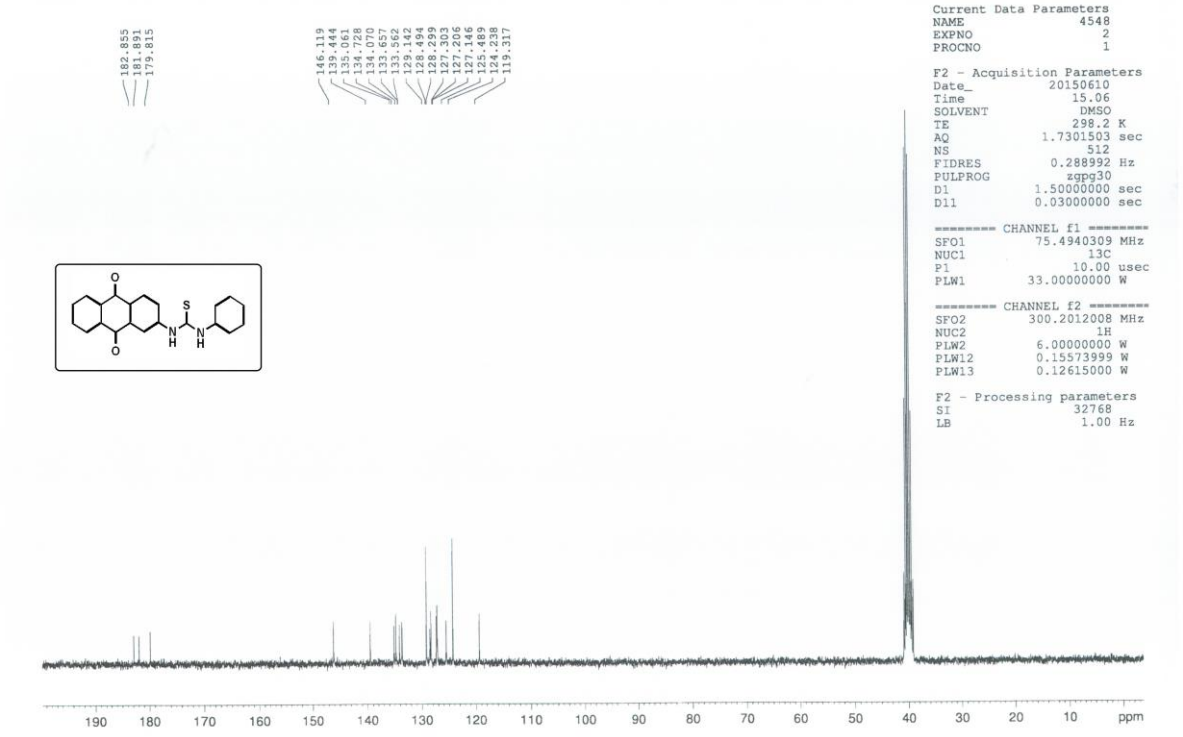
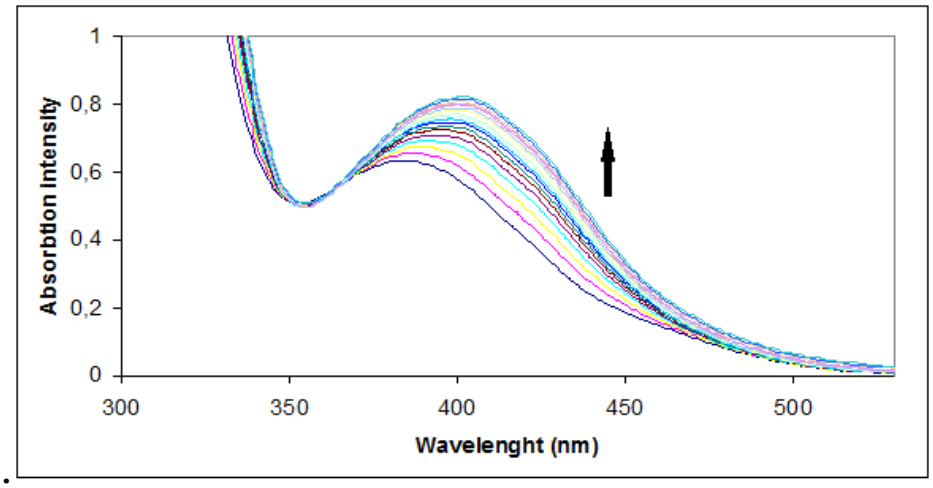


Fig. S14: Representative UV-Vis titration spectra of receptor 1 (upon gradual addition of tetrabutylammonium chloride in the presence of 1 eq. of sodium perchlorate)



DILUTION AND JOB PLOTS.

Fig. S15: Job plot (Host: Receptor **1**, guest: Cl^-)

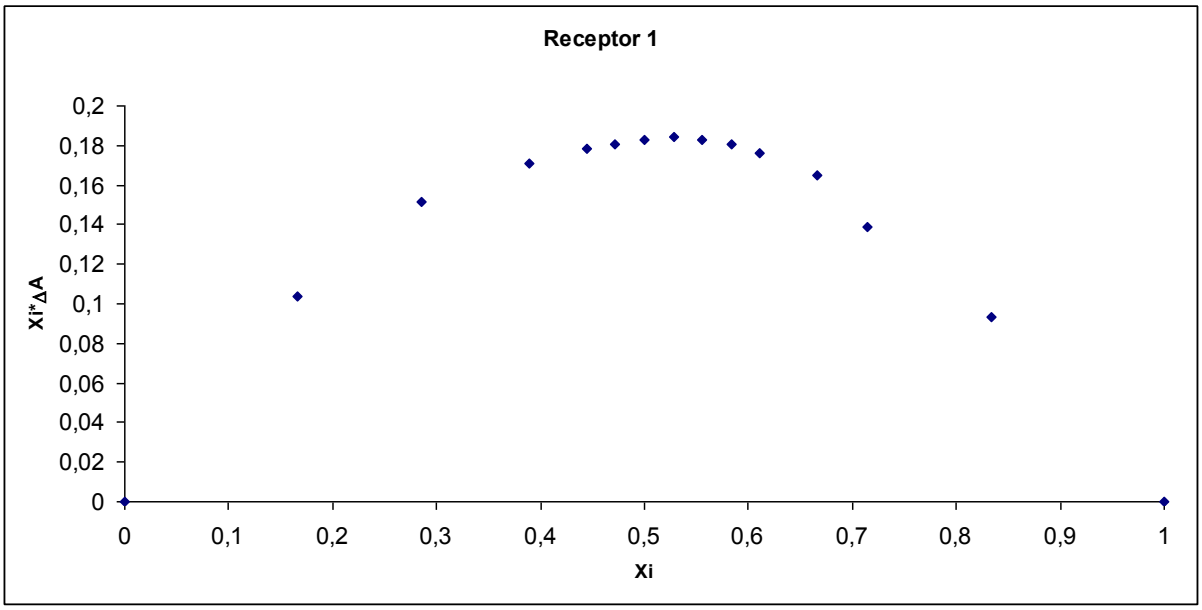


Fig. S16: Dilution curve of receptor **1**.

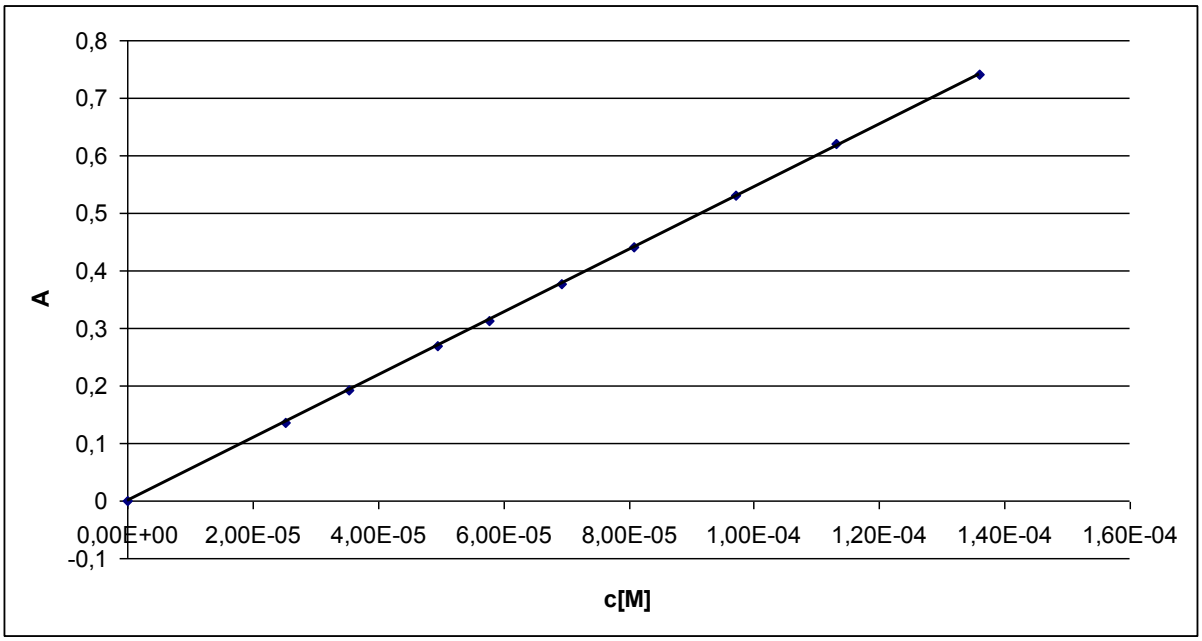
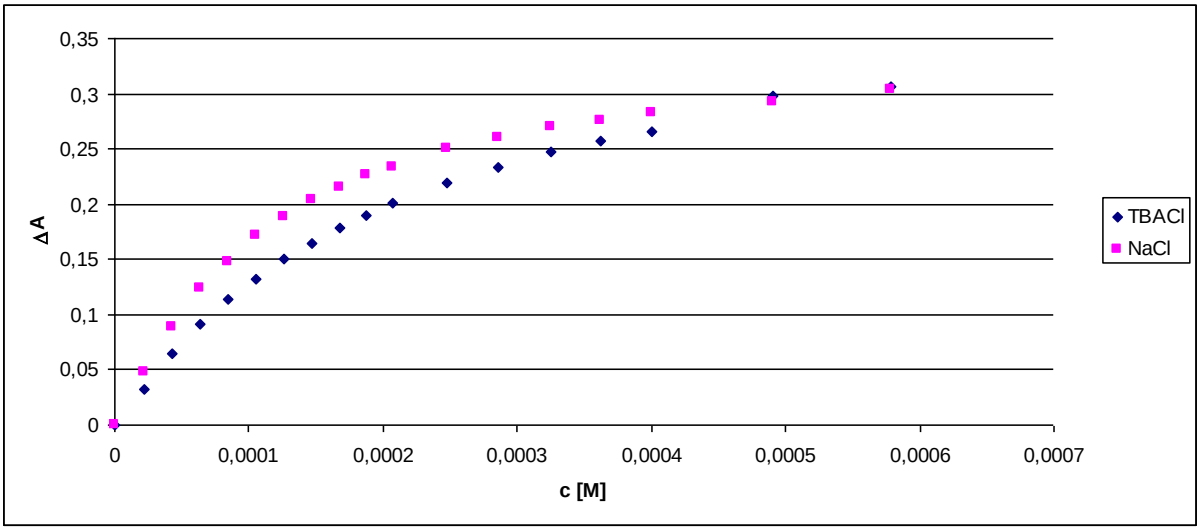


Fig. S17: UV-Vis titration binding isotherms of receptor **1** with TBACl and TBACl in the presence of 1 equivalent of $NaClO_4$.



.

Fig. S18: UV-Vis titration binding isotherms of receptor **1** with $TBANO_2$ and $TBANO_2$ in the presence of 1 equivalent of $NaClO_4$.

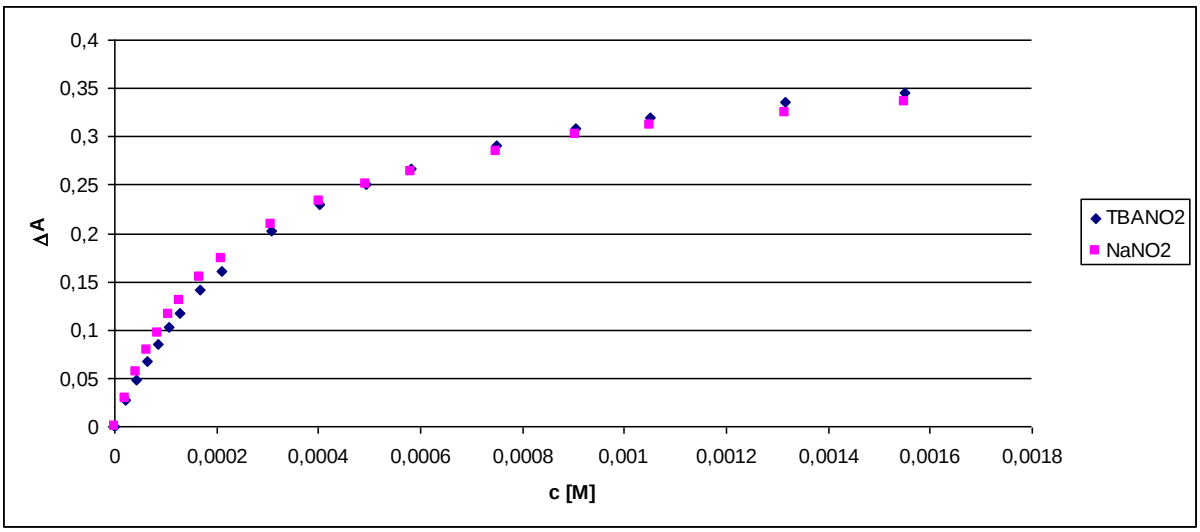


Fig. S19: UV-Vis titration binding isotherms of receptor **1** with TBAPhCOO and TBAPhCOO in the presence of 1 equivalent of $NaClO_4$.

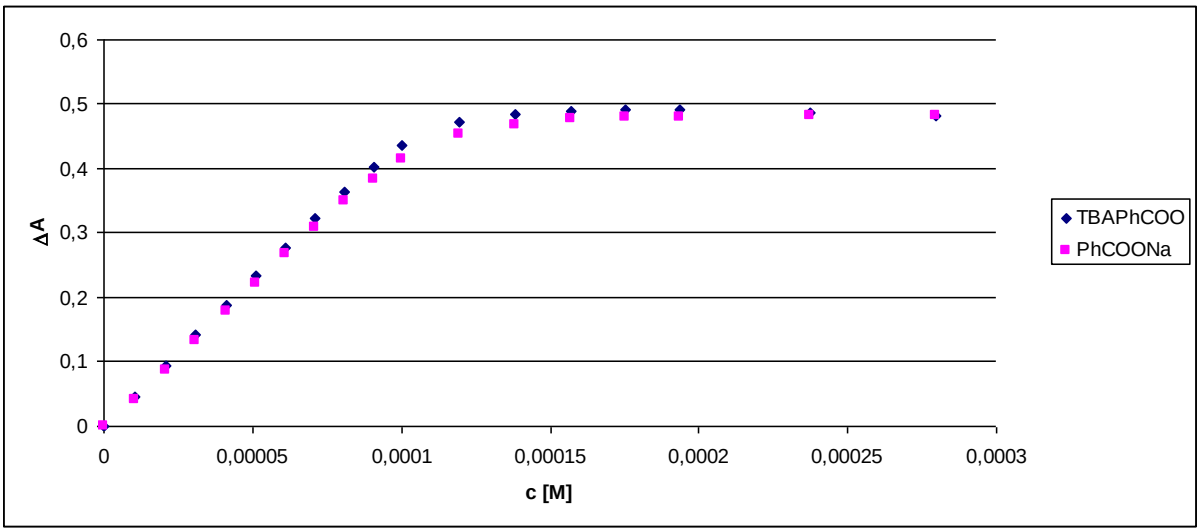


Fig. S20: UV-Vis titration binding isotherms of receptor **2** with TBACl and TBACl in the presence of 1 equivalent of $NaClO_4$.

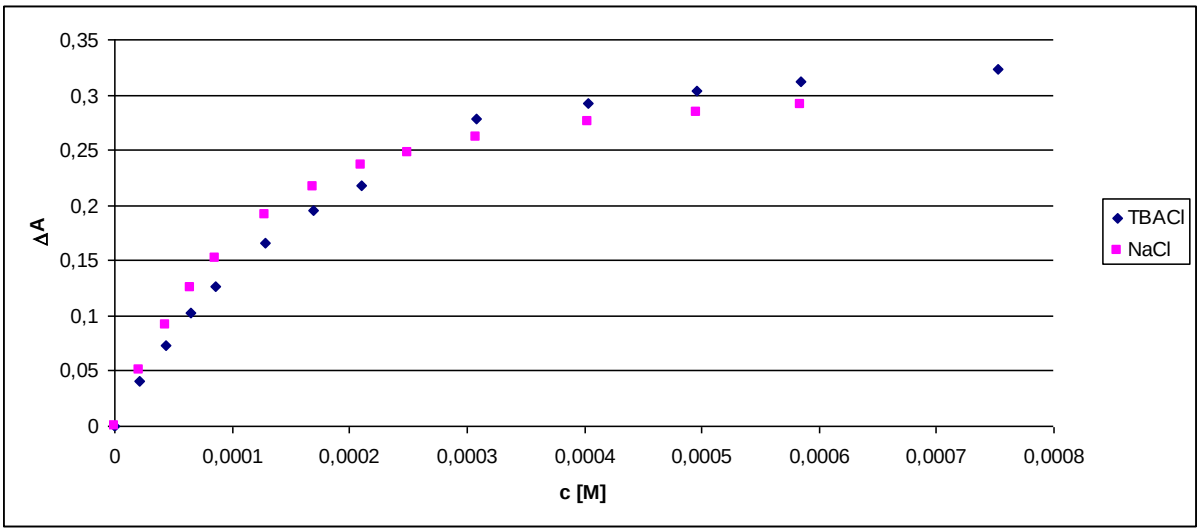


Fig. S21: UV-Vis titration binding isotherms of receptor **3** with TBACl and TBACl in the presence of 1 equivalent of $NaClO_4$.

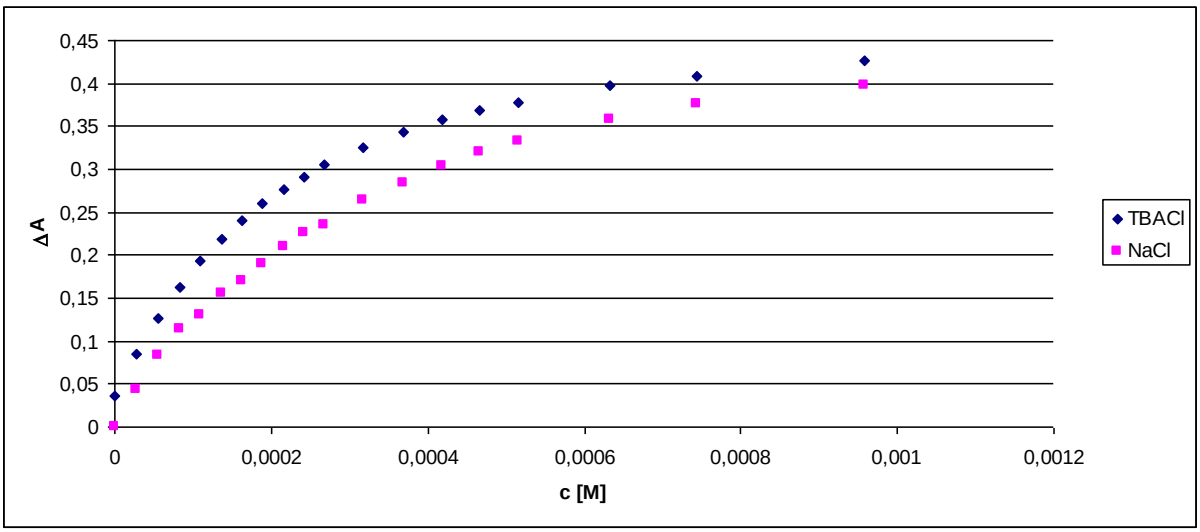


Fig. S22: Color changes upon addition of acetate and benzoate anions into receptor **1** solution

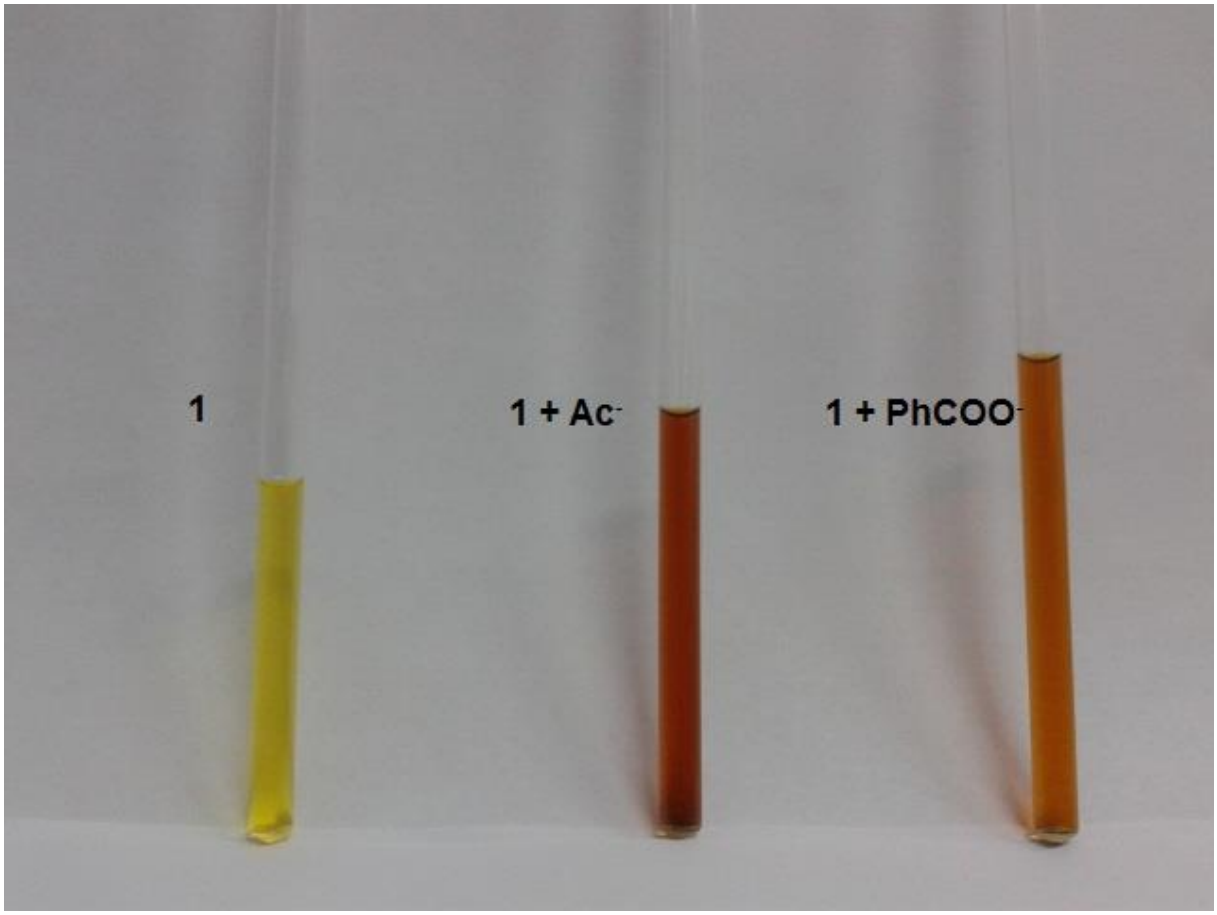


Fig. S23: UV-Vis titration spectra of receptor 1 (upon gradual addition of tetrabutylammonium benzoate)

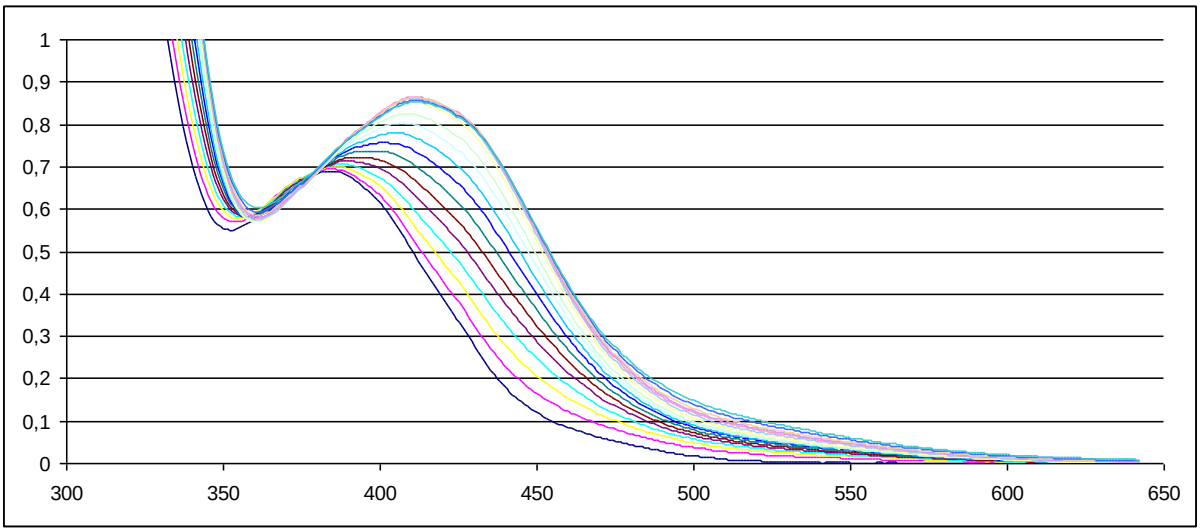


Fig. S24: UV-Vis titration spectra of receptor 1 (upon gradual addition of tetrabutylammonium acetate)

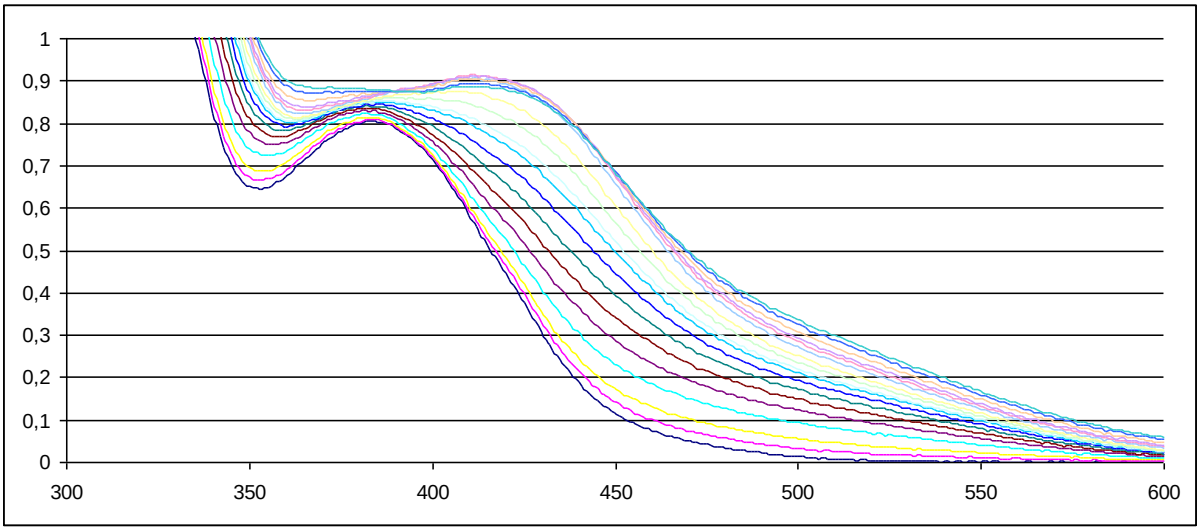
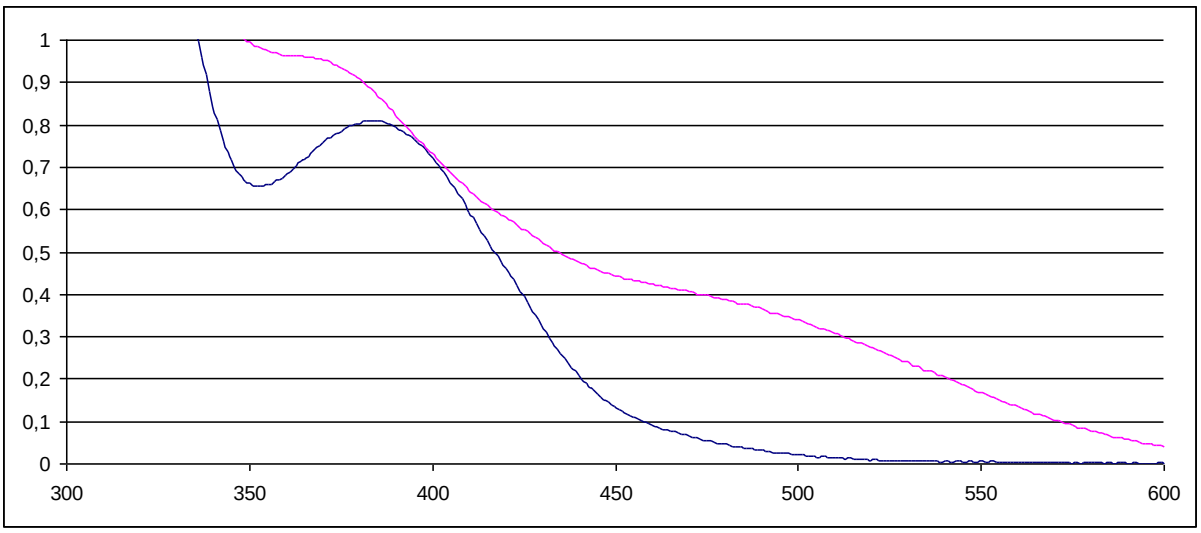


Fig. S25: UV-Vis spectra of receptor 1 and 1 + TBAOH



NMR TITRATION

The ^{1}H NMR titration was performed on a Bruker 300 spectrometer, at 298K in CD_3CN. $NaClO_4$ were dried under high vacuum at 30−45 °C prior to use. In this case, a 500 µL of freshly prepared 3.25 mM solution of receptor **1** was added to a 5mm NMR tube. Small aliquots of 46 mM solution of $NaClO_4$, containing **1** at 3.25 mM concentration, were added and a spectrum was acquired after each addition. Titration isotherms for NH protons were fitted to a 1:1 binding model using the HypNMR 2000 program.

Fig. S26: NMR titration binding isotherm of receptor 1 with Na^+

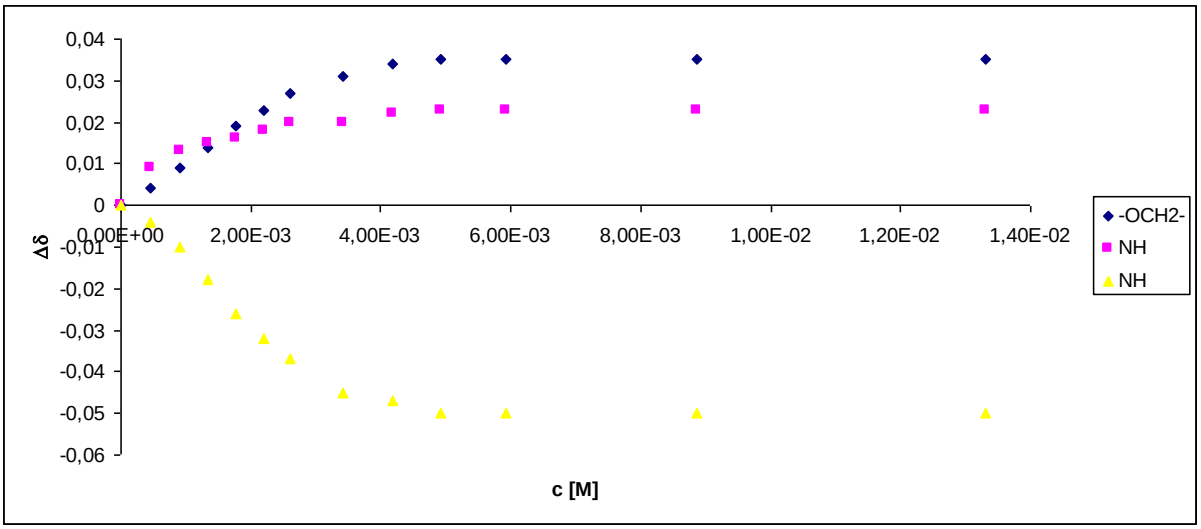
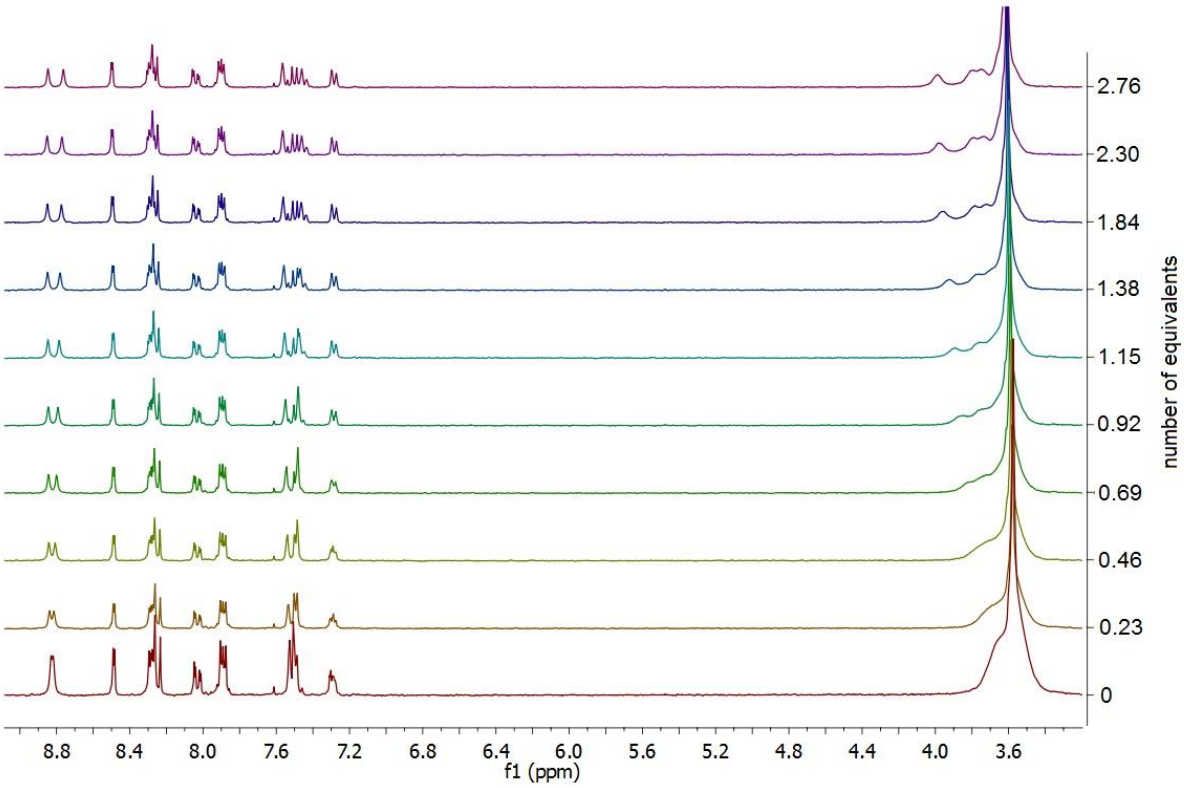


Fig. S27. Variation of the ^{1}HNMR spectrum of receptor **1** in CD_3CN upon addition of increasing amounts of sodium perchlorate



.

Fig. S28. Variation of the ^{1}HNMR spectrum of receptor **1** in CD_3CN upon addition of increasing amounts of TBABr

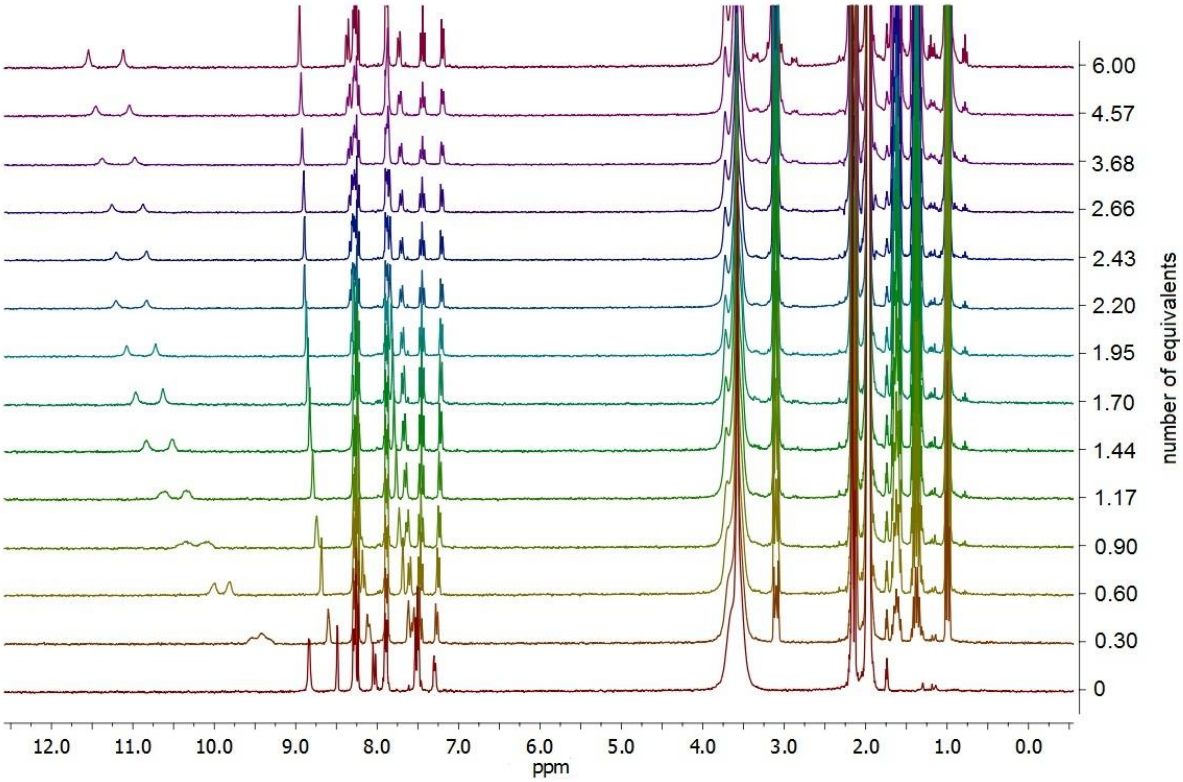


Fig. S29. Variation of the ^{1}HNMR spectrum of receptor **1** in CD_3CN upon addition of increasing amounts of TBABr in the presence of one equivalent of $NaClO_4$

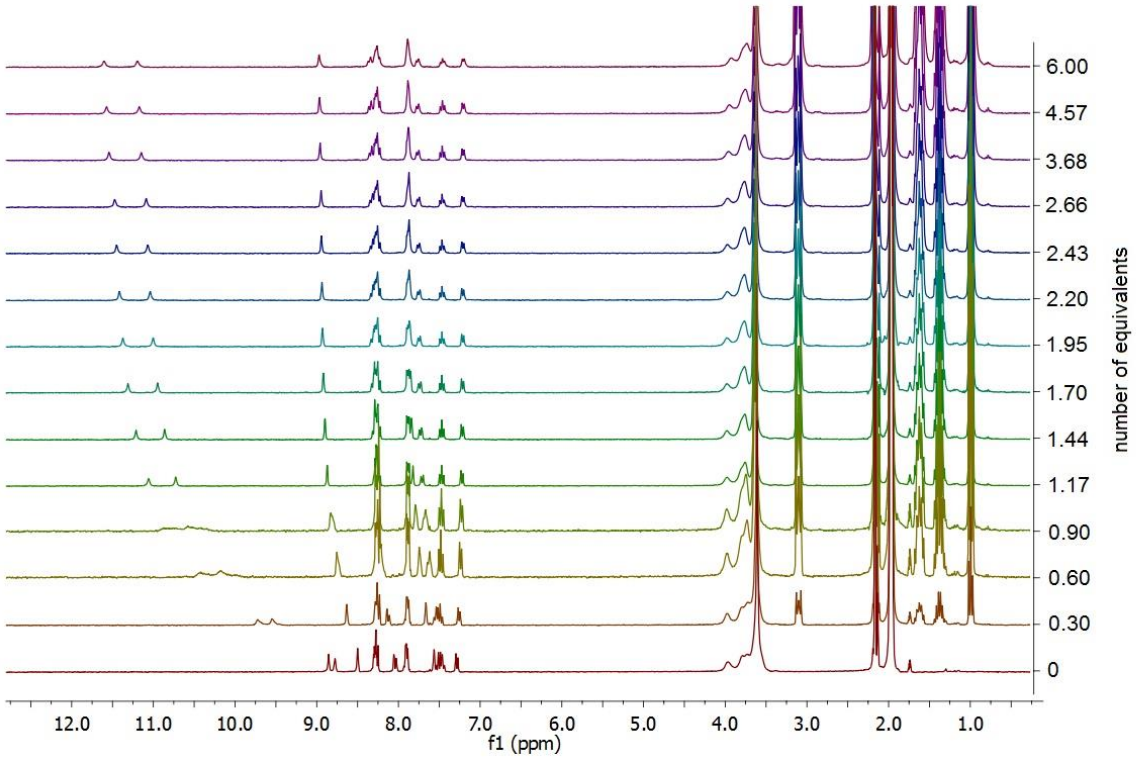


Fig. S30. Variation of the ^{1}HNMR spectrum of receptor **1** in CD_3CN upon addition of increasing amounts of TBAAcO

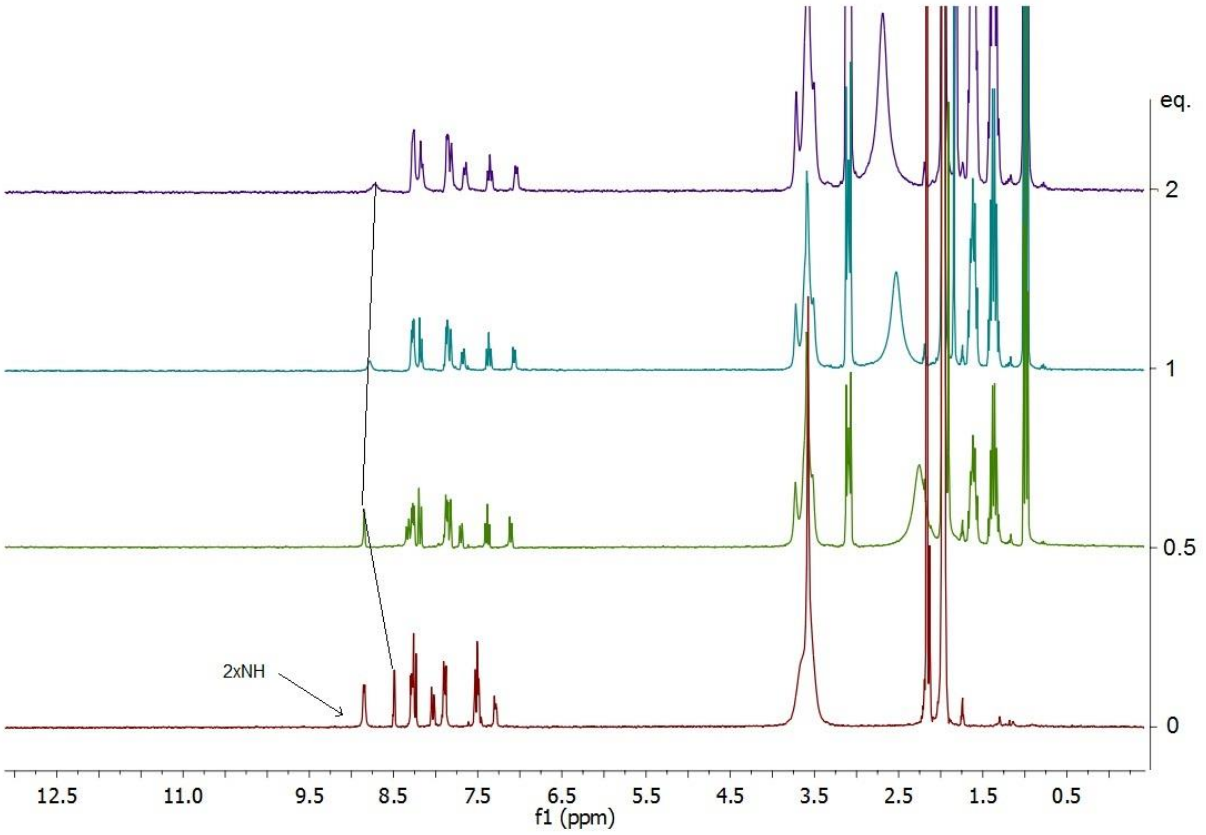
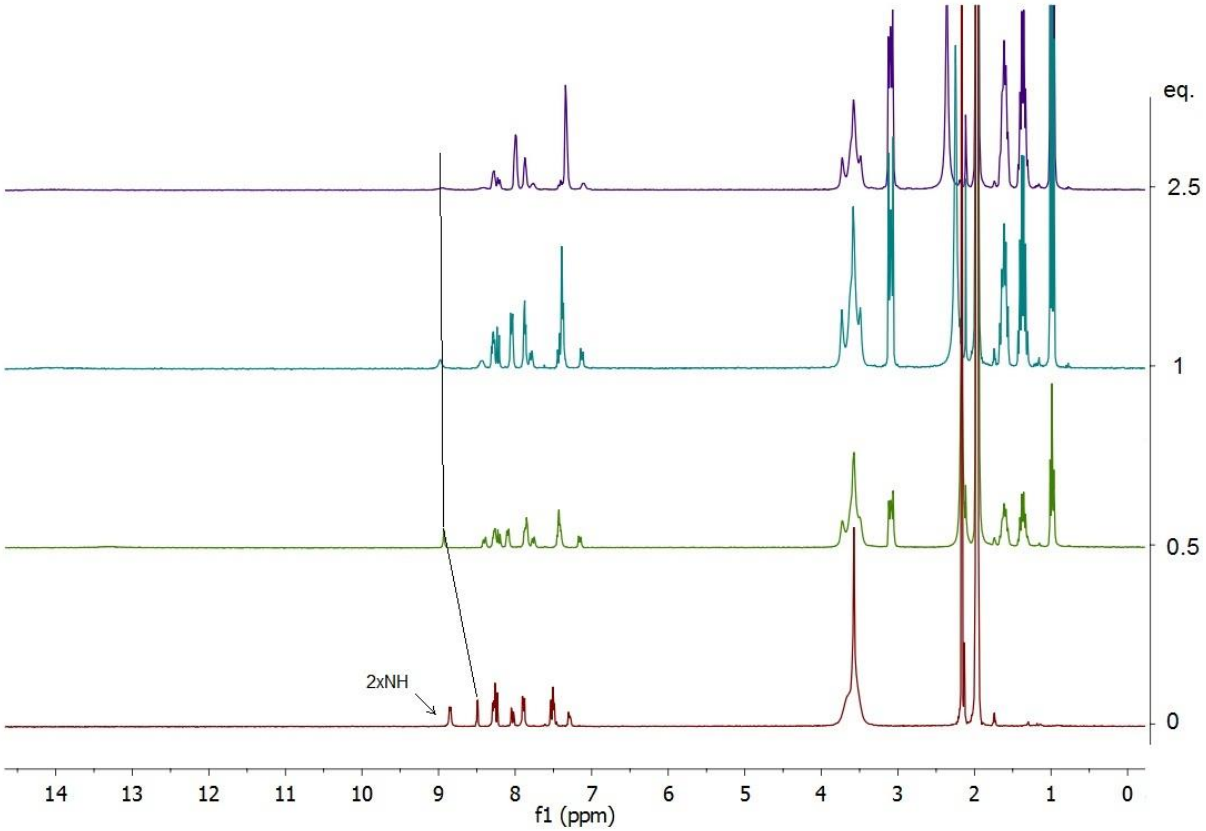


Fig. S31. Variation of the ^{1}HNMR spectrum of receptor **1** in CD_3CN upon addition of increasing amounts of TBAPhCOO



CRYSTAL DATA of [2·Na^+] complex

Identification code	p_EleRac
Chemical formula	$C_{35.29}H_{40.71}ClN_{3.29}NaO_{12.80}S$
Formula weight	806.24 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.055 x 0.103 x 0.450 mm
Crystal system	monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 8.5544(5) Å α = 90° b = 15.2860(8) Å β = 91.532(2)° c = 28.4211(15) Å γ = 90°
Volume	3715.1(4) $Å^3$
Z	4
Density (calculated)	1.441 g/cm^3
Absorption coefficient	0.241 mm^{-1}
F(000)	1687
Diffractometer	Bruker D8 VENTURE
Radiation source	fine focus sealed tube, MoKα
Theta range for data collection	2.47 to 25.05°
Index ranges	-9<=h<=10, -18<=k<=18, -33<=l<=33
Reflections collected	33913
Independent reflections	6573 [R(int) = 0.0406]
Coverage of independent reflections	99.9%
Absorption correction	multi-scan
Max. and min. transmission	0.9870 and 0.8990
Structure solution technique	direct methods
Structure solution program	SHELXS-2014 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	Σ w(Fo2 - Fc2)2
Data / restraints / parameters	6573 / 0 / 513
Goodness-of-fit on F2	1.052
Δ/σmax	0.001
Final R indices	4920 data; I>2σ(I) R1 = 0.0403, wR2 = 0.0842

	all data	R1 = 0.0649, wR2 = 0.0937
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0390P)^2+1.9271P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.272 and -0.327 eÅ^{-3}	
R.M.S. deviation from mean	0.049 eÅ^{-3}	

Fig. S32: ORTEP diagram of [2·Na+] complex (arbitrary atom numbering). Ellipsoids are represented at the 50% probability level.

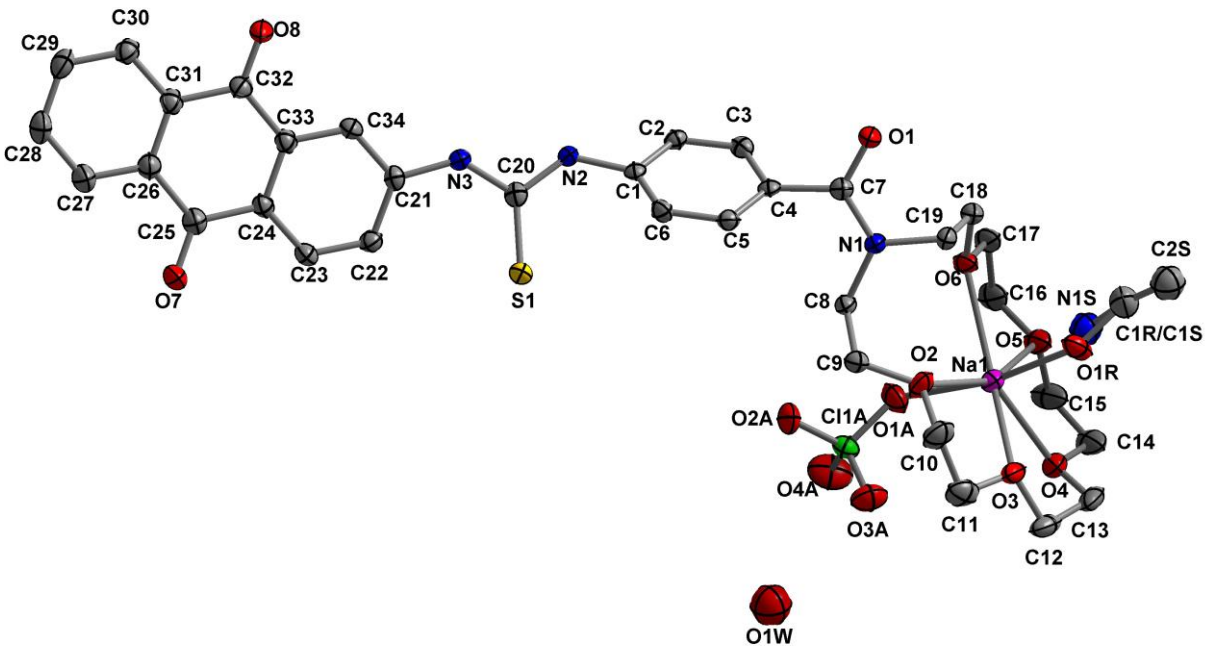


Fig. S33: Crystal packing of **[2·Na+]** along the a-axis

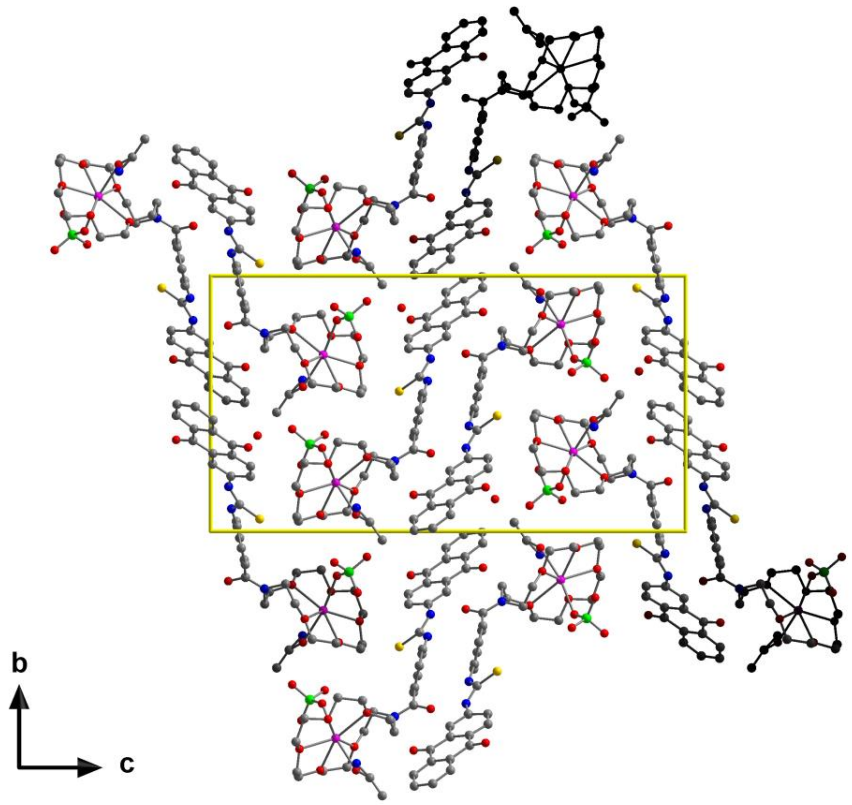


Fig. S34: Crystal packing of **[2·Na+]** along the b-axis

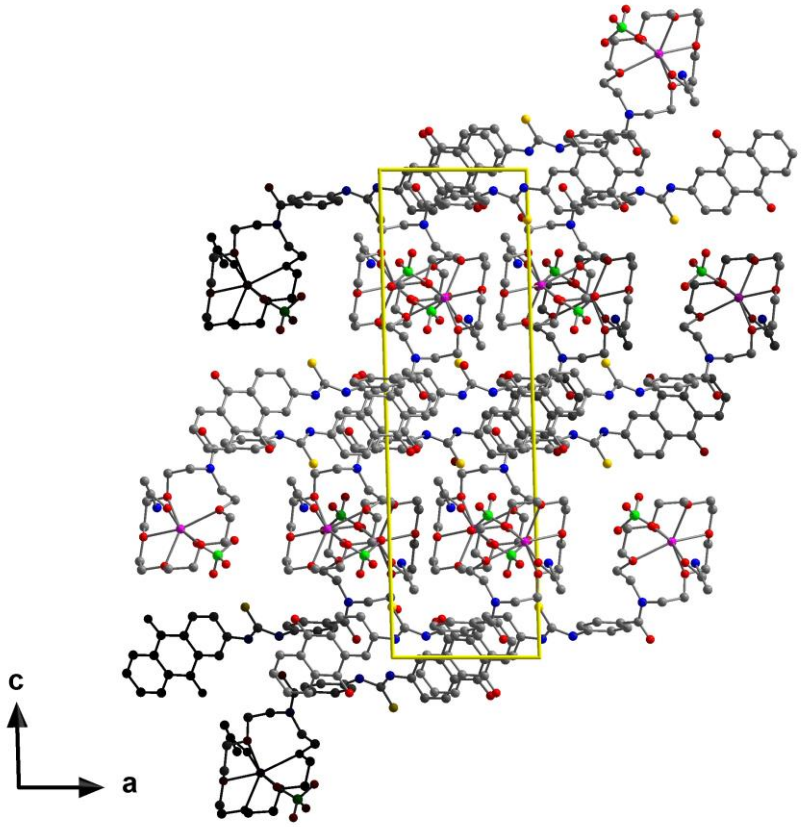
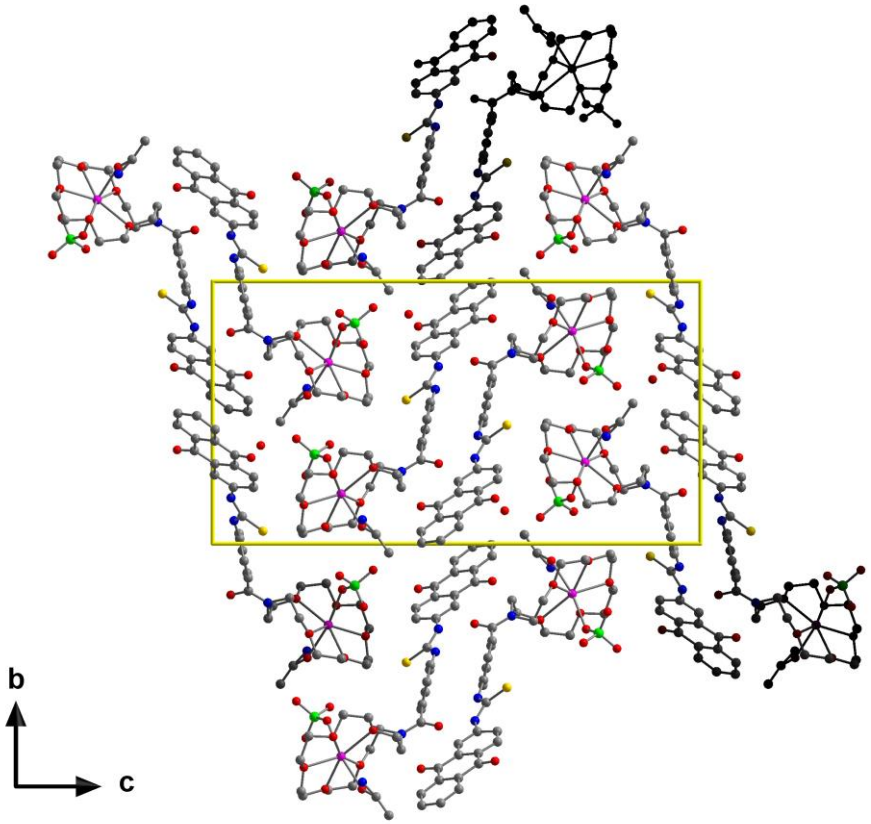


Fig. S35: Crystal packing of **[2·Na+]** along the c-axis



Electrochemical experiments.

Before recording of cyclic voltammograms a 3 mL of freshly prepared 0.5 mM solution of receptor, containing also supporting electrolyte (0.1 M $TBAPF_6$), was degassed with argon. After receiving reproducible voltammograms small aliquots of freshly prepared solution containing appropriated salt was added. The solution of the salt containing also receptor (0.5 mM) to keep constants concentration of the receptor. The concentration of salts was 30 mM (50 μL salt solution had the same number of moles as the starting receptor solution). After adding appropriate volume of salt solution the solution of receptor was degassed with argon and cyclic voltammograms were recorded. Before each experiment, the microelectrode was polished with aluminum oxide powder.

Fig. S36: Cyclic voltammograms recorded for 0.5 mM solution of receptor **2** (solid black line) (**A**), and changes after adding 1 eq., 3 eq. and 5 eq. TBACl (gray lines) (**B**); and after adding 1 eq. $NaClO_4$ (dashed black line) and then after adding 1 eq., 3 eq. and 5 eq. TBACl (gray lines) (**C**) in acetonitrile. The concentration of supporting electrolyte $TBAPF_6$ was 0.1 M and scan rate was 100 mV s^{-1}.

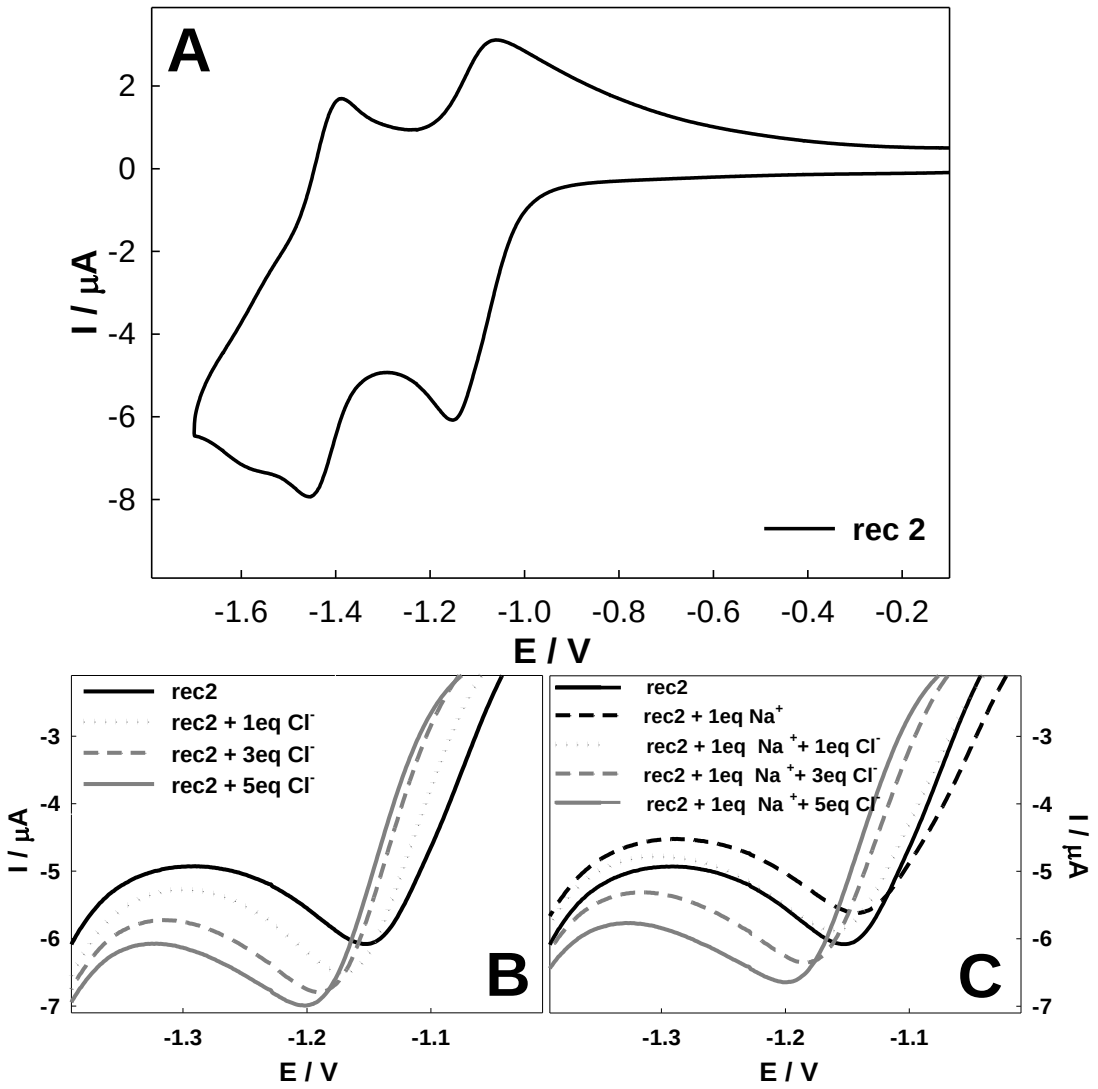


Fig. S37: Cyclic voltammograms recorded for 0.5 mM solution of receptor **3** (solid black line) (**A**), and changes after adding 1 eq., 3 eq. and 5 eq. TBACl (gray lines) (**B**); and after adding 1 eq. $NaClO_4$ (dashed black line) and then after adding 1 eq., 3 eq. and 5 eq. TBACl (gray lines) (**C**) in acetonitrile. The concentration of supporting electrolyte $TBAPF_6$ was 0.1 M and scan rate was 100 mV s^{-1}.