Electronic Supplementary Information (ESI) for

Metal cations recognition by bowl-shaped N-pyrrolic polycyclic aromatic hydrocarbons

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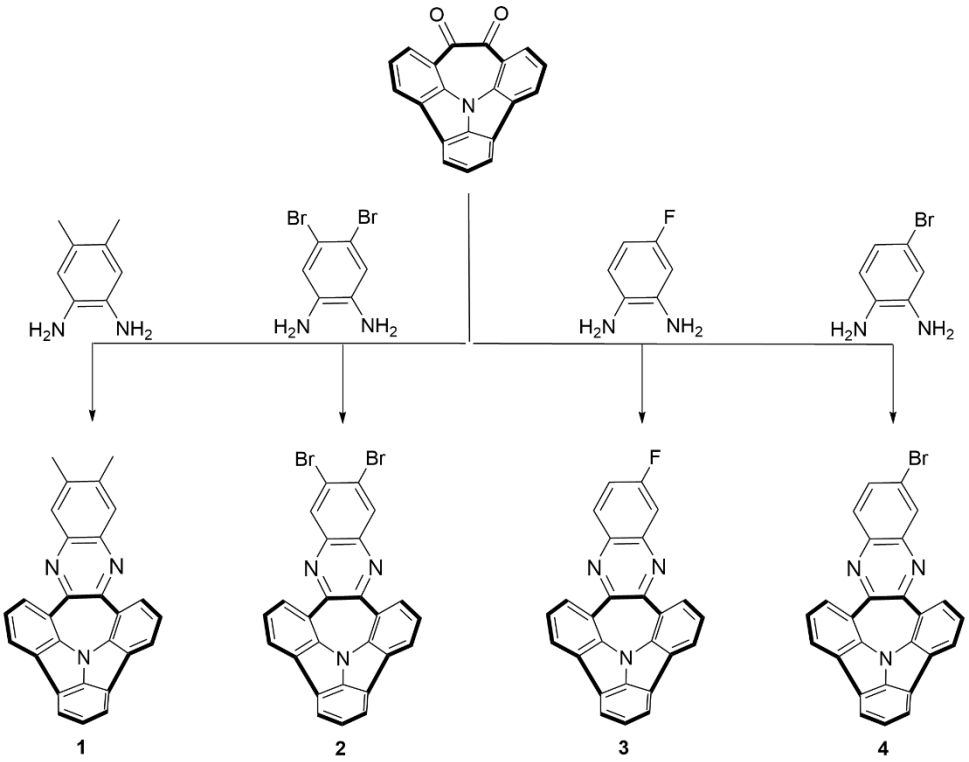
S1. Materials and methods

Chemical reagents and solvents for the synthesis were commercially purchased and purified according to the standard methods, if necessary. All inorganic salts, 1-morpholinoethanesulfonic acid (MES), were of analytical grade and were purchased from Fluka. The solutions of inorganic salts (0.01 M) were prepared with deionised water. High-molecular-weight poly(vinyl chloride) (PVC), o-nitrophenyl octyl ether (o-NPOE), potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), were obtained from Fluka (Selectophore). Freshly distilled tetrahydrofuran (THF, Fluka) was used as a solvent for membrane components.

Synthesis of receptors

Receptors were synthesised according to the literature.[1] The titled receptors **1**-**4** were reproduced according to recently published protocol (**Scheme 1**) starting from corresponding diketone (0.34 mmol). Acidic condensation with four different diamines (0.34 mmol) provided receptors **1**-**4** with satisfied yields.



Scheme. 1 The synthesis of receptors **1-4.**

N-PAH **1**: obtained as yellow powder (yield 70%, 95mg). The structure complies with previously reported spectral data: ^{1}H NMR (500 MHz, 300K, $CDCl_3$) δ 8.46 (d, *J* = 7.8 Hz, 2H), 7.96 – 7.89(m, 4H), 7.68 (s, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.33 – 7.27 (m, 2H), 2.43(s, 6H). HRMS (EI) calcd. for $C_{28}H_{17}N_3$: 395.1422 [M]+, found: 395.1419.

N-PAH **2**: obtained as orange powder (yield 57%, 102mg). The structure complies with previously reported spectral data: ^{1}H NMR (500 MHz, 300K, Tetrachloroethane-d_2) δ

8.45 (d, *J* = 8.0 Hz, 2H), 8.33 (s, 2H), 8.02 (m, 4H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H).; HRMS (EI) calcd. for $C_{26}H_{11}Br_2N_3$: 522.9320 [M]+, found: 522.9326.

N-PAH **3**: obtained as yellow powder (yield 55%, 73mg). The structure complies with previously reported spectral data: ^{1}H NMR (600 MHz, 300K, $CDCl_3$) δ 8.46 (m, 2H), 7.98 – 7.94 (m, 5H),7.62-7.54 (m, 2H), 7.43 (td, *J* = 8.6, 2.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), HRMS (EI) calcd for $C_{26}H_{12}F_1N_3$: 385.1015 [M]+, found: 385.1025

N-PAH **4**: obtained as dark-yellow powder (yield 60%, 90mg). The structure complies with previously reported spectral data: ^{1}H NMR (600 MHz, 300K, Tetrachloroethane-d_2) δ 8.47 (dd, *J* = 7.9, 4.3Hz, 2H), 8.20 (s, 1H), 8.01 (m, 4H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.79 – 7.75(m, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H); HRMS (EI) calcd for $C_{26}H_{12}BrN_3$: 445.0215 [M]+, found: 445.0232.

Preparation of sensors and EMF measurements

The method of the membranes and sensors preparation was the same as for standard ion-selective electrodes. The membranes contained: 1% wt receptor **1-2**, 65% wt plasticizer, 33% wt PVC and 50% mol (vs receptor) KTFPB. The membrane components (200 mg in total) were dissolved in 1.5 ml of THF. The solution was poured into a glass ring placed on a glass. After solvent evaporation, membrane discs of appropriate size were cut off and mounted in electrode bodies (type IS 561, Philips) for electromotive force (EMF) measurements. NaCl solution (0.01 M) was used as an internal filling; the electrodes were conditioned overnight in NaCl solution (0.001 M). For each membrane composition three sensor specimens were prepared.

All measurements were carried out with cells of the following type: Ag, AgCl; KCl 1 M / CH_3COOLi 1 M / sample solution // membrane // internal filling solution; AgCl, Ag.

Potentiometric multiplexer (EMF 16 Interface, Lawson Labs Inc., Malvern, USA) was used for the EMF measurements. The values of the potentiometric selectivity coefficients ($\log K_{Na, X}$) of the ion-selective electrodes were determined by the separate solution method (SSM) using 0.01 M solutions of nitrate salts containing 0.01M MES, pH 5.0. The calibration curves of the sensors were examined by measuring the EMFs in 0.01 M solution of sodium nitrate, increasing the activity of the Cs^+ in steps of 0.5 log a (concentration range $10^{-6.5}$ – 10^{-2} M), pH 5.0. The activities of ions in aqueous solutions were calculated according to the Debye-Hueckel approximation.

Spectroscopic studies

Emission spectra were recorded with a HITACHI F-7100 FL spectrometer, parameters: scan speed: 240 nm/min, delay: 0.0 s, EX slit: 5.0 nm, EM slit: 5.0 nm, PMT voltage: 250 V for **1**, 400 V for **3**-**4**. The measurements were performed at room temperature. To eliminate any background emission, the spectrum of pure solvent was subtracted from the samples' spectra.

Stock solutions were prepared by dissolving weighted amount of receptor in THF or analyte in distilled water to yield concentration of $2 \cdot 10^{-3}$ M. Analysed samples were prepared by mixing the receptor's stock solution with analyte stock solution and

adding proper amounts of THF and distilled water to achieve final solvent system THF/H_2O 1:1 *vol*/*vol*. Concentration on receptor in the analysed sample was $2 \cdot 10^{-5}$ M. Following analytes were used: caesium hexafluorophosphate ($CsPF_6$), sodium hexafluorophosphate ($NaPF_6$), rubidium tetrafluoroborate ($RbBF_4$), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$). Apparent binding constant values were taken as a ratio of intercept-to-slope of $1/(I - I_0)$ vs. $1/C$(cation) linear plots, following Benesi-Hildebrand method.[4] The limit of detection (LOD) values were calculated from the intercept and slope of the linear plots[5–7] of ΔI *versus* log(C_{cation}); At first, the *x* value for *y* =1 was calculated, and subsequently, LOD was calcualted as $10^{x(y=1)}$.

Theoretical calculations

Theoretical calculations were performed using NWChem[8] software. Calculations with NWChem were carried out using Plane Wave Pseudo Potential method (PSPW)[9] with simulation cell of 100 Å Initial geometries were prepared in Avogadro molecular editor.[10,11] Then, molecules were subjected to optimization procedure in NWChem. Following geometry optimization, the vibrational frequencies were calculated. Optimised structures were found to be stable geometric structures, since no imaginary frequencies were observed. In optimization processes no symmetry constraints were applied.

S2. Potentiometry

Table S1. Values of selectivity coefficients (log $K_{Na, X}$) of PVC/o-NPOE membranes formulated with receptor 1 or 2 (50 mol% KTFPB) and without receptor (blank membrane); mean values were calculated for 3 electrode specimens.

X =	Blank	1	2
Cs^+	2.05	2.55	2.25
Rb^+	1.55	2.10	2.05
Li^+	−0.50	−0.50	−0.55
Ba^{2+}	−0.70	−0.55	−0.65
Pb^{2+}	−0.70	−0.50	−0.60
Ni^{2+}	−1.00	−0.85	−0.90
Co^{2+}	−1.30	−1.15	−1.15
Zn^{2+}	−1.30	−1.15	−1.25
Cu^{2+}	−1.30	−1.05	−1.15

log $K_{Na, X}$ ↑ higher selectivity

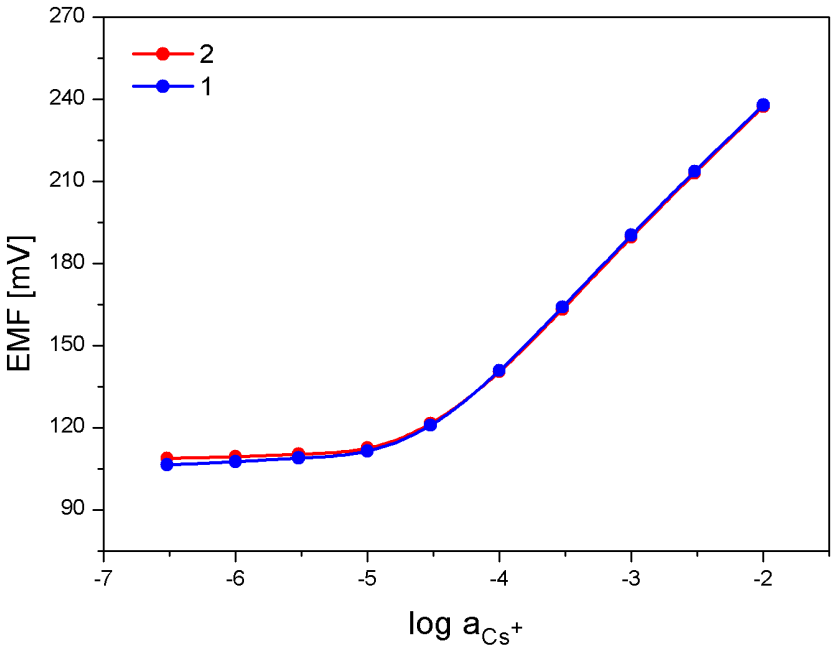


Fig. S1. Calibration plots of exemplary ion-selective electrodes based on membranes doped with receptors 1 or 2 (50 mol% KTFPB, PVC/o-NPOE) towards caesium cations measured in 0.01 M $NaNO_3$ solution.

S3. Spectrofluorimetry

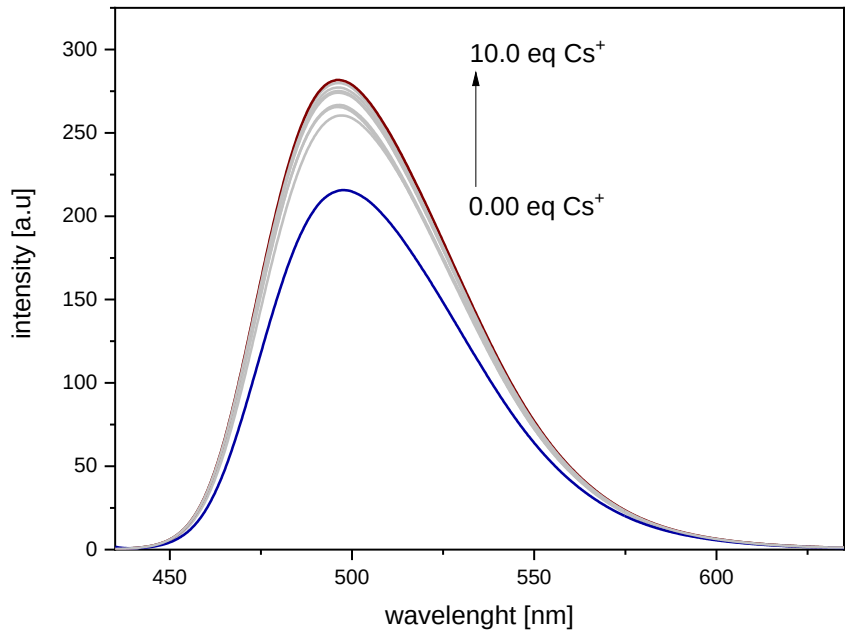


Fig. S2. Fluorescence Cs^+ titration of receptor **1** (λ_{ex} = 320 nm).

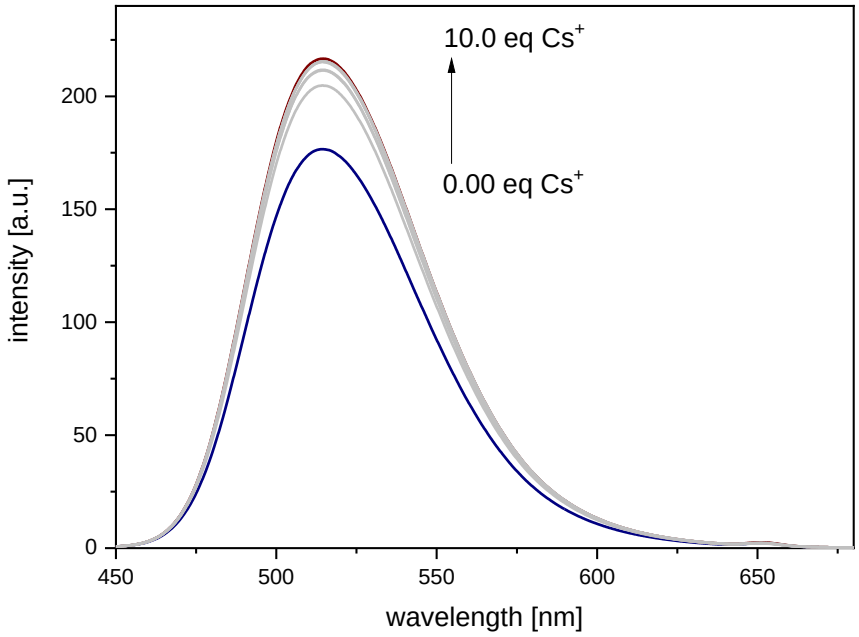


Fig. S3. Fluorescence Cs^+ titration of receptor **3** (λ_{ex} = 324 nm).

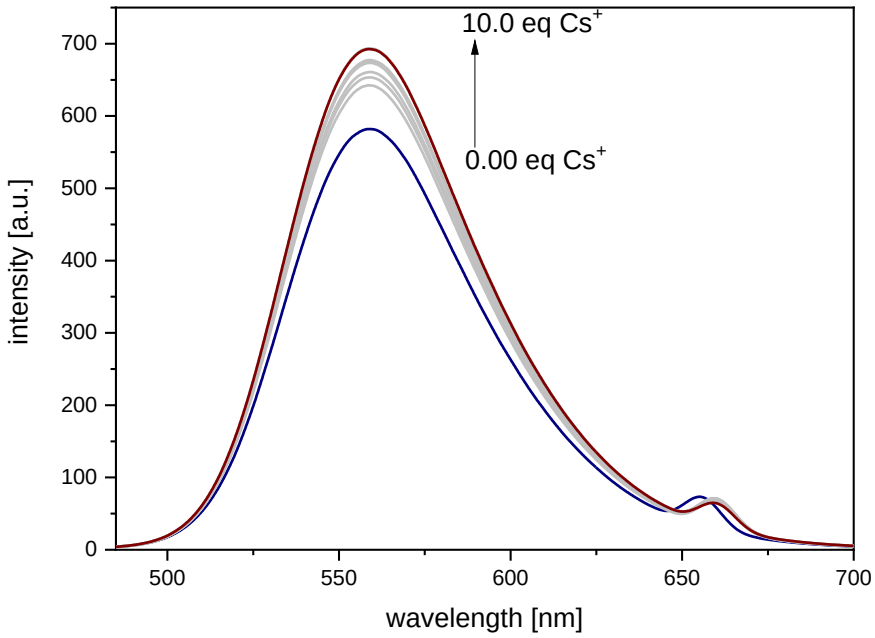


Fig. S4. Fluorescence Cs^+ titration of receptor **4** (λ_{ex} = 328 nm).

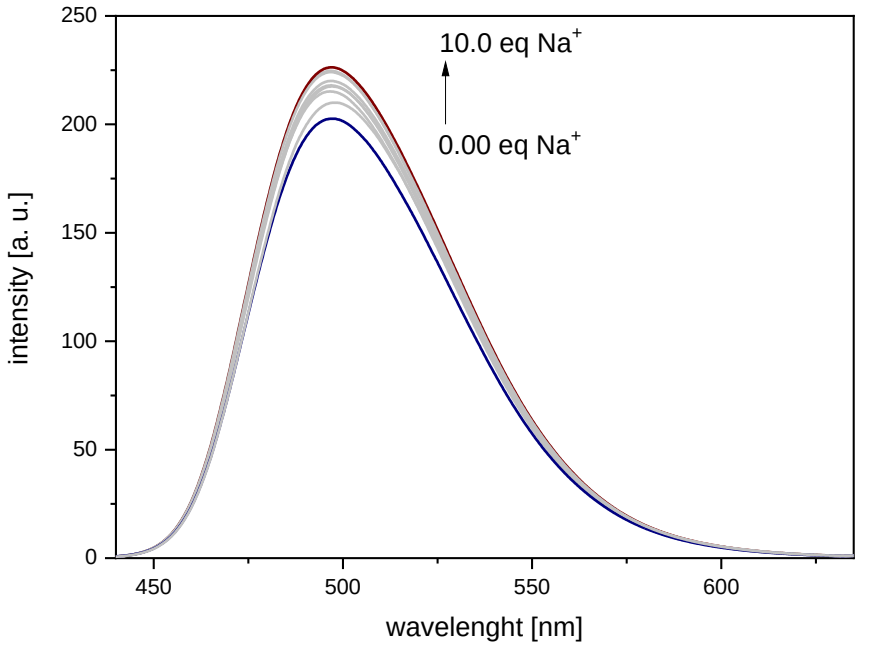


Fig. S5. Fluorescence Na^+ titration of receptor **1** (λ_{ex} = 320 nm).

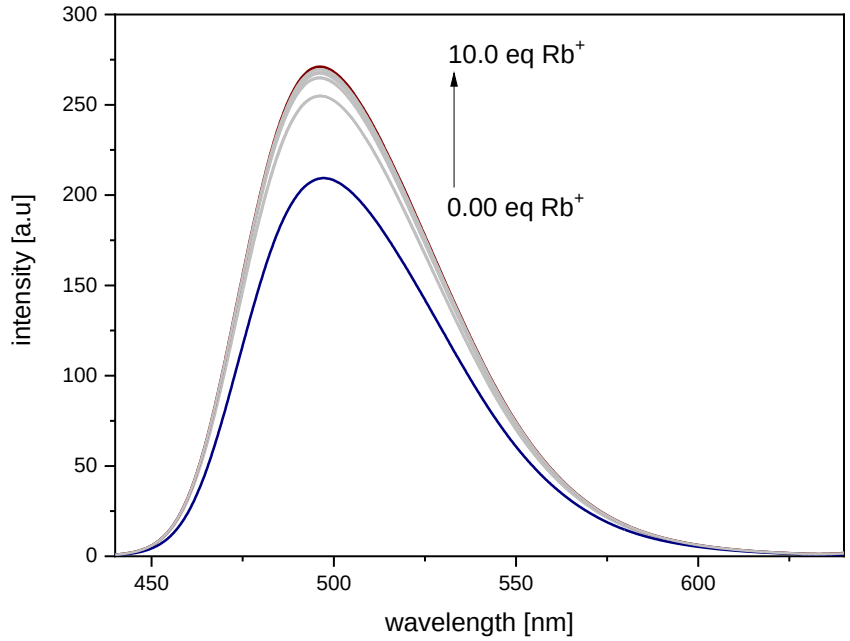


Fig. S6. Fluorescence Rb^{+} titration of receptor **1** (λ_{ex} = 320 nm).

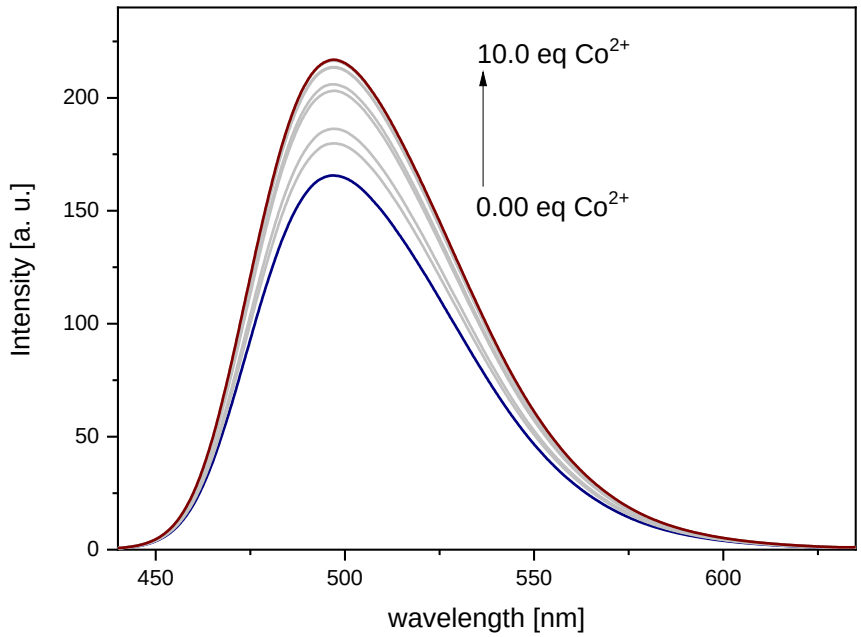


Fig. S7. Fluorescence Co^{2+} titration of receptor **1** (λ_{ex} = 320 nm).

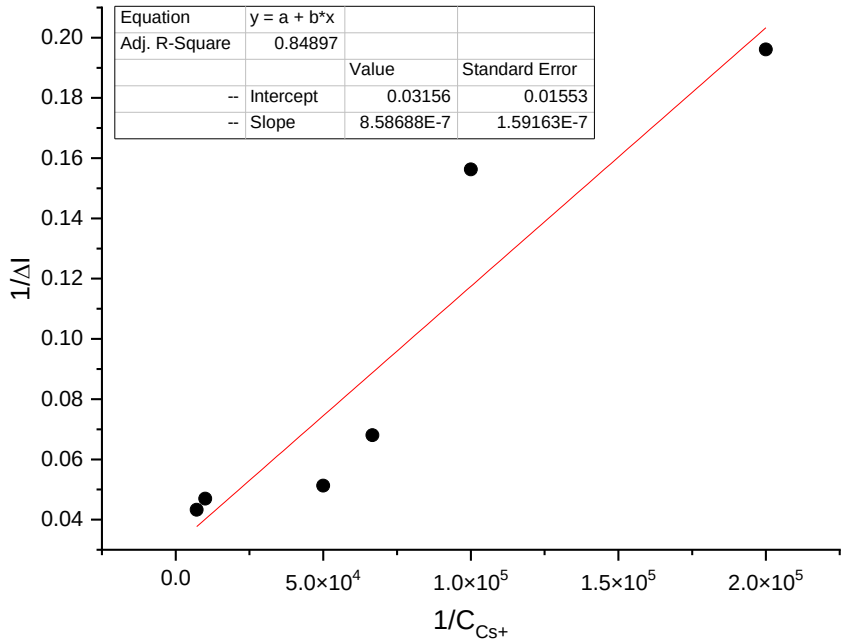


Fig. S8. Plots based on the Benesi-Hildebrand for the interactions between Cs^+ and receptor **1** (data were collected for $\lambda_{em,max}$ = 496 nm). Linear plot data are also presented.

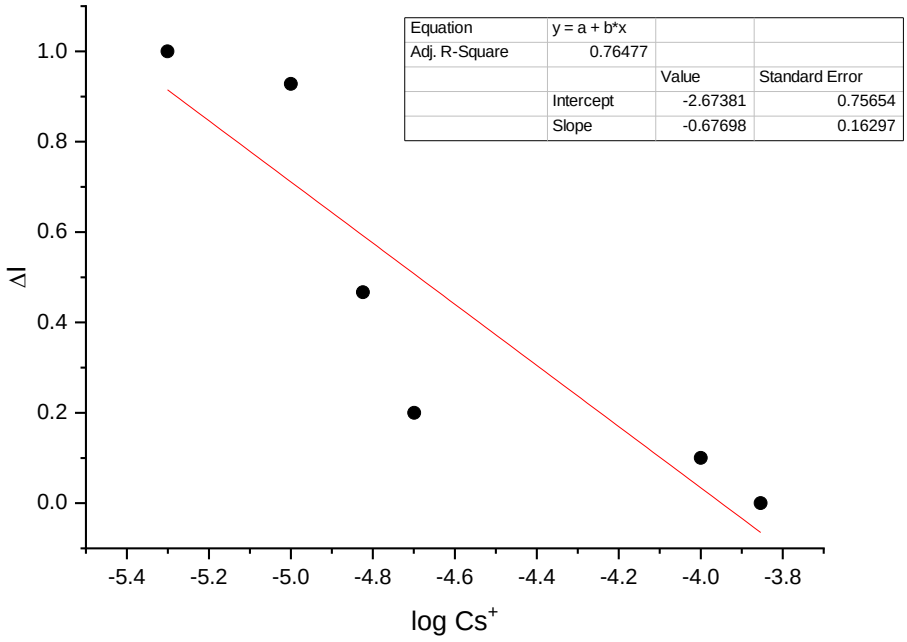


Fig. S9. ΔI *versus* log(C_{Cs+}) plots for the interactions between Cs^+ and receptor **1** used to calculate LOD (data were collected for $\lambda_{em,max}$ = 496 nm). Linear plot data are also presented.

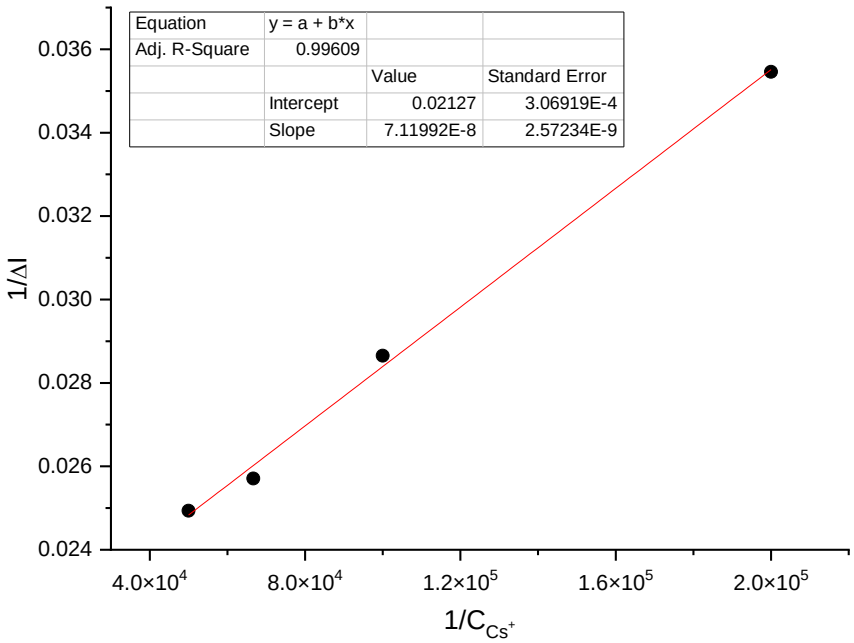


Fig. S10. Plots based on the Benesi-Hildebrand for the interactions between Cs^+ and receptor **3** (data were collected for $\lambda_{em,max}$ = 514 nm). Linear plot data are also presented.

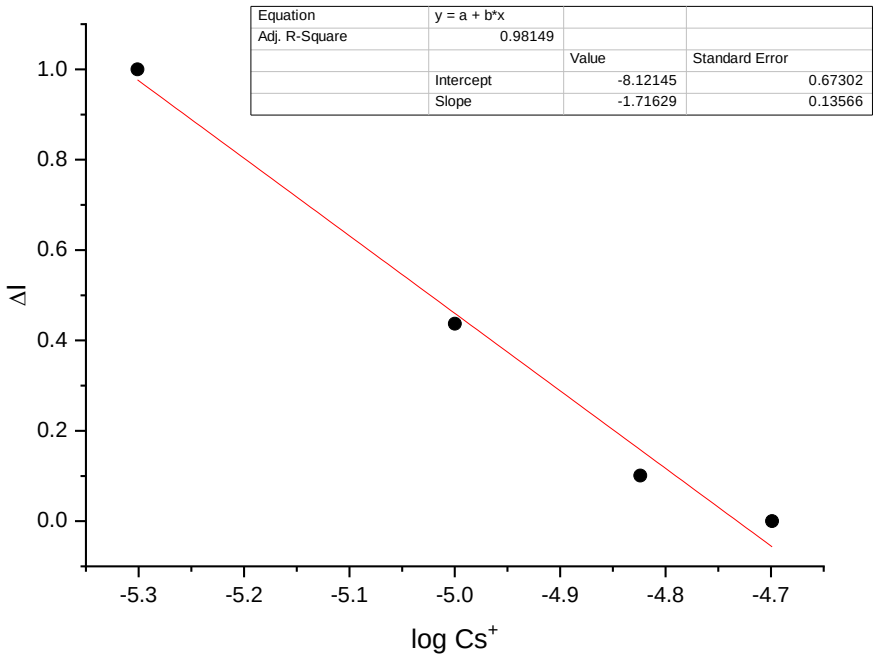


Fig. S11. ΔI *versus* log(C_{Cs+}) plots for the interactions between Cs^+ and receptor **3** used to calculate LOD (data were collected for $\lambda_{em,max}$ = 514 nm). Linear plot data are also presented.

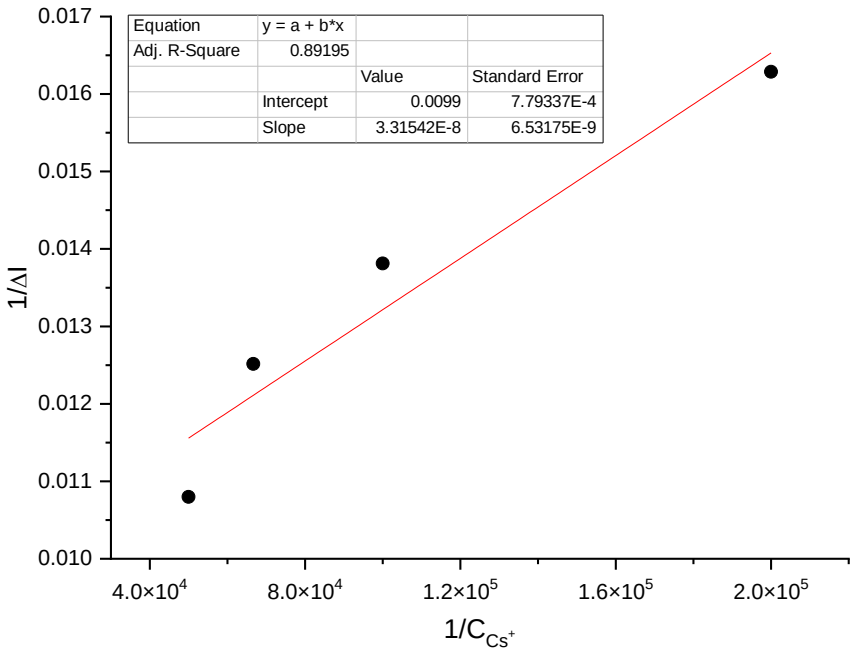


Fig. S12. Plots based on the Benesi-Hildebrand for the interactions between Cs^+ and receptor **4** (data were collected for $\lambda_{em,max}$ = 558 nm). Linear plot data are also presented.

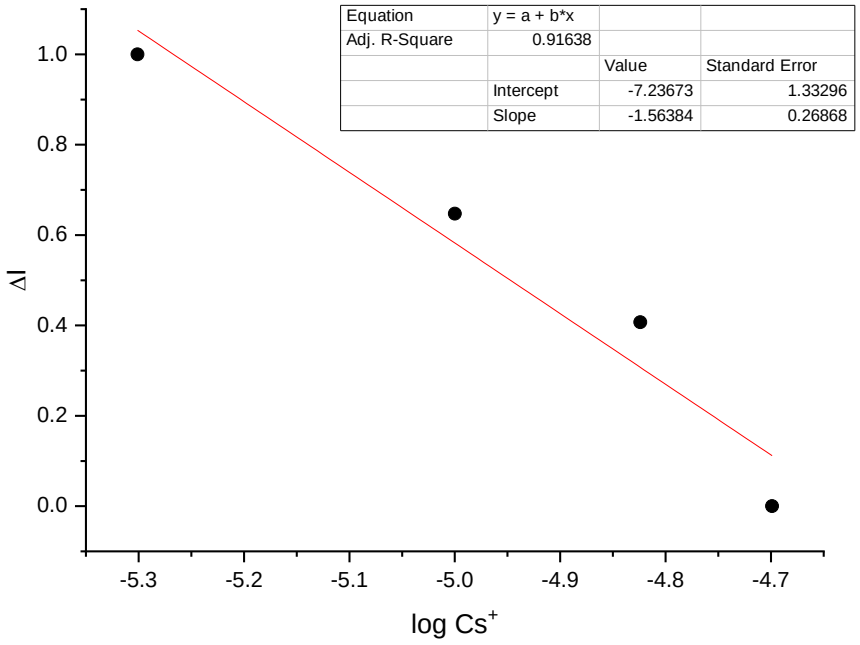


Fig. S13. ΔI *versus* log(C_{Cs+}) plots for the interactions between Cs^+ and receptor **4** used to calculate LOD (data were collected for $\lambda_{em,max}$ = 558 nm). Linear plot data are also presented.

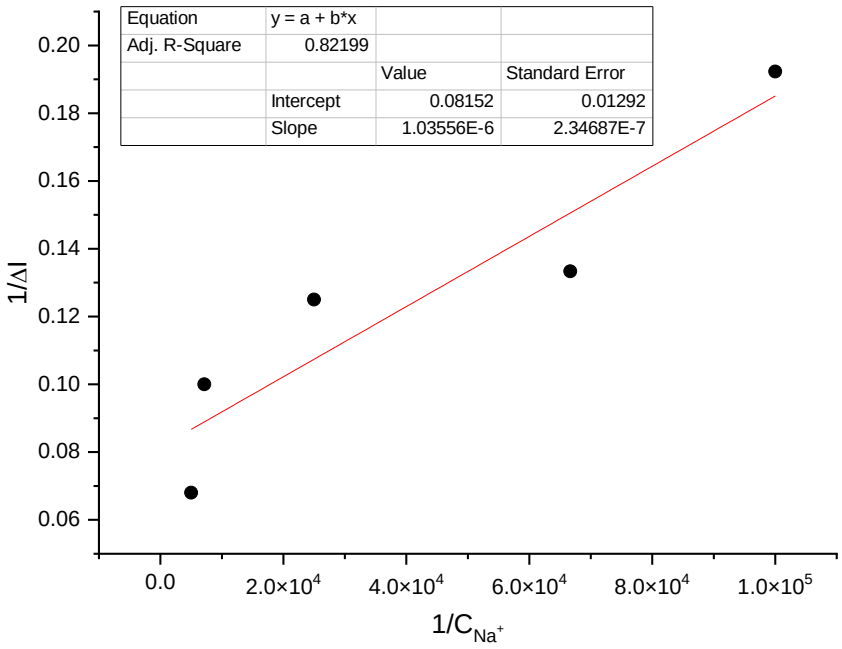


Fig. S14. Plots based on the Benesi-Hildebrand for the interactions between Na^+ and receptor **1** (data were collected for $\lambda_{em,max}$ = 496 nm). Linear plot data are also presented.

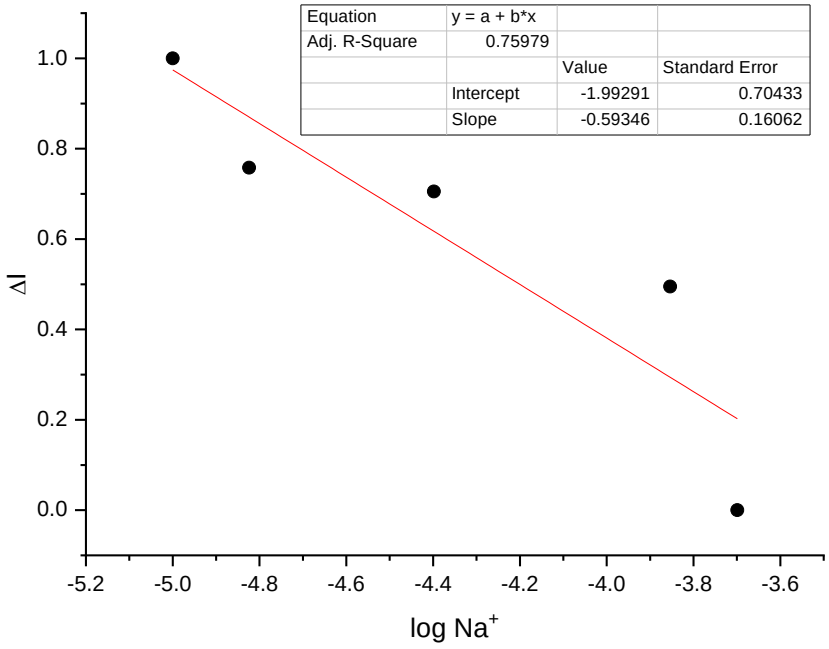


Fig. S15. ΔI *versus* log(C_{Na+}) plots for the interactions between Na^+ and receptor **1** used to calculate LOD (data were collected for $\lambda_{em,max}$ = 496 nm). Linear plot data are also presented.

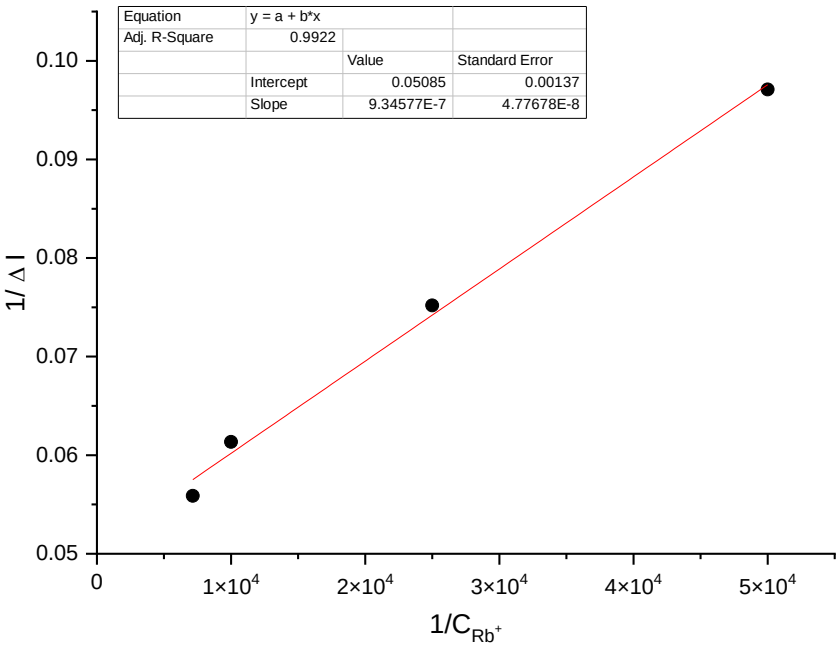


Fig. S16. Plots based on the Benesi-Hildebrand for the interactions between Rb^+ and receptor **1** (data were collected for $\lambda_{em,max}$ = 496 nm). Linear plot data are also presented.

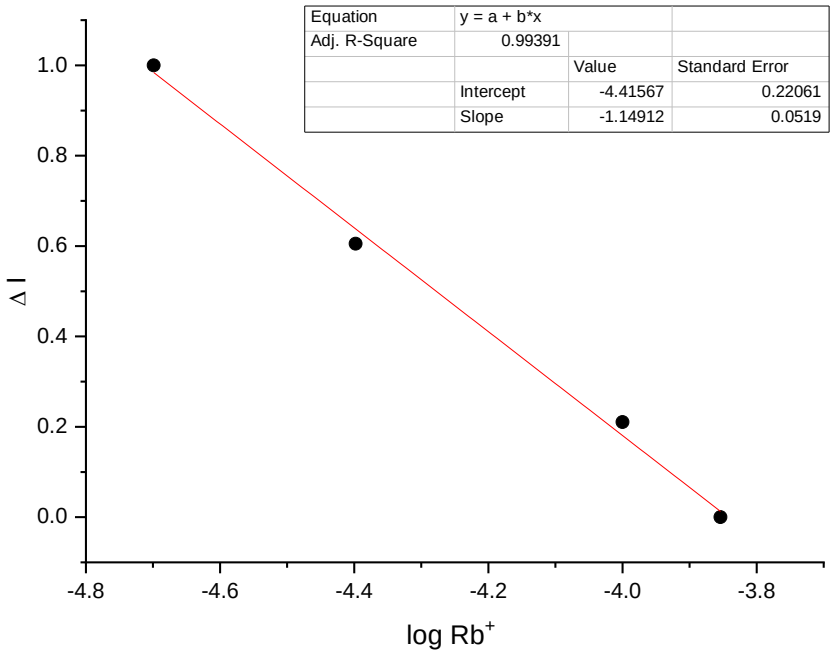


Fig. S17. ΔI *versus* log(C_{Rb+}) plots for the interactions between Rb^+ and receptor **1** used to calculate LOD (data were collected for $\lambda_{em,max}$ = 496 nm). Linear plot data are also presented.

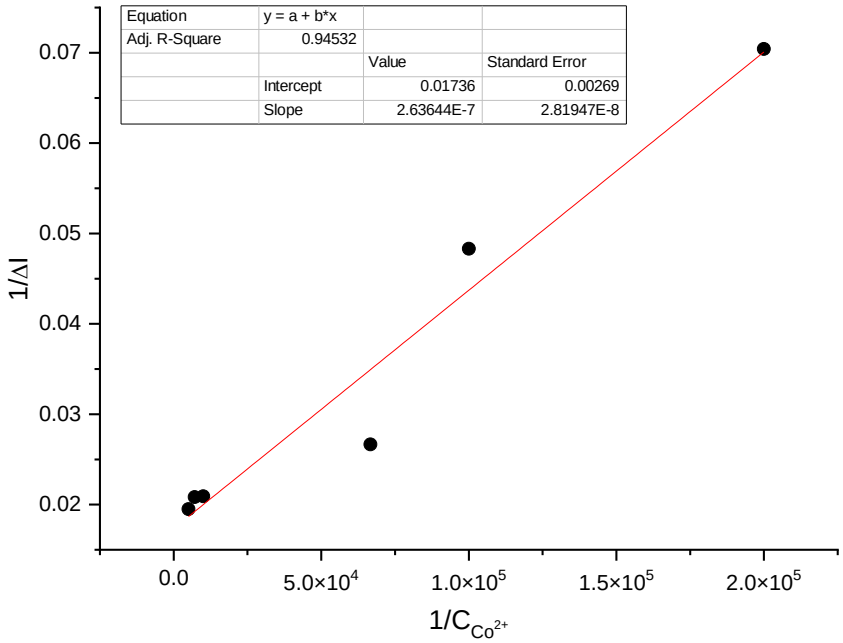


Fig. S18. Plots based on the Benesi-Hildebrand for the interactions between Co^{2+} and receptor **1** (data were collected for $\lambda_{em,max}$ = 496 nm). Linear plot data are also presented.

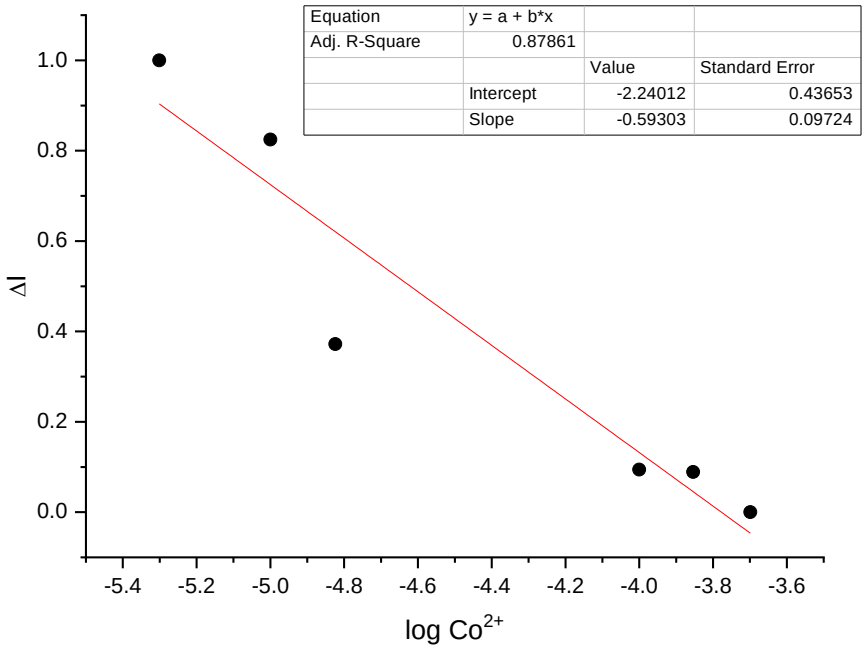


Fig. S19. ΔI *versus* log(C_{Co2+}) plots for the interactions between Co^{2+} and receptor **1** used to calculate LOD (data were collected for $\lambda_{em,max}$ = 496 nm). Linear plot data are also presented.

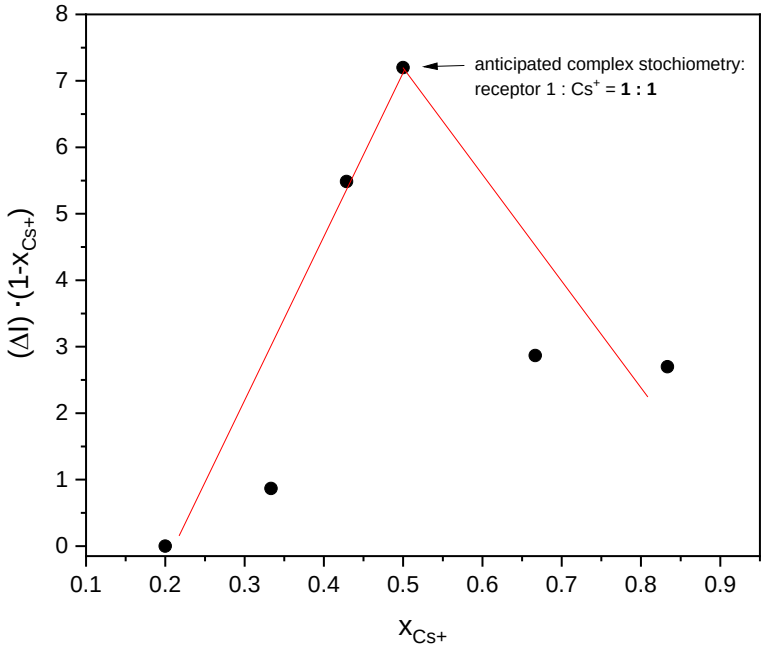


Fig. S20. Job's plot regarding interactions between receptor **1** and Cs^+.

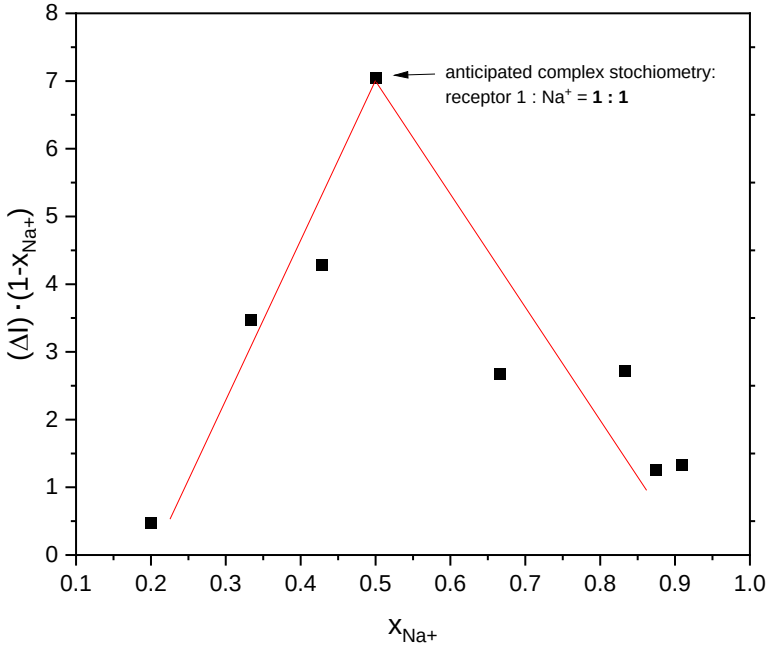


Fig. S21. Job's plot regarding interactions between receptor **1** and Na^+.

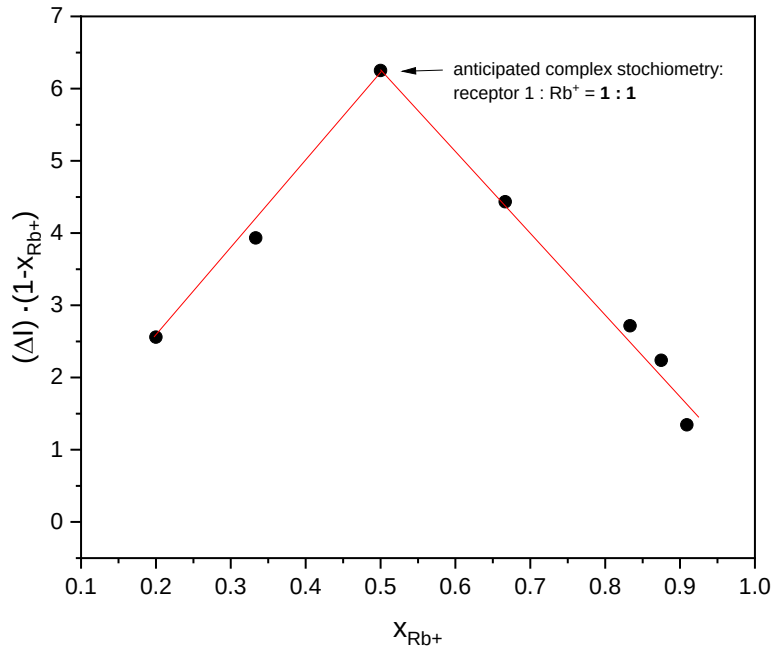


Fig. S22. Job's plot regarding interactions between receptor **1** and Rb^{+}.

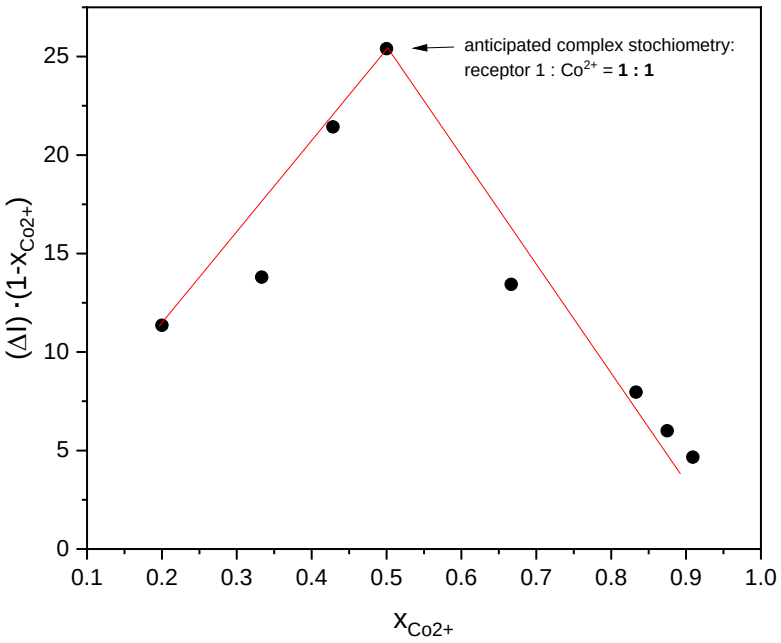


Fig. S23. Job's plot regarding interactions between receptor **1** and Co^{2+}.

S4. DFT computations

Table S2. Atomic coordinates for optimised structure **1** (DFT/PSPW/Vosko).

	x	*y*	*z*
C	0.0004400000	-3.4966500000	-0.5015500000
C	-1.2540400000	-4.0010400000	-0.2335000000
H	2.1010100000	-5.9041000000	0.4435100000
H	-4.8239700000	-1.1029700000	0.7837700000
C	-1.2545600000	-5.3420900000	0.1178900000
H	-3.2464700000	0.7706500000	0.6551300000
C	-0.0303700000	-5.9934700000	0.2531600000
H	-2.1651600000	-5.8737400000	0.3676000000
C	1.2062900000	-5.3619800000	0.1618500000
H	-0.0445200000	-7.0367000000	0.5467400000
C	1.2350000000	-4.0231500000	-0.1932500000
N	0.0161000000	-2.1368200000	-0.5901300000
C	2.9881200000	-0.3061000000	0.4901300000
H	4.8356200000	-1.2385900000	0.9728800000
C	1.2726200000	-1.7208600000	-0.2017700000
C	2.0850500000	-2.8649200000	-0.0275400000
C	1.6695400000	-0.4313700000	0.0742400000
H	3.3401500000	0.6901800000	0.7235900000
C	0.7919400000	0.7419900000	0.0013800000
C	3.3871100000	-2.6849400000	0.3847700000
H	4.0417700000	-3.5329900000	0.5434800000
C	3.8216200000	-1.3986700000	0.6307500000
C	-1.2389300000	-1.7012200000	-0.2350100000
C	-1.5867200000	-0.4049500000	0.0478800000
C	-2.0880500000	-2.8212000000	-0.1025200000
H	-4.0973900000	-3.4140900000	0.3609400000
C	-3.4023900000	-2.5910100000	0.2420800000
C	-2.9185800000	-0.2311500000	0.4149600000
C	-0.6523900000	0.7339900000	-0.0007700000
C	-3.8002600000	-1.2916100000	0.4865100000
C	-0.6307800000	3.0372900000	0.0041100000
N	-1.3090400000	1.8838900000	0.0040000000
N	1.4666800000	1.8937200000	-0.0041400000
C	0.7687200000	3.0507100000	-0.0108100000
C	-1.3496300000	4.2272400000	0.0175200000
C	1.4146300000	4.2867600000	-0.0438600000
H	2.4985300000	4.2989600000	-0.0758500000
C	-1.4877500000	6.6800300000	0.0021800000
C	-0.7117900000	5.4294300000	-0.0096500000
C	0.7000700000	5.4563200000	-0.0602900000
H	-2.4326100000	4.1564400000	0.0457900000

C	1.3715800000	6.7611700000	-0.1579300000
H	-1.2991700000	7.2852200000	-0.8894300000
H	-2.5563800000	6.4703800000	0.0473700000
H	-1.2305800000	7.3087900000	0.8598200000
H	1.1033500000	7.4114700000	0.6805600000
H	2.4546800000	6.6562500000	-0.1815500000
H	1.0561300000	7.2931000000	-1.0614500000

Table S3. Atomic coordinates for optimised structure of 1:1 non-covalent complex labelled as **1_A_concave** (DFT/PSPW/Vosko).

	x	*y*	*z*
C	-0.0225800000	-2.9970000000	-0.8340700000
C	-1.2908100000	-3.5040300000	-0.6352800000
H	2.0420500000	-5.4657900000	-0.0032700000
H	-4.8627700000	-0.6255300000	0.4612400000
C	-1.3070500000	-4.8633500000	-0.3596600000
H	-3.2680900000	1.2322000000	0.4688700000
C	-0.0870100000	-5.5189500000	-0.2174200000
H	-2.2301800000	-5.4065100000	-0.1951500000
C	1.1581400000	-4.8926400000	-0.2507400000
H	-0.1145700000	-6.5784500000	0.0010700000
C	1.2127100000	-3.5359000000	-0.5388700000
N	-0.0041900000	-1.6445200000	-0.8442500000
C	2.9785200000	0.1940900000	0.1834100000
H	4.8599000000	-0.7249100000	0.5272500000
C	1.2552200000	-1.2310900000	-0.4689900000
C	2.0745800000	-2.3752200000	-0.3515700000
C	1.6496000000	0.0584500000	-0.1839000000
H	3.3286700000	1.1927400000	0.4111700000
C	0.7689400000	1.2323800000	-0.2169000000
C	3.3968200000	-2.1775200000	-0.0033300000
H	4.0798000000	-3.0125200000	0.0809600000
C	3.8283700000	-0.8910100000	0.2483700000
C	-1.2664100000	-1.2054700000	-0.5231800000
C	-1.6061200000	0.0809500000	-0.1697000000
C	-2.1256500000	-2.3278200000	-0.4641500000
H	-4.1682600000	-2.9139300000	-0.0989100000
C	-3.4476800000	-2.1059200000	-0.1293200000
C	-2.9408100000	0.2375300000	0.1929800000
C	-0.6660600000	1.2247100000	-0.1524900000
C	-3.8318400000	-0.8194200000	0.1916200000
C	-0.6409900000	3.5286800000	-0.0165800000
N	-1.3148300000	2.3669100000	-0.0068000000
N	1.4498100000	2.3783200000	-0.2233500000
C	0.7565700000	3.5423300000	-0.1700500000
C	-1.3485700000	4.7215700000	0.1062600000
C	1.4013700000	4.7781400000	-0.2371600000
H	2.4771000000	4.7969100000	-0.3708600000
C	-1.4586300000	7.1862700000	0.1747600000
C	-0.7093100000	5.9247900000	0.0447400000
C	0.6941500000	5.9481700000	-0.1460100000
H	-2.4251700000	4.6676600000	0.2331500000

C	1.3668200000	7.2512100000	-0.2324000000
H	-1.3446200000	7.8159300000	-0.7137000000
H	-2.5221900000	7.0083300000	0.3258400000
H	-1.0918600000	7.7887800000	1.0116200000
H	1.1886600000	7.8517400000	0.6656200000
H	2.4412400000	7.1508400000	-0.3714900000
H	0.9683100000	7.8449700000	-1.0621400000
Cs	-0.3451400000	-2.2771900000	2.5042300000

Table S4. Atomic coordinates for optimised structure of 1:1 non-covalent complex labelled as **1_A_convex** (DFT/PSPW/Vosko).

	x	*y*	*z*
C	0.3944900000	-3.0168800000	0.5325900000
C	-0.7699000000	-3.5806500000	1.0080800000
H	2.7333600000	-5.3535300000	0.7517600000
H	-4.4397300000	-0.7899100000	2.0799500000
C	-0.6315500000	-4.9399200000	1.2667600000
H	-3.0454200000	1.1548700000	1.5507300000
C	0.6242500000	-5.5165700000	1.0904400000
H	-1.4413400000	-5.5470400000	1.6515200000
C	1.7872500000	-4.8267200000	0.7437800000
H	0.7213800000	-6.5725500000	1.3087800000
C	1.6942700000	-3.4693300000	0.4725300000
N	0.3091100000	-1.6755300000	0.4192700000
C	3.2613700000	0.4180500000	0.2839200000
H	5.2403300000	-0.3491900000	0.1837400000
C	1.5815000000	-1.1664700000	0.3675500000
C	2.4851200000	-2.2520900000	0.3386400000
C	1.8967900000	0.1674000000	0.3484300000
H	3.5834600000	1.4505700000	0.2700200000
C	0.8982300000	1.2536800000	0.3455500000
C	3.8272600000	-1.9386700000	0.2516100000
H	4.5837300000	-2.7126600000	0.2255600000
C	4.1903300000	-0.6067300000	0.2305800000
C	-0.9055000000	-1.2737000000	0.8963000000
C	-1.3351900000	0.0303000000	1.0003600000
C	-1.6506300000	-2.4386100000	1.2218500000
H	-3.5889000000	-3.0851300000	1.9076700000
C	-2.9554100000	-2.2480400000	1.6411500000
C	-2.6449800000	0.1548900000	1.4463500000
C	-0.5150000000	1.2079800000	0.6475600000
C	-3.4252900000	-0.9518700000	1.7390400000
C	-0.6421800000	3.4936700000	0.3565700000
N	-1.2480000000	2.3219300000	0.6368600000
N	1.4660800000	2.4067800000	0.0078700000
C	0.7193500000	3.5297900000	0.0131100000
C	-1.3618500000	4.6869500000	0.3994700000
C	1.3107100000	4.7467900000	-0.3117200000
H	2.3598600000	4.7438200000	-0.5861500000
C	-1.5127900000	7.1470800000	0.1840100000
C	-0.7647300000	5.8835100000	0.1102500000
C	0.6014000000	5.9124300000	-0.2679100000
H	-2.4098900000	4.6430900000	0.6770900000

C	1.2337900000	7.1932700000	-0.6166600000
H	-1.5015600000	7.6737800000	-0.7753600000
H	-2.5505100000	6.9842400000	0.4700500000
H	-1.0622000000	7.8343400000	0.9062100000
H	1.1630400000	7.9118800000	0.2054700000
H	2.2840100000	7.0663700000	-0.8717800000
H	0.7292600000	7.6651000000	-1.4660900000
Cs	-1.8560000000	-2.3377200000	-2.1224000000

Table S5. Atomic coordinates for optimised structure of 1:1 non-covalent complex labelled as **1_B_concave** (DFT/PSPW/Vosko).

	x	*y*	*z*
C	-0.0621400000	-3.8086400000	-0.7454400000
C	-1.3002000000	-4.3361900000	-0.4604300000
H	2.1051600000	-6.2158700000	-0.0215700000
H	-4.8834100000	-1.4926800000	0.6878600000
C	-1.2701100000	-5.6952600000	-0.1919700000
H	-3.3907400000	0.4152300000	0.4073900000
C	-0.0265300000	-6.3221700000	-0.1360000000
H	-2.1669200000	-6.2601600000	0.0333200000
C	1.1981600000	-5.6620600000	-0.2242000000
H	-0.0149500000	-7.3834600000	0.0767300000
C	1.1995500000	-4.2991400000	-0.5059700000
N	-0.0870500000	-2.4571800000	-0.8426100000
C	2.8341400000	-0.4540500000	-0.0334300000
H	4.7280700000	-1.2978200000	0.4451800000
C	1.1634300000	-1.9863700000	-0.5671300000
C	2.0217400000	-3.0999600000	-0.3920100000
C	1.5119400000	-0.6619100000	-0.4112300000
H	3.1778100000	0.5685500000	0.0705200000
C	0.5961900000	0.4702500000	-0.5993300000
C	3.3260500000	-2.8255000000	-0.0328900000
H	4.0327900000	-3.6288500000	0.1315600000
C	3.7085400000	-1.5086900000	0.1511800000
C	-1.3324800000	-2.0279700000	-0.4706600000
C	-1.7085200000	-0.7251900000	-0.2177500000
C	-2.1481200000	-3.1695900000	-0.2882700000
H	-4.1288300000	-3.7913700000	0.2704300000
C	-3.4479600000	-2.9627300000	0.1193900000
C	-3.0267200000	-0.5843200000	0.2082900000
C	-0.8356900000	0.4458900000	-0.3802700000
C	-3.8655300000	-1.6679500000	0.3624100000
C	-0.8348900000	2.7631800000	-0.4151700000
N	-1.4859200000	1.5994400000	-0.2156800000
N	1.2344700000	1.6256600000	-0.8262600000
C	0.5163500000	2.7743000000	-0.8022700000
C	-1.5109800000	3.9708500000	-0.2476000000
C	1.1283400000	3.9957500000	-1.0757500000
H	2.1657600000	3.9871500000	-1.3930500000
C	-1.6420000000	6.4268700000	-0.4029300000
C	-0.9031600000	5.1617500000	-0.5223100000
C	0.4435400000	5.1732000000	-0.9551100000
H	-2.5526400000	3.9350800000	0.0538900000

C	1.0849200000	6.4574500000	-1.2658100000
H	-1.6756800000	6.9570800000	-1.3598400000
H	-2.6649200000	6.2687300000	-0.0664300000
H	-1.1529500000	7.1145700000	0.2947300000
H	1.0680300000	7.1330900000	-0.4048200000
H	2.1194800000	6.3264200000	-1.5774200000
H	0.5530500000	6.9838000000	-2.0642700000
Cs	0.5881500000	1.3562100000	2.5876300000

Table S6. Atomic coordinates for optimised structure of 1:1 non-covalent complex labelled as **1_B_convex** (DFT/PSPW/Vosko).

	x	*y*	*z*
C	0.0028600000	-3.8358300000	-0.2157600000
C	-1.2564900000	-4.3544900000	-0.0252900000
H	2.1194500000	-6.3184000000	0.3755500000
H	-4.8750900000	-1.4792300000	0.9438100000
C	-1.2501300000	-5.7256800000	0.1755600000
H	-3.3074100000	0.3867800000	0.9908100000
C	-0.0176100000	-6.3737800000	0.2300800000
H	-2.1579200000	-6.2903100000	0.3467200000
C	1.2233600000	-5.7400800000	0.1927800000
H	-0.0266100000	-7.4434700000	0.3929500000
C	1.2521500000	-4.3689700000	-0.0036600000
N	0.0110900000	-2.4822800000	-0.1975600000
C	2.9995700000	-0.6376900000	0.7911800000
H	4.8855500000	-1.5550900000	1.1002200000
C	1.2705300000	-2.0679600000	0.1444200000
C	2.1027400000	-3.2058700000	0.2023200000
C	1.6647500000	-0.7812800000	0.4394600000
H	3.3511100000	0.3527300000	1.0472100000
C	0.7825600000	0.3823400000	0.4311400000
C	3.4258000000	-2.9988800000	0.5285400000
H	4.1180700000	-3.8286200000	0.5861000000
C	3.8533800000	-1.7170500000	0.8204200000
C	-1.2457500000	-2.0542700000	0.1203700000
C	-1.6051400000	-0.7622900000	0.4303700000
C	-2.0972200000	-3.1829500000	0.1571200000
H	-4.1377300000	-3.7733100000	0.4787300000
C	-3.4269300000	-2.9578700000	0.4352200000
C	-2.9584500000	-0.6007400000	0.7197200000
C	-0.6670800000	0.3739000000	0.4909300000
C	-3.8365500000	-1.6643200000	0.7006900000
C	-0.6245700000	2.6904000000	0.6894700000
N	-1.3066900000	1.5275000000	0.6309600000
N	1.4547300000	1.5382400000	0.4059900000
C	0.7695000000	2.7063900000	0.5259900000
C	-1.3235600000	3.8837000000	0.8545100000
C	1.4177600000	3.9437900000	0.4788100000
H	2.4946000000	3.9620000000	0.3491300000
C	-1.4248300000	6.3415400000	1.0608900000
C	-0.6783700000	5.0889700000	0.8458400000
C	0.7215500000	5.1158500000	0.6399900000
H	-2.3971000000	3.8292600000	1.0081200000

C	1.4109400000	6.4150700000	0.6333400000
H	-1.3076800000	7.0396800000	0.2262300000
H	-2.4886800000	6.1568100000	1.2033100000
H	-1.0575600000	6.8763200000	1.9428900000
H	1.2885100000	6.9275100000	1.5936600000
H	2.4762100000	6.3169000000	0.4361900000
H	0.9814000000	7.0948500000	-0.1100400000
Cs	-0.4479100000	1.9883600000	-2.5931300000

Table S7. Atomic coordinates for optimised structure of 1:1 non-covalent complex labelled as **1_C_concave** (DFT/PSPW/Vosko).

	x	*y*	*z*
C	0.1199100000	-3.2758500000	-1.0604800000
C	-1.1390100000	-3.8103100000	-0.8739400000
H	2.2023700000	-5.7200600000	-0.1537200000
H	-4.7840200000	-1.0283000000	0.2032000000
C	-1.1422800000	-5.1732900000	-0.6047000000
H	-3.2394000000	0.8769800000	0.2059600000
C	0.0798600000	-5.8213800000	-0.4366400000
H	-2.0601900000	-5.7318500000	-0.4635100000
C	1.3111000000	-5.1671300000	-0.4268200000
H	0.0685300000	-6.8857800000	-0.2332900000
C	1.3429700000	-3.8063900000	-0.7046600000
N	0.1180800000	-1.9170600000	-1.0517900000
C	2.9883200000	-0.0818900000	0.2368600000
H	4.8359900000	-1.0002900000	0.7523700000
C	1.3457100000	-1.5043300000	-0.5847000000
C	2.1660800000	-2.6435100000	-0.4272400000
C	1.6966900000	-0.2164400000	-0.2509400000
H	3.3174200000	0.9140800000	0.5048000000
C	0.8082200000	0.9445500000	-0.3899800000
C	3.4492100000	-2.4503000000	0.0451100000
H	4.1327400000	-3.2817300000	0.1680900000
C	3.8363800000	-1.1666800000	0.3730300000
C	-1.1576300000	-1.5114200000	-0.7250300000
C	-1.5359200000	-0.2295900000	-0.3978700000
C	-1.9940900000	-2.6522400000	-0.6885600000
H	-4.0202000000	-3.3021200000	-0.3568700000
C	-3.3275300000	-2.4691100000	-0.3736500000
C	-2.8794500000	-0.1105100000	-0.0536700000
C	-0.6283900000	0.9331900000	-0.4179800000
C	-3.7461500000	-1.1922400000	-0.0569500000
C	-0.6150700000	3.2365100000	-0.4327600000
N	-1.2959900000	2.0814100000	-0.4258000000
N	1.4817400000	2.0942100000	-0.4126000000
C	0.7892200000	3.2483100000	-0.4392300000
C	-1.3155000000	4.4376300000	-0.4342500000
C	1.4530800000	4.4735100000	-0.4490700000
H	2.5370700000	4.4677200000	-0.4588800000
C	-1.4222600000	6.8909300000	-0.4550800000
C	-0.6612300000	5.6332900000	-0.4411400000
C	0.7566500000	5.6515700000	-0.4465300000
H	-2.3992500000	4.3894200000	-0.4377800000

C	1.4522600000	6.9458500000	-0.4580800000
H	-1.1869100000	7.4866700000	-1.3426000000
H	-2.4947100000	6.7027200000	-0.4493100000
H	-1.1773100000	7.5214500000	0.4041500000
H	1.1666300000	7.5577100000	0.4023600000
H	2.5330700000	6.8228900000	-0.4543700000
H	1.1761300000	7.5285400000	-1.3428800000
Cs	-0.1244600000	-3.2038300000	2.3054600000

Table S8. Atomic coordinates for optimised structure of 1:1 non-covalent complex labelled as **1_C_convex** (DFT/PSPW/Vosko).

	x	*y*	*z*
C	-0.0240500000	-3.4374400000	-0.2208500000
C	-1.2860400000	-3.9131100000	0.0600600000
H	2.0295100000	-5.8099100000	0.8767900000
H	-4.8287200000	-0.8985400000	0.9109700000
C	-1.3090500000	-5.2395400000	0.4666800000
H	-3.2283600000	0.9480200000	0.6580000000
C	-0.0963900000	-5.8933500000	0.6514900000
H	-2.2319800000	-5.7426000000	0.7272000000
C	1.1467700000	-5.2747100000	0.5518700000
H	-0.1252200000	-6.9196400000	0.9933500000
C	1.2020600000	-3.9530000000	0.1338000000
N	0.0042200000	-2.0826200000	-0.3911800000
C	2.9732800000	-0.1940400000	0.6341800000
H	4.8130900000	-1.1010100000	1.1781400000
C	1.2614300000	-1.6503700000	0.0062700000
C	2.0643800000	-2.7836600000	0.2435500000
C	1.6620700000	-0.3441000000	0.2040500000
H	3.3239800000	0.8118700000	0.8247900000
C	0.7933600000	0.8307800000	0.0541700000
C	3.3695400000	-2.5728700000	0.6419500000
H	4.0275400000	-3.4072600000	0.8466200000
C	3.8035500000	-1.2767700000	0.8318900000
C	-1.2506000000	-1.6196400000	-0.0461200000
C	-1.5890200000	-0.2993500000	0.1314600000
C	-2.1119700000	-2.7204800000	0.1401200000
H	-4.1437500000	-3.2342800000	0.6268500000
C	-3.4261700000	-2.4400000000	0.4621300000
C	-2.9200000000	-0.0734200000	0.4764200000
C	-0.6429900000	0.8208400000	-0.0176000000
C	-3.8080500000	-1.1197700000	0.6252100000
C	-0.6457200000	3.1277200000	-0.1525300000
N	-1.3031400000	1.9561800000	-0.2098700000
N	1.4588600000	1.9898600000	0.0277200000
C	0.7513000000	3.1467000000	0.0118900000
C	-1.3803200000	4.3119800000	-0.1564300000
C	1.3727700000	4.3848100000	0.1841200000
H	2.4475000000	4.4112100000	0.3269200000
C	-1.5400900000	6.7540900000	0.2008000000
C	-0.7669900000	5.5087200000	0.0712000000
C	0.6409600000	5.5403500000	0.2321700000
H	-2.4590000000	4.2456900000	-0.2565100000

C	1.2832700000	6.8374900000	0.4776500000
H	-1.2444000000	7.5004800000	-0.5425800000
H	-2.6101200000	6.5774100000	0.0974200000
H	-1.3713500000	7.2246300000	1.1747600000
H	0.8647300000	7.3203100000	1.3676800000
H	2.3574900000	6.7442900000	0.6195400000
H	1.1001600000	7.5380700000	-0.3431600000
Cs	-0.8759200000	-0.2472700000	-3.2072300000

Table S9. Atomic coordinates for optimised structure of 1:1 non-covalent complex labelled as **1_D_concave** (DFT/PSPW/Vosko).

	x	*y*	*z*
C	-1.0598100000	-2.9670600000	-0.6624200000
C	-2.3137200000	-3.3448700000	-0.2395800000
H	0.7693500000	-5.7273400000	-0.8704400000
H	-5.3585600000	-0.0683600000	1.3212500000
C	-2.4383600000	-4.7207900000	-0.1601300000
H	-3.6074200000	1.6179100000	1.0120400000
C	-1.3170600000	-5.5086500000	-0.4389300000
H	-3.3583000000	-5.2021800000	0.1476300000
C	-0.0457900000	-5.0273000000	-0.7402900000
H	-1.4414800000	-6.5817300000	-0.3745300000
C	0.1220400000	-3.6490100000	-0.8336600000
N	-0.8837600000	-1.6349300000	-0.6189400000
C	2.4081100000	-0.1359600000	-0.6082200000
H	4.1978600000	-1.2280400000	-0.9717000000
C	0.4451600000	-1.3688800000	-0.6667400000
C	1.1292100000	-2.5985600000	-0.8687000000
C	1.0206200000	-0.1310200000	-0.5051700000
H	2.9152600000	0.8174900000	-0.5231100000
C	0.2544200000	1.1165600000	-0.2889100000
C	2.5073800000	-2.5318800000	-0.9988300000
H	3.0932600000	-3.4184400000	-1.2082000000
C	3.1232300000	-1.2978900000	-0.8595400000
C	-2.0061000000	-1.0617200000	-0.0736700000
C	-2.1691900000	0.2672200000	0.2343200000
C	-2.9588000000	-2.0878000000	0.1248900000
H	-4.9798600000	-2.4325200000	0.7826700000
C	-4.1913600000	-1.7084700000	0.6235600000
C	-3.4181900000	0.5834400000	0.7556600000
C	-1.1435700000	1.3018600000	0.0266200000
C	-4.3992100000	-0.3765700000	0.9255900000
C	-0.8139600000	3.5873300000	0.0514300000
N	-1.6403000000	2.5299500000	0.1953700000
N	1.0565700000	2.1676400000	-0.4124400000
C	0.5474200000	3.4044900000	-0.2534400000
C	-1.2997800000	4.8824600000	0.2152100000
C	1.3749800000	4.5164700000	-0.3993500000
H	2.4191100000	4.3520700000	-0.6438700000
C	-1.0015600000	7.3363600000	0.2362700000
C	-0.4831200000	5.9682900000	0.0698700000
C	0.8837900000	5.7819300000	-0.2455900000
H	-2.3487900000	5.0103200000	0.4584200000

C	1.7460900000	6.9630800000	-0.4070300000
H	-0.8562600000	7.9314900000	-0.6708300000
H	-2.0610200000	7.3431300000	0.4840700000
H	-0.4623600000	7.8713000000	1.0254600000
H	1.7715800000	7.5671100000	0.5058400000
H	2.7691100000	6.6859800000	-0.6567000000
H	1.3724600000	7.6291100000	-1.1906900000
Cs	1.9566200000	-1.8382400000	2.3912000000

Table S10. Atomic coordinates for optimised structure of 1:1 non-covalent complex labelled as **1_D_convex** (DFT/PSPW/Vosko).

	x	*y*	*z*
C	-1.1144600000	-3.0387700000	-0.1521100000
C	-2.4369000000	-3.3537200000	-0.3783800000
H	0.1259400000	-5.6971700000	1.4373900000
H	-5.6880500000	0.0433000000	-0.7208300000
C	-2.7555500000	-4.6669700000	-0.0775600000
H	-3.9241300000	1.6880700000	-0.3086300000
C	-1.7719500000	-5.4854900000	0.4760200000
H	-3.7630300000	-5.0506100000	-0.1830900000
C	-0.5137400000	-5.0409000000	0.8611300000
H	-2.0453700000	-6.5043900000	0.7193900000
C	-0.1718500000	-3.7219700000	0.5838700000
N	-0.8804700000	-1.6969500000	-0.2025800000
C	1.6676000000	-0.1992200000	1.9219300000
H	3.0584400000	-1.3360600000	3.0670700000
C	0.1757100000	-1.4412600000	0.6290500000
C	0.7085000000	-2.6779700000	1.0736500000
C	0.6023900000	-0.1915300000	1.0273800000
H	2.0197900000	0.7555700000	2.2919300000
C	0.0159600000	1.0711500000	0.5409900000
C	1.7922000000	-2.6208500000	1.9310800000
H	2.2315300000	-3.5269500000	2.3306100000
C	2.2530900000	-1.3822700000	2.3447100000
C	-2.1064100000	-1.0724000000	-0.3473400000
C	-2.3442600000	0.2765900000	-0.2303800000
C	-3.0902900000	-2.0658400000	-0.5408900000
H	-5.2016500000	-2.3643800000	-0.8258700000
C	-4.3987600000	-1.6510200000	-0.6876100000
C	-3.6761800000	0.6379000000	-0.3881800000
C	-1.3100000000	1.2879000000	0.0351700000
C	-4.6656400000	-0.2973200000	-0.6200200000
C	-0.8744500000	3.5612800000	-0.0408200000
N	-1.7189600000	2.5290800000	-0.2180900000
N	0.8685600000	2.0895200000	0.6477200000
C	0.4507400000	3.3361900000	0.3547900000
C	-1.2970200000	4.8642800000	-0.2957400000
C	1.3300400000	4.4118900000	0.4394400000
H	2.3542000000	4.2142600000	0.7372200000
C	-0.8718100000	7.2878600000	-0.4801100000
C	-0.4313800000	5.9158700000	-0.2003300000
C	0.9172900000	5.6824800000	0.1623000000
H	-2.3295000000	5.0165800000	-0.5908600000

C	1.8637700000	6.8047300000	0.2162700000
H	-0.3000600000	7.7294700000	-1.3025800000
H	-1.9272400000	7.3255900000	-0.7440600000
H	-0.7102900000	7.9436400000	0.3807200000
H	1.5349600000	7.5755500000	0.9196000000
H	2.8596300000	6.4765900000	0.5080400000
H	1.9372100000	7.3033900000	-0.7555200000
Cs	3.1551900000	-0.9375000000	-1.0143800000

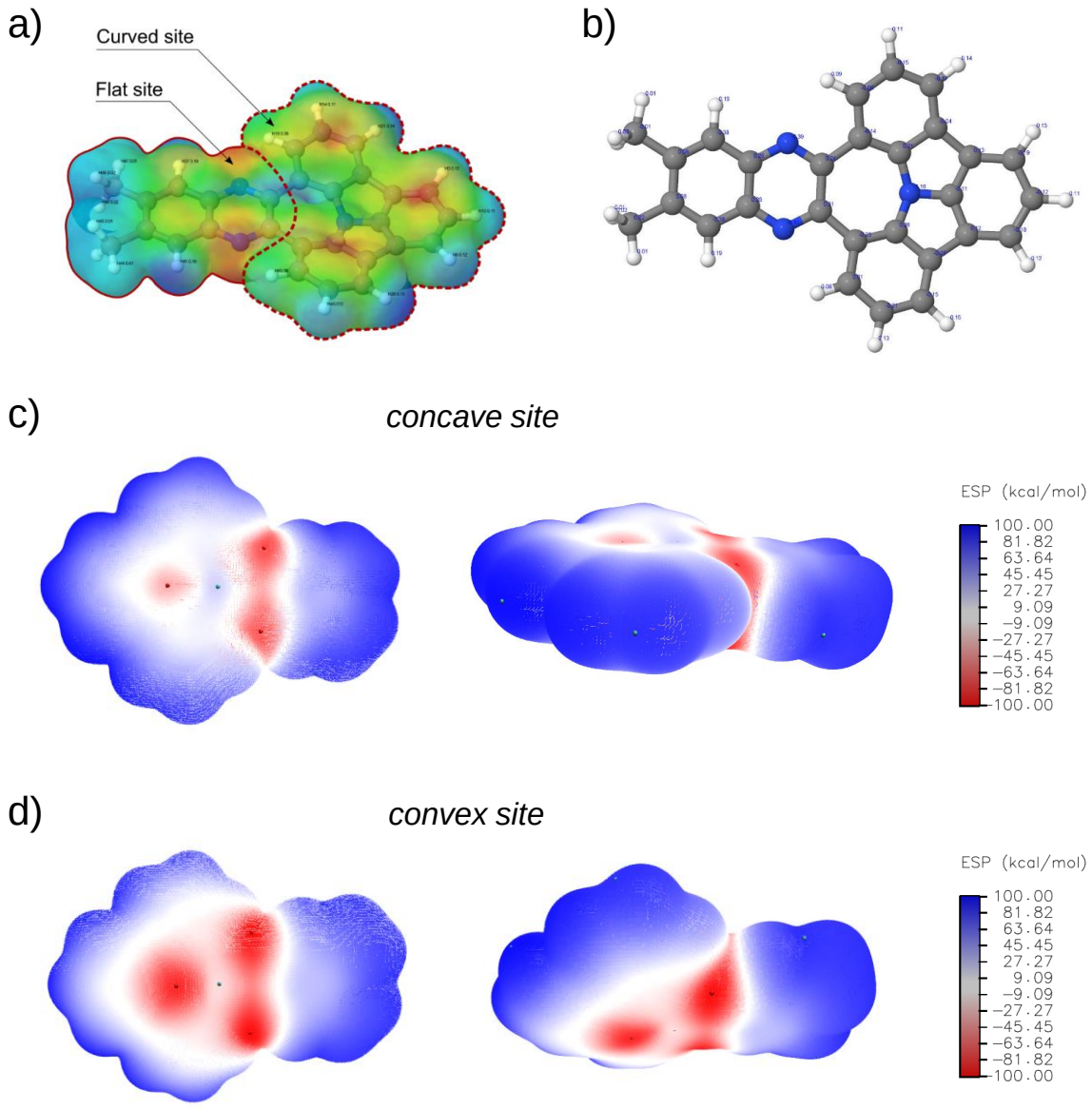


Fig. S24. Values of molecular electrostatic potential calculated around the molecule of receptor **1** using DFT (M06-2X/6-311G**) and NWChem, visualized with (**a**) Jmol, (**b**) Avogardo and (**c,d**) Multiwfn and VMD. Partial charges (electrostatic potentials) of atoms assigned to the bowl and flat site of the molecule were summed (values for each atom, presented in **b**), are given in Hartree). Sum of partial charges on atoms in the flat site is equal to 95.11 kcal/mol, whereas negative value of −95.11 kcal/mol was calculated for the bowl moiety, indicating a non-uniform charge distribution within the receptor molecule, concentrated mainly in the bowl part.

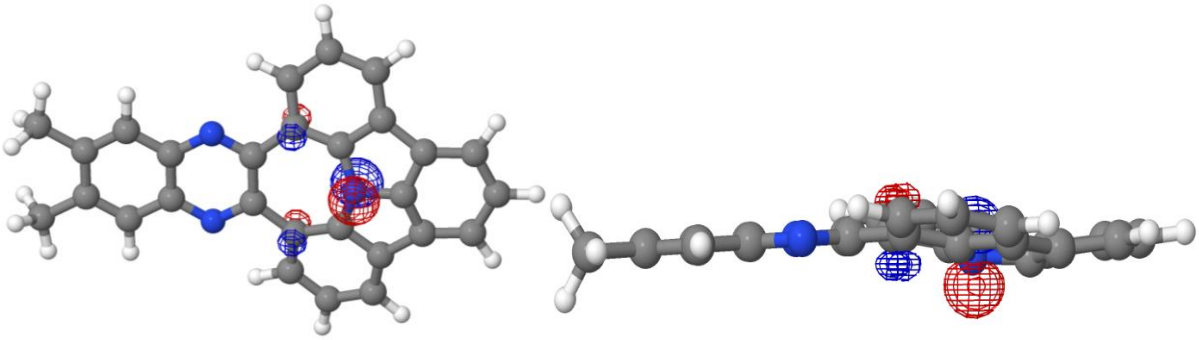


Fig. S25. 3D models of HOMO molecular orbitals in the molecule of receptor **1** calculated using DFT with M06-2X functional and 6-311G** basis set using NWChem (orbital geometry was visualized using Jmol). Similar geometry of HOMOs (localized mainly on nitrogen atom in the centre of the curved part of molecule) was calculated at both concave and convex side of the receptor molecule. Comparable charge distribution at both sides of molecule align with the previous results, indicating the formation of both concave- and convex-bound complexes.

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