Supplementary information

Selective recognition of oxalate in water: effect of pH on binding strength and sensing mechanisms

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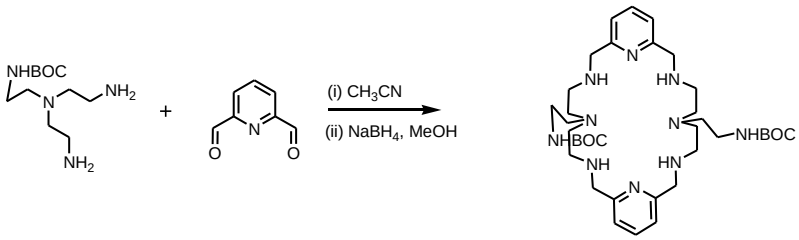
CONTENT

1 GENERAL

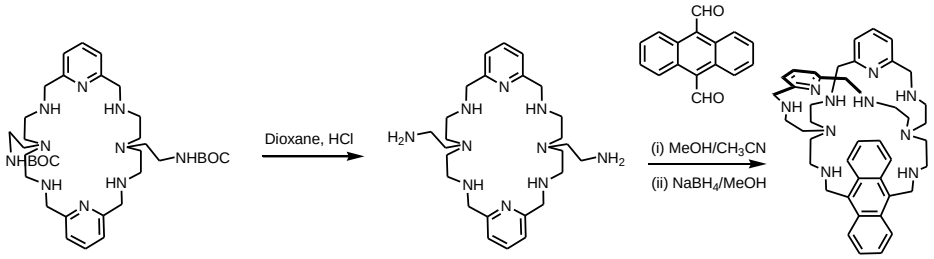
All the solvents were dried according to standard procedures. Reactions were performed in oven-dried round bottom flask. The flasks were fitted with rubber septa and the reactions were conducted under nitrogen atmosphere. Crude products were purified by column chromatography on silica gel 100-200 mesh. TLC plates were visualized by exposure to ultraviolet light and/or by exposure to acidic ethanolic solution of ninhydrin followed by heating (<1 min) on a heat gun (~250 °C). Organic solutions were concentrated on rotary evaporator at 35–40 °C. NMR Spectra**:** 1H: 400.1 MHz, 13C: 100.6 MHz, T = 300 K. The chemical shifts are reported in δ [ppm] relative to external standards (solvent residual peak). The spectra were analysed by first order, the coupling constants are given in Hertz [Hz]. Characterisation of the signals: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = double doublet. Integration is determined as the relative number of atoms. The solvent used is reported for each spectrum. Mass Spectra: ESI. Absorption and emission spectra were recorded with temperature control by use of a 1 cm quartz cuvettes and aqueous buffered solutions.

2. SYNTHESIS OF COMPOUNDS

1.1 RECEPTOR 1.

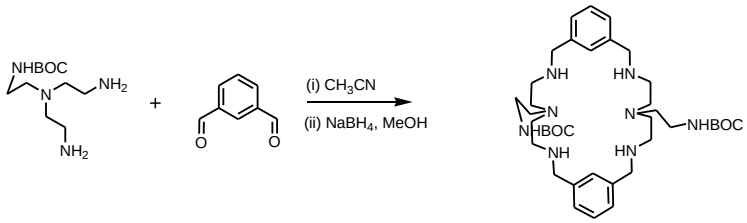


N,N-Bis(2-aminoethyl)-N-[2-(tert-butylcarbamoyl)ethyl]-amine[1] (1.4 g, 0.006 mol) was dissolved in 280 mL of CH_3CN. Under stirring, a solution of 2,6-Pyridinedicarboxaldehyde (0.8 g, 0.006 mol) in CH_3CN 150 mL was added drop wise over 2h at RT. After 20 h stirring, the solvent was removed under reduced pressure, and the crude product was diluted with 200 mL of methanol. The solution was heated to 50 °C and $NaBH_4$ was added (1.38g, 34 mmol). When the addition was complete, the reaction mixture was stirred at 70 °C for 2 h. The solvent was then removed and the residue was dissolved in basic water (20 mL, pH=9) and extracted with CH_2Cl_2 (2 x 50 mL). The collected organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography using as 94% THF/ 3% MeOH/ 3% aq.NH_3 eluent, giving the product in 45% yield as a transparent oil. ^{1}H NMR (400 MHz, CD^3OD): δ (ppm) 7.64 (t, *J* = 7.6 Hz, 2H), 722 (d, *J* = 7.6 Hz, 4H), 3.82 (s, 8H), 3.72-3.69 (m, 2H), 3.13 (t, *J* = 6.0 Hz, 4H), 2.70-2.49 (m, 20H), 1.86-1.83 (m, 3H), 1.34 (s, 18 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 160.0, 158.5, 138.7, 122.2, 79.9, 68.9, 56.0, .3, 54.8, 48.0, 39.9, 28.9, 26.6. HRMS (ESI): *m/z* calcd for $C_{36}H_{63}N_{10}O_4$: 699.5028; found: 699.5025.

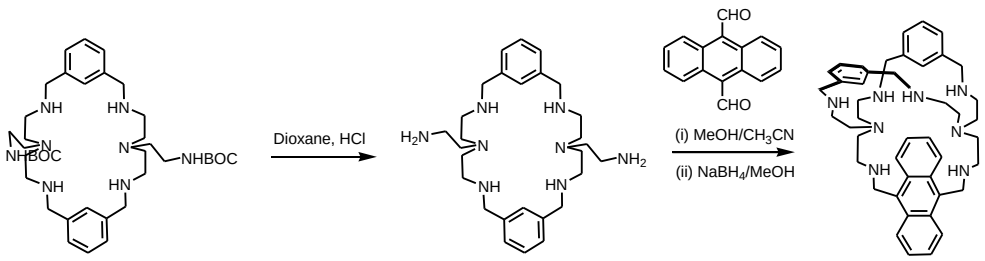


To a stirred solution of compound (200 mg) in dioxane (30 mL) was added conc. HCl (1 mL) dropwise under the nitrogen atmosphere at 0 °C. The reaction was continued stirring for 1 h at room temperature. After the solvent was removed in vacuo and the crude product was dissolved in basic water (20 mL, pH=9) and extracted with CH_2Cl_2 (2 x 50 mL). The collected organic phases were combined and dried over Na_2SO_4. The solvent was removed and the crude product(160 mg) was used in the next step without further purification. A solution of 9,10-anthracenedicarboxaldehyde[2] (0.13 g, 0.56mmol) in 100 ml of CH_3CN was added dropwise to a stirred solution of the BOC-protected intermediate macrocycle (0.28 g, 0.56 mmol) in 350 mL MeOH:CH_3CN mixture (1:1 ratio) over 2 h at room temperature. After 24 h stirring, CH_3CN was removed in vacuum. Then, 200 ml of MeOH was added to the reaction mixture, heated to 50 °C and reacted with $NaBH_4$(0.5 g). When the addition was complete, the reaction was stirred and refluxed for 2 h. The solvent was removed and the residue was dissolved in basic water (20 mL, 3 M NaOH) and extracted with CH_2Cl_2. The collected organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography using as 90% THF/ 5% MeOH/ 5% aq. NH_3 eluent, giving the product in 40% yield as a white solid M.p. 65-69 °C.. ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 8.388.30 (m, 4H), 7.41-7.30 (m, 6H), 6.99 (d, , *J* = 8.0 Hz, 4H), 4.66 (s, 4H), 3.42-3.21 (m, 8H), 2.90 (t, *J* = 4.0 Hz, 4H), 2.62 (t, *J* = 8.0 Hz, 4H), 2.54-2.24 (m, 16H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 159.9, 138.3, 133.3, 131.4, 127.0, 126.1, 121.5, 57.4, 55.3, 55.1, 48.7, 46.3, 31.1. HRMS (ESI): *m/z* calcd for $C_{38}H_{64}N_8O_4$: 696.5051; found: 696.5055.

1.2 RECEPTOR 2



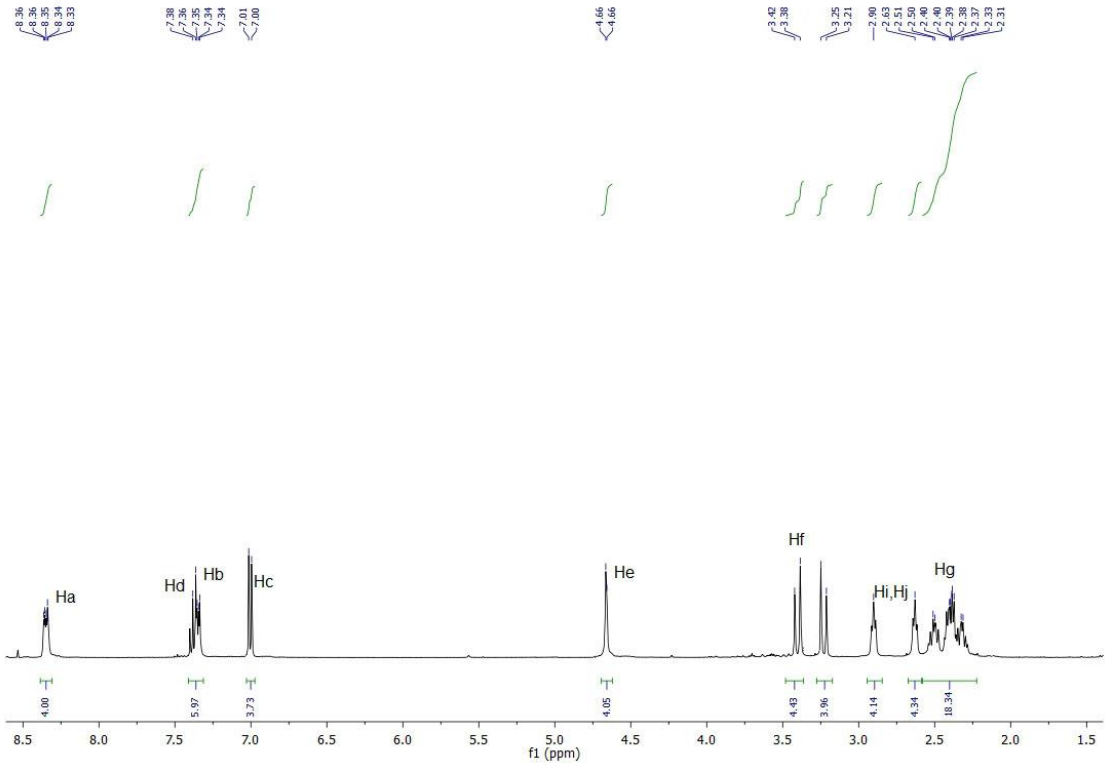
N,N-Bis(2-aminoethyl)-N-[2-(tert-butylcarbamoyl)ethyl]-amine[3] (1.4 g, 0.006 mol) was dissolved in 280 mL of CH_3CN. Under stirring, a solution of Isophthalaldehyde (0.8 g, 0.006 mol) in CH_3CN 150 mL was added drop wise over 2h at RT. After 20 h stirring, solvent was removed under reduced pressure, and the crude product was dilution with 200 mL of methanol. The solution was heated to 50 °C and hydrogenated with $NaBH_4$ (1.38g, 34 mmol). When the addition was complete, the reaction mixture was stirred at 70 °C for 2 h. The solvent was then removed and the residue was dissolved in basic water (20 mL, pH=9) and extracted with CH_2Cl_2 (2 x 50 mL). The collected organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography using as 94% THF/ 3% MeOH/ 3% aq.NH_3 eluent, giving product as a transparent oil in a 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.32 (s, 2H), 7.20-7.11 (m, 6H), 3.78-3.65 (m, 12H), 3.14 (bs, 4H), 2.68-2.48 (m, 20H), 1.88-1.79 (m, 4H), 1.32 (s, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 156.4, 140.2, 127.9, 126.6, 78.2, 67.9, 54.4, 53.6, 52.9, 46.6, 28.3, 25.5. HRMS (ESI): *m/z* calcd for $C_{36}H_{64}N_{10}O_4$: 697.5123; found: 697.55124.

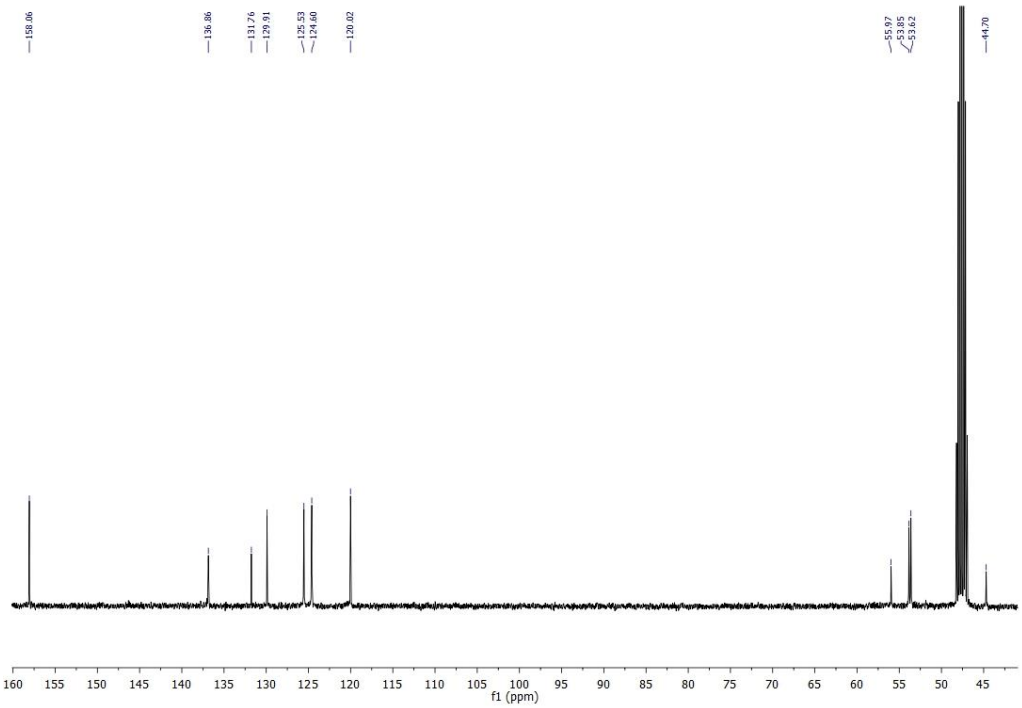


To a stirred solution of compound **7a** (200 mg) in dioxane (30 mL) at room temperature was added con. HCl (1 mL) drop wise under nitrogen atmosphere at 0 ^{o}C. The reaction was continued stirring for 1 h at room temperature. After the solvent was removed in vacuo and the crude product was dissolved in basic water (20 mL, pH=9) and extracted with CH_2Cl_2 (2 x 50 mL). The collected organic phases were dried over Na_2SO_4. The solvent was removed under reduced and crude product was used to next step without further purification (150 mg). A solution of 9,10-anthracenedicarboxaldehyde[4] (0.13 g, 0.56mmol) in 100 ml of CH_3CN was added drop wise to a stirred solution of the intermediate macrocycle **7b** (0.28 g, 0.56 mmol) in 350 mL MeOH:CH_3CN mixture (1:1 ratio) over 2 h at room temperature. After 24 h stirring, CH_3CN was removed in vacuum. Then, 200 ml of MeOH was added to the reaction mixture, heated to 50 °C and hydrogenated with $NaBH_4$(0.5 g). When the addition was complete, the reaction was stirred and refluxed for 2 h. Then solvent was removed and the residue was dissolved in basic water (20 mL, 3 M NaOH) and extracted with CH_2Cl_2. The collected organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography using as 88% DCM/ 10% MeOH/ 2% aq. NH_3 eluent, giving product **7** in 38% yield. Solid, m.p. 55-59 °C.; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.44 (dd, *J* = 3.2 Hz, 3.6 Hz, 4H), 7.46 (dd, *J* = 3.2 Hz, 3.6 Hz, 4H), 6.85 (bs, 6H), 6.23 (s, 2H), 4.71 (s, 4H), 3.42 (s, 2H), 3.17-2.95 (m, 12H), 2.67-2.35 (m, 20H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 140.1, 12.3, 10.0, 127.6, 127.1, 126.2, 125.7, 125.0, 55.6, 54.2, 53.0, 48.4, 47.0, 46.4. HRMS (ESI): m/z calcd for $C_{44}H_{58}N_8$: 699.4857; found: 699.4862.

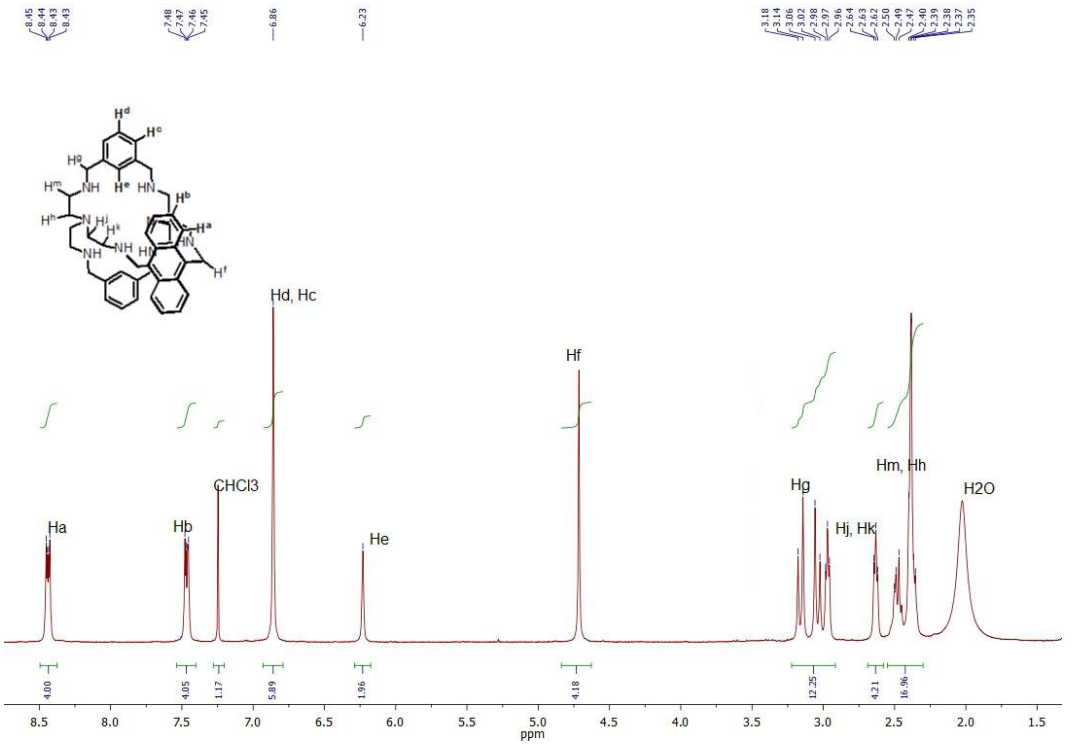
2 NMR SPECTRA

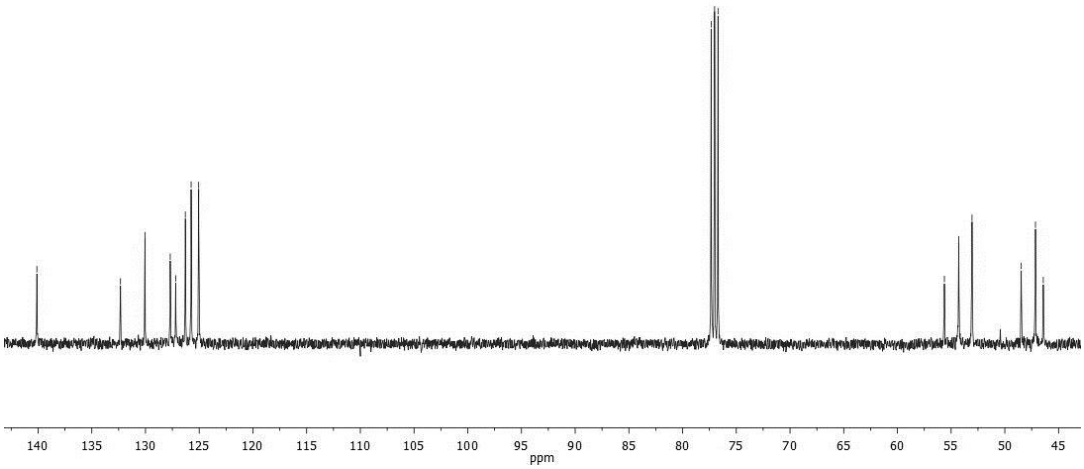
Receptor 1 (^{1}H, ^{13}C)



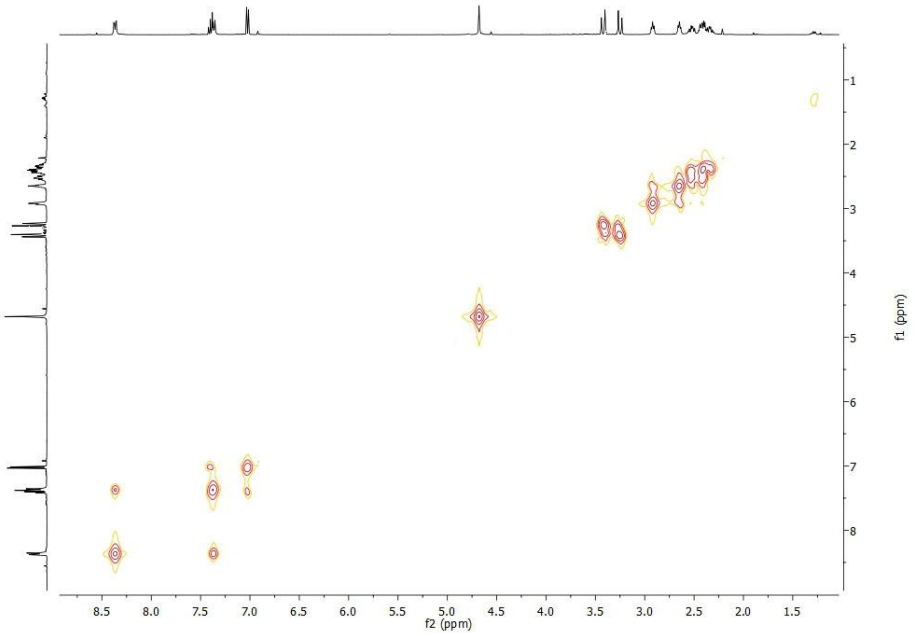


Receptor 2 (^{1}H, ^{13}C)

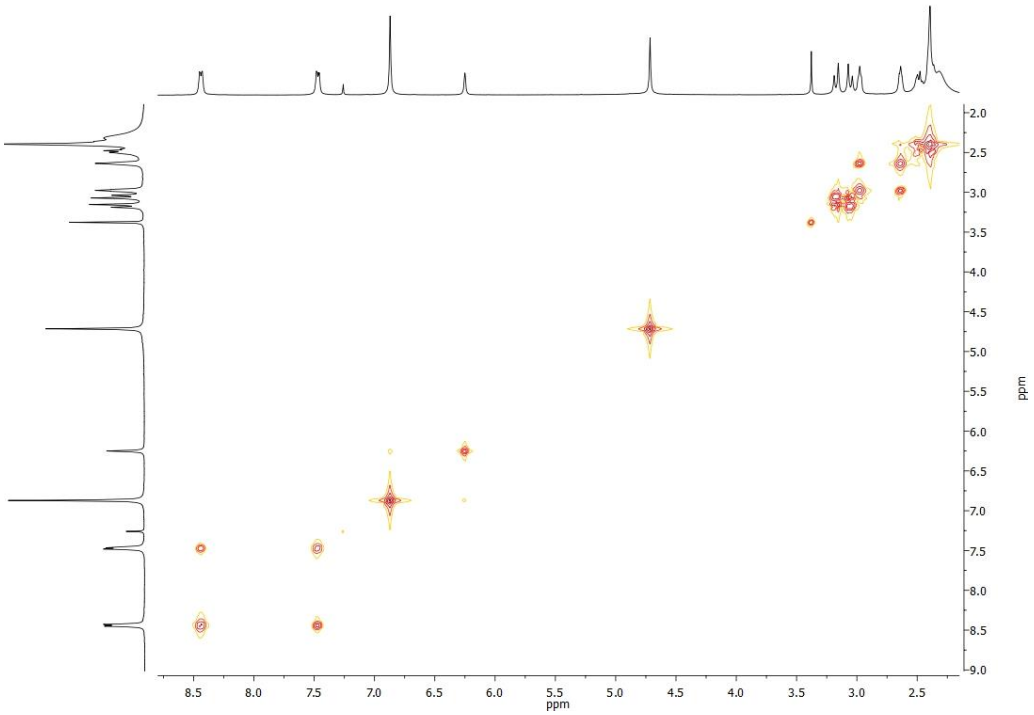

Hd, Hc
Hf
CHCl3
Ha
Hb
He
Hg
Hj, Hk
Hm, Hh
H2O
ppm


ppm

Receptor 1 (^{1}H- ^{1}H COSY) $CDCl_3$



Receptor 2 (^{1}H- ^{1}H COSY) $CDCl_3$



3 X-RAY ANALYSIS

The ligand was crystallized from MeOH-water solution in the presence of 5 equiv. of oxalic acid by slow evaporations. Data were collected with an Oxford Gemini S diffractometer, with graphite monochrmated Cu $K_{\square}$ radiation ($\square$ = 1.54184 Å). The structure were solved by direct methods and refined by full-matrix least-squares procedures on F^2.[5] All non-hydrogen atoms were refined anisotropically. All hydrogen atom positions, except for *N*-bonded hydrogen atoms, were refined using a riding model. The position of the *N*-bonded hydrogen atom of the ligand was taken from the difference Fourier map and refined isotropically.

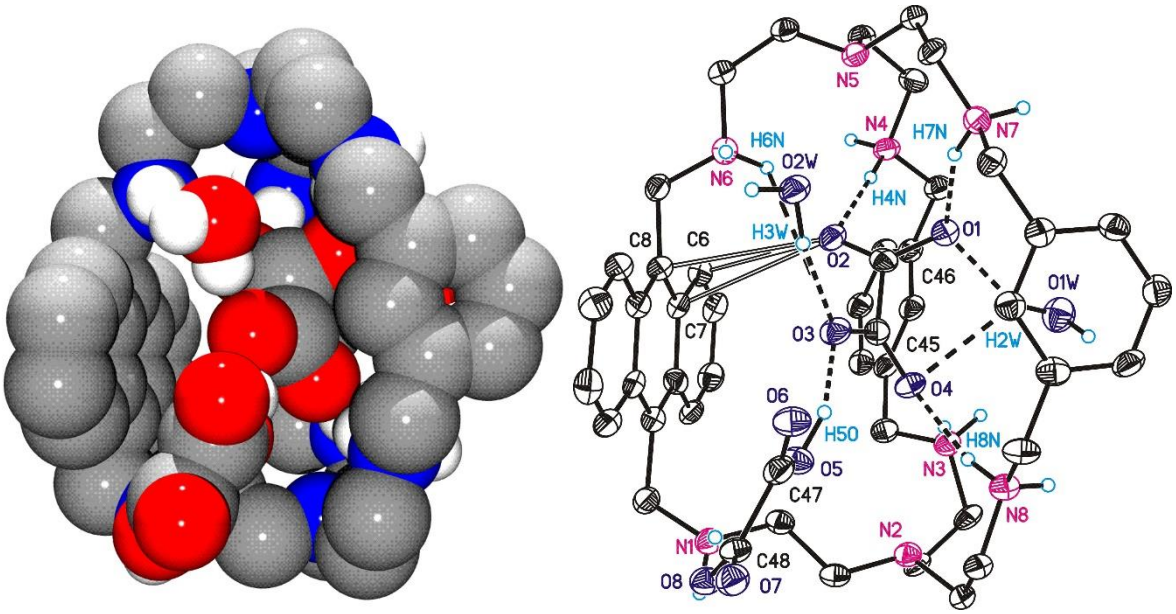
CCDC- 1557902 of the ligand contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Selected data of bond distances (Å) and angles (°) of the hydrogen bonds of the oxalate complex.

D–H···A[1)]	D···A	D–H···A
*Hydrogen bonds involving the encapsulated oxalate of $[H_6$**2**$(Ox)]^{4+}$*		
O1W–H2W···O1	2.78(1)	146(10)
O2W–H3W···O3	2.789(9)	163(8)
O1W–H2W···O4	3.303(9)	131(19)
N7–H7N···O1	2.806(10)	159(7)
N4–H4N···O2	2.845(9)	174(11)
N6–H6N···O2	2.758(9)	152(6)
O5–H5O···O3	2.532(8)	153(9)
N3–H3N···O4	2.91(1)	164(6)
N8–H8N···O4	2.908(10)	166(5)
*Hydrogen bonds between Ox^{2-}, HOx^- and H_2Ox species and $\{H_6$**2**$\}^{6+}$*		
N1–H1N···O5	3.153(10)	134(4)
N1–H1N···O8	2.848(10)	151(5)
N4–H4N1···O18^{i}	2.798(10)	171(4)
N6–H6N1···O10^{ii}	3.211(10)	133(9)
N7–H7N1···O15	2.740(9)	165(6)
N7–H7N1···O16	3.106(10)	117(5)
*Hydrogen bonds between H_2O and $\{H_6$**2**$\}^{6+}$*		
N1–H1N1···O5W^{iii}	2.776(10)	154(10)
N3–H3N1···O10W^{iv}	2.68(1)	156(8)
N6–H6N1···O2W	2.857(10)	140(9)
N8–H8N1···O11W^{iv}	2.793(10)	163(6)
Hydrogen bonds between the species Ox^{2-}, HOx^- and H_2Ox		
O10–H10O···O7	2.597(9)	175(14)
O18–H18O···O13	2.558(9)	178(10)
Hydrogen bonds H_2O and the species Ox^{2-}, HOx^- and H_2Ox		
O2W–H4W···O6^{ii}	2.918(8)	143(11)
O2W–H4W···O10^{ii}	3.059(8)	111(6)
O10W–H2OW···O15	2.761(9)	168(6)
O3W–H5W···O11^{i}	2.826(11)	161(9)
O3W–H6W···O12^{iii}	2.943(11)	150(17)
O4W–H7W···O12W^{v}	2.796(11)	167(13)
O4W–H8W···O8^{vi}	2.796(10)	148(6)
O5W–H9W···O11	2.982(11)	165(7)
O5W–H10W···O12^{vii}	2.728(10)	174(9)
O6W–H11W···O7	2.840(8)	148(7)
O6W–H12W···O7W^{ii}	2.738(12)	168(7)

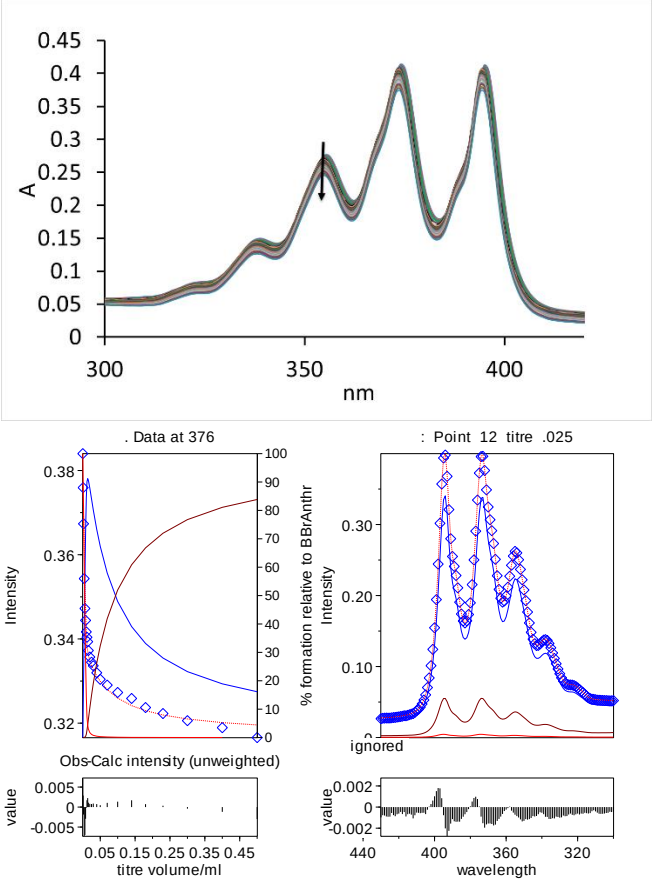
O7W–H13W···O16	2.767(13)	152(13)
O7W–H14W···O4W^{viii}	2.850(13)	118(9)
O9W–H17W···O3W^{iv}	2.896(10)	120(9)
O9W–H18W···O13	3.072(10)	131(11)
O9W–H18W···O14	2.745(10)	147(8)
O10W–H19W···O1W	2.841(10)	170(11)
O11W–H21W···O6W^{ix}	2.78(1)	169(5)
O11W–H22W···O12W	2.759(11)	174(9)
O12W–H23W···O17^{x}	2.895(11)	164(12)
O12W–H24W···O9W	2.708(12)	165(10)

[1)] Notice: Symmetry codes given here apply to hydrogen bonds of chemical species outside of the asymmetric unit to chemical species inside of the crystallographically refined asymmetric unit. Symmetry codes: *i* = –1 + *x*, *y*, *z*. *ii* = 2 – x, –y, –z. *iii* = 2 – *x*, 1 – *y*, –*z*. *iv* = 2 – *x*, 1 – *y*, 1 – *z*. *v* = 2 – *x*, –*y*, 1 – *z*. *vi* = 1 – *x*, –*y*, –*z*. *vii* = 3 – *x*, 1 – *y*, –*z*. *viii* = 1 + *x*, *y*, *z*. *ix* = *x*, *y*, 1 + *z*. x = 3 – *x*, –*y*, 1 – *z*.



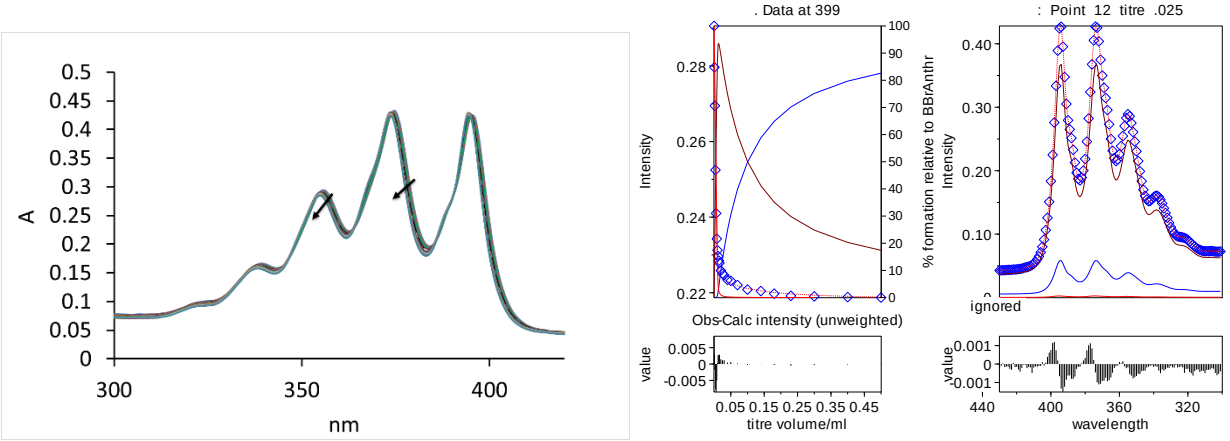
Perspective view on [H_6**2**(Ox)][HOx]·2H_2O in form of a van-der-Waals plot (left) and an ORTEP (right, 40 % probability ellipsoids). Dotted lines indicate all hydrogen bonds in which the encapsulated oxalate is involved. Open lines indicate short oxygen···carbon distance with C8–O2 = 3.348 Å, C7–O2 = 3.286 Å and C6–O2 = 3.230 Å. All carbon bonded hydrogen atoms were omitted for clarity.

4 UV-VIS TITRATIONS



$\log K_{11}$ = 6.08(6); $\log K_{12}$=2.73(7)

Figure S1. Titration of **2** with $Na_2C_2O_4$ in a 50mM acetate buffer at pH 3.6 and fitted to stepwise 1:1 and 1:2 binding mode.



$\log K_{11}$ = 6.35(9); $\log K_{12}$=3.30(7)

Figure S2. Titration of **2** with $Na_2C_2O_4$ in a 50mM acetate buffer at pH 5.6 and fitted to stepwise 1:1 and 1:2 binding mode.

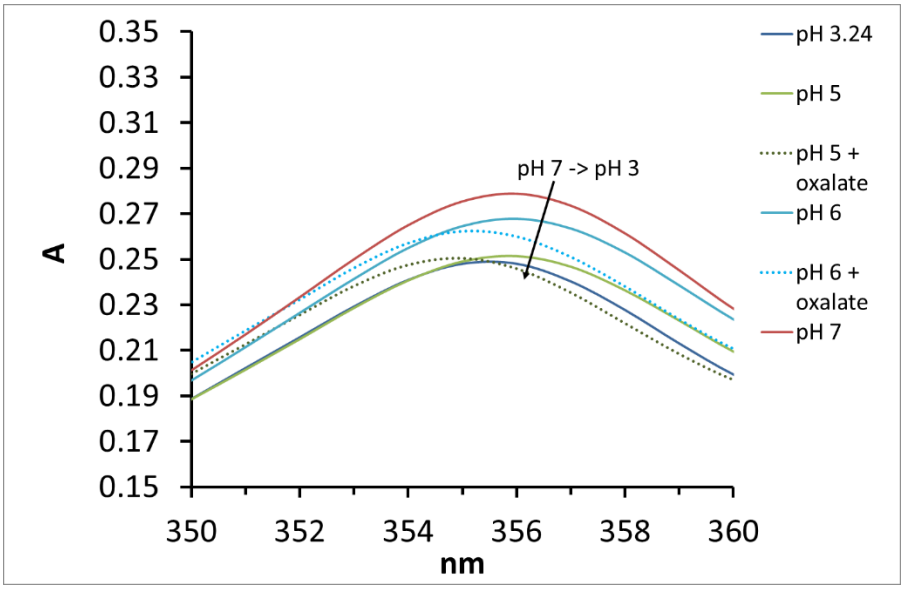


Figure S3. Overlay of UV-Vis spectra of **2** in solutions with different pH values. Corresponding spectra after addition of one equivalent of oxalate are also shown. The solutions were prepared from 50mM aqueous solution of acetic acid (+receptor) and adjusted with NaOH to a required pH value.

5 QUANTUM YIELDS

The quantum yields of the compounds were measured in a 50mM acetate buffer pH 3.6 relative to anthracene (in ethanol ϕ=0.27) and quinine sulfate (in 0.1M H_2SO_4 solution ϕ=0.54) used as references.[3]

Table S1. Quantum yields of cryptands.

Cryptand	**1**	**2**
reference	anthracene	anthracene
quantum yield	0.67	0.73

6 FLUORESCENCE TITRATIONS

The stock solutions of cryptands (10^{-5}M) in buffer were prepared in 50 ml volumetric flasks. The solutions of sodium salts (0.001-0.04M) were prepared in the solution of cryptands to keep the concentration of the cryptand constant throughout the titrations. The receptor solution in a 10mm cuvette (1.6 ml) was then titrated with the salt solution and each time the fluorescence spectrum was recorded. Following setup parameters were used; for anthracene-containing cryptands ex. 370 nm, slit 2/2, em: 380-460 nm; for naphthalimide-containing cryptands: ex. 440 nm, slit 2/2; em: 500-600 nm. The resulting data was imported in HypSpec program and the data was fitted to obtain stability constants with anions. For titrations 3 buffers were used:

1. pH 3.6: 50mM acetate buffer
2. pH 5.6: 50 mM acetate buffer
3. pH 6.2: 50 mM MOPSO buffer

6.1.1 Binding constants

Table S2. Apparent binding constants ($logK_{11}$ and $logK_{12}$ in cases when the isotherm was fitted to a 1:2 binding mode) of cryptands with anions as determined from fluorescence titrations in a 50mM acetate buffer at pH 3.6 and pH 5.6 at 23°C.

Ligand/Anion	**1**	**2**
$NaReO_4$, pH 3.6	2.52(1)	3.43(1)
pH 5.6	2.14(1)	2.72(1)
NaF, pH 3.6	3.76(1) 1:1 6.44(1) 1:2	2.00(1)
pH 5.6	1.89(1)	2.56(1)
NaCl, pH 3.6	2.66(1)	2.98(1)
pH 5.6	4.20(1) 1:1 7.42(3) 1:2	4.36(1)
NaBr, pH 3.6	4.16(1)	2.70(1)
pH 5.6	3.18(1)	2.46(1)
NaI, pH 3.6	2.83(2)	2.99(1)
pH 5.6	2.50(1)	2.56(1)
NaN_3, pH 3.6	3.15(1)	3.89(1)
pH 5.6	3.00(1)	3.80(1)

	$Na_2S_2O_3$	**$NaNO_3$**
1, pH 3.6	4.90(1)	2.91(1)
pH 5.6	3.04(1)	3.25(1)
pH 6.2	[a]	[a]
2, pH 3.6	6.55(2)	3.04(1)
pH 5.6	4.80(1)	[a]
pH 6.2	2.64(1)	1.76(3)

[a] no fluorescence changes were observed.

Table S3. Apparent binding constants ($logK_{11}$) of receptors for sodium salts of dicarboxylic acids and sodium carbonate measured in a 50 mM MOPSO buffer at 23°C.

Ligand/Anion	**2**
Fumarate	3.07(1)
Maleate	2.59(1)
Malonate	2.67(1)
Succinate	<2
Carbonate	<2

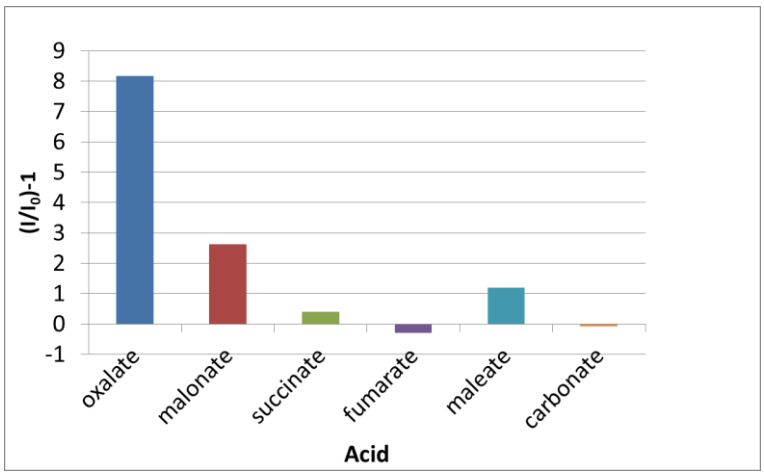


Figure S4. Fluorescence response of **2** in a 50mM MOPSO buffer (pH 6.2) after addition of 60 equiv. of diacids and carbonate.

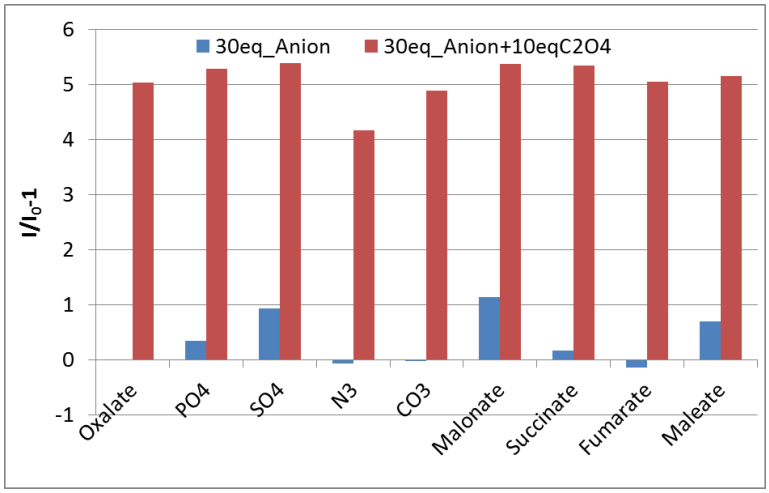


Figure S5. Detection of oxalate by **2** in the presence of other anions. Conditions: 50 mM MOPSO buffer, [**2**]=10^{-5}M.

6.1.2 Effect of pH on fluorescence intensity.

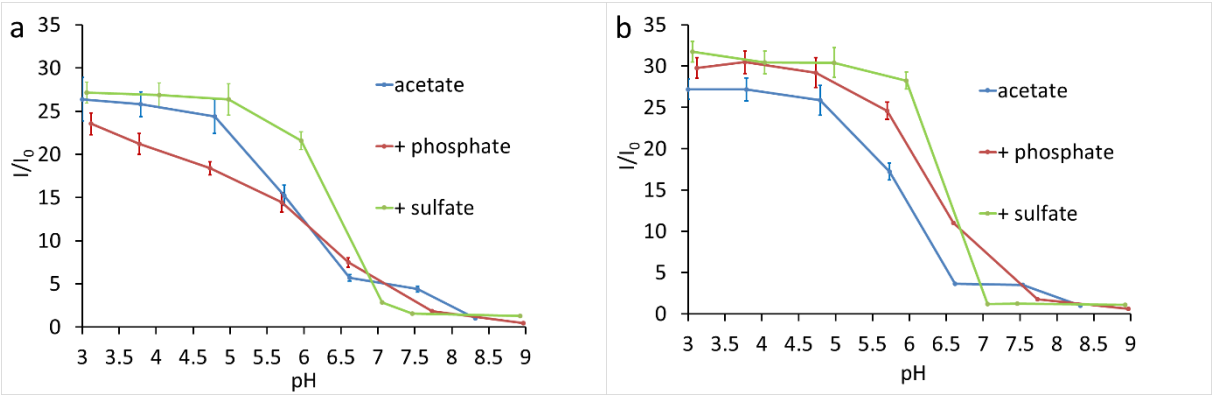


Figure S6. Effect of pH on fluorescence intensity of receptors in the presence of sulfate and phosphate: **a**, **1**; **b**, **2**. Conditions: ex. 370 nm for; 10^{-5}M receptor in a 50 mM acetate solution (acetate), 50 mM acetate solution containing 10 mM Na_2SO_4 (+ sulfate), 50 mM acetate solution containing 10mM NaH_2PO_4 (+ phosphate).

6.1.3 Titration curves for receptor 1

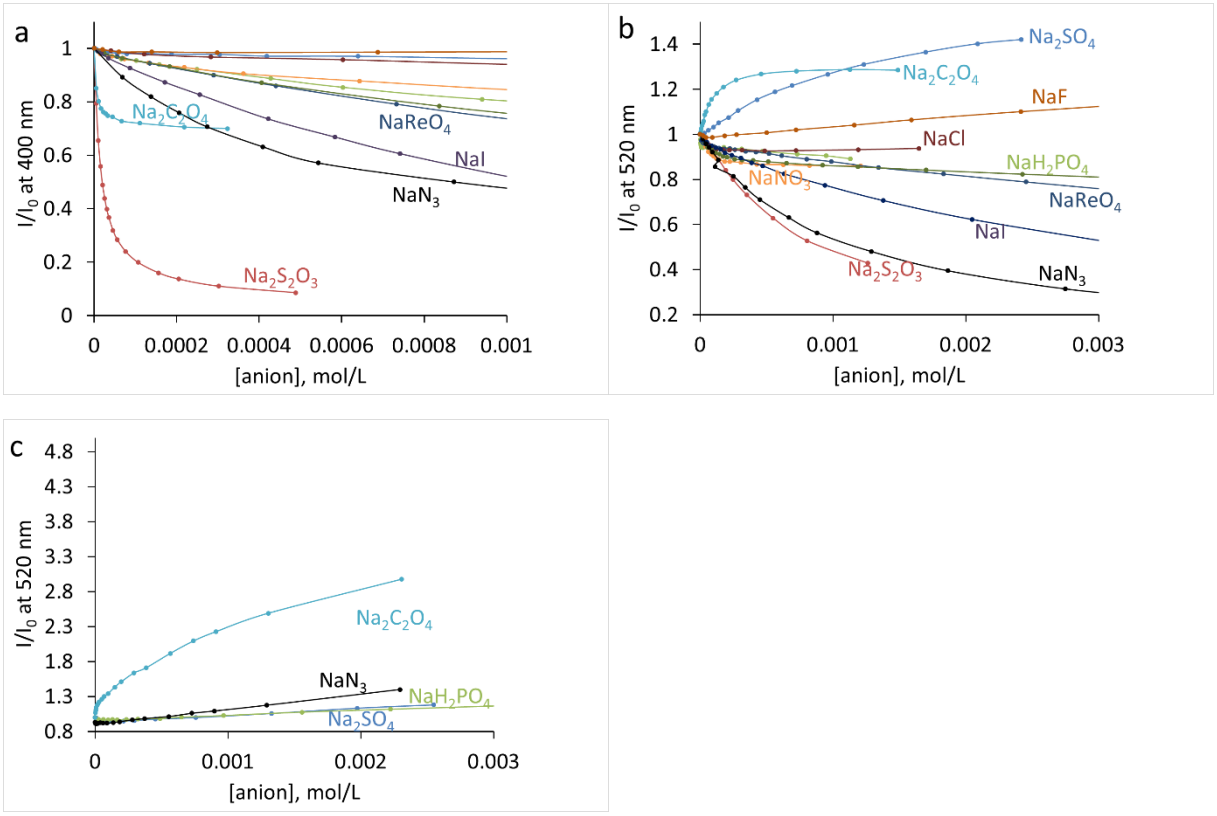
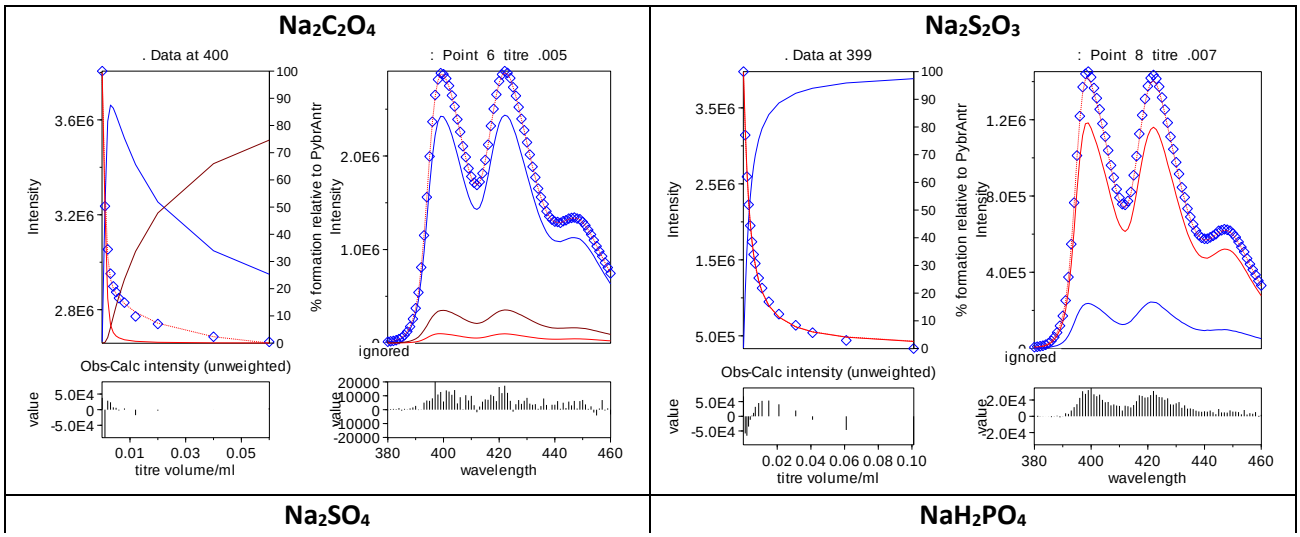
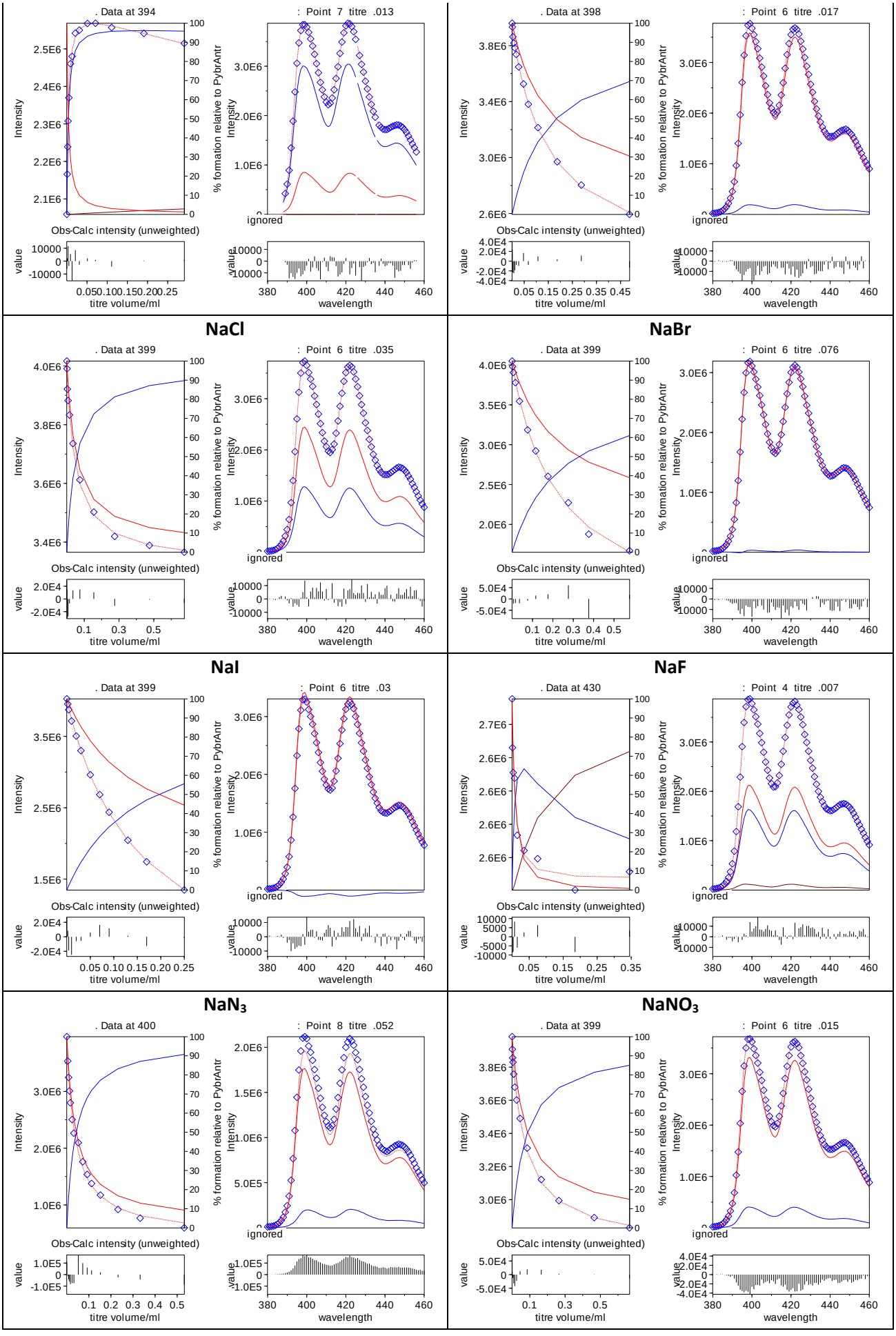
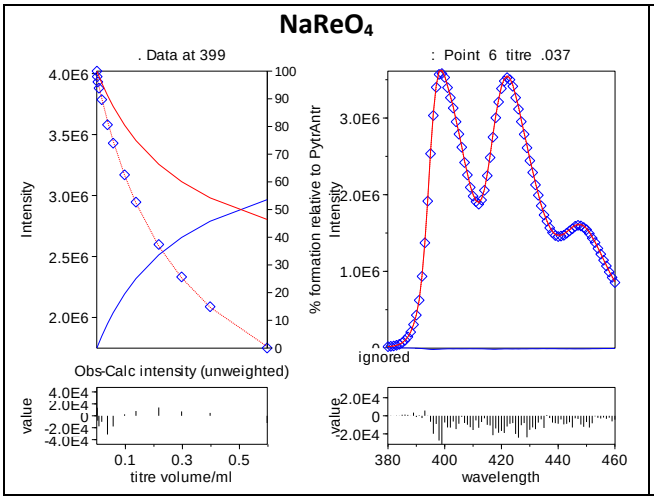


Figure S7. Fluorescence titration of receptor **1** with anions at pH 3.6 (a), pH 5.6 (b), pH 6.2 (c)

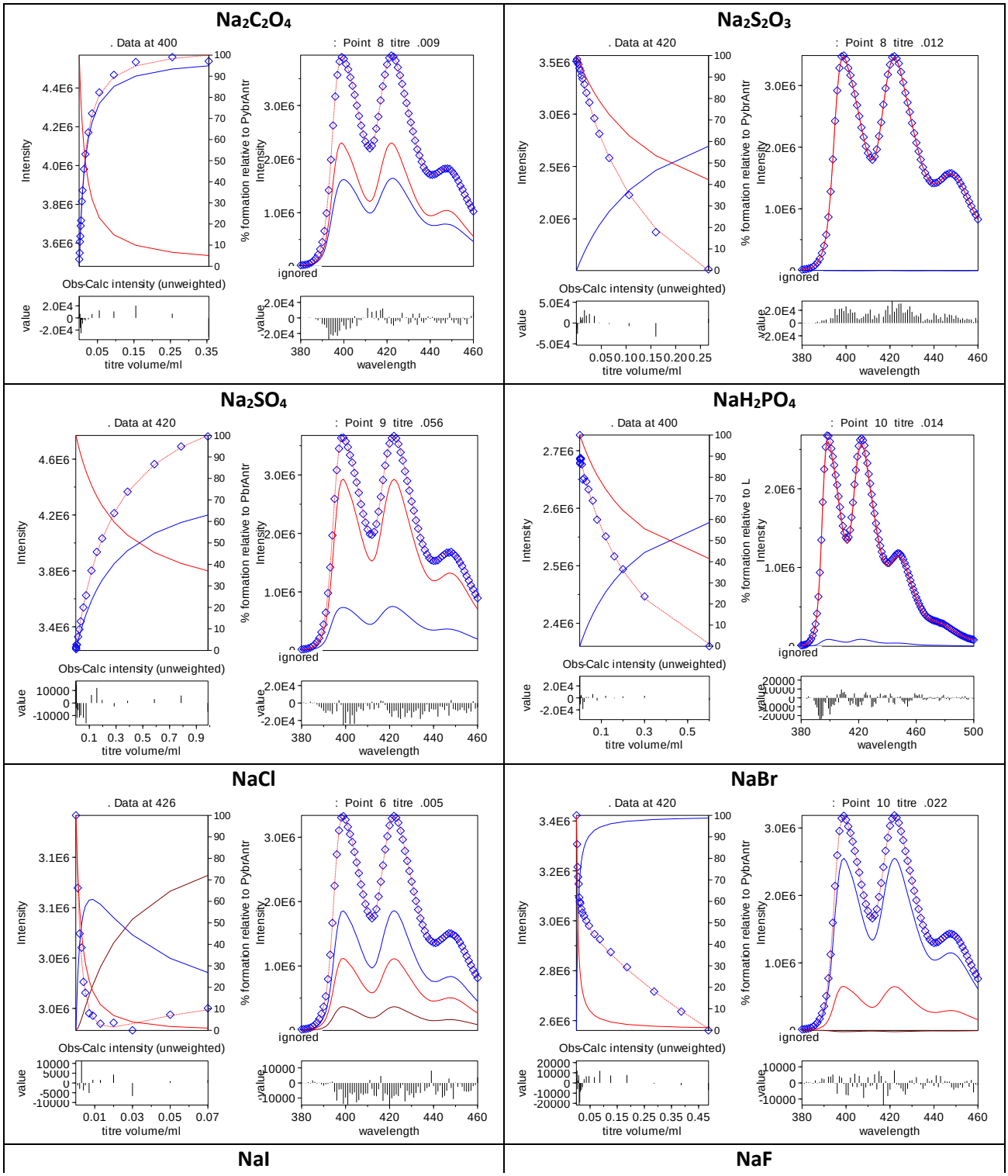
6.1.4 Receptor 1 (pH 3.6)

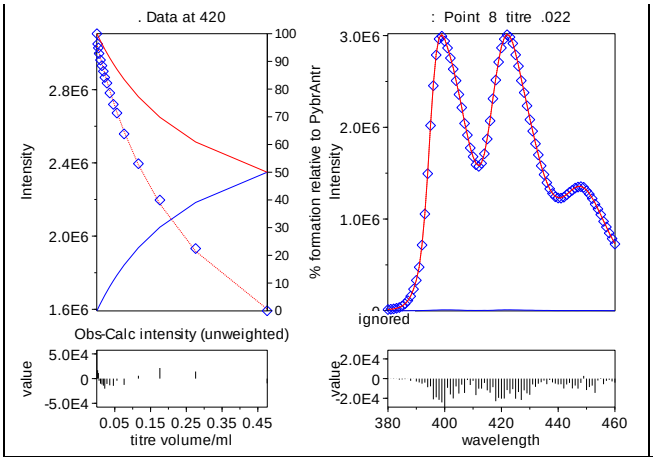


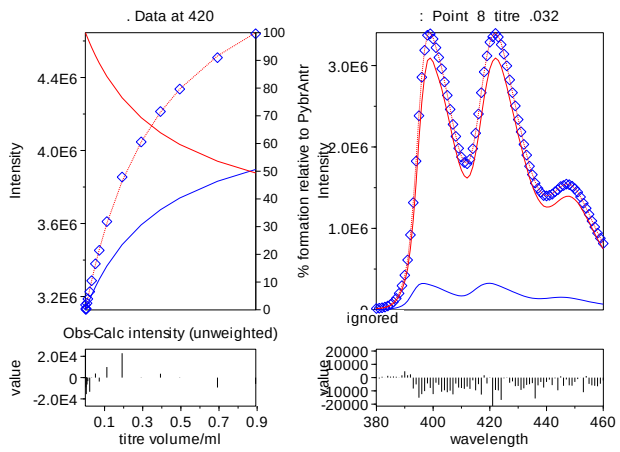

. Data at 394
: Point 7 titre .013
. Data at 398
: Point 6 titre .017
NaCl
. Data at 399
: Point 6 titre .035
NaBr
. Data at 399
: Point 6 titre .076
NaI
. Data at 399
: Point 6 titre .03
NaF
. Data at 430
: Point 4 titre .007
NaN3
. Data at 400
: Point 8 titre .052
NaNO3
. Data at 399
: Point 6 titre .015
Intensity
% formation relative to PybrAntr Intensity
ignored
Obs-Calc intensity (unweighted)
value
titre volume/ml
wavelength


NaReO4
. Data at 399
: Point 6 titre .037
Intensity
% formation relative to PytrAntr
Intensity
ignored
Obs-Calc intensity (unweighted)
value
titre volume/ml
wavelength

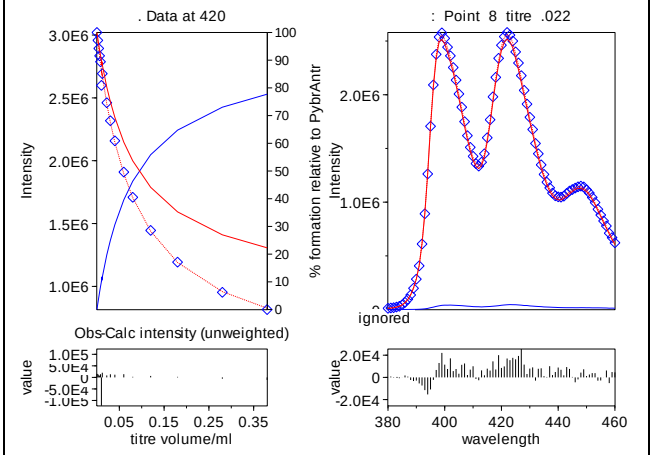
6.1.5 Receptor 1 (pH 5.6)



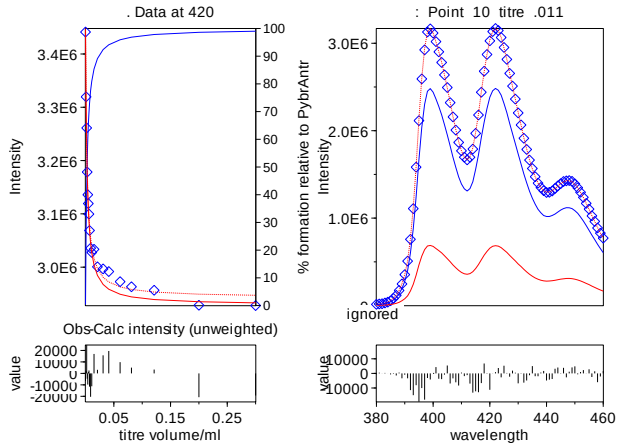




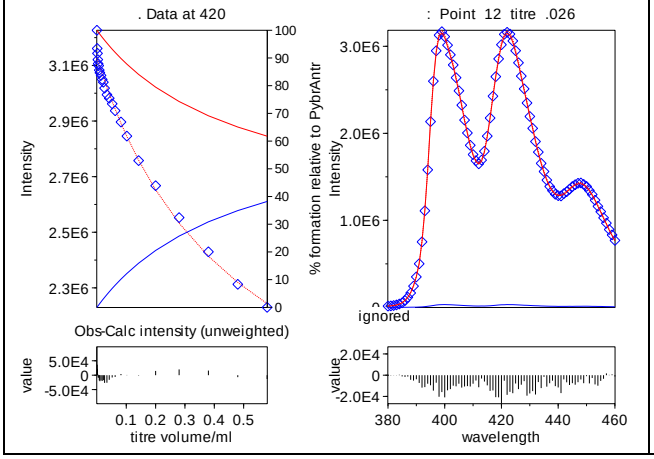
NaN_3



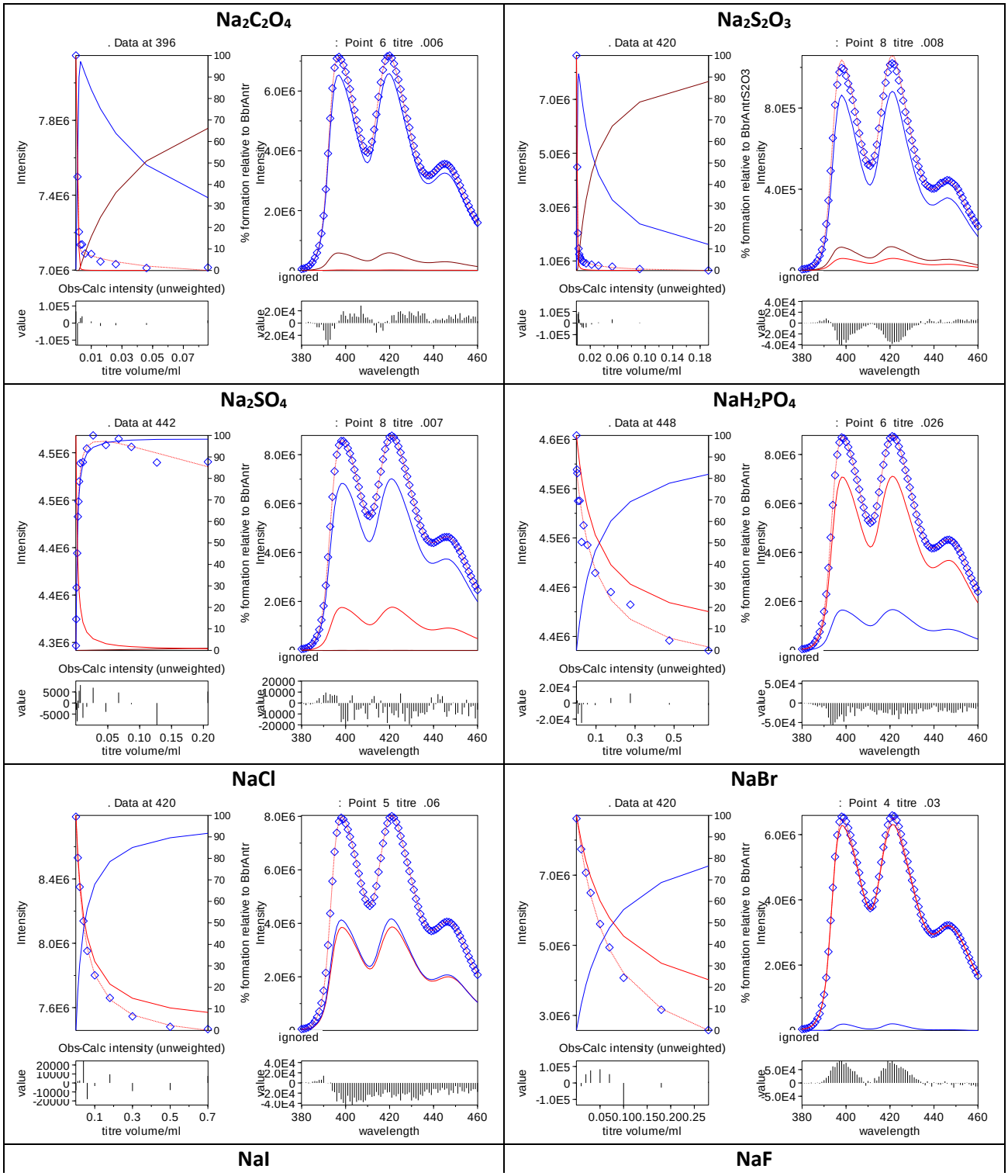
$NaNO_3$

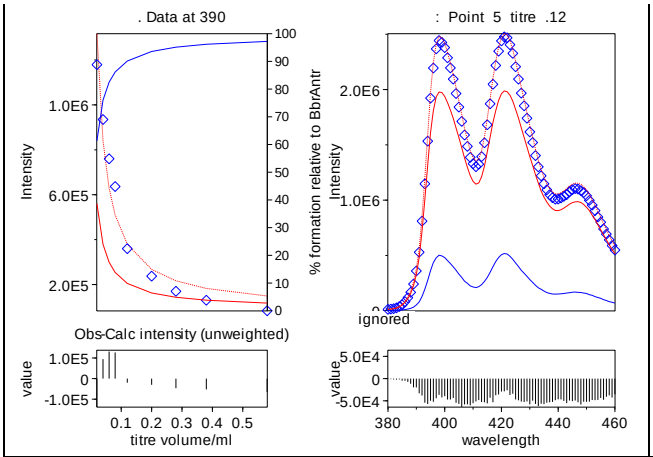


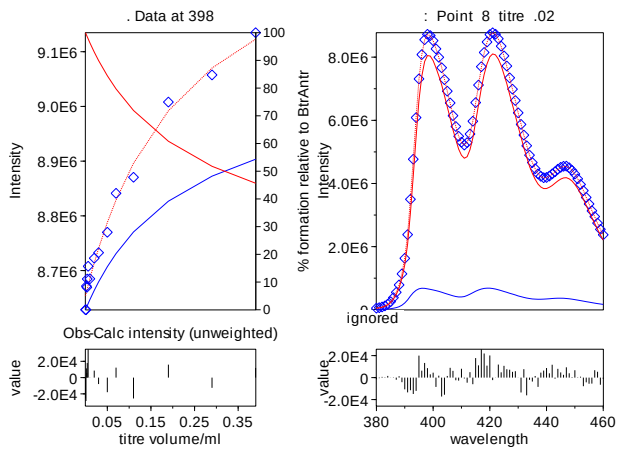
$NaReO_4$



6.1.6 Receptor 2 (pH 3.6)







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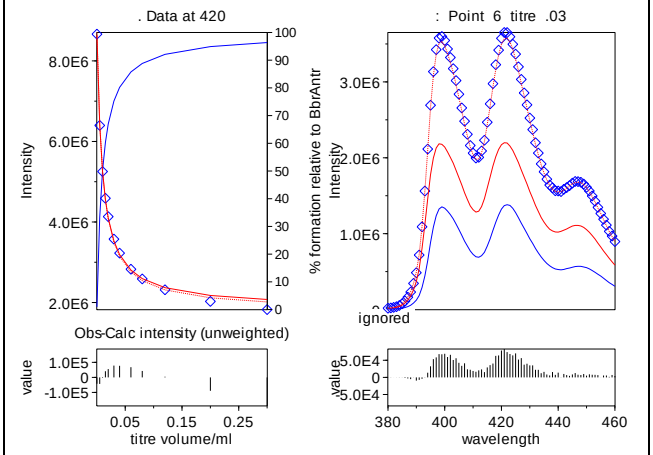
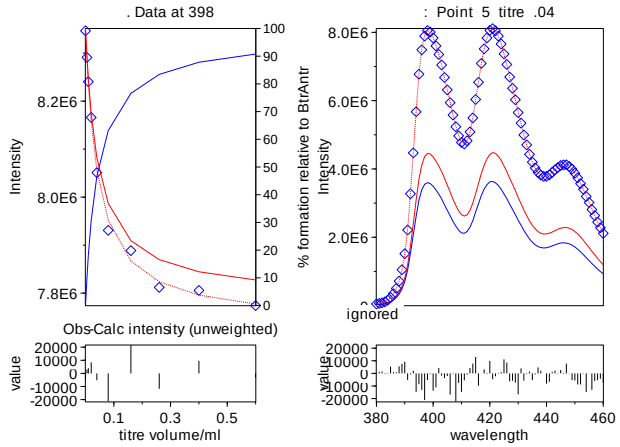
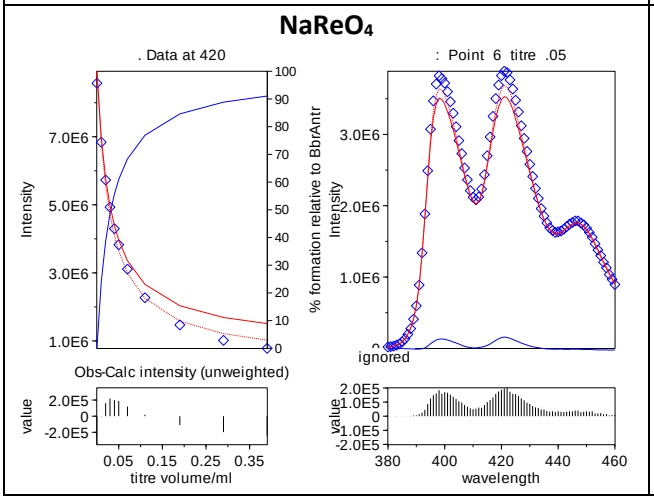


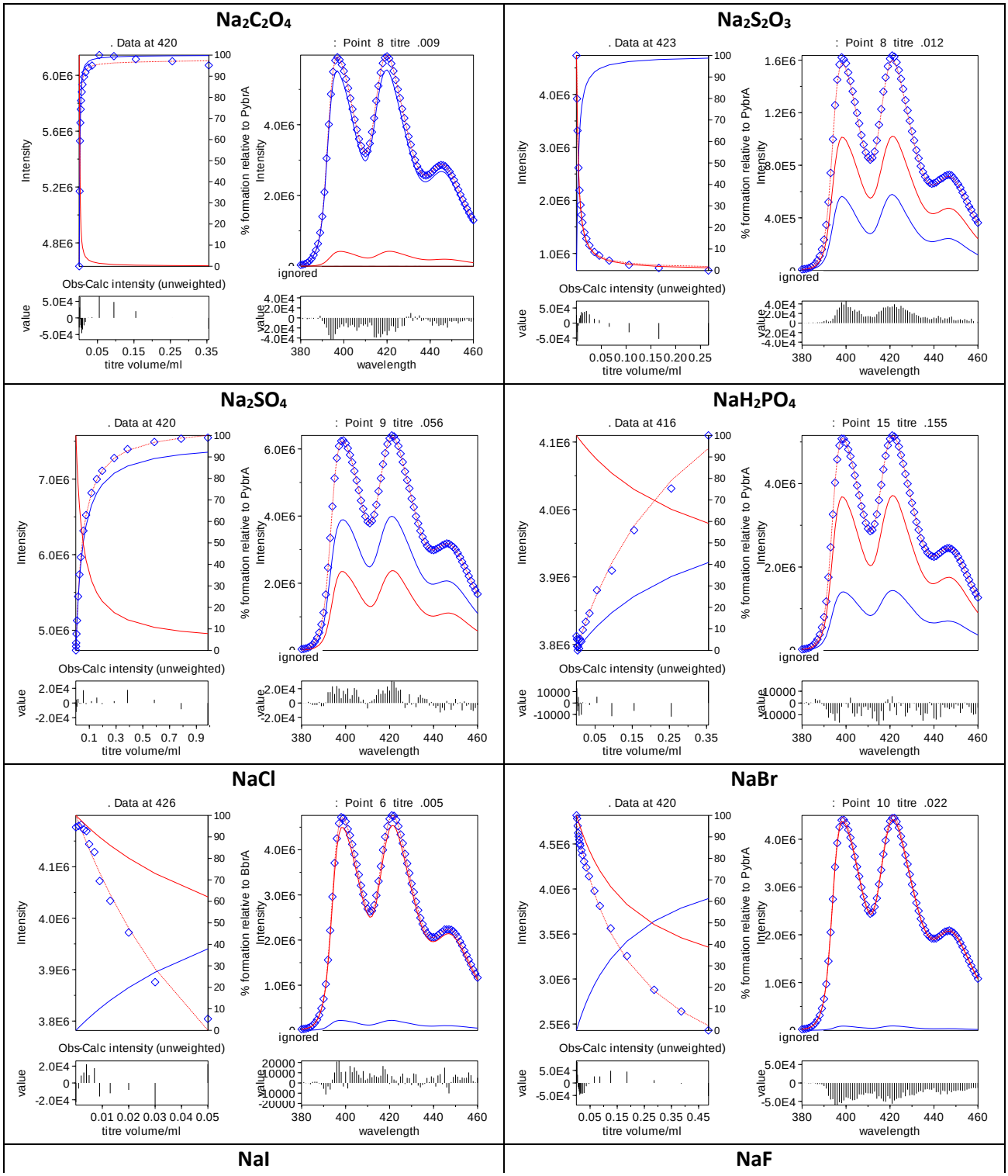
$NaNO_3$

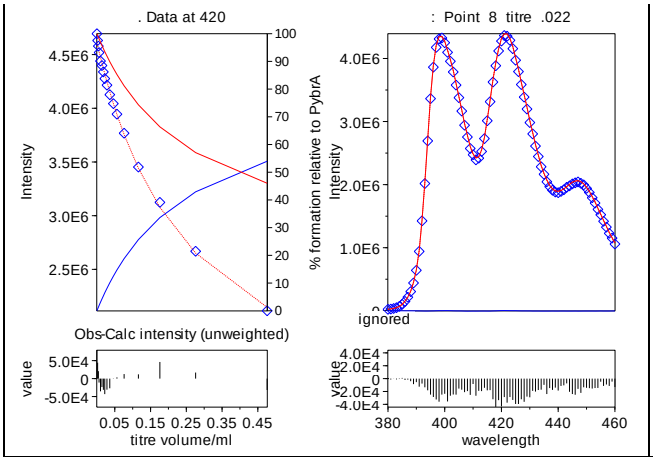


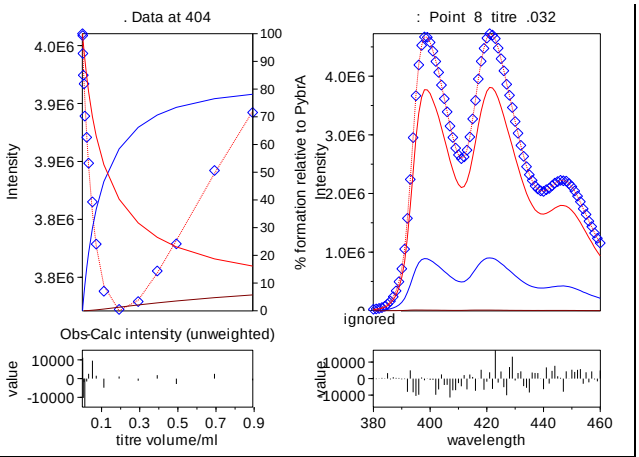
$NaReO_4$



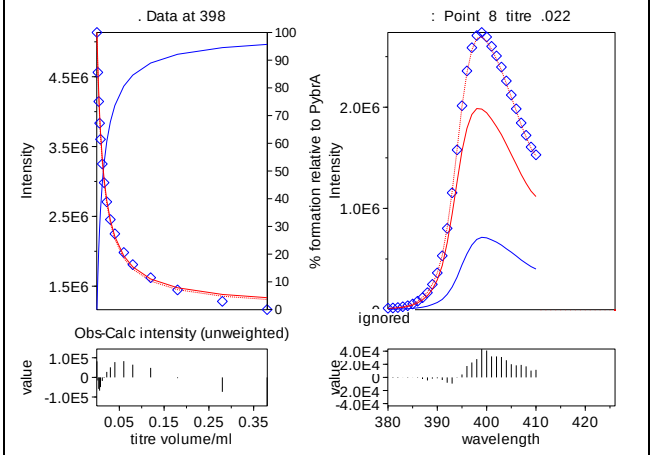
6.1.7 Receptor 2 (pH 5.6)



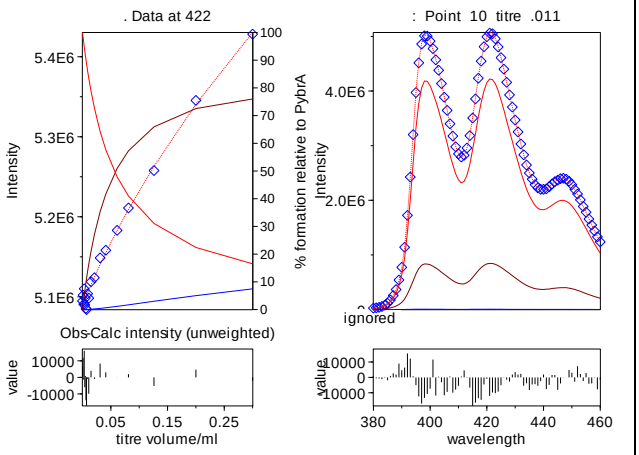




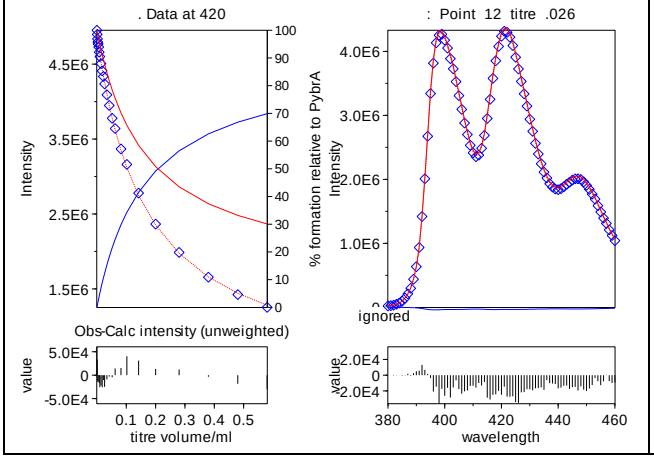
NaN_3



$NaNO_3$

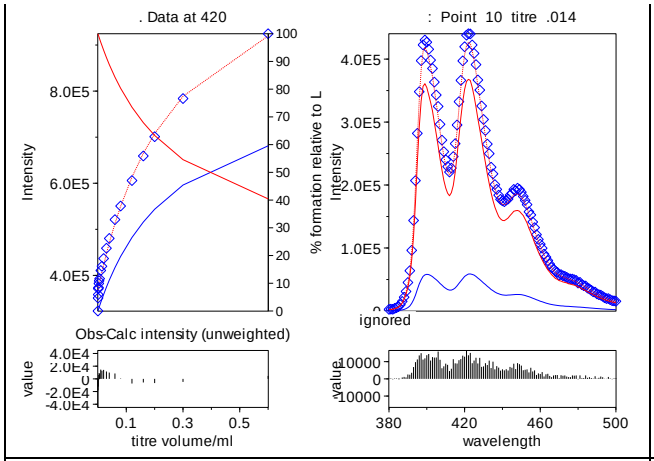


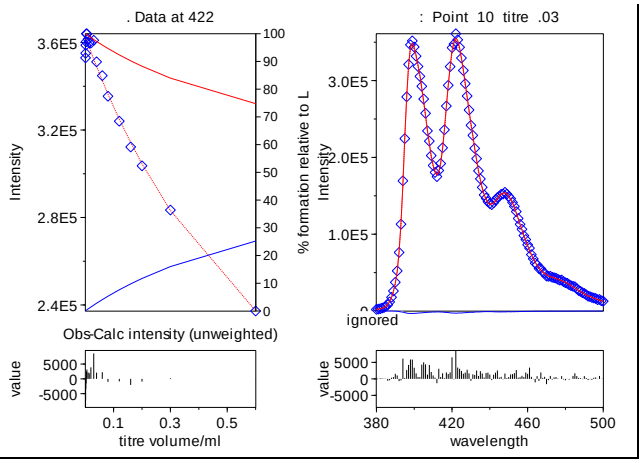
$NaReO_4$



6.1.8 Receptor 1 (pH 6.2)

$Na_2C_2O_4$	NaN3

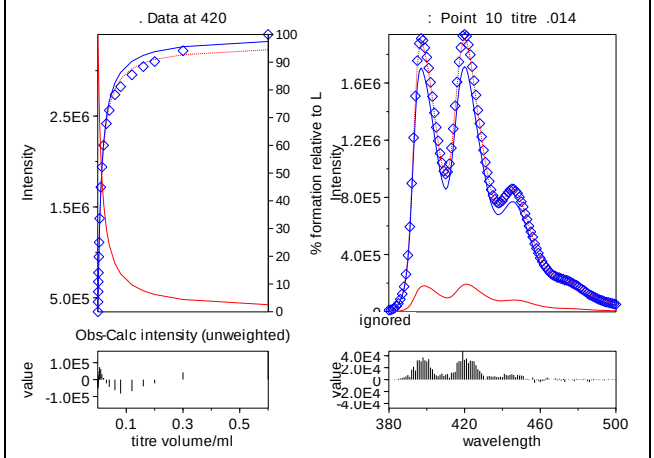




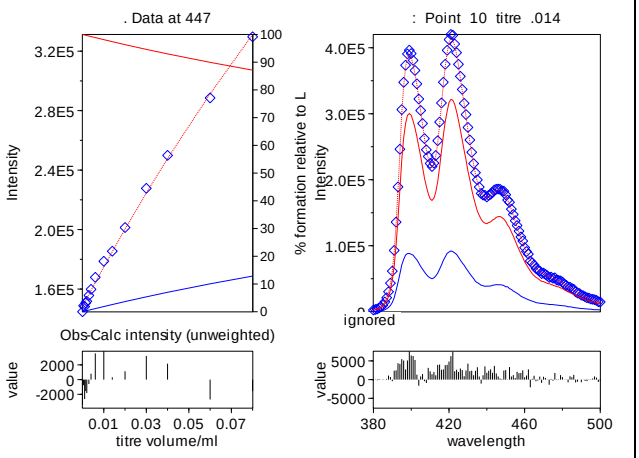
For Na_2SO_4, NaH_2PO_4, $NaNO_3$ and NaN_3 the changes in spectrum were very small

6.1.9 Receptor 2 (pH 6.2)

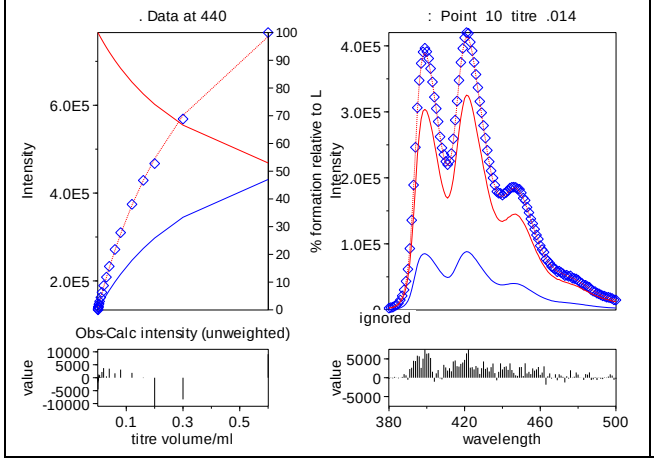
$Na_2C_2O_4$



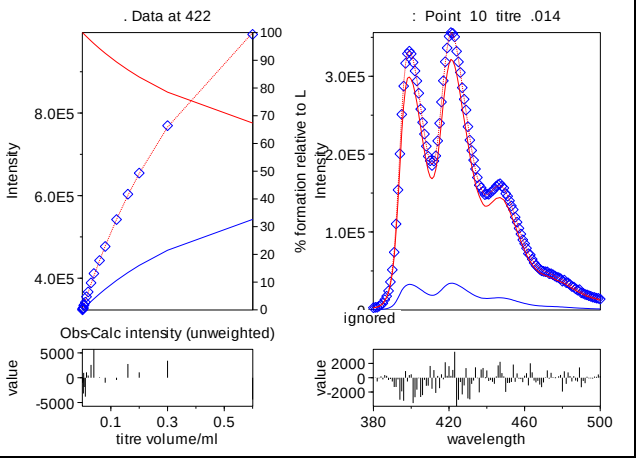
$Na_2S_2O_3$



Na_2SO_4

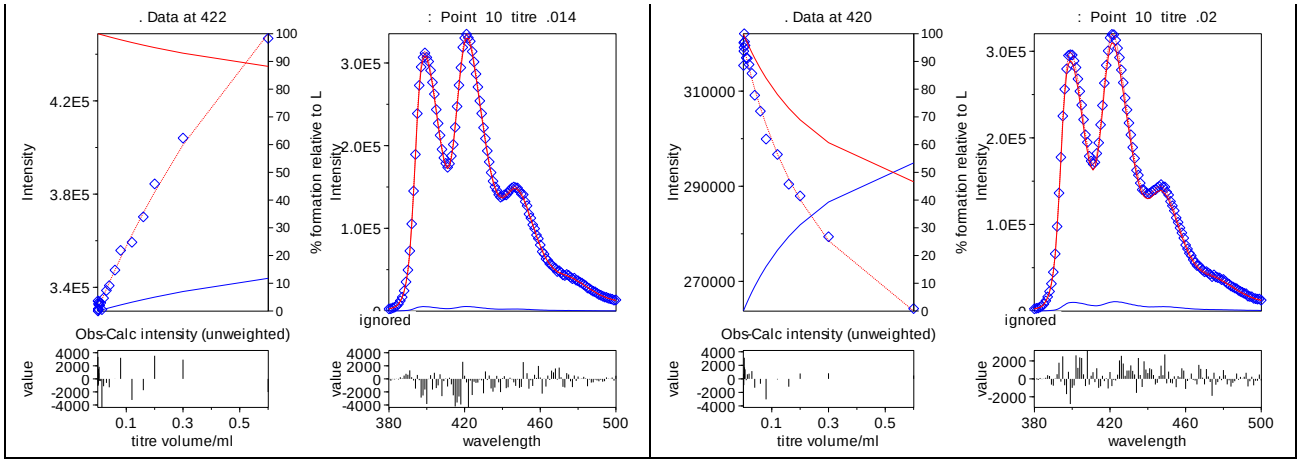


NaH_2PO_4



NaNO3

NaN_3


. Data at 422
Intensity
4.2E5
3.8E5
3.4E5
100
90
80
70
60
50
40
30
20
10
0
% formation relative to L
: Point 10 titre .014
Intensity
3.0E5
2.0E5
1.0E5
ignored
Obs-Calc intensity (unweighted)
value
4000
2000
0
-2000
-4000
0.1
0.3
0.5
titre volume/ml
380
420
460
500
wavelength
. Data at 420
310000
290000
270000
: Point 10 titre .02

7 STOICHIOMETRY DETERMINATION

Determination of stoichiometry of interaction is based on the best fit of the experimental data and described earlier by Jurczak.[5]

In case of binding of oxalate by **2** the following residual plots were obtained by HypSpec program. These two figures show that more random distribution of residuals is observed in case of a 1:2 binding mode. This indicates that the second binding exists at pH 3.6. The fitting of the data yielded a small value and a large error in the calculation of the second binding event. However, for example, in case of oxalate binding by **2** at pH 5.6 the fitting yielded binding constants for both events 1:1 and 1:2 binding.

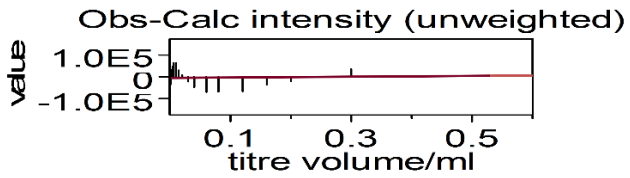
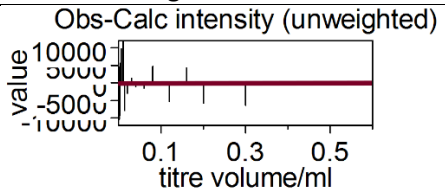
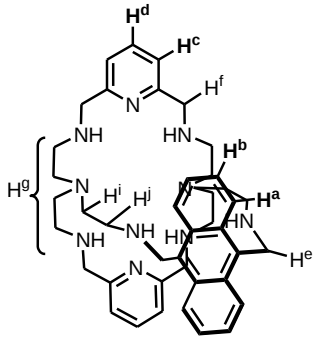
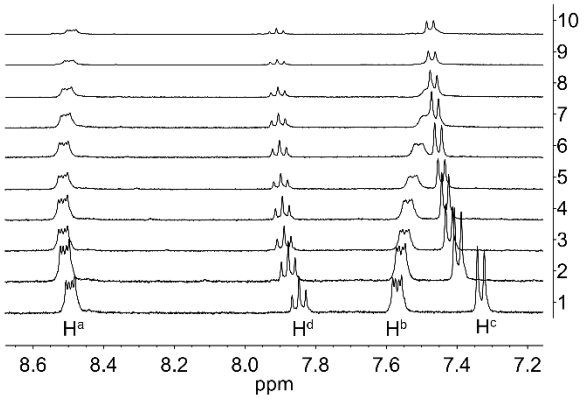
For 1:1 binding mode	For 1:2 binding mode
	

Figure S8. Comparison of residual plots exported from HypSpec program constructed for 1:1 and 1:2 binding of oxalate by **2** at pH 3.6.

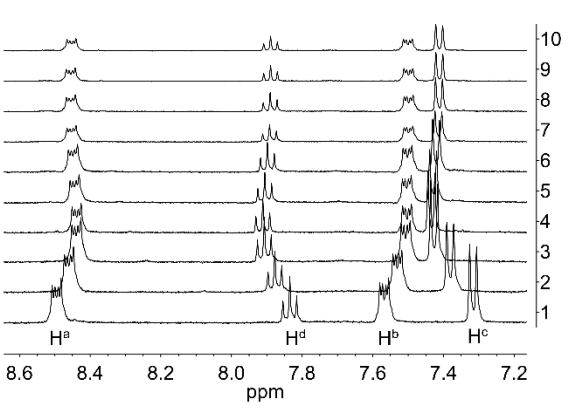
8 ^{1}H NMR TITRATIONS

The titrations were carried out by sequential addition of salts to the NMR tube containing the cryptands followed by the measurements. The methanol-buffer solution was used because at mM concentration all cryptands were not soluble in pure buffer. The following conditions were used: 0.002 M solution of a cryptand in a 7:5 CD_3OD–D_2O (50mM acetate buffer, pH3.6); sodium salts were added in following amounts (equiv): 1:0; 2:0.2, 3:0.4; 4:0.6; 5:1.1; 6:2.1; 7: 4.2; 8: 6.4; 9:13.2, 10:17.6. Since binding constants are high in water, the expected binding constants in methol-buffer solution were expected to be even higher. Thus, the fitting of the proton shifts with HypNMR program did not yield any reliable binding constants because their values exceed the limit of the NMR titration method, which is 10^4 M^{-1}.

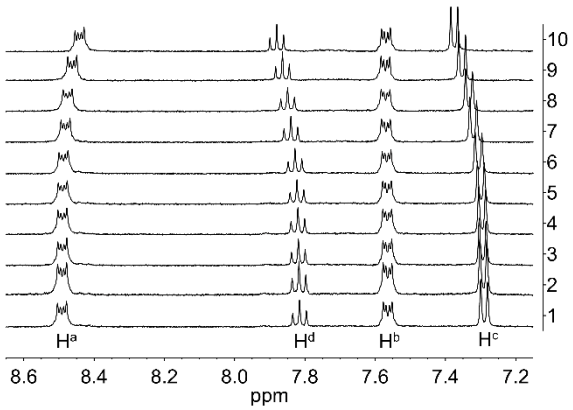




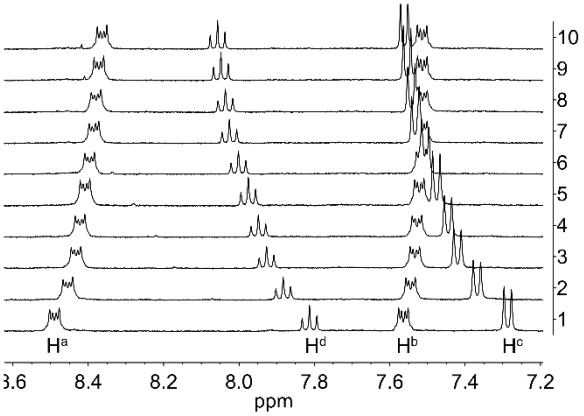
1 with NaH_2PO_4



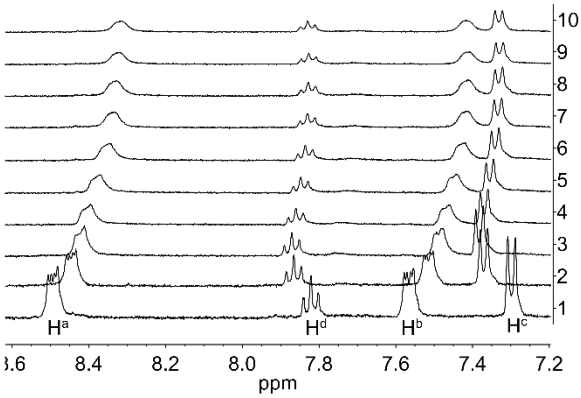
1 with Na_2SO_4



1 with $NaReO_4$

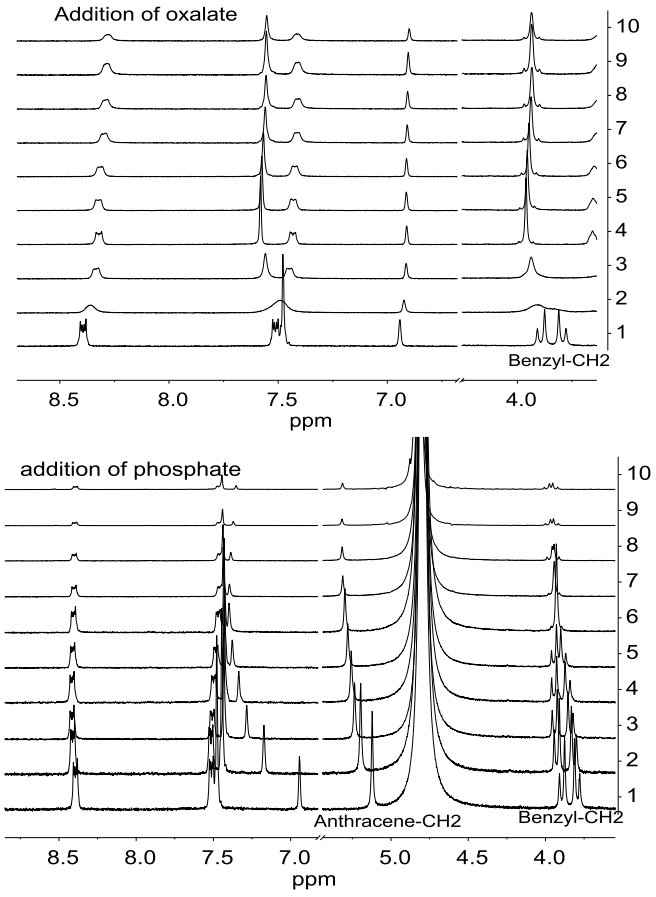


1 with NaN_3



1 with $Na_2C_2O_4$

Figure S9. ^{1}H NMR titrations of **1** with anions.



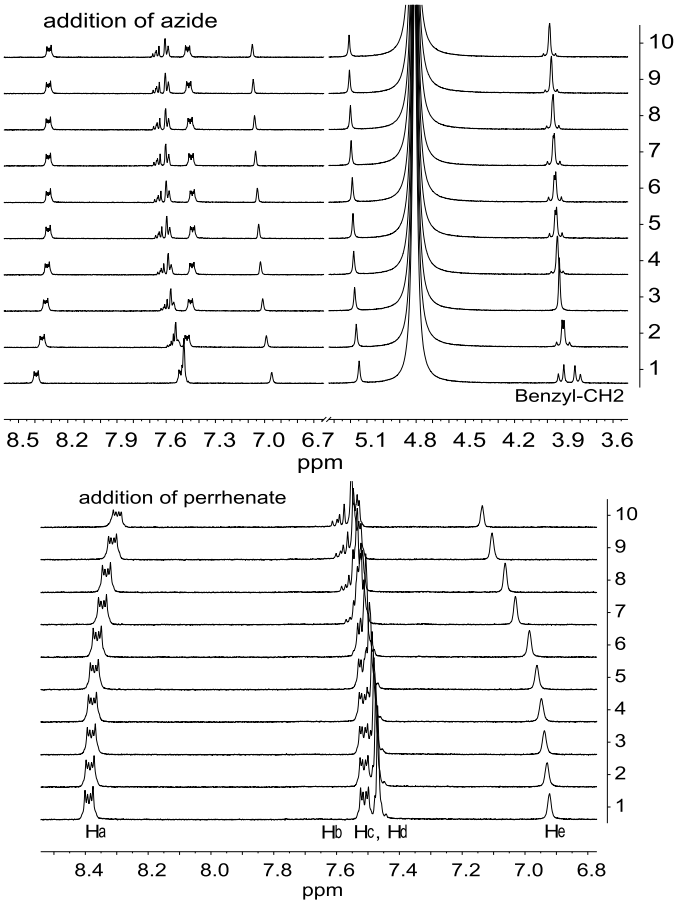


Figure S10. ^{1}H NMR titrations of **2** with anions.

9 POTENTIOMETRIC MEASUREMENTS

All solutions were prepared in 1:1 water (0.1M $NaClO_4$)-methanol mixed solvent. A stock solution of receptors was prepared at ca. 0.0025 M. Anions solutions were prepared at 0.1M of the corresponding sodium salts. For titrations standard 0.1M solution of NaOH was used. The carbonate-free solutions were prepared with freshly boiled (at least 2h) water that was cooled under nitrogen atmosphere.The reaction vessel was kept at constant temperature 23°C. The value of K'_w was determined from data obtained in the alkaline range of the titration, and found to be equal to $10^{-14.66}$ in our experimental conditions. The titration experiment was carried out as follows: in the reaction vessel was placed a solution of a cryptand and $HClO_4$ (0.037M); after stirring the solution for 5 minutes the titrations was started. The experiment was repeated 3-5 times. The obtained data was imported to the HYPEQUAD 2008 program and fitted to obtained protonation constants. The errors quoted in the tables are standard deviations of the overall association constants calculated from the repeating experiments.

Table S4. Protonation constants determined for 1 and 2 in a 1:1 methanol-water mixture at 23°C.

Species	**1**, logβ_{1i}	Standard deviation	**2**, logβ_{1i}	Standard deviation
LH^{1+}	10.51	0.11	10.72	0.15
LH_2^{2+}	9.75	0.15	8.80	0.15
LH_3^{3+}	8.75	0.20	7.77	0.21
LH_4^{4+}	7.56	0.21	7.11	0.22
LH_5^{5+}	6.42	0.32	6.25	0.35
LH_6^{6+}	6.20	0.34	6.40	0.27

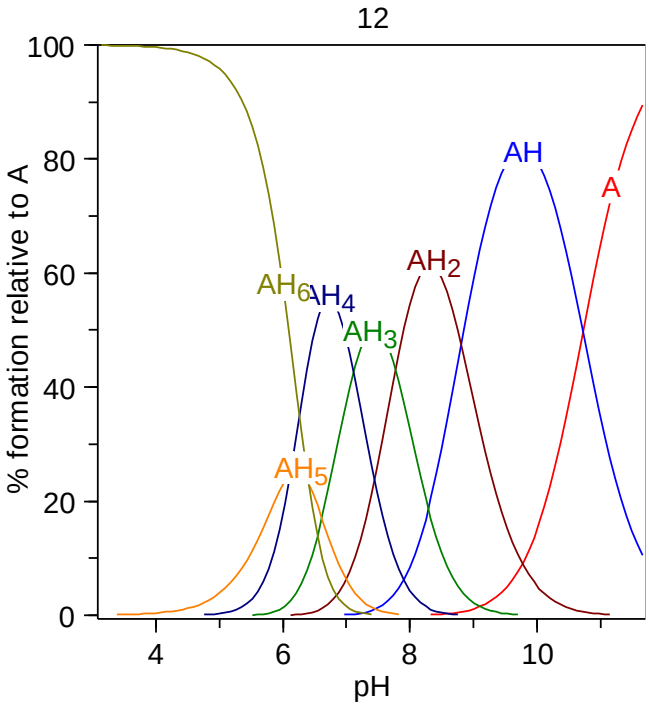


Figure S11. Species distribution of **2** (A=**2**) calculated from the protonation constants.

10 REFERENCES

(1) Boon, J. M.; Lambert, T. N.; Smith, B. D.; Beatty, A. M.; Ugrinova, V.; Brown, S. N. *J Org Chem* **2002**, *67*, 2168.

(2) Popp, N.; Homburg, T.; Stock, N.; Senker, J. *Journal of Materials Chemistry A* **2015**, *3*, 18492.

(3) Lakowicz, J. R. *Principles of fluorescence spectroscopy*; 3rd ed.; Springer: New York, 2006.

(4) Vosburgh, W. C.; Cooper, G. R. *J Am Chem Soc* **1941**, *63*, 437.

(5) Ulatowski, F.; Dabrowa, K.; Balakier, T.; Jurczak, J. *J Org Chem* **2016**, *81*, 1746.