Supporting Information

Fluorescence detection of bisphosphonates in water by a naphthalimide-based receptor and derived cryopolymers

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Content

General

All the solvents were dried according to standard procedures. Reactions were performed in oven-dried round bottom flask. 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** were measured on ASCEND 600 FT spectrometer (Bruker Corp., Billerica, MA), 600 MHz for ^{1}H NMR and 150.9 MHz for ^{13}C NMR. The chemical shifts are reported in δ [ppm] relative to external standards (solvent residual peak). The solvent used is reported for each spectrum. **Mass Spectra:** Finnigan MAT TSQ 7000 (ESI). **Melting Point:** Melting Points were determined on Büchi SMP or a Lambda PhotometricsOptiMelt MPA 100. **Absorption spectra** were measured in 1 cm quartz cuvettes with Varian Cary BIO 50 UV/VIS/NIR Spectrometer. **Emission spectra** were recorded with aqueous buffered solution in 1 cm quartz cuvettes (Hellma) on a FluoroMax 4 (Horiba) with a temperature control. **pH-Measurements** were carried out on a Mettler Toledo G20 Titrator equipped with a DG115-SC pH-electrode. The electrode was calibrated with standard calibrating solutions from Mettler Toledo. The reaction vessels were kept at constant temperature 23°C. The starting compounds were purchased from TCI, Sigma-Aldrich and Acros Chemicals.

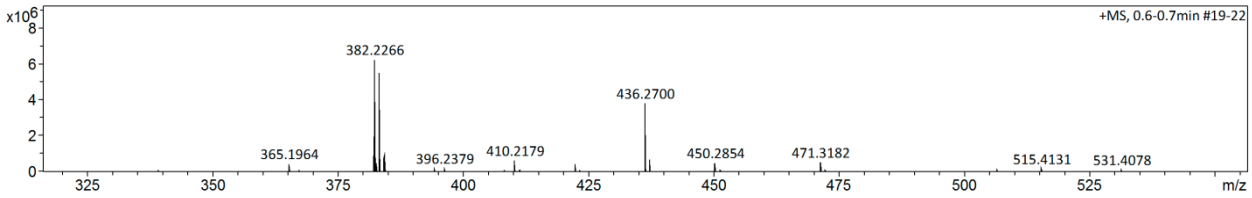
Synthetic procedures

12-allyl-6-bromo-1H-benzo[de]isoquinoline-1,3(2H)-dione was prepared according to literature procedure[1]

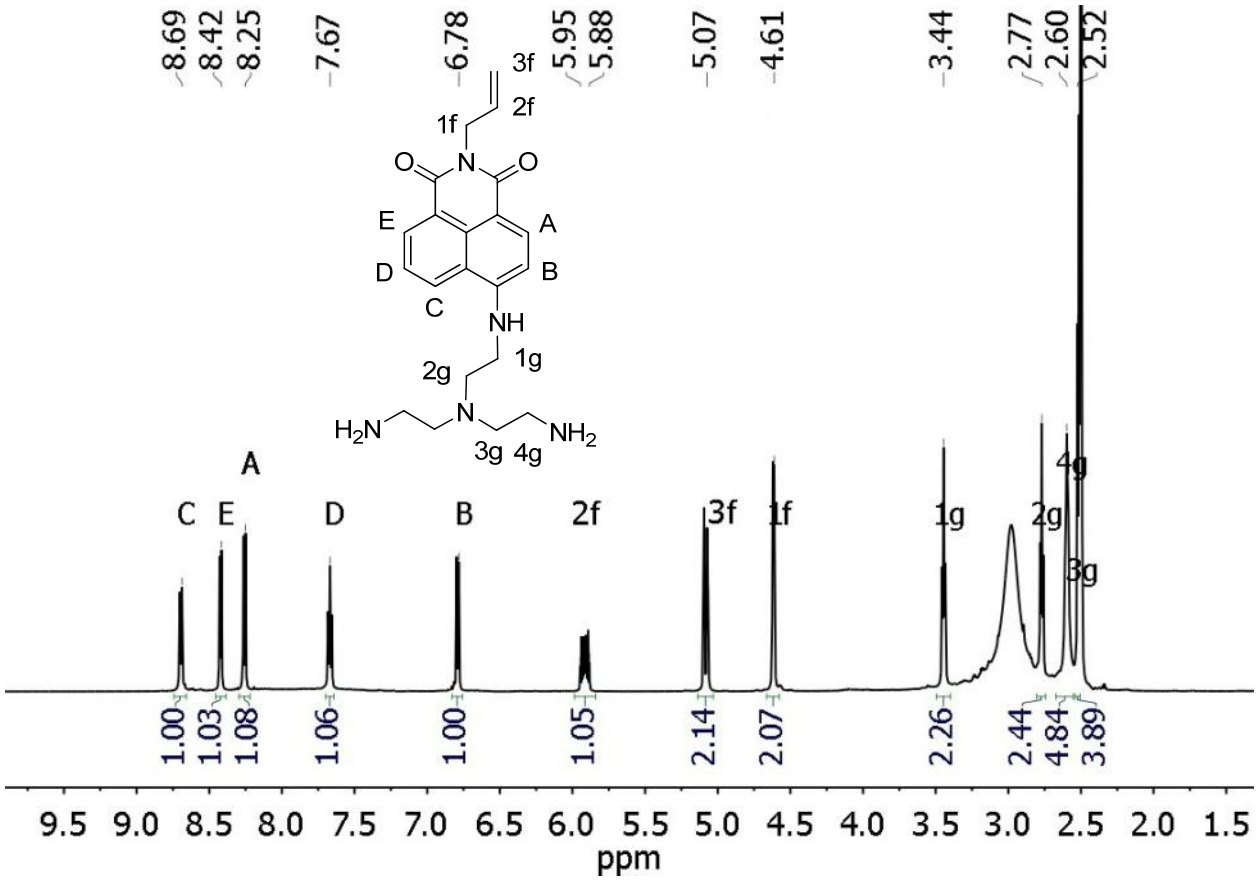
M

2-Allyl-6-(2-(bis(2-aminoethyl)amino)ethylamino)-1H-benzo[de]isoquinoline-1,3(2H)-dione

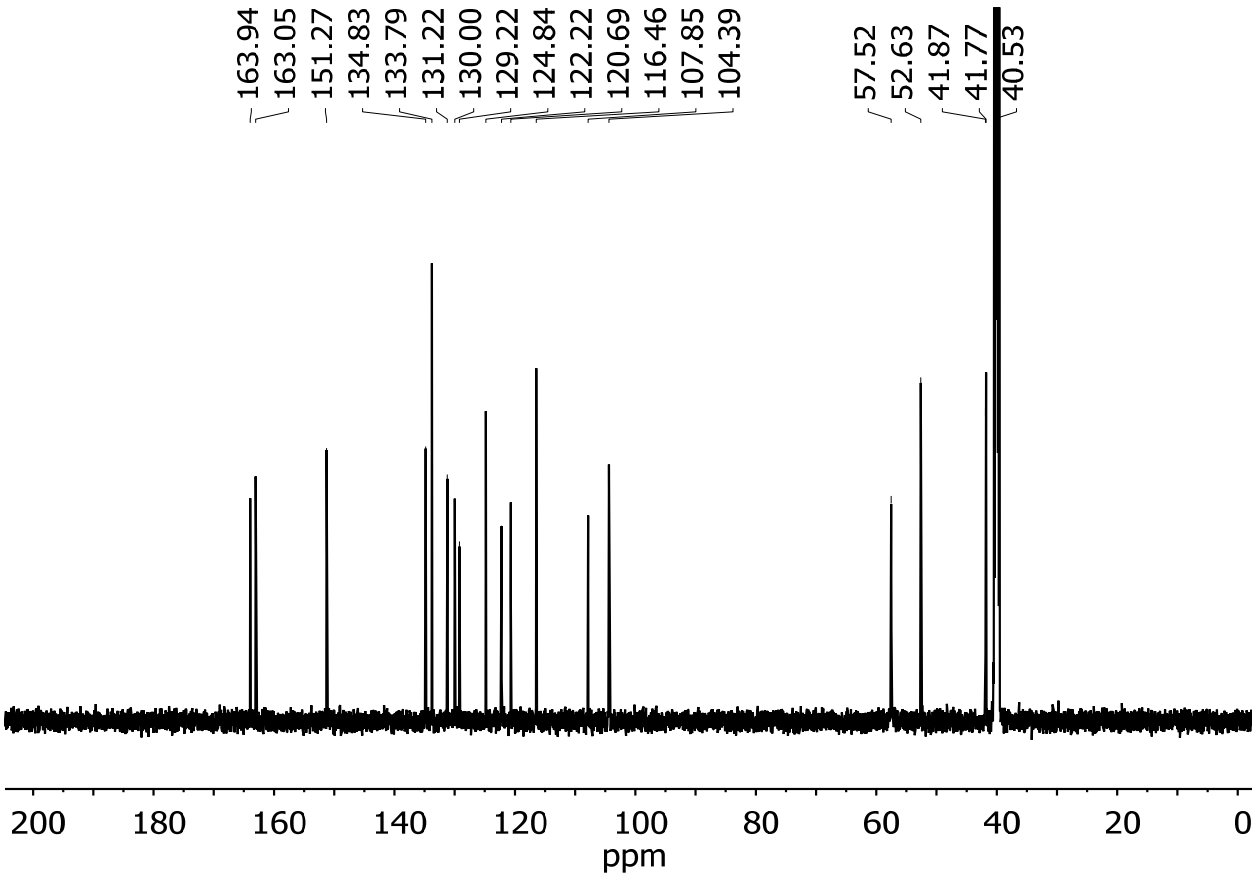
Compound **2** (1.27 g, 4 mmol) was suspended in 6 ml of TREN. The reaction mixture was stirred for 5 days at room temperature. The saturated brine solution (30 ml) was added to quench the reaction and the product was extracted by chloroform (4x50 ml). Organic layers were collected and the solvent was removed. The extraction procedure was repeated to remove traces of amine. The extracts were dried over anhydrous Na_2CO_3 and concentrated in vacuum to give a red-orange amorphous solid (1.38 g, 3.6 mmol, 91%). M.p. 85-87^{0}C. ^{1}H NMR (600 MHz, DMSO-*d6*, 25°C): δ= 2.52 (br.s, 4H) 2.60 (br.s, 4H), 2.77 (t, *J* = 6.6 Hz, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 4.61 (d, *J* = 5.0 Hz, 2H), 5.07-5.10 (m, 2H), 5.97 – 5.87 (m, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 7.67 (dd, *J* = 7.5 Hz, *J* = 8.3 Hz , 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 7.5 Hz, 1H), 8.69 (d, *J* = 8.3 Hz, 1H) ^{13}C NMR (150.9 MHz, DMSO-*d6*): δ = 40.5, 41.8, 41.9, 52.6, 57.5, 104.4, 107.9, 116.5, 120.7, 122.2, 124.8, 129.2, 130.0, 131.2, 133.8, 134.8, 151.3, 163.1, 163.9. HRMS-ES for **M**; (CH_2Cl_2); Calcd for $C_{21}H_{28}N_5O_2$: *m/z*= 382.2243 $[M+H]^+$; Found: 382.2266 $[M+H]^+$.



^{1}H NMR spectrum (600 MHz, DMSO-*d6*, 298 K) of **M**



^{13}C NMR spectrum (150.9 MHz, DMSO-*d6*, 298 K) of **M**



Synthesis of the polymers

An aqueous solution of monomer M (2.6 ml) was added to an aqueous solution of *N,N*-dimethylacrylamide (2.2 mL, 1 M). The resulting solution was bubbled with argon for 15 min and cooled in an ice bath, and the initiator was added (200 µL of a 1% solution of ammonium persulfate and 6 µL of *N,N,N′,N′* - tetramethylethylenediamine). A sealed tube with the reaction mixture was placed in the chamber of a Proline RP 1840 precision cryostat (Lauda, Germany), where the mixture was allowed to stand for 24 h at the predetermined temperature –20°C. The samples were thawed in a water bath at 25 ° C. The resulting polymer cryogel was washed with deionized water from the low molecular mass and oligomeric fractions during repeated changing of the water. The polymeric product was lyophilically dried with an Alpha 1-2 LD plus sublimation device (Martin Christ, Germany) and subsequently in a vacuum desiccator over calcined granular $CaCl_2$. The synthesis of cryogels was performed at least three times.

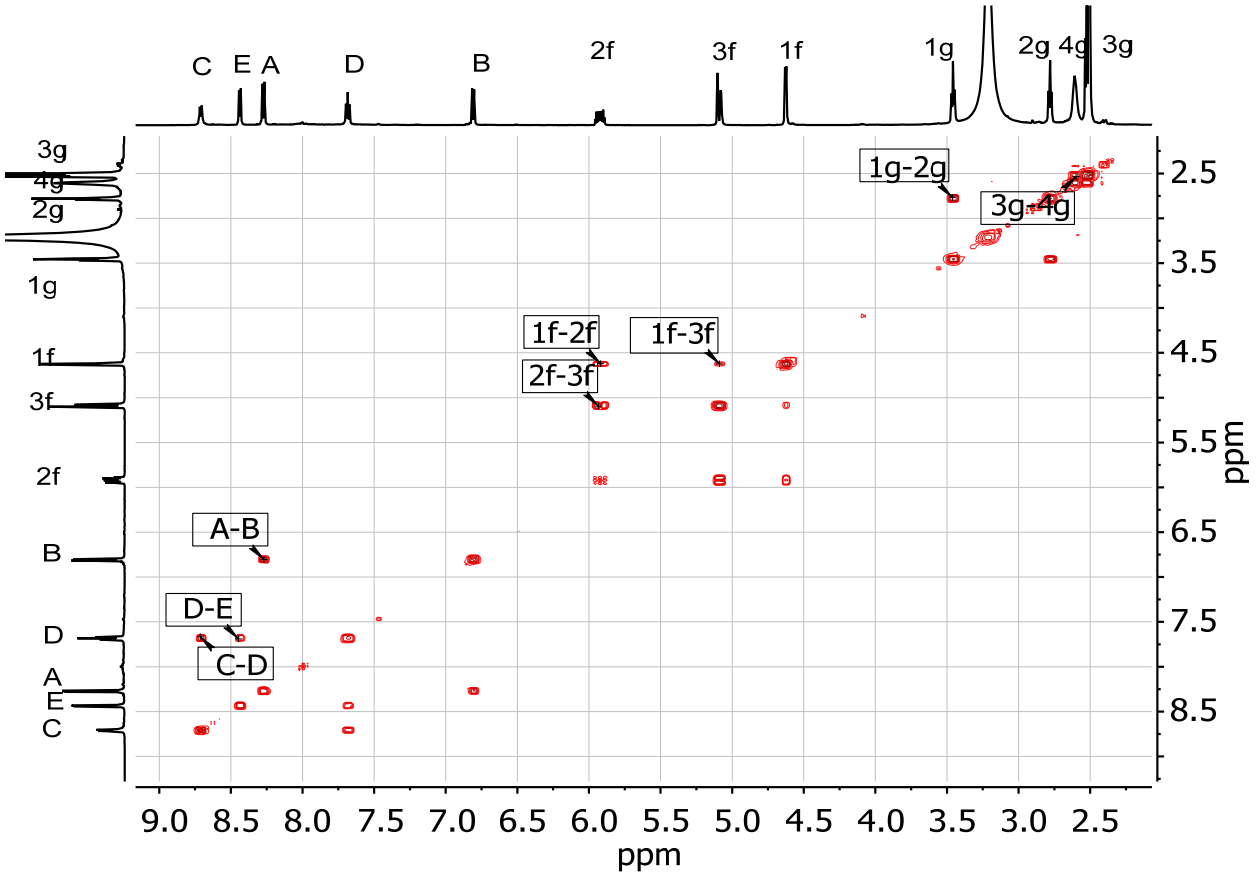


Figure S1. Annotated 2D ^{1}H-^{1}H COESY NMR spectrum (600 MHz, DMSO-*d6*, 298K) of **M**.

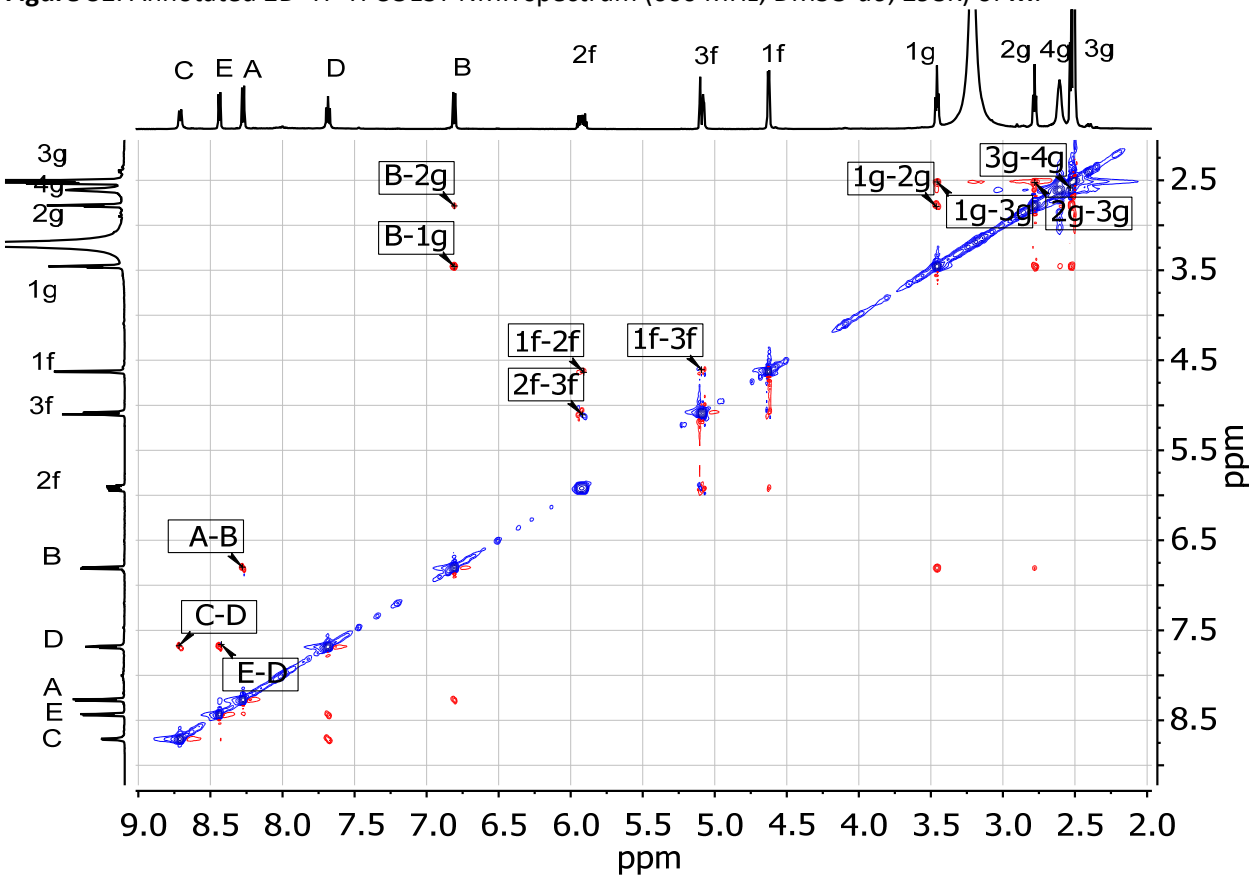


Figure S2. Annotated ROESY NMR spectrum (600 MHz, DMSO-*d6*, 298K) of **M**.

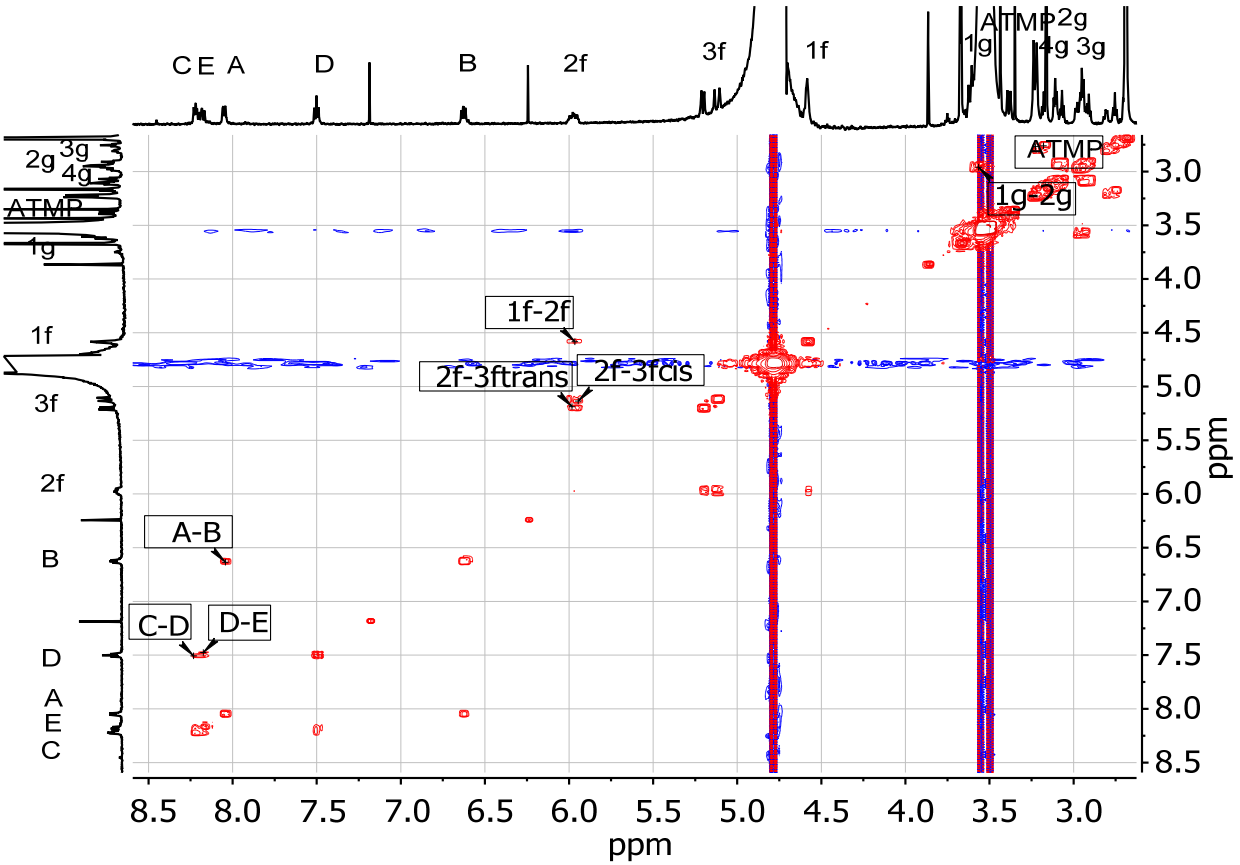


Figure S3. Annotated 2D ^{1}H-^{1}H COESY NMR spectrum of **M** in presence 30 equivalents of ATMP. Conditions: 50 mmol TRIS buffer in D_2O (pH 7.2. 10% DMSO-*d6*), 1 mmol receptor concentration.

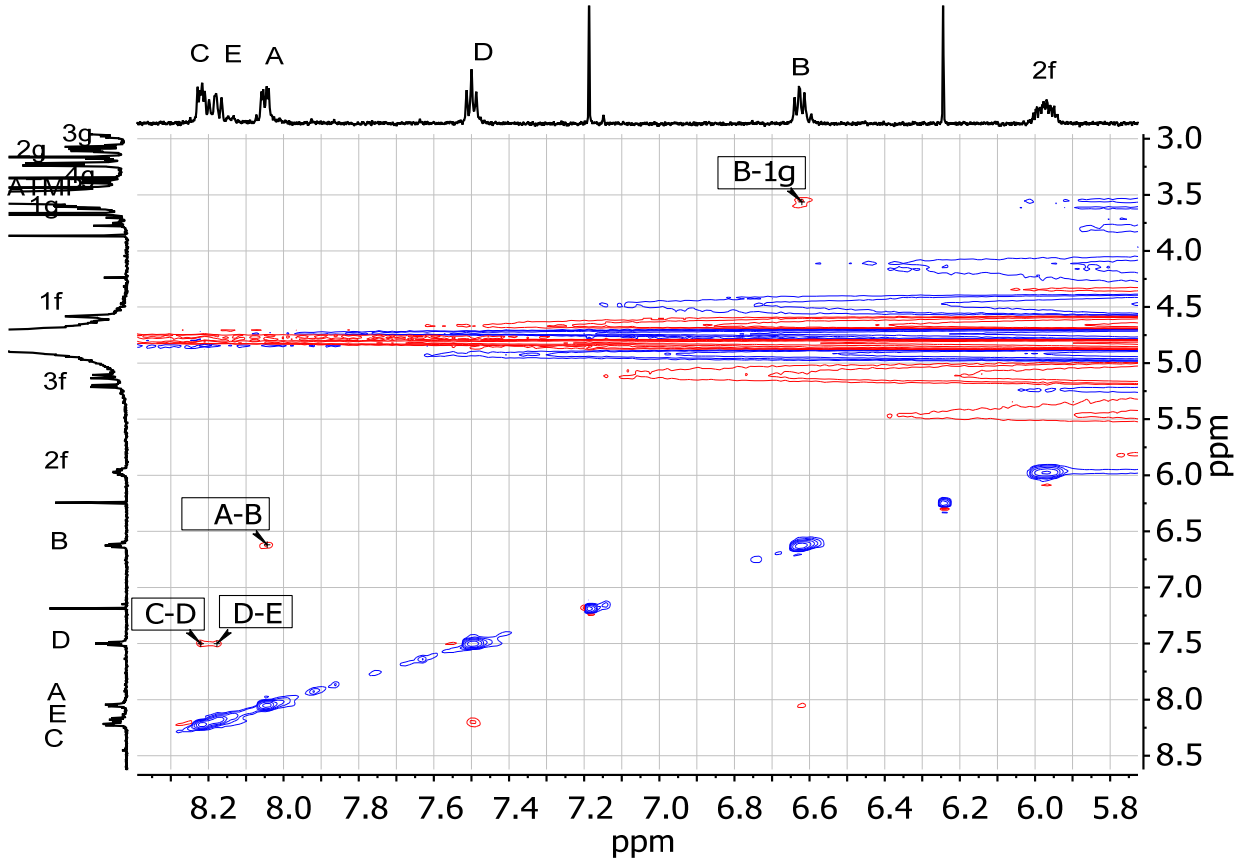


Figure S4. Annotated ROESY NMR spectrum of **M** in presence 30 equivalents of ATMP.

^{1}H NMR titrations

The titrations were carried out by sequential addition of sodium salts to the NMR tube containing the receptors followed by the measurements. The 10%DMSO–buffer mixture was used because of solubility limitation of mixture receptor with BP`s at 1 mM concentration. The following conditions were used: 0.5 mL of 1 mM solution of receptors in a 1:9 DMSO-d_6–D_2O (50 mM TRIS buffer, pH 7.2) mixture. Sodium salts dissolved in the same D_2O-based buffer (0.125 M) were added as follows (equiv): 0.25; 0.5; 1; 2; 5; 10; 30. The fitting was performed by HypNMR program.

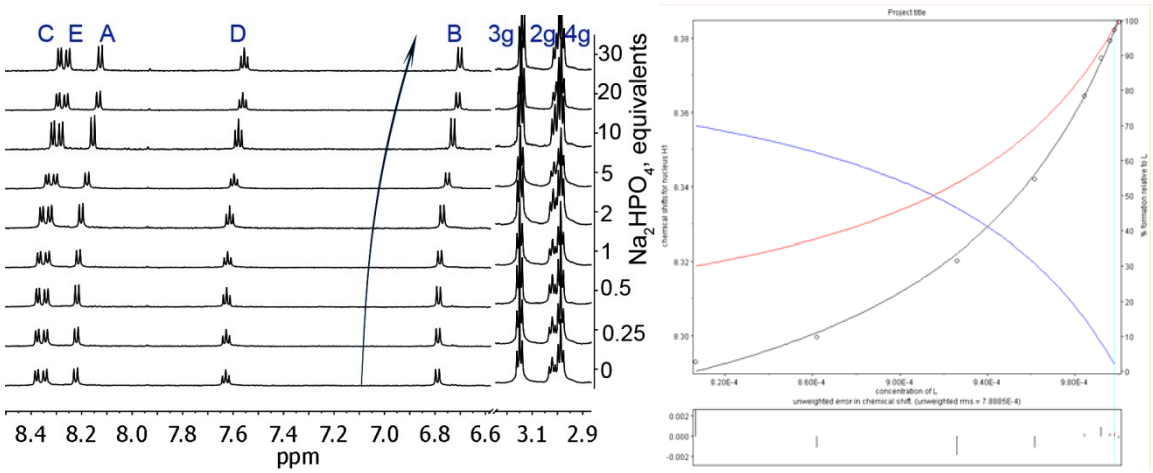


Figure S5. ^{1}H NMR titration of **2** with Na_2HPO_4 and the fitting (black line) of experimental points (circles) to a 1:1 binding mode.

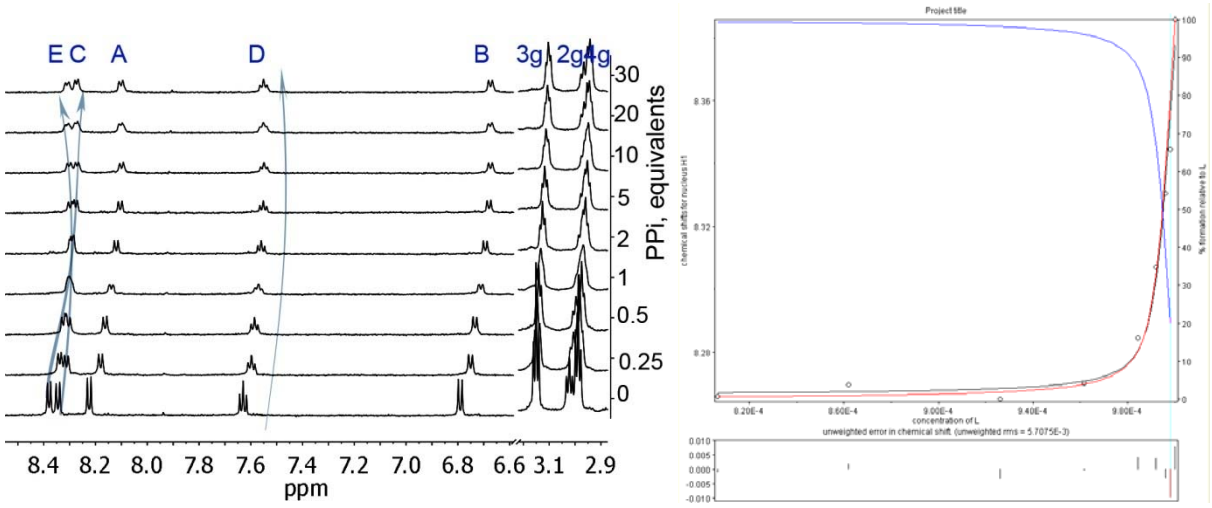


Figure S6. ^{1}H NMR titration of **2** with PPi and the fitting (black line) of experimental points (circles) to a 1:1 binding mode.

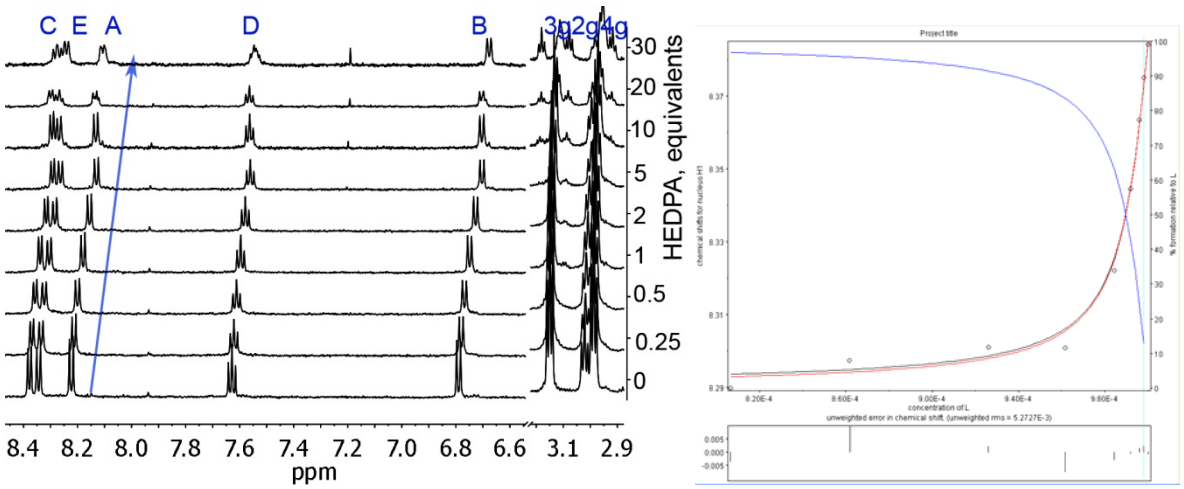


Figure S7. ^{1}H NMR titration of **2** with HEDPA and the fitting (black line) of experimental points (circles) to a 1:1 binding mode.

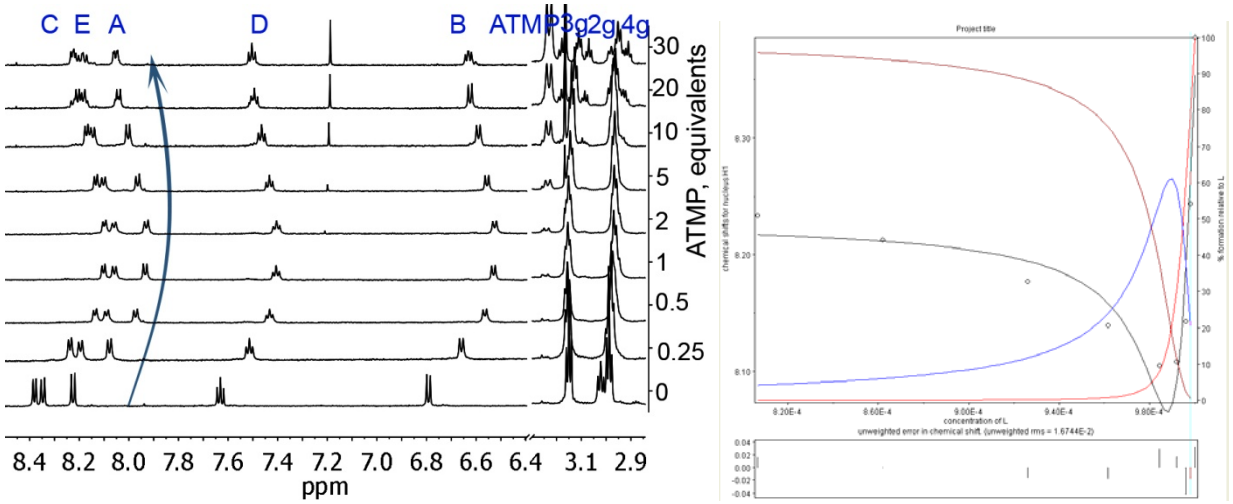


Figure S8. ^{1}H NMR titration of **2** with ATMP and the fitting (black line) of experimental points (circles) to a 1:1 and 1:2 binding mode.

Absorption and fluorescence properties

The quantum yields of the compounds were measured in a 50 mmol acetate buffer pH 3.6 and in 50 mmol TRIS buffer pH 9.2 relative to quinine sulphate (in 0.1M H_2SO_4 solution ϕ=0.54) used as a reference.[2]

Fluorescence spectroscopy

M

Stock solutions of receptors with concentrations of 0.01mmol in a 50 mmol TRIS buffer pH 9.2 were prepared for fluorescence binding studies. The titrant (sodium salt, 0.01M) was sequentially added to a 2 mL sample of the host stock solution in the spectrometric cell and the changes in the spectral features were monitored. The receptor solution in a 10mm cuvette (2 ml) was then titrated with the salt solution and each time the fluorescence spectrum was recorded. The following setup parameters were used for fluorescence titration experiments: ex. 440 nm, slit 2/2, em: 460-700 nm. The resulting data was imported in HypSpec program.[3]

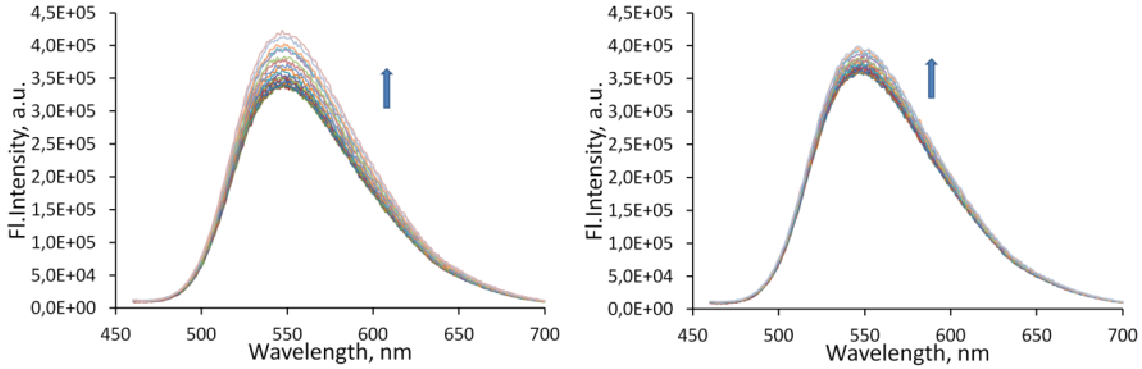
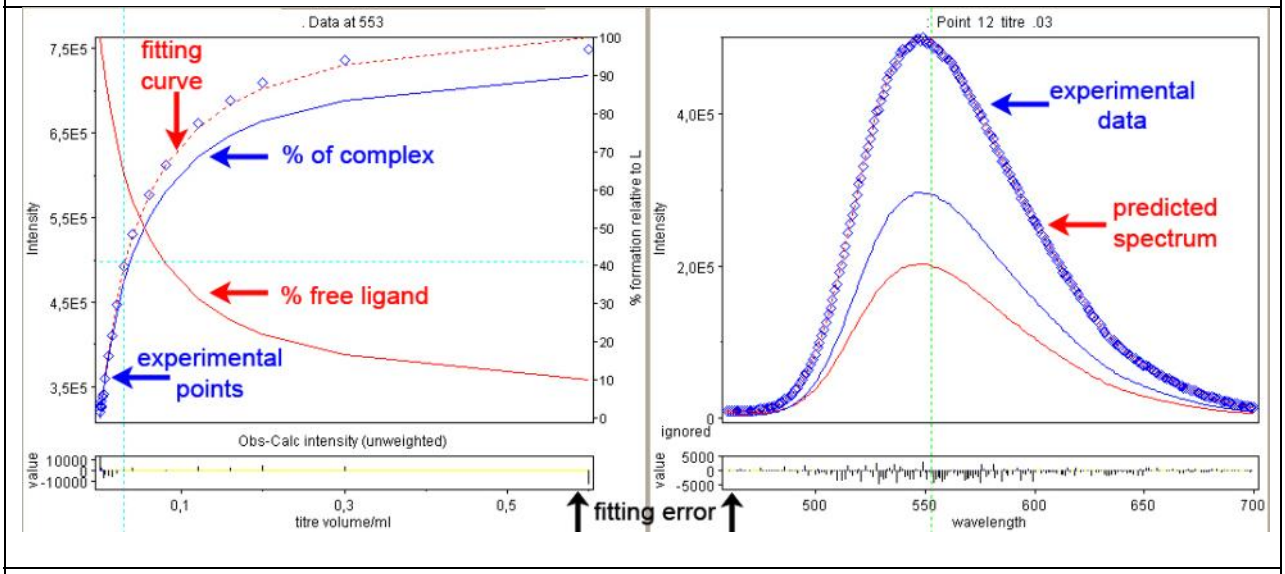


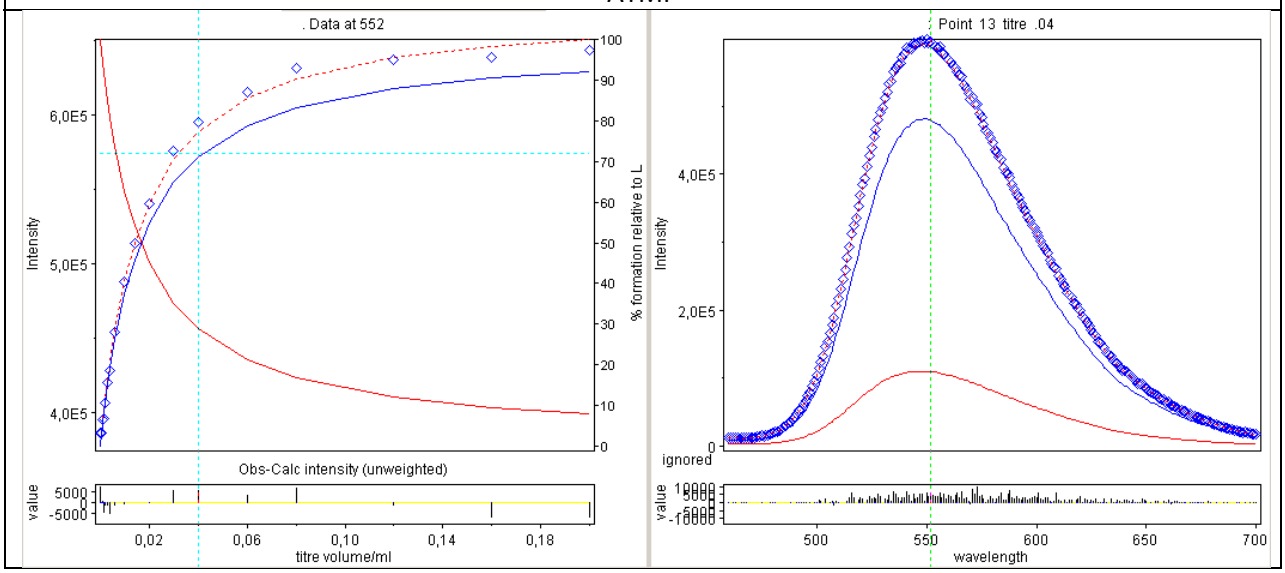
Figure S9. Fluorescence titrations of receptor **M** with a) HEDPA and b) Na_2HPO_4. Conditions: 0.01 mmol receptor in a 50 mM TRIS buffer (pH 9.2).

The fitting curves for the titration of anion were exported from HypSpec program showing fitting over the whole spectrum.

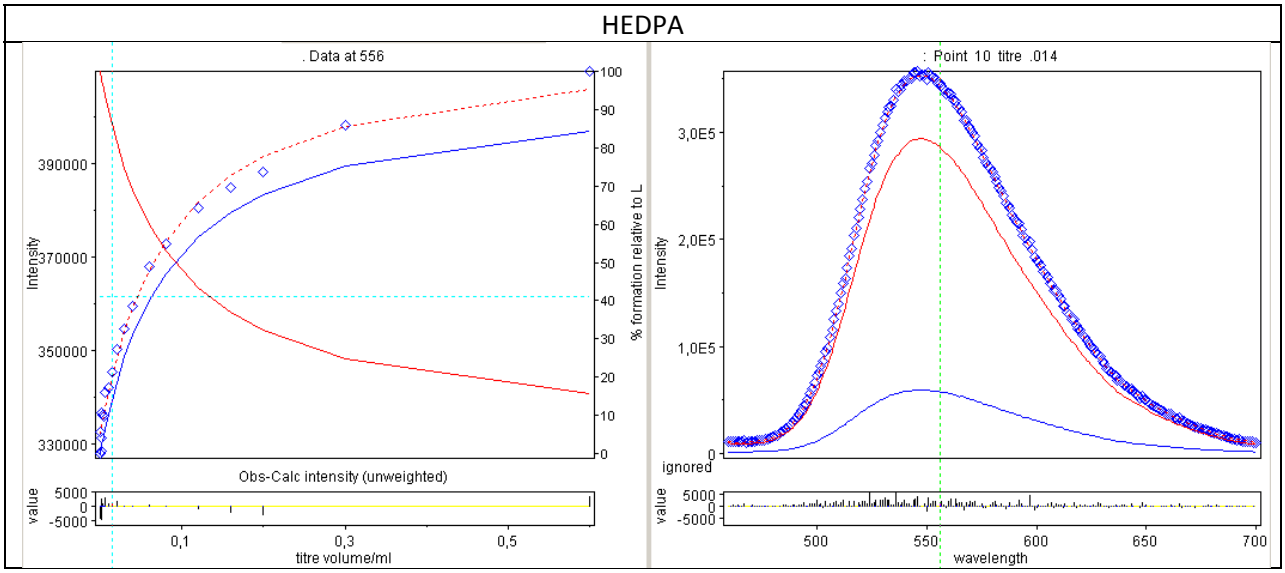
PPi

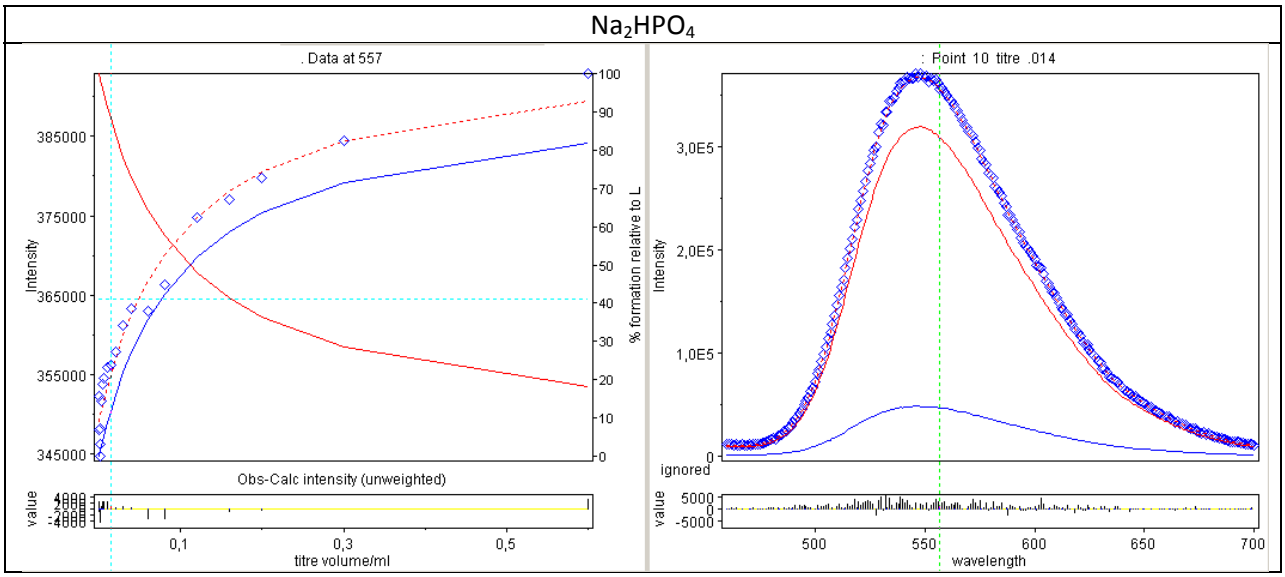


ATMP



HEDPA





Studies of polymers

Stock solutions of polymers with relative concentration of fluorophore of 0.01mmol/L (0.001 mmol/L for **P2**) in a 50 mmol TRIS buffer pH 9.2 were prepared for fluorescence binding studies (2 days under stirring at room temperature). The titrant (sodium salt, 0.01 mol/L, 0.001 mol/L for **P2**) was sequentially added to a 2 mL sample of the host stock solution in the spectrometric cell and the changes in the spectral features were monitored. The receptor solution in a 10mm cuvette (2 ml) was then titrated with the salt solution and each time the fluorescence spectrum was recorded. The following setup parameters were used for fluorescence titration experiments: ex. 440 nm, slit 2/2 (slit 3/3 for **P2**), em: 460-650 nm.

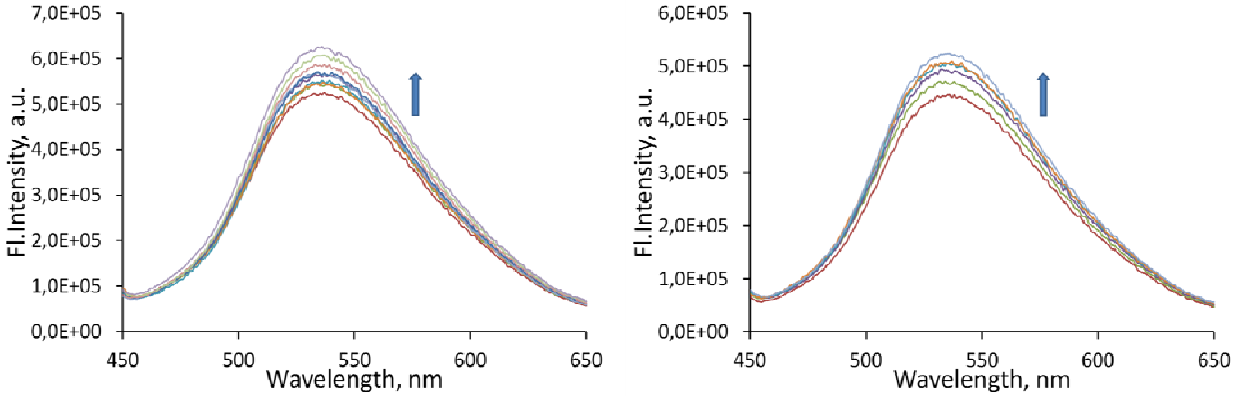


Figure S10. Fluorescence titrations of **P2** with a) PPi 0-100 equiv and b) ATMP 0-100 equiv.

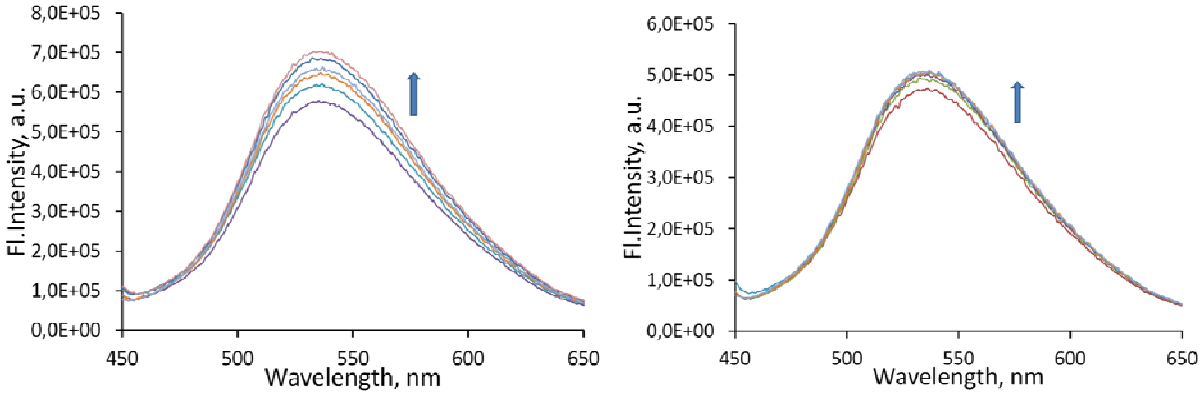


Figure S11. Fluorescence titrations of **P2** with a) HEDPA 0-100 equiv and b) Na_2HPO_4 0-100 equiv.

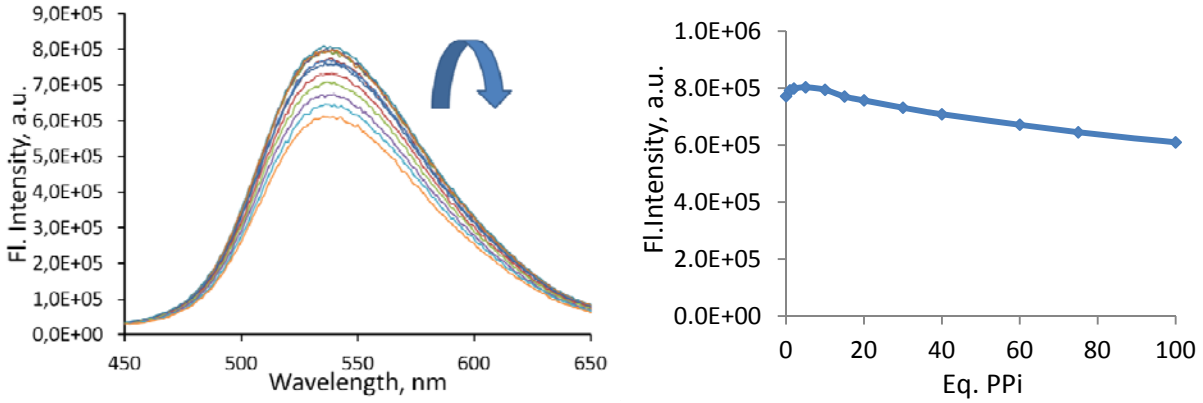


Figure S12. Fluorescence spectrum of **P3** after addition 0-100 equiv PPi together with the b) curve at 537 nm. Conditions: 0.01 mmol receptor in a 50 mmol TRIS buffer (pH 9.2).

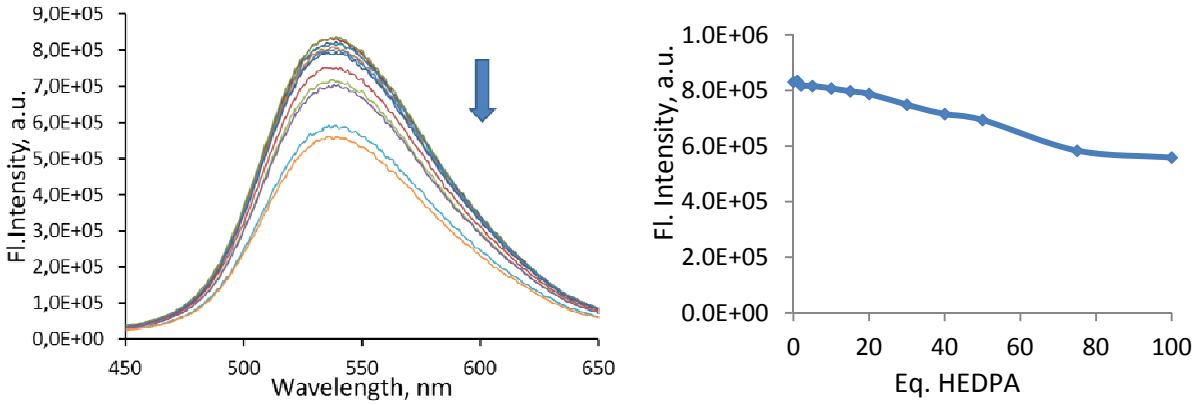


Figure S13. Fluorescence spectrum of **P3** after addition 0-100 equiv HEDPA together with the b) curve at 537 nm. Conditions: 0.01 mmol receptor in a 50 mmol TRIS buffer (pH 9.2).

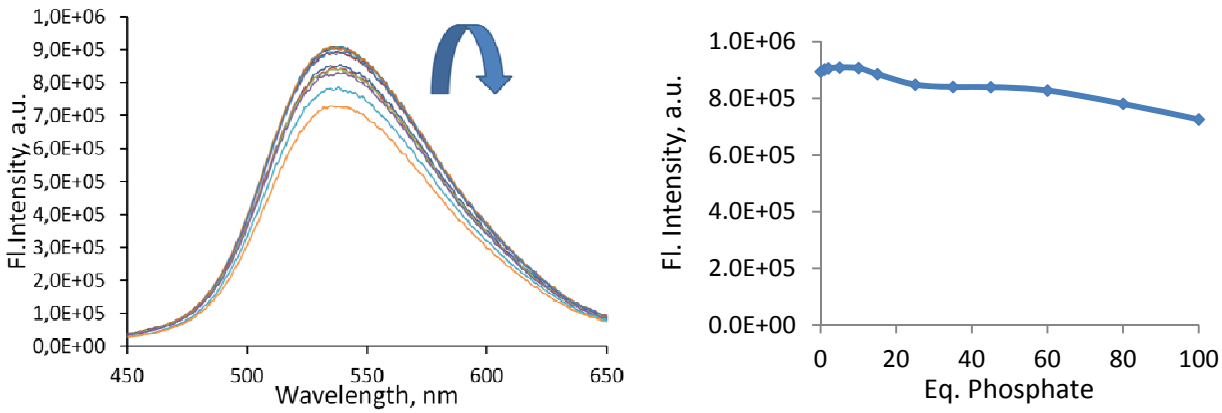


Figure S14. Fluorescence spectrum of **P3** after addition 0-100 equiv Na_2HPO_4 together with the b) curve at 537 nm. Conditions: 0.01 mmol receptor in a 50 mmol TRIS buffer (pH 9.2).

Job plots

The plots were constructed according to the classical method described by Cooper.[4] The measurements demonstrate that binding of BPs is close to 1:1 binding mode. However, in a case of ATMP the maximum at the Job plots was diffused between values 0.35 and 0.45, so exact stoichiometry (1:1 of 1:2) could not be accurately assessed. Thus, in all cases we used the other method to determine the stoichiometry. This methods is based on the best fit of the experimental data and described earlier by Jurczak.[5]

The stock solution of compounds and anions with identical concentration (10^{-5}M) were mixed together producing different mol fractions of guest: Assuming that in this concentration range there is a linear relationship between absorbance intensity and concentration, one can predict the intensity of the receptor at each concentration as follows: $k = I_0/c_0$, where k is a coefficient; the predicted intensity I_c at concentration c will be $I_c = c*k$. The difference between the expected value and measured $D = I_{obs} - I_c$ is plotted versus mol fraction of the guest to find the maximum.

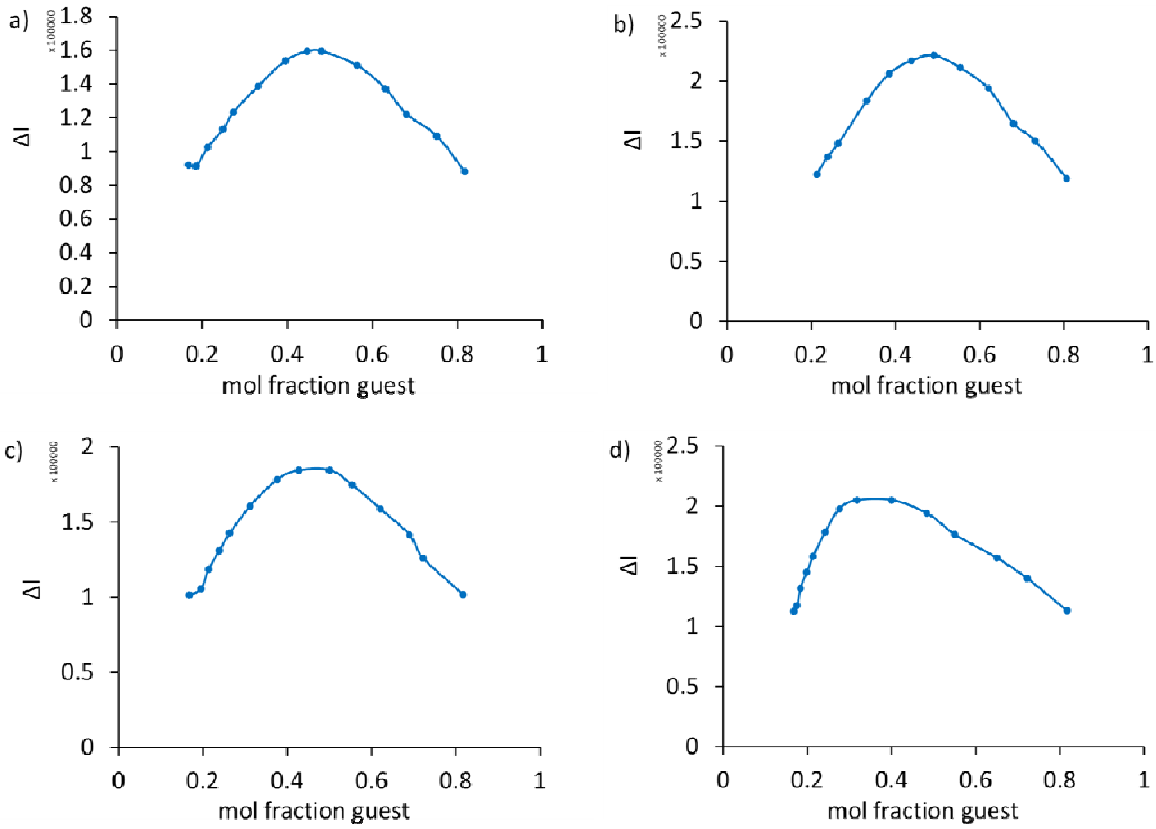


Figure S15. Job plot: stoichiometry determination of M in the presence of a) Na_2HPO_4, b) PPi, c) HEDPA and d) ATMP. Indicating 1:2 for ATMP, 1:1 for the rest of BPs major binding mode. Conditions: 0.01 mM receptor and BPs concentration in 50 mmol TRIS buffer pH 9.2.

UV-Vis spectroscopy

Stock solutions of receptor with concentrations of 0.05 mM in a 50 mM TRIS buffer pH 9.2 were prepared for UV-Vis binding studies. The titrant (sodium salt, 0.05 mol/L) was sequentially added to a 2 mL sample of the host stock solution in the spectrometric cell (10 mm cuvette (2 ml)) and the changes in the spectral features were monitored. The following setup parameters were used for UV-Vis titration experiments: slit 2, λ_{abs}: 340-530 nm. The resulting data was imported in HypSpec program and the data was fitted to obtain stability constants with anions.

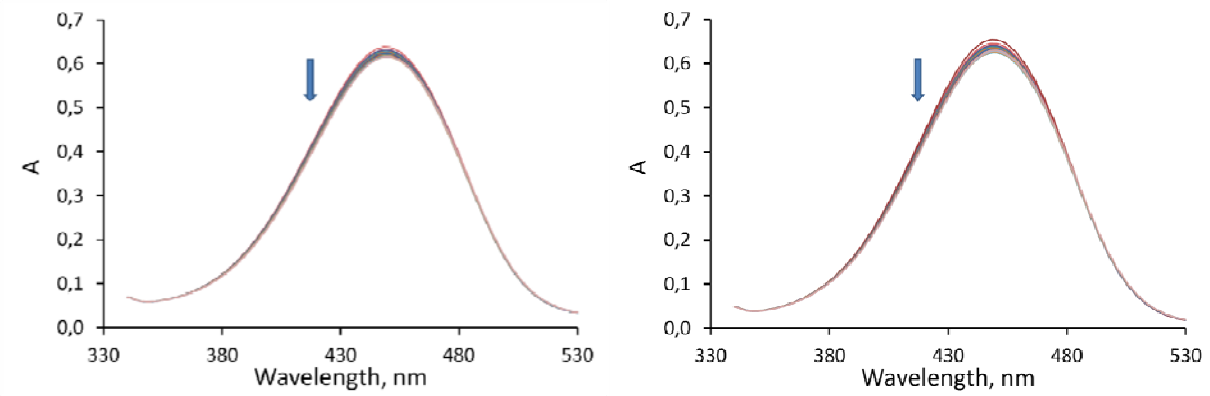


Figure S16. UV-Vis titrations of receptor **M** with a) PPi and b) ATMP. Conditions: 0.05 mmol receptor in a 50 mmol TRIS buffer (pH 9.2).

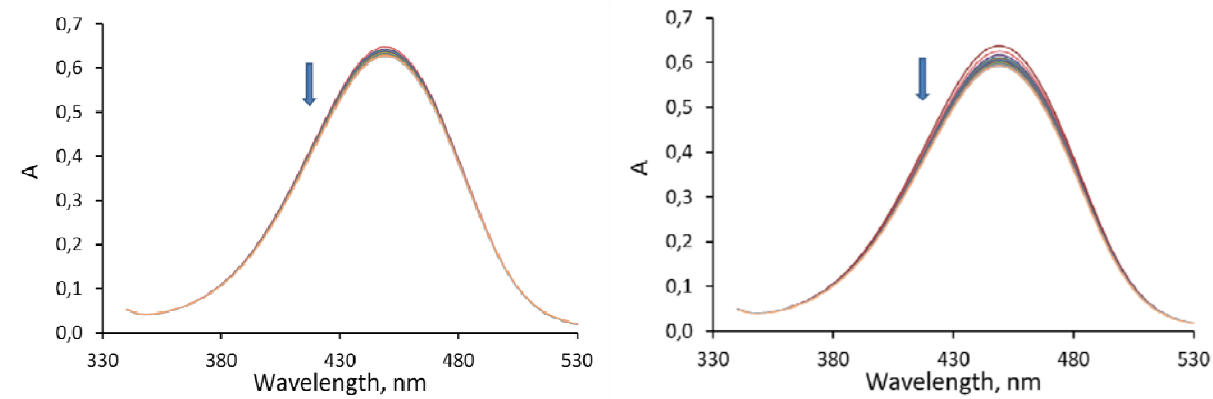
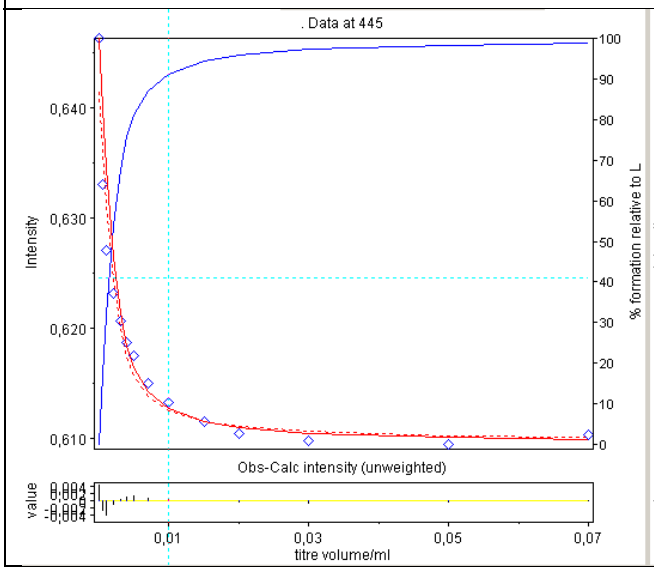
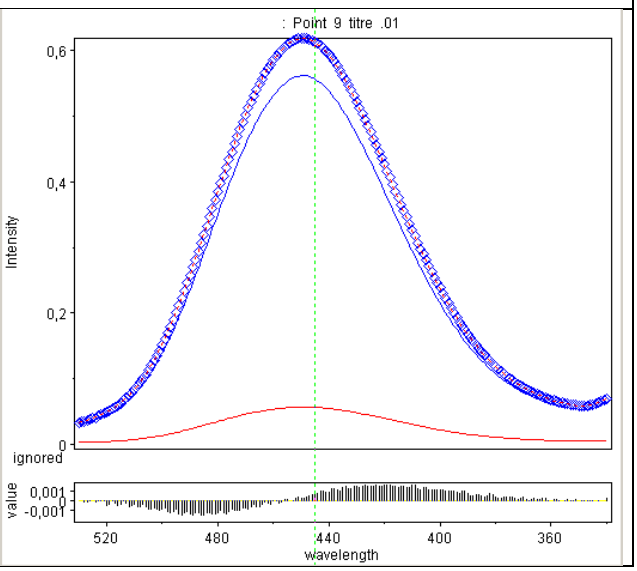


Figure S17. UV-Vis titrations of receptor **M** with a) HEDPA and b) Na_2HPO_4. Conditions: 0.05 mmol receptor in a 50 mmol TRIS buffer (pH 9.2).

PPi


. Data at 445
Intensity
% formation relative to L
Obs-Calc intensity (unweighted)
value
titre volume/ml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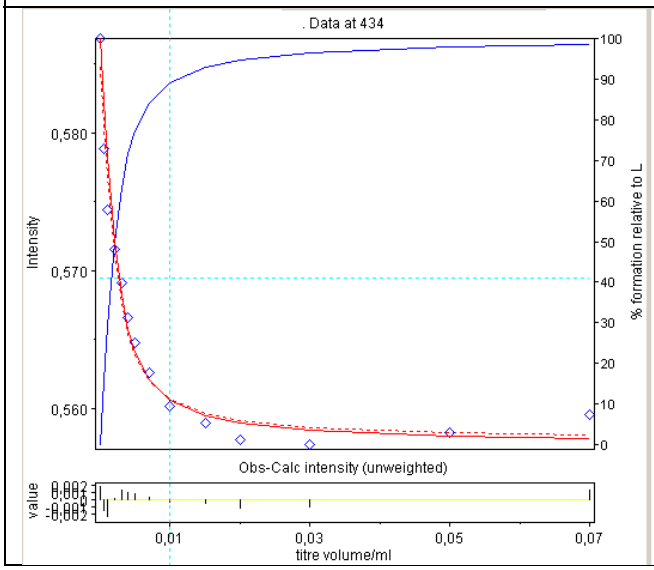
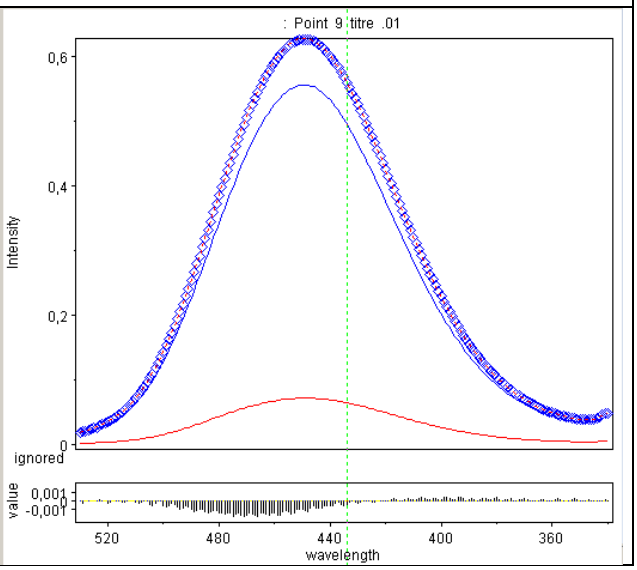
Intensity
ignored
value
wavelength

ATMP


. Data at 434
Intensity
% formation relative to L
Obs-Calc intensity (unweighted)
value
titre volume/ml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Intensity
ignored
value
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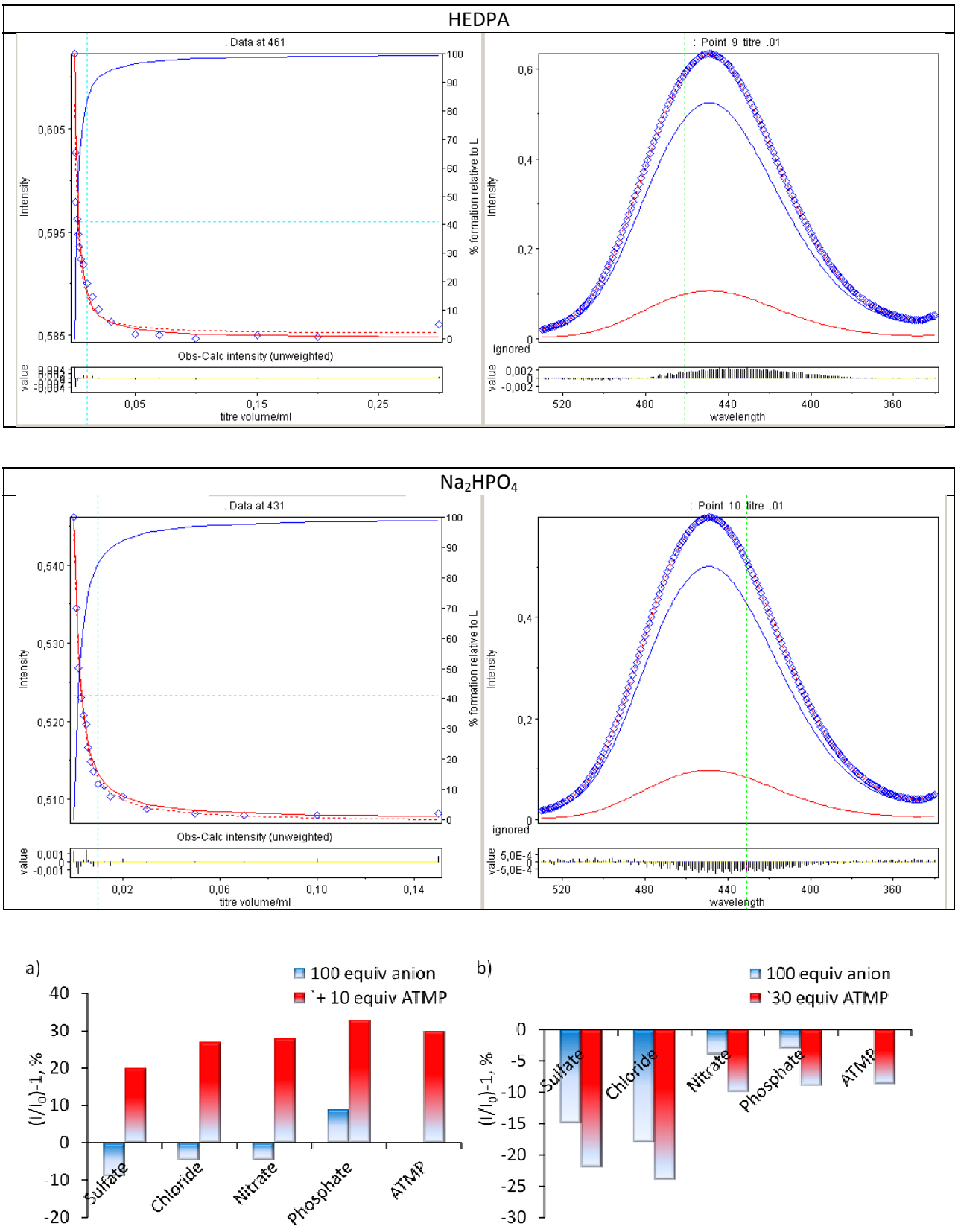

Figure S18. Fluorescence studies of probe responses in the presence of different anions for a) **M**, b) **P3**. The spectra were recorded after addition of 10-30 equiv of ATMP (red bars) to a 0.01 mmol solution of receptors + 100 equiv of a competing anion (blue bars) in 50 mmol TRIS buffer pH 9.2

DFT calculations and geometry optimization

The tables contain the atomic coordinates (Cartesian, in angstroms) for the four structures of complexes M with PPi, shown in Fig. 6.

M···$H_2P_2O_7^{2-}$

66
Coordinates from ORCA-job

C	-0.16982181341239	0.25482891501801	0.02479774094879
C	1.16019129456472	0.17463315859337	0.08259991306823
C	2.07545068224463	1.36217193979415	0.13457885995204
N	3.01555045124637	1.39489927705588	-0.98603192259914
H	-0.79527107890791	-0.64263137947166	0.01112678319629
H	-0.68142203866146	1.22297196078181	-0.00600532328517
H	1.65059027669911	-0.80629818860686	0.10892819947271
H	1.50054747398412	2.29542502670341	0.11304777476839
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C	4.22170233591018	0.69769355493459	-0.83421244713344
C	2.63035302522470	2.09031660177978	-2.12537780732292
O	1.54742659905771	2.65224754989115	-2.17548580027673
O	4.44039237213290	0.09206411551429	0.20699968610208
C	5.15429399474557	0.74432522248164	-1.95356496951200
C	4.83740422240989	1.45270632898961	-3.13819893661490
C	3.59173073254885	2.11935338051378	-3.24740565667396
C	6.37751930271201	0.08337005509997	-1.87451969360372
C	7.29498637693534	0.10889222722929	-2.91786634818205
C	7.03044567720596	0.81756792679000	-4.10571757041274
C	5.75488267111409	1.50060426745760	-4.22872591151086
C	3.25829308297079	2.81028087674979	-4.40204602982110
C	4.15513439166600	2.85613363362902	-5.47779197614753
C	5.37806817767442	2.21353713363899	-5.38781986248628
H	6.61335739888084	-0.46783338110294	-0.96126209843929
H	8.23694458116863	-0.42728675671335	-2.80451467459828
H	2.29022827113493	3.31264072519968	-4.45423800719393
H	3.89081862859050	3.39766930504141	-6.38817466591021
H	6.04794818501880	2.27066813353900	-6.24863820768035
N	7.92951777746665	0.88752496415972	-5.10590551052730
C	9.20087328742369	0.20587250874714	-5.14959633906130
C	9.09345299370817	-1.23445247432078	-5.65856310559713
H	7.66966836668896	1.39341644386535	-5.94180830132659
H	9.85993351017857	0.79081681926171	-5.80731842146834
H	9.67000403449693	0.20894188172493	-4.15412334861860
H	8.45597603889270	-1.80299219834829	-4.96203519027719
H	8.55744124352514	-1.22609377880165	-6.63208877913274
N	10.38607004851517	-1.88203958377429	-5.72431598794305
C	10.34619685590701	-3.31902176056519	-5.50710256242314
C	9.56502323283287	-4.14609619692395	-6.53668784870198
N	9.96781787928698	-5.54433290847314	-6.57751345509028
H	9.94795194865632	-3.51286364508578	-4.49511179012983
H	11.37985174917850	-3.69590662130600	-5.51788960888902
H	8.47985700082077	-4.07964871122309	-6.34916311036203
H	9.73650199395495	-3.73588535420929	-7.54412118006802
H	9.84176716605941	-5.98984352567527	-5.66865982427259
H	10.97613264548546	-5.55695692520193	-6.80493548918384
C	11.19222208873037	-1.49245939285734	-6.86785855600556
C	12.68635484506465	-1.62561558392024	-6.60834981281883
N	13.42942362136764	-1.40562659597341	-7.84348612369661
H	10.95258060841011	-2.08061041430187	-7.77725590512568
H	10.96972913118611	-0.44171594034691	-7.11554468006345
H	12.90574844608794	-2.65379911222270	-6.28616562116212
H	12.97900916768027	-0.93792280345547	-5.79269494603379
H	14.43105428460843	-1.49007699744501	-7.67469007059861
H	13.28598665911681	-0.45496470094202	-8.18712810782587
H	12.94146251721424	-2.59245225144746	-8.92022273731830
H	9.38506071167869	-6.21726879317360	-7.94235859898366
O	9.15341553189304	-6.52600482740243	-8.88988926588357
P	10.51560312627040	-6.77713196866823	-9.72993907529310
O	12.60746056467611	-3.26752867919916	-9.59988009237866
P	12.64540652142361	-4.80497260728801	-9.07980909564643
O	12.60569511257768	-4.84852532179472	-7.56028420579818
O	13.73556231133650	-5.55946332642608	-9.79901649195951
O	11.17478714464915	-5.24695201103353	-9.69122625130686
O	11.43534747701922	-7.72075346832506	-8.99350224832965
O	10.12736937285679	-7.05463636454628	-11.16032053663056

$MH_2^{2+} \cdot HP_2O_7^{3-}$

67
Coordinates from ORCA-job

C	0.02312524665673	0.14673262403023	0.13261678909633
C	1.35657156701797	0.15765768034424	0.11121040336952
C	2.18849675690629	1.40186213072974	0.00831231406310
N	3.05361071765885	1.40185872150403	-1.17174831199414
H	-0.53795452580887	-0.78718298120404	0.23157012574512
H	-0.55555540903626	1.07372841143649	0.05672833547249
H	1.91472150509808	-0.78383650097950	0.18492438656778
H	1.54997451769783	2.29124006873989	-0.04822950038993
H	2.84961679846931	1.48217678097665	0.88211289938770
C	4.31143753283891	0.79731538561952	-1.04705531755957
C	2.55122364710890	1.97313411871245	-2.33436511009977
O	1.43050777775953	2.45704900721646	-2.35635336967784
O	4.63535964404488	0.29451534144941	0.02097640337245
C	5.16787142285310	0.80997275479181	-2.22724550378303
C	4.73009563959284	1.39539617712196	-3.44025324082526
C	3.43753541168151	1.97099693213546	-3.51710345299142
C	6.43655672541585	0.23894381554494	-2.17788882359170
C	7.28417458258826	0.23669630402454	-3.27958775521649
C	6.89701390782755	0.82271250736713	-4.49971951652592
C	5.57243986931230	1.40991719338925	-4.59070812092102
C	2.98686334061252	2.54183631307520	-4.69715322935293
C	3.80988583585141	2.55441284403482	-5.83139387846935
C	5.07660604075006	1.99902233185162	-5.77447554439071
H	6.76633610335923	-0.21713939454014	-1.24156314219353
H	8.26666451570445	-0.22553141376508	-3.18645172235580
H	1.98560824059271	2.97664499087728	-4.72303788498036
H	3.45307272367475	3.00104057623985	-6.76155331039435
H	5.68553441092682	2.02576058365183	-6.68091974760275
N	7.72507890992807	0.86455607924759	-5.56204456875602
C	9.04179947156485	0.27967899163871	-5.62799305394973
C	9.01956149587222	-1.20730810981857	-5.99238566994984
H	7.37851383859559	1.27621680211413	-6.41777239757354
H	9.61200822099526	0.84652603282642	-6.37823063284255
H	9.56703610544495	0.41223938250527	-4.66995030214007
H	8.44648609760195	-1.74615743679022	-5.22119427704372
H	8.45946485609711	-1.33491781435326	-6.94261493054107
N	10.35312026506056	-1.77322048116434	-6.03806968433410
C	10.42900684310226	-3.17019062730223	-5.65644604928136
C	9.71708628970118	-4.15266155679254	-6.59574486689150
N	10.36983660479064	-5.46658541877828	-6.59674299234658
H	10.03774625155467	-3.27710690700877	-4.63150135833599
H	11.49001810599068	-3.46033373470165	-5.61532436625595
H	8.65636027679986	-4.27721853800812	-6.33480862761960
H	9.76217190048750	-3.79373505924522	-7.63333486550249
H	10.29992182218575	-5.94454003667789	-5.69697852621046
H	11.38570796929002	-5.31894223288917	-6.85240909627961
C	11.11189493520908	-1.43836961398976	-7.22653737972076
C	12.60773242732810	-1.40697307298729	-6.94946697709148
N	13.35802844846496	-1.21752017791021	-8.20248015341735
H	10.92204583179388	-2.13352366874661	-8.07110264505616
H	10.79916311016683	-0.44339708507317	-7.57915121393607
H	12.94552042823622	-2.36574601028134	-6.53438766517837
H	12.85447820831159	-0.60211565140688	-6.24320819088062
H	14.35955873236961	-1.11997011604265	-8.02120332686389
H	13.06866733163139	-0.37041728201034	-8.69869137462759
H	13.21786990087163	-2.09801270646373	-8.87275051471843
H	9.97463439586883	-6.09797074125395	-7.40782789984037
O	9.59654417675857	-6.81050356468195	-8.64844253721322
P	10.44511028203421	-6.49735734178967	-9.89789168942150
O	13.00180527125482	-3.25858437255704	-9.69956994270573
P	12.65528037992483	-4.62690020739054	-9.10696375595057
O	12.76248877235827	-4.73055539393566	-7.58785917161449
O	13.50168566893153	-5.75428565606515	-9.84736894342457
O	11.12123487941005	-4.96338411463497	-9.55243060047878
O	11.70653301624159	-7.39928544300514	-10.00285563544924
O	9.66539849882941	-6.31129077085882	-11.17596711336256
H	12.81962543178568	-6.57497964809298	-9.95902217695238

$MH^+ \cdot H_2P_2O_7^{2-}$ (N_3 protonated)

67
Coordinates from ORCA-job

C	0.05431703054966	-0.05115984424115	0.02854748351365
C	1.38592871941842	0.02218556892590	0.03815566388968
C	2.16065017987301	1.30328312980074	-0.05875167615262
N	3.05188283220592	1.33205193936691	-1.21924564899457
H	-0.46451566423439	-1.00952679988847	0.12422092185462
H	-0.56529275733327	0.84670049786772	-0.07072585880901
H	1.98543061332772	-0.89140980656069	0.13477546228673
H	1.48270105164576	2.16096788352746	-0.13997363270487
H	2.79677202543822	1.42405612370002	0.82878851567383
C	4.33382090276242	0.79292844276377	-1.05960638424993
C	2.54803850440350	1.86373276875093	-2.40044427624001
O	1.40727401786184	2.29383114553252	-2.45227120881388
O	4.66239515992453	0.32318743050895	0.02089234586649
C	5.21455587206888	0.82903042572651	-2.22457045025151
C	4.77265120146213	1.37108559562581	-3.45605371154654
C	3.45739502242014	1.88605052146220	-3.56590827681247
C	6.50669453617373	0.32413581656469	-2.13844140786308
C	7.37347916853288	0.33944035778361	-3.22796202695694
C	6.97714494132874	0.87246102722114	-4.46507474306515
C	5.63471620586610	1.40340470568807	-4.59102961764466
C	3.00541344759113	2.41948945566559	-4.76219215262980
C	3.85035848321256	2.45493009235753	-5.88047006141794
C	5.13796886314025	1.95640034617608	-5.79277871986562
H	6.84199766895047	-0.09499215252155	-1.18710390005898
H	8.37509901354295	-0.07239129585190	-3.10427417644222
H	1.98651791352539	2.80849331832718	-4.81418169447798
H	3.49315902391009	2.87563947633749	-6.82245703234241
H	5.76368887715712	2.00254229732637	-6.68677395401595
N	7.81525364661589	0.91439383748039	-5.52683177768434
C	9.15439441541193	0.39592687867038	-5.55817174175629
C	9.16014493754308	-1.10426682319090	-5.84585322415057
H	7.46172886451624	1.27527467489766	-6.40233233185155
H	9.70288178172304	0.94448832269259	-6.33616489340141
H	9.66713086444065	0.60321386564015	-4.60499935011692
H	8.60647959846243	-1.64097749655727	-5.06341851864815
H	8.68814899963169	-1.31726669087754	-6.81403156373167
N	10.53814467176030	-1.67754226856563	-5.87667876654475
C	10.53460388104355	-3.15887618128464	-5.62372558781977
C	9.62801428658265	-3.95860426047251	-6.55353963805348
N	9.98904510166816	-5.36221919511090	-6.55951194564151
H	10.25161088954245	-3.29432928710029	-4.57048621123165
H	11.56522153718513	-3.50353319744792	-5.76890579381009
H	8.57148417289620	-3.84666528512872	-6.26495504073635
H	9.72160597897359	-3.59224829960137	-7.58716029877667
H	9.88872052137871	-5.77839110694977	-5.63445941464860
H	10.97897506222730	-5.41833542984874	-6.84538904061981
C	11.29000914464749	-1.31309242236313	-7.11736411667127
C	12.79356369901087	-1.42326182191000	-6.93290341614549
N	13.43387381525688	-1.20398978333982	-8.21975773034786
H	10.95846969525052	-1.98237573251928	-7.92077432310671
H	11.00942970271767	-0.28628590507061	-7.38652122677632
H	13.04820601561400	-2.44491269316169	-6.61858268642840
H	13.12620787571685	-0.71679241150871	-6.14892858187410
H	14.43710809655381	-1.36454504579406	-8.13944388439145
H	13.32868184244811	-0.23424287313881	-8.52051627132908
H	12.76737742436887	-2.37096370228912	-9.27501901937315
H	9.34731390318605	-6.10922757691152	-7.92184294349470
O	9.12227315209899	-6.44055396294880	-8.85053147518158
P	10.50175307475013	-6.72806565891032	-9.65760806523811
O	12.31810253279579	-3.08210523817189	-9.82986785504612
P	12.51637930738546	-4.58090466910020	-9.22339340296440
O	12.48682099805108	-4.52523858240771	-7.70180829566438
O	13.67179187112500	-5.27242195637312	-9.89774413479693
O	11.08912696469817	-5.17270212990758	-9.79499157964151
O	11.45705764275543	-7.52789498269875	-8.80798825896489
O	10.13313460747893	-7.18056033283375	-11.04560794498720
H	11.04938656775984	-1.26465304382933	-5.08667943008088

$MH^+ \cdot H_2P_2O_7^{2-}$ (N_1 protonated)

67
Coordinates from ORCA-job

C	0.02126538161298	0.08866478853392	0.16016673031914
C	1.35435825628253	0.12411840809954	0.14382669460326
C	2.16383111022053	1.38309694774691	0.04073032201016
N	3.02564007352843	1.39788388891171	-1.14167957845783
H	-0.52294702088686	-0.85530795509693	0.25798660231805
H	-0.57402092751542	1.00474051061470	0.08043387502189
H	1.92928702314609	-0.80705147787045	0.22042726330472
H	1.50940254472551	2.26100993530265	-0.01382242988493
H	2.82573746529201	1.47474942895239	0.91266254080652
C	4.29984481396982	0.82839465079915	-1.01764646078330
C	2.50331123631126	1.94673805599335	-2.30632620228196
O	1.37145745946053	2.40393520766894	-2.32567697150271
O	4.64384711984702	0.34719772982261	0.05394485854967
C	5.14820094010181	0.84818238192621	-2.20394709931357
C	4.68589821689221	1.40378223134479	-3.42183271123987
C	3.38132380183301	1.95203060782693	-3.49500679957127
C	6.43225089881975	0.31232821442335	-2.15596524569656
C	7.26782643319298	0.30761116592986	-3.26707743803917
C	6.85008229286487	0.85102174676807	-4.49601640652058
C	5.51658965680954	1.41771433679303	-4.58049144504694
C	2.91056396772574	2.50182376488485	-4.67712618899329
C	3.72515572788116	2.52057549407284	-5.81738328879084
C	5.00160725628716	1.98780566529056	-5.76558864657220
H	6.78305450635132	-0.11709963884394	-1.21470277081630
H	8.26100992554047	-0.13209630734994	-3.17698709917325
H	1.90086715516081	2.91683128666408	-4.69953916636678
H	3.35439958394640	2.95475675999067	-6.74797512720782
H	5.60421739305340	2.02126225604931	-6.67598475531489
N	7.65568226149210	0.87168111891461	-5.57643690971865
C	8.98636152355332	0.32090431658113	-5.65780374763182
C	8.96287364552731	-1.17583005274258	-5.97642920358453
H	7.27789148339387	1.23400472395343	-6.44134389809374
H	9.51720868866141	0.84928840466030	-6.46077812986383
H	9.52776920975315	0.53358309042431	-4.72374460697808
H	8.48017319553666	-1.72915236720799	-5.14378717745035
H	8.32453932303040	-1.29207365225937	-6.86400483035325
N	10.27825863954177	-1.73754884238153	-6.28786643101216
C	10.19592985610960	-3.16798780812034	-6.62503618387360
C	9.16614911855359	-3.61246085763892	-7.64789185575787
N	9.42119758968601	-3.12777919066459	-9.01126838648944
C	11.24594356958904	-1.57056019744284	-5.18143733102737
C	12.38464012249008	-0.59031818002767	-5.41477136737240
N	13.35943888852646	-1.07591973946650	-6.38869535575239
H	11.19157285007942	-3.47422150404631	-6.97874416465193
H	9.97331416512373	-3.75135180511890	-5.70931964740192
H	9.20823634908142	-4.71073934426407	-7.66496931783394
H	8.14198229445374	-3.34035451810885	-7.35570170717872
H	8.89984742673177	-3.67504409306476	-9.69775956905946
H	9.16611296045134	-2.09531468135326	-9.16202022744522
H	10.71291325676740	-1.27336798439864	-4.26244176703853
H	11.69021946969230	-2.55234740935530	-4.94905673706357
H	11.99694218013563	0.37912688479551	-5.76185011081655
H	12.84850918105383	-0.41316496594711	-4.42644347891985
H	13.70108195349011	-1.99398327635736	-6.09845494712210
H	14.18189840045353	-0.47219354538482	-6.35638776963344
H	13.27991572814044	-1.04786439148722	-8.10709902548761
H	10.47055017793318	-3.17155614966542	-9.24764842322800
H	10.80823441122967	-0.65135370049767	-7.52429259224643
O	9.03884695242422	-0.56746198377900	-9.47472396267681
P	10.37028025795592	0.17903205286968	-9.54427265935305
O	11.39514967115286	-0.73321176114124	-10.46253127875526
P	12.62011949276582	-1.79186817693403	-10.10415291112317
O	10.39407256914071	1.57571137697029	-10.08423746929159
O	13.35995220079728	-2.00776279587769	-11.38988319898045
O	11.06297281131512	0.14817800566257	-8.08700710647076
O	11.99770537563896	-2.99145167118872	-9.38936003517046
O	13.55686045609079	-0.98921541415825	-9.07835953345042

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