Molecular Tweezers with Varying Anions - A Comparative Study

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Supporting Information

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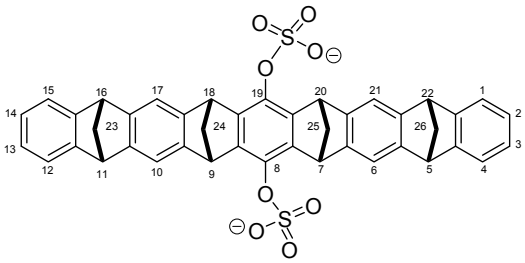
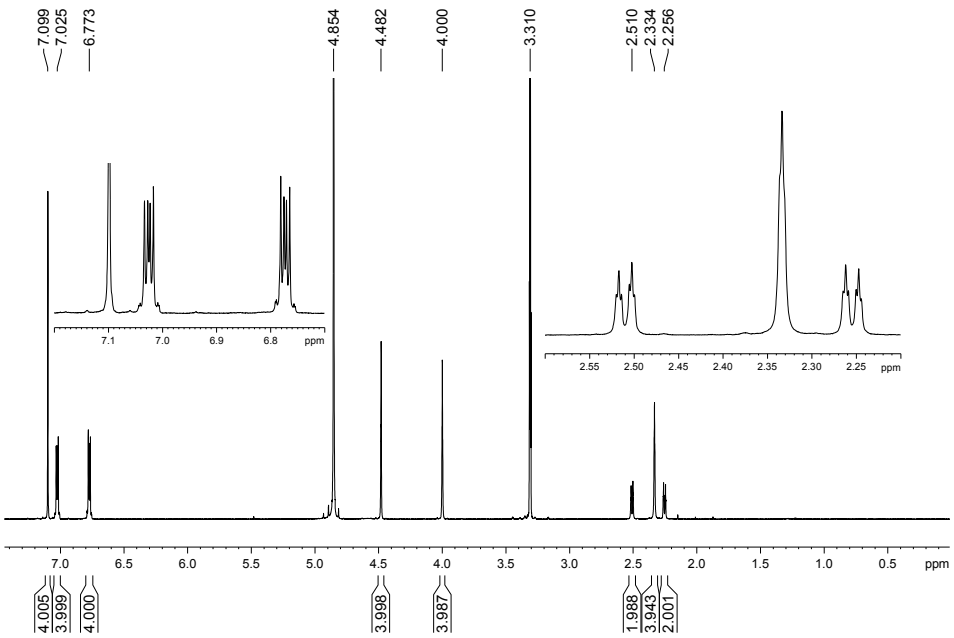
1 Experimental Section

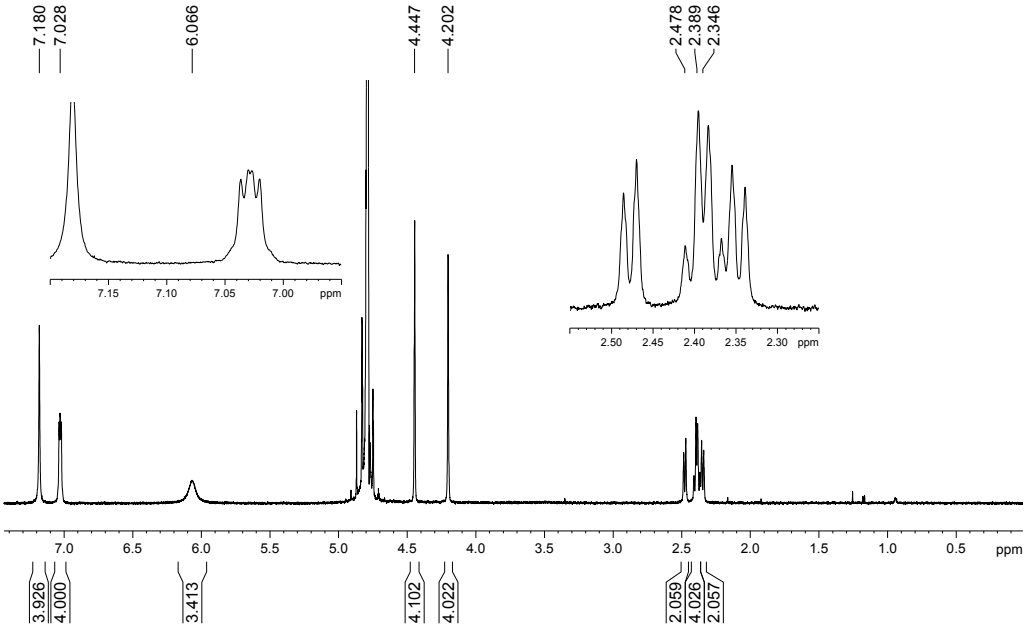
1.1 ^{1}H NMR and ^{13}C NMR spectra of the tweezers 1c, 1g, and 1d



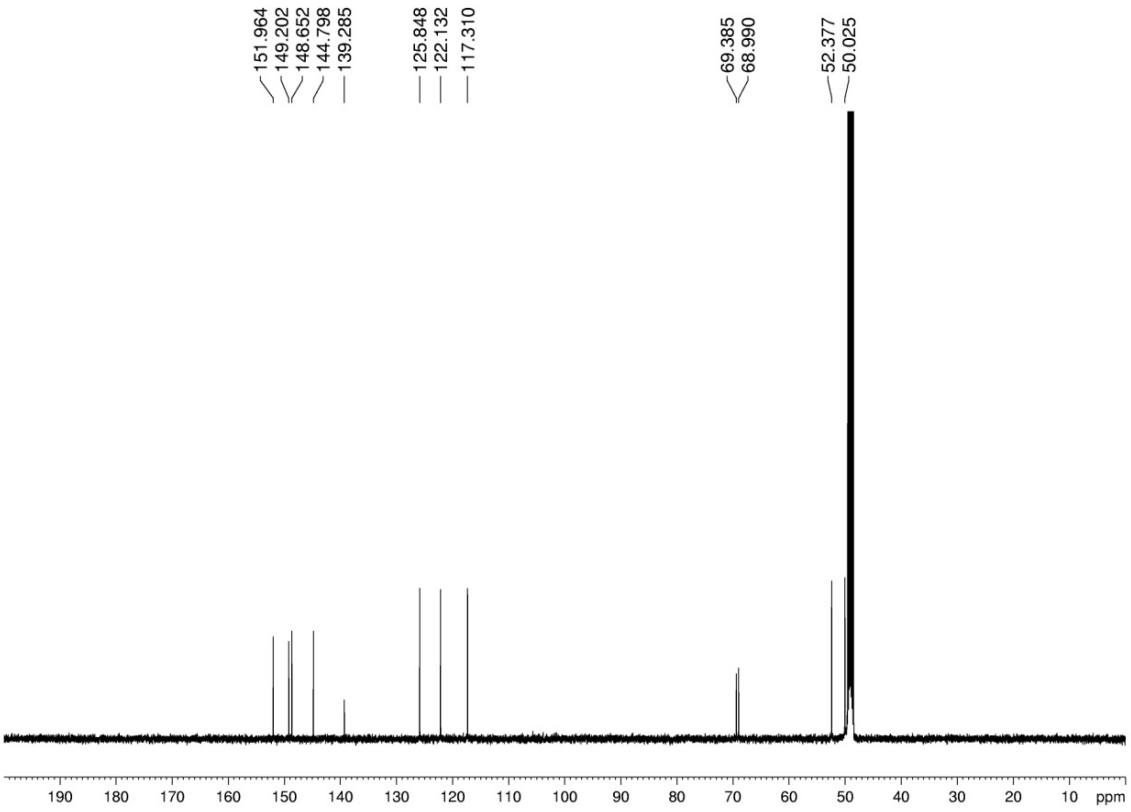
^{1}H-NMR in CD_3OD: **1c**

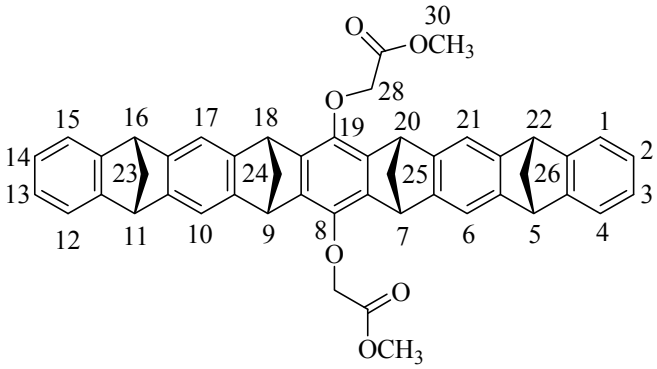


^{1}H-NMR in D_2O: **1c**

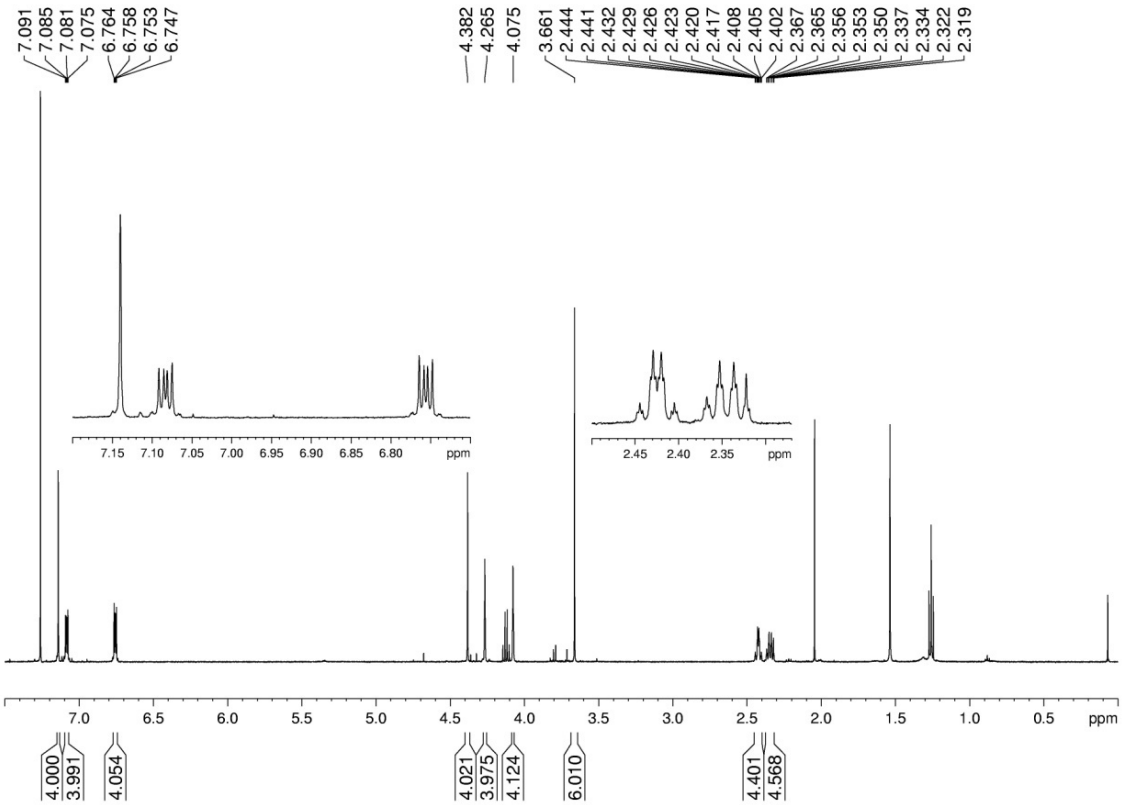


^{13}C-NMR in CD_3OD: **1c**

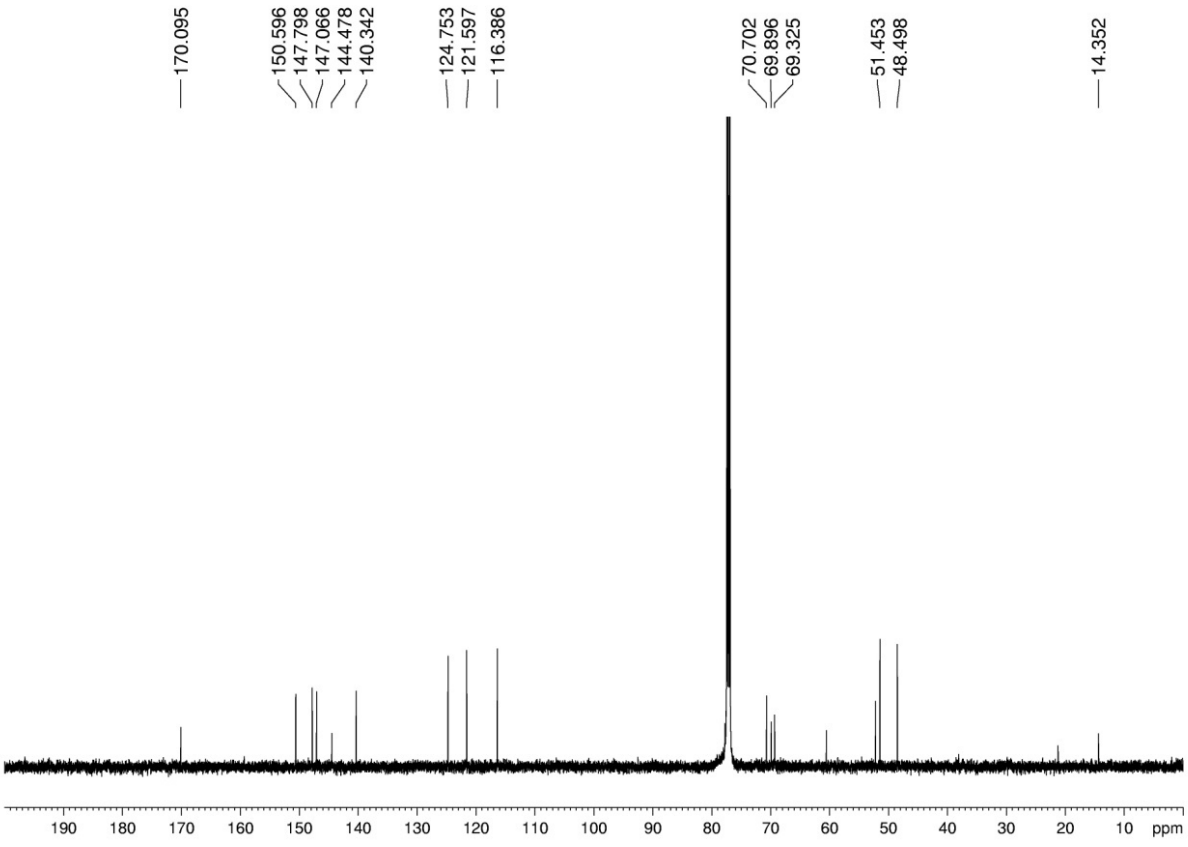


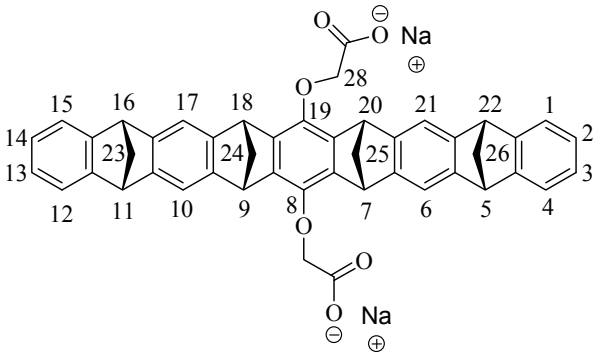


^{1}H-NMRin $CDCl_3$: **1g**

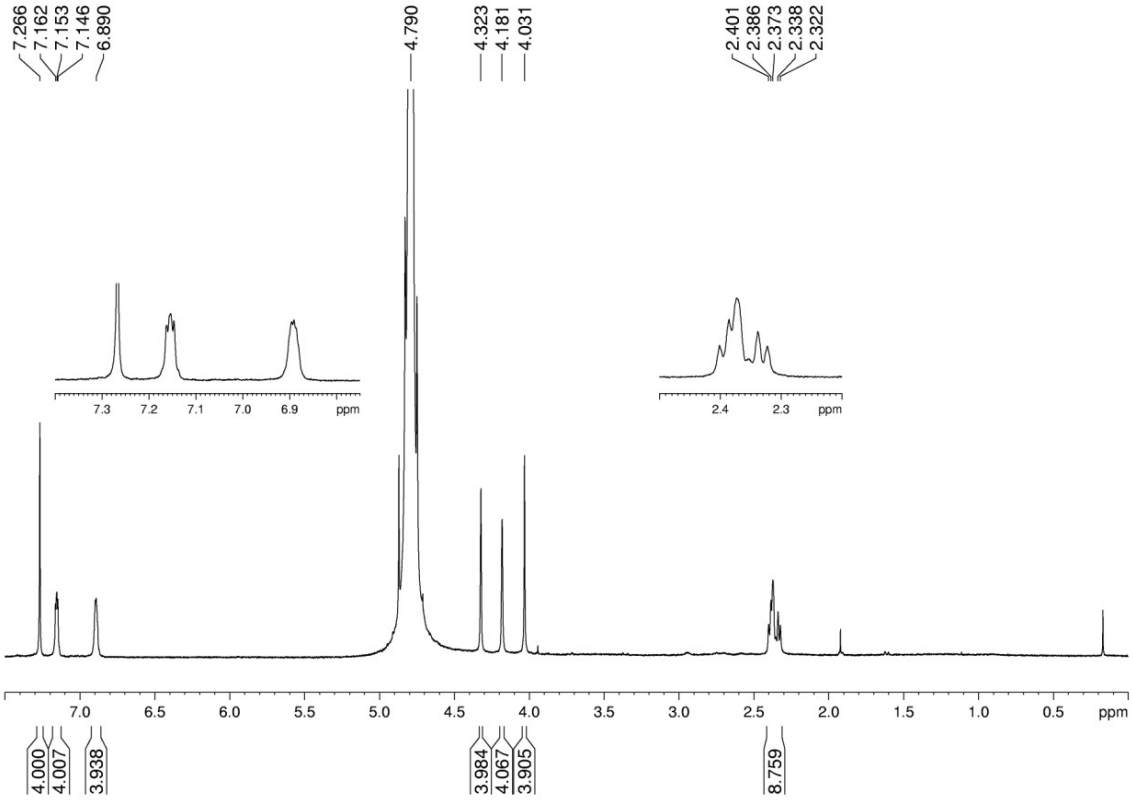


^{13}C-NMRin $CDCl_3$: **1g**

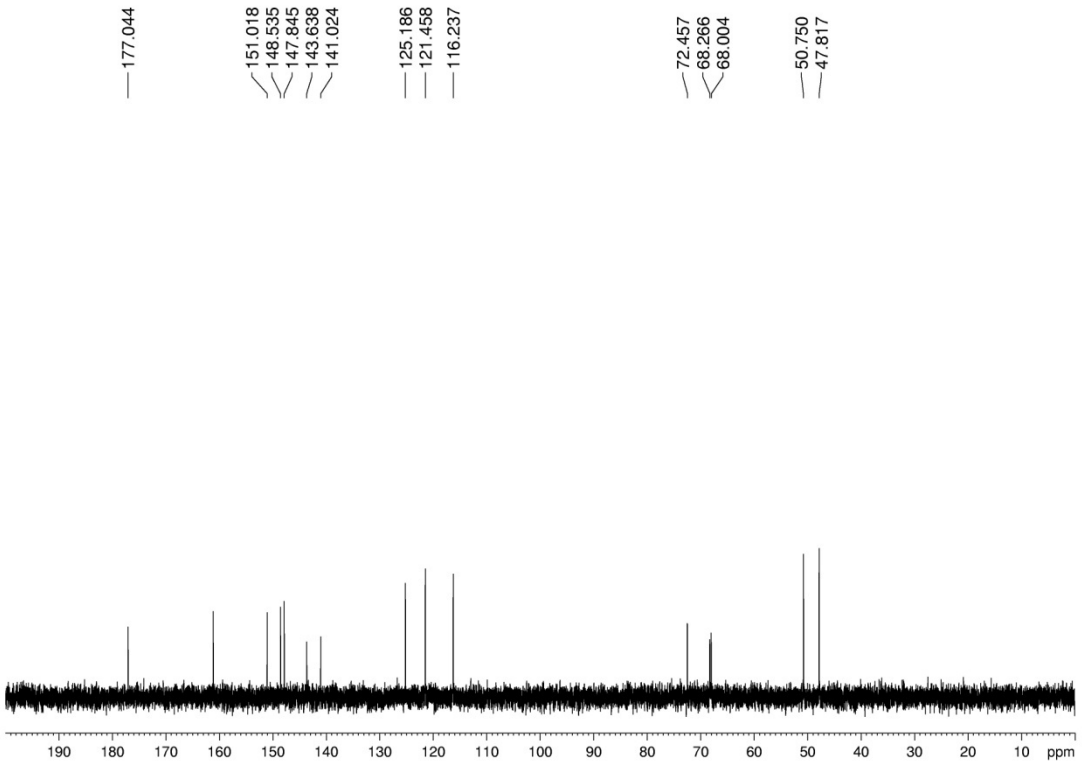




^{1}H-NMR in D_2O: **1d**



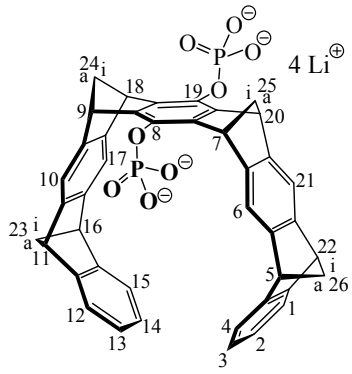
^{13}C-NMR in D_2O: **1d**



1.2 Dimerisation of the molecular tweezers determined by NMR titration

1.2.1 Dilution titration of the phosphate tweezer 1a

Receptor (R)	**1a**	M_Rg/mol]	1a.19
Solvent	Phosphate buffer	m_R(**1a**) [mg]	10.10
Substrate	**Itself**	V_0 [mL]	2
T [°C]	25	[**R**]$_0$ [mM]	7.40



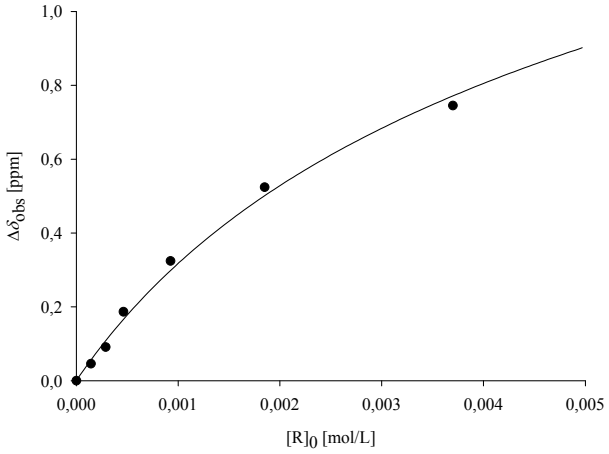
δ_0 (5-H, 11-H, 16-H, 22-H) = 4.162

δ_0 (6-H, 10-H, 17-H, 21-H) = 7.260

δ_0 (1-H, 4-H, 12-H, 15-H) = 7.142

δ_0 (2-H, 3-H, 13-H, 14-H) = 6.865

[1a] [mM]	δ_{obs}(2-H, 3-H, 13-H, 14-H)	**$\Delta\delta_{obs}$**	**$\Delta\delta_{calc}$**
7.40	6.120	0.745	0.771
3.70	6.341	0.524	0.501
1.85	6.541	0.324	0.298
0.92	6.679	0.186	0.166
0.58	6.775	0.091	0.109
0.29	6.820	0.046	0.057



K_{dim} [M^{-1}] = 60 ± 10

$\Delta\delta_{max}$ (5-H, 11-H, 16-H, 22-H) = - 0.20

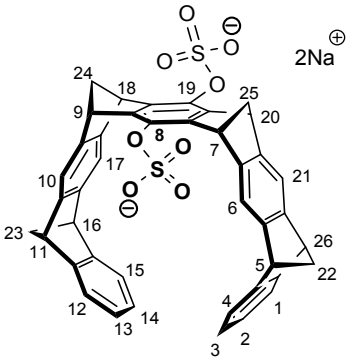
$\Delta\delta_{max}$ (6-H, 10-H, 17-H, 21-H) = - 0.28

$\Delta\delta_{max}$ (1-H, 4-H, 12-H, 15-H) = 0.37

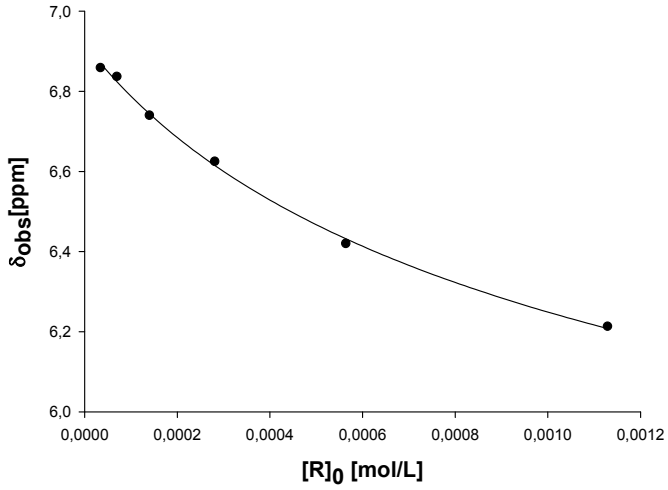
$\Delta\delta_{max}$(2-H, 3-H, 13-H, 14-H) = 2.23

1.2.2 Dilution titration of the sufate tweezer 1c

Receptor(R)	**1c**	M_R[g/mol]	770.78
Solvent	Phosphate buffer	m_R[mg]	1.13
T[°C]	25	V_0 [ml]	2.3
Substrate	**Itself**	$[R]_0$[mM]	1.13



[R][mM]	δ_{obs}[ppm]	$\delta_{monomercalc}$- δ_{obs} = $\Delta\delta_{calc}$[ppm]
1.13	6.212	0.707
0.565	6.419	0.500
0.282	6.624	0.295
0.141	6.733	0.186
0.0706	6.836	0.083
0.0353	6.858	0.061



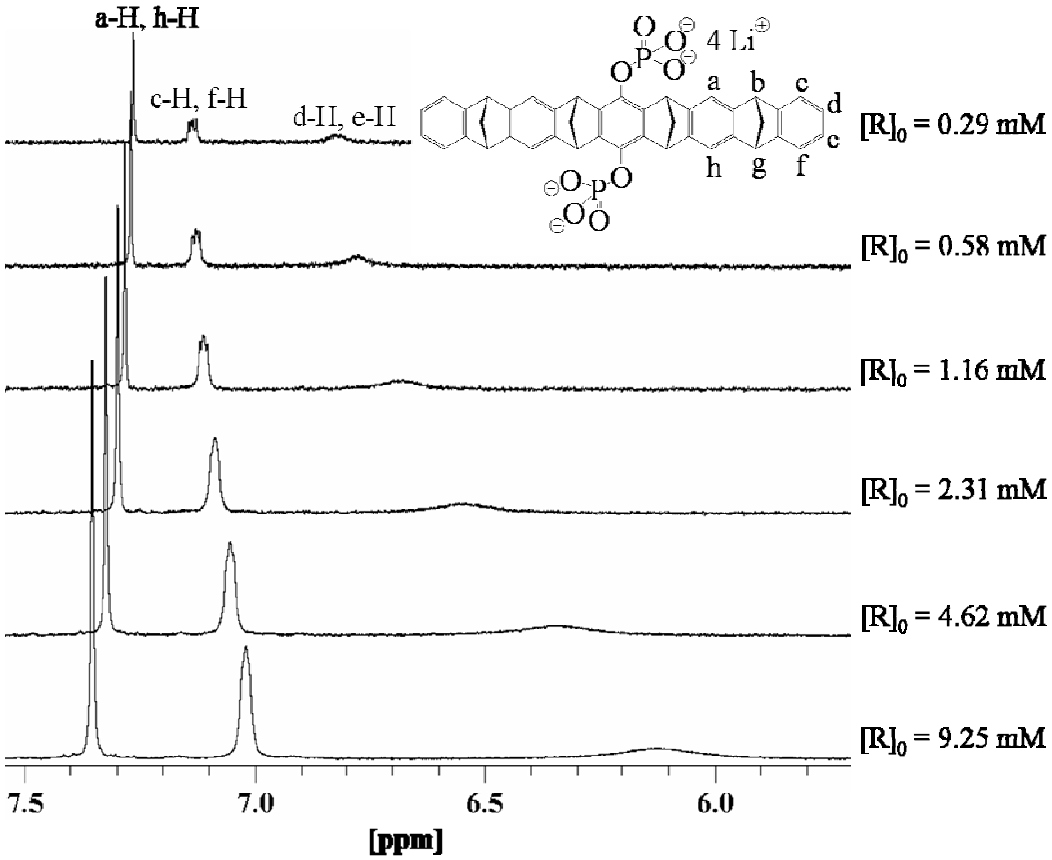
$K_{dim}[M^{-1}]$ = 370 ± 80

$\Delta\delta_{max}$[ppm] = 2.02

$\delta_{monomercalc}$[ppm] = 6.92

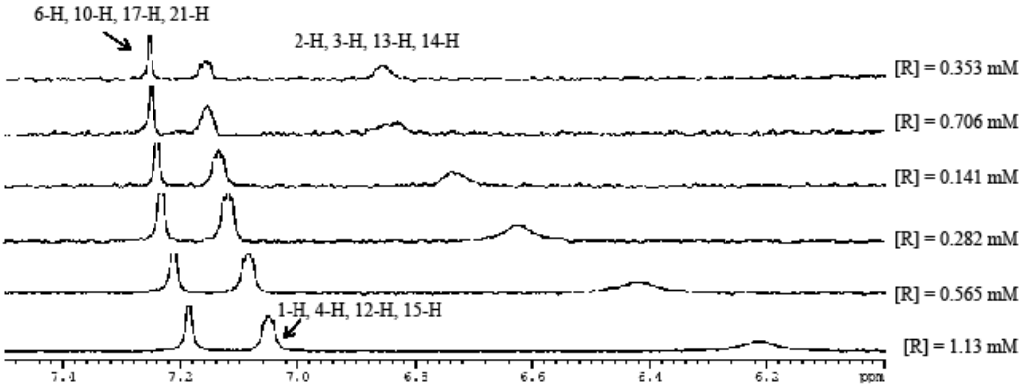
1.2.3 Concentration-dependent ^{1}H NMR spectra of tweezer 1a

in aqueous phosphate buffer (70 mM, pH 7.2, 25°C)



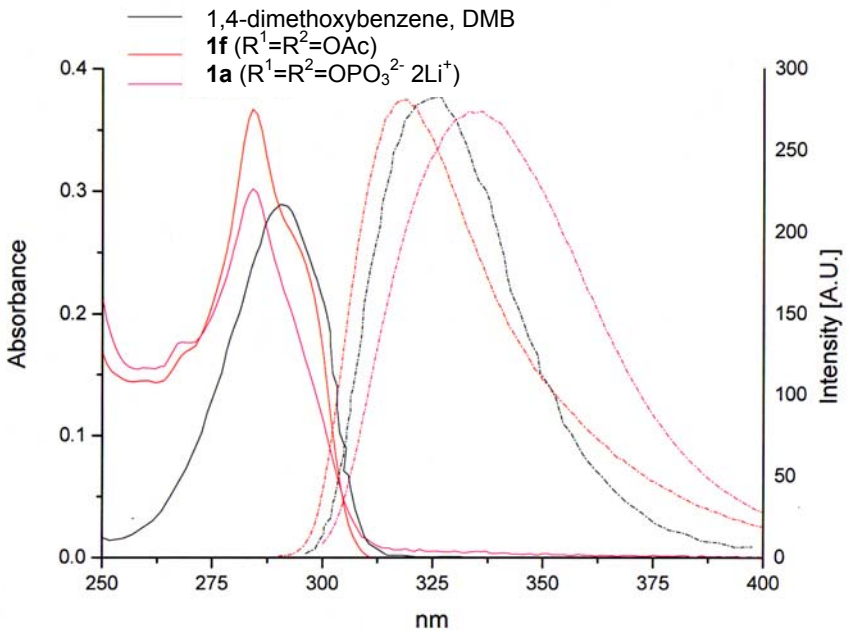
1.2.3 Concentration-dependent ^{1}H NMR spectra of tweezer 1c

in aqueous phosphate buffer (10 mM, pH 7.2, 25°C)



1.3 Fluorescence titrations

1.3.1 UV-Vis and Fluorescence spectra of molecular tweezers and 1,4-dimethoxybenzene



Compound	Solvent	Absorption		Emission		
		$\lambda_{max}\varepsilon_{max}$		$\lambda_{max}\Phi_{em}\tau$		
		[nm]	[M^{-1} cm^{-1}]	[nm]		[ns]
1a (R^1=R^2= OPO_3^{2-} $2Li^+$)	H_2O	284	-	336	0.10	3.1
1f:(R^1=R^2= OAc)	CD_3CN	284	-	318	0.11	3.8
1,4-dimethoxybenzene	CD_3CN	290	2800	320	0.11	2.5

Figure S1. UV-VIS and fluorescence spectra of the molecular tweezers substituted by phosphate or acetoxy groups in the central benzene bridge and of 1,4-dimethoxybenzene (determined by P. Ceroni, Dipartimento di ChimicaCiamicianUniversita' di Bologna Via Selmi, 2, 40126 Bologna, Italy).

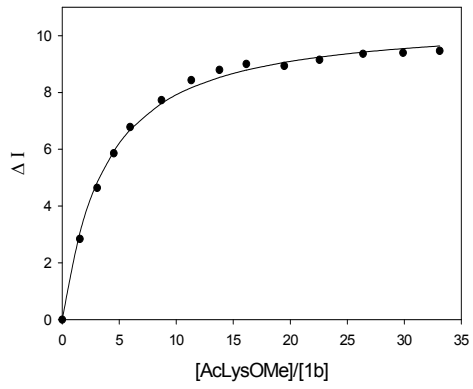
1.3.2 Fluorescence titrations

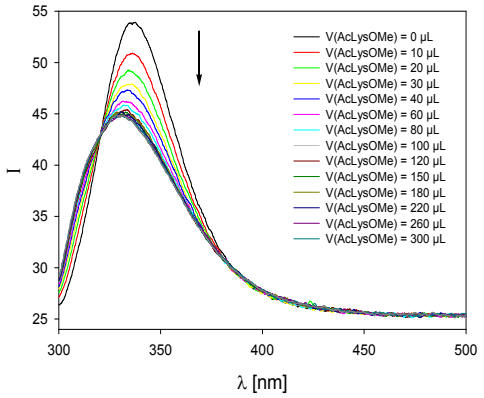
Fluorescence titrations for Ac Lys OMe

Titration of **Ac Lys OMe** and tweezer **1b** in phosphate buffer (200mM, pH 7.64)

λ_{exc}= 280 nm	Receptor **1b**	Guest Ac Lys OMe· HCl
Amount [mg]:	0.165	0.38
Volume [mL]:	10.277	0.66
Concentration [mol/L]:	$2.18 \cdot 10^{-05}$	$2.4 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{336})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.19E-05	0.00E+00	0.00	53.7	0.0	0.0
10	710	2.19E-05	3.40E-05	1.55	50.9	2.8	3.1
20	720	2.19E-05	6.70E-05	3.07	49.1	4.6	4.8
30	730	2.19E-05	9.91E-05	4.54	47.9	5.9	5.9
40	740	2.19E-05	1.30E-04	5.97	46.9	6.8	6.7
60	760	2.19E-05	1.90E-04	8.71	46.0	7.7	7.6
80	780	2.19E-05	2.47E-04	11.32	45.3	8.4	8.2
100	800	2.19E-05	3.01E-04	13.79	44.9	8.8	8.5
120	820	2.19E-05	3.53E-04	16.15	44.7	9.0	8.8
150	850	2.19E-05	4.26E-04	19.47	44.8	8.9	9.1
180	880	2.19E-05	4.93E-04	22.57	44.6	9.1	9.2
220	920	2.19E-05	5.77E-04	26.39	44.4	9.4	9.4
260	960	2.19E-05	6.53E-04	29.89	44.3	9.4	9.5
300	1000	2.19E-05	7.24E-04	33.11	44.3	9.5	9.6





K_a [M^{-1}] = 14766 ± 1%, K_d[µM] = 68 ± 1%

Titration of **AcLysOMe** and tweezer **1c** in phosphate buffer (200mM, pH 7.64)

λ_{exc}= 285 nm	Receptor **1c**	Guest Ac Lys OMe ·HCl
Amount [mg]:	0.156	0.410
Volume [mL]:	8.69	0.673
Concentration [mol/L]:	$2.33 \cdot 10^{-05}$	$2.55 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{337})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.33E-05	0.00E+00	0.00	918.114	0.000	0
10	710	2.33E-05	3.59E-05	1.54	725.153	192.961	193.3159
20	720	2.33E-05	7.09E-05	3.04	642.548	275.566	272.2011
30	730	2.33E-05	1.05E-04	4.50	611.539	306.575	309.9996
40	740	2.33E-05	1.38E-04	5.92	584.480	333.634	331.4145
60	760	2.33E-05	2.01E-04	8.65	565.857	352.257	354.424
80	780	2.33E-05	2.62E-04	11.23	551.001	367.113	366.4685
100	800	2.33E-05	3.19E-04	13.69	548.189	369.925	373.8478
120	820	2.33E-05	3.73E-04	16.03	541.879	376.235	378.8253
150	850	2.33E-05	4.50E-04	19.33	532.487	385.627	383.8455
180	880	2.33E-05	5.22E-04	22.40	527.754	390.360	387.2144
220	920	2.33E-05	6.10E-04	26.19	526.147	391.967	390.2914
260	960	2.33E-05	6.91E-04	29.66	525.849	392.265	392.4293
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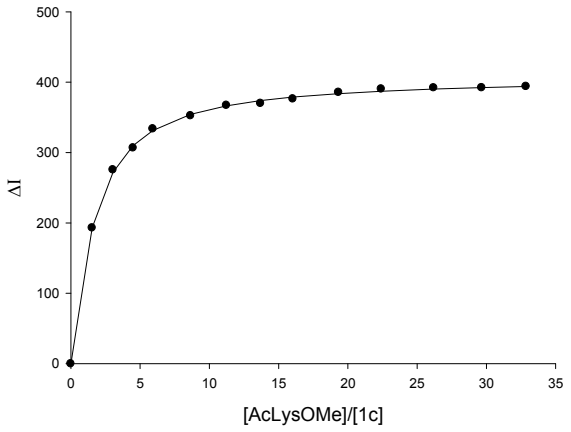
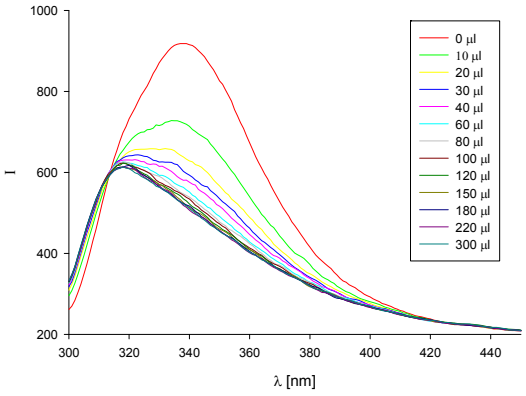




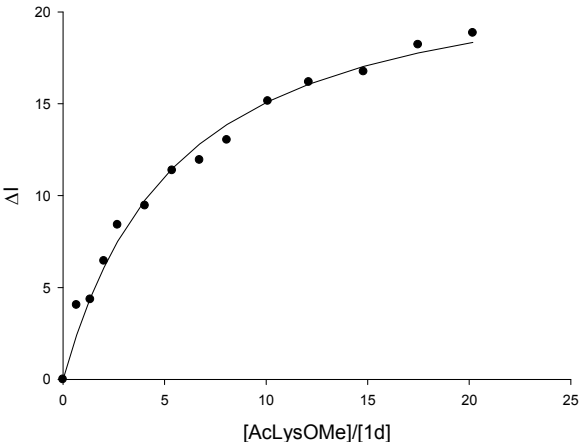
K_a [M^{-1}] = 36000 ± 2 %

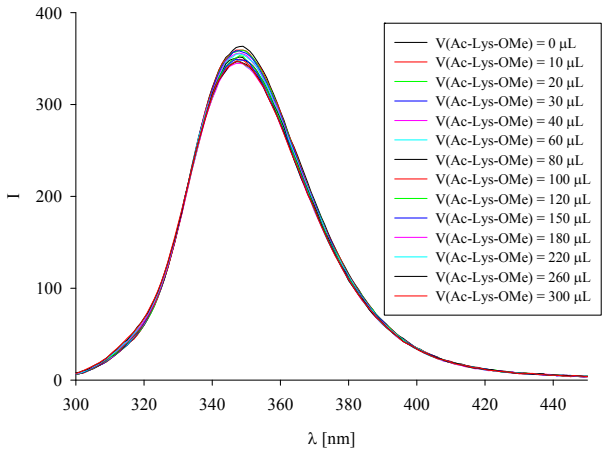
K_d[µM] = 28 ± 2 %

Titration of **AcLysOMe** and tweezer **1d** in phosphate buffer (200mM, pH 7.64)

λ_{exc}= 285 nm	Receptor **1d**	Guest Ac Lys OMe ·HCl
Amount [mg]:	0.119	0.184
Volume [mL]:	4.00	0.40
Concentration [mol/L]:	$4.094 \cdot 10^{-05}$	$1.93 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{349})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	4.09E-05	0.00E+00	0.000	363.402	0.000	0.0000
10	710	4.09E-05	2.71E-05	0.663	359.354	4.048	2.4168
20	720	4.09E-05	5.35E-05	1.308	359.055	4.347	4.4184
30	730	4.09E-05	7.92E-05	1.934	356.959	6.443	6.0942
40	740	4.09E-05	1.04E-04	2.544	354.993	8.409	7.5123
60	760	4.09E-05	1.52E-04	3.716	353.948	9.454	9.7697
80	780	4.09E-05	1.98E-04	4.828	352.032	11.370	11.4768
100	800	4.09E-05	2.41E-04	5.884	351.464	11.938	12.8070
120	820	4.09E-05	2.82E-04	6.889	350.378	13.024	13.8699
150	850	4.09E-05	3.40E-04	8.307	348.260	15.142	15.1132
180	880	4.09E-05	3.94E-04	9.628	347.229	16.173	16.0644
220	920	4.09E-05	4.61E-04	11.256	346.654	16.748	17.0304
260	960	4.09E-05	5.22E-04	12.749	345.190	18.212	17.7638
300	1000	4.09E-05	5.78E-04	14.122	344.553	18.849	18.3391





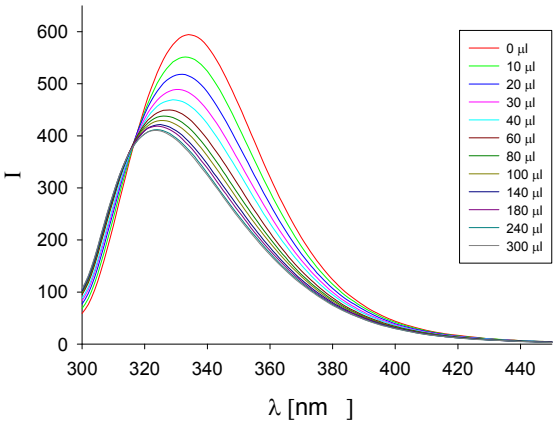
K_a [M^{-1}] = 4434 ± 14%

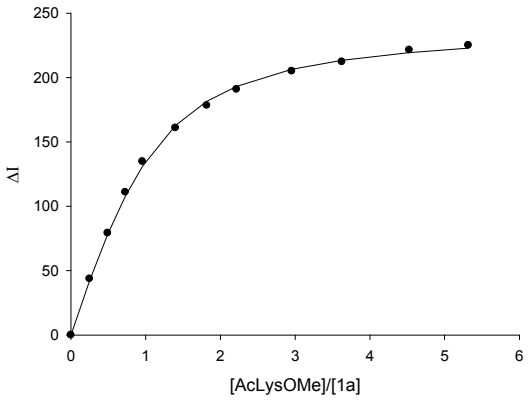
K_d[µM] = 226 ± 14%

Titration of **AcLysOMe** and tweezer **1a** in phosphate buffer (10 mM, pH 7.6)

λ_{exc}= 285 nm λ_{em}= 334 nm	Receptor **1a**	Guest AcLysOMe ·HCl
Amount [mg]:	0.225	0.263
Volume [mL]:	10.710	0.780
Concentration [mol/L]:	$2.579 \cdot 10^{-05}$	$4.573 \cdot 10^{-04}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. ($I_{334\ nm}$)**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.58E-05	0.00E+00	0.00	594.451	0.000	0.000
10	710	2.58E-05	6.44E-06	0.25	550.838	43.613	42.321
20	720	2.58E-05	1.27E-05	0.49	515.279	79.172	78.336
30	730	2.58E-05	1.88E-05	0.73	483.590	110.861	107.795
40	740	2.58E-05	2.47E-05	0.96	459.677	134.774	131.058
60	760	2.58E-05	3.61E-05	1.40	433.532	160.919	162.749
80	780	2.58E-05	4.69E-05	1.82	416.212	178.239	181.512
100	800	2.58E-05	5.72E-05	2.22	403.594	190.857	193.191
140	840	2.58E-05	7.62E-05	2.95	389.476	204.975	206.378
180	880	2.58E-05	9.35E-05	3.63	382.237	212.214	213.434
240	940	2.58E-05	1.17E-04	4.53	373.044	221.407	219.364
300	1000	2.58E-05	1.37E-04	5.32	369.385	225.066	222.793





K_a [M^{-1}] = 113000 ± 6 %

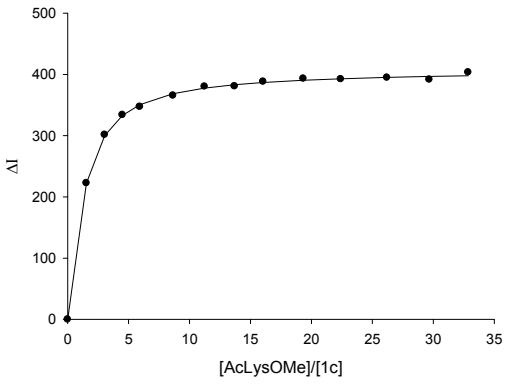
K_d[µM] = 9 ± 6 %

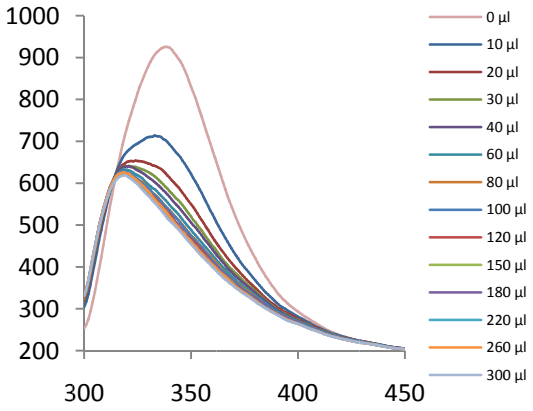
ΔI_{max} = 240 (40 %)

Titration of **AcLysOMe** and tweezer **1c** in phosphate buffer (10 mM, pH 7.2)

λ_{exc}= 285 nm	Receptor **1c**	Guest Ac Lys OMe ·HCl
Amount [mg]:	0.100	0.354
Volume [mL]:	5.568	0.581
Concentration [mol/L]:	$2.33 \cdot 10^{-05}$	$2.55 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{338})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.33E-05	0.00E+00	0.00	925.462	0.000	0.000
10	710	2.33E-05	3.60E-05	1.54	702.801	222.661	222.446
20	720	2.33E-05	7.09E-05	3.04	623.958	301.504	299.942
30	730	2.33E-05	1.05E-04	4.50	591.476	333.986	332.975
40	740	2.33E-05	1.38E-04	5.92	578.192	347.270	350.558
60	760	2.33E-05	2.02E-04	8.65	559.736	365.726	368.613
80	780	2.33E-05	2.62E-04	11.24	545.225	380.237	377.746
100	800	2.33E-05	3.19E-04	13.69	544.797	380.665	383.242
120	820	2.33E-05	3.74E-04	16.03	537.159	388.303	386.908
150	850	2.33E-05	4.50E-04	19.33	532.127	393.335	390.573
180	880	2.33E-05	5.22E-04	22.41	533.112	392.350	393.015
220	920	2.33E-05	6.10E-04	26.20	530.630	394.832	395.234
260	960	2.33E-05	6.91E-04	29.67	533.667	391.795	396.769
300	1000	2.33E-05	7.66E-04	32.86	522.077	403.385	397.893





K_a [M^{-1}] = 51500 ± 3 %

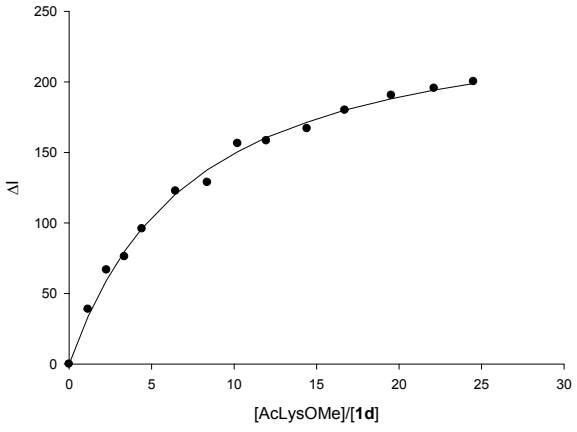
K_d[µM] = 19 ± 3 %

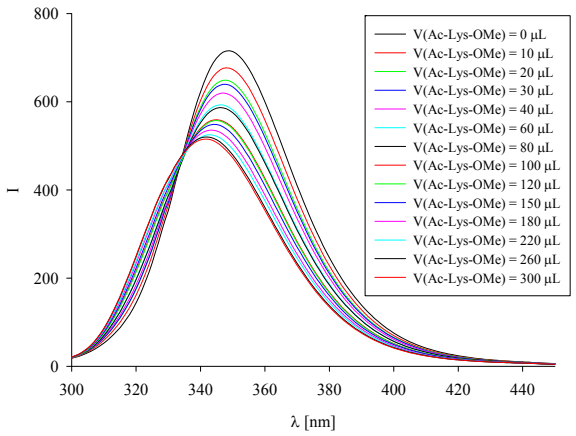
ΔI_{max} = 408 (44 %)

Titration of **AcLysOMe** and tweezer **1d** in phosphate buffer (10 mM, pH 7.2)

λ_{exc}= 285 nm	Receptor **1d**	Guest Ac Lys OMe· HCl
Amount [mg]:	0.492	1.509
Volume [mL]:	7.00	0.800
Concentration [mol/L]:	$9.67 \cdot 10^{-05}$	$7.90 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{348})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	9.67E-05	0.00E+00	0.00	715.684	0.000	0.0000
10	710	9.67E-05	1.11E-04	1.151	676.845	38.839	33.7203
20	720	9.67E-05	2.19E-04	2.269	648.935	66.749	59.5512
30	730	9.67E-05	3.25E-04	3.358	639.607	76.077	79.9818
40	740	9.67E-05	4.27E-04	4.416	619.840	95.844	96.1721
60	760	9.67E-05	6.24E-04	6.450	593.112	122.572	120.5213
80	780	9.67E-05	8.10E-04	8.380	586.929	128.755	137.6953
100	800	9.67E-05	9.88E-04	10.213	559.378	156.306	150.5497
120	820	9.67E-05	1.16E-03	11.956	557.382	158.302	160.5912
150	850	9.67E-05	1.39E-03	14.418	548.790	166.894	171.3778
180	880	9.67E-05	1.62E-03	16.712	535.738	179.946	179.9713
220	920	9.67E-05	1.89E-03	19.537	525.169	190.515	188.0593
260	960	9.67E-05	2.14E-03	22.127	520.197	195.487	194.1389
300	1000	9.67E-05	2.37E-03	24.510	515.458	200.226	198.8329





K_a [M^{-1}] = 1555 ± 7%

K_d[µM] = 643 ± 7%

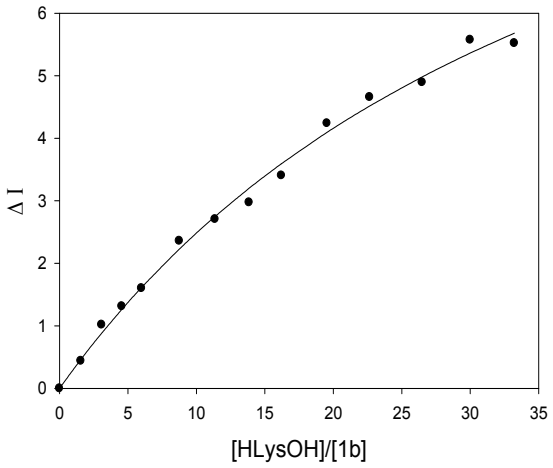
ΔI_{max} = 225 (36 %)

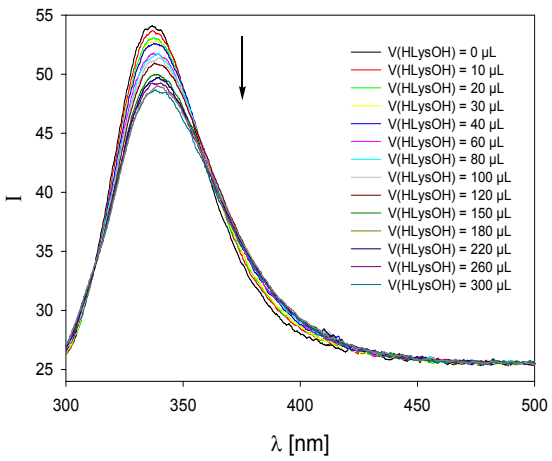
Fluorescence titrations for H Lys OH

Titration of **H LysOH** and tweezer **1b** in phosphate buffer (200 mM, pH 7.6)

λ_{exc}= 280 nm	Receptor **1b**	Guest H Lys OH · HCl
Amount [mg]:	0.165	0.314
Volume [mL]:	10.277	0.71
Concentration [mol/L]:	$2.18 \cdot 10^{-5}$	$2.4 \cdot 10^{-3}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{336})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.19E-05	0.00E+00	0.00	54.0	0.0	0.0
10	710	2.19E-05	3.41E-05	1.56	53.6	0.4	0.5
20	720	2.19E-05	6.72E-05	3.08	52.9	1.0	0.9
30	730	2.19E-05	9.95E-05	4.55	52.7	1.3	1.3
40	740	2.19E-05	1.31E-04	5.99	52.4	1.6	1.6
60	760	2.19E-05	1.91E-04	8.74	51.6	2.4	2.2
80	780	2.19E-05	2.48E-04	11.36	51.3	2.7	2.8
100	800	2.19E-05	3.03E-04	13.84	51.0	2.9	3.2
120	820	2.19E-05	3.54E-04	16.21	50.6	3.4	3.6
150	850	2.19E-05	4.27E-04	19.54	49.8	4.2	4.1
180	880	2.19E-05	4.95E-04	22.65	49.4	4.7	4.5
220	920	2.19E-05	5.79E-04	26.48	49.1	4.9	4.9
260	960	2.19E-05	6.56E-04	29.99	48.4	5.6	5.4
300	1000	2.19E-05	7.26E-04	33.23	48.5	5.5	5.7





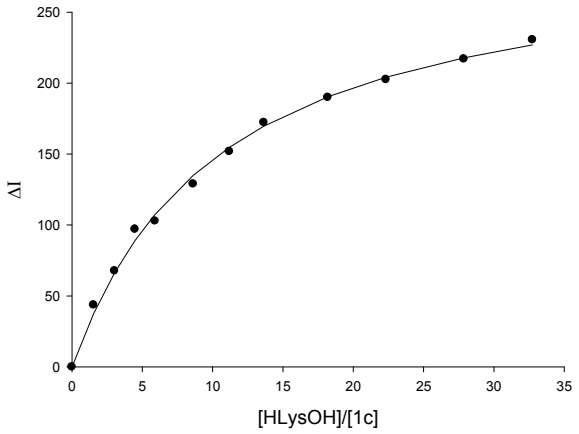
K_a [M^{-1}] = 1144 ± 1%

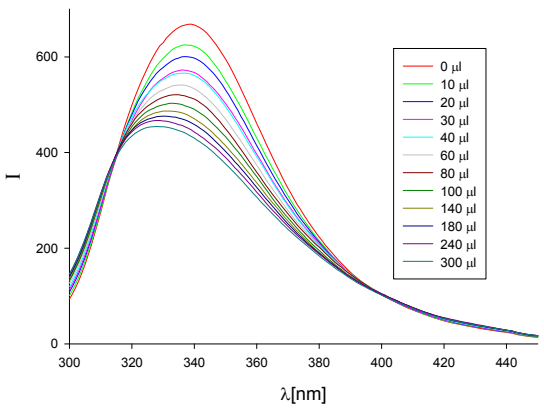
K_d[µM] = 874 ± 1%

Titration of **HLysOH** and tweezer **1c** in phosphate buffer (10mM, pH 7.6)

λ_{exc}= 285 nm λ_{em}= 338 nm	Receptor **1c**	Guest H LysOH · HCl
Amount [mg]:	0.154	0.282
Volume [mL]:	8.58	0.607
Concentration [mol/L]:	$2.33 \cdot 10^{-05}$	$2.54 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{338})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.33E-05	0.00E+00	0.00	668.101	0.000	0.000
10	710	2.33E-05	3.58E-05	1.54	624.460	43.641	37.471
20	720	2.33E-05	7.06E-05	3.03	600.417	67.684	66.272
30	730	2.33E-05	1.05E-04	4.49	571.074	97.027	88.995
40	740	2.33E-05	1.37E-04	5.90	565.345	102.756	107.324
60	760	2.33E-05	2.01E-04	8.62	539.165	128.936	134.979
80	780	2.33E-05	2.61E-04	11.19	516.322	151.779	154.784
100	800	2.33E-05	3.18E-04	13.64	495.840	172.261	169.631
140	840	2.33E-05	4.24E-04	18.19	478.098	190.003	190.359
180	880	2.33E-05	5.20E-04	22.32	465.560	202.541	204.114
240	940	2.33E-05	6.49E-04	27.86	451.082	217.019	217.799
300	1000	2.33E-05	7.63E-04	32.74	437.507	230.594	226.874





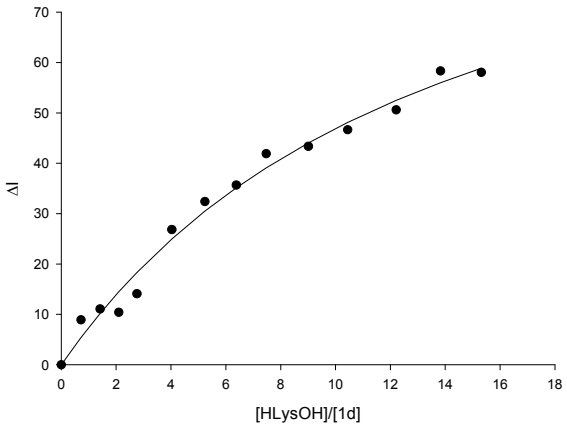
K_a [M^{-1}] = 4410 ± 6 %

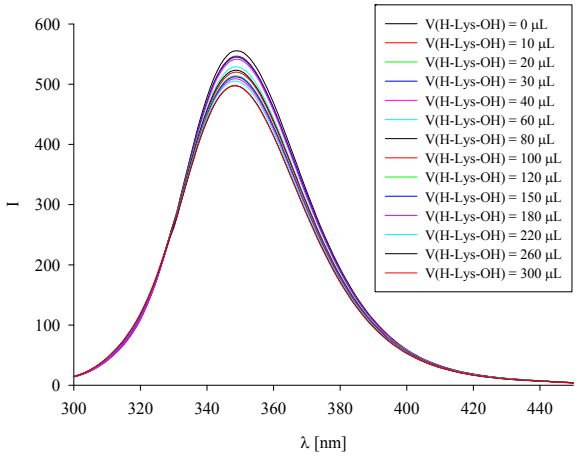
K_d[µM] = 227 ± 6%

Titration of **HLysOH** and tweezer **1d** in phosphate buffer (10 mM, pH 7.2)

λ_{exc}= 285 nm λ_{em}= 348 nm	Receptor **1d**	Guest H LysOH · HCl
Amount [mg]:	0.259	0.655
Volume [mL]:	4.00	0.80
Concentration [mol/L]:	$8.91 \cdot 10^{-05}$	$4.55 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{348})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	8.91E-05	0.00E+00	0.000	555.580	0.000	0.0000
10	710	8.91E-05	6.41E-05	0.719	546.684	8.896	5.4037
20	720	8.91E-05	1.26E-04	1.418	544.499	11.081	10.2046
30	730	8.91E-05	1.87E-04	2.099	545.179	10.401	14.4953
40	740	8.91E-05	2.46E-04	2.760	541.476	14.104	18.3508
60	760	8.91E-05	3.59E-04	4.031	528.748	26.832	24.9908
80	780	8.91E-05	4.67E-04	5.237	523.192	32.388	30.4993
100	800	8.91E-05	5.69E-04	6.383	519.935	35.645	35.1385
120	820	8.91E-05	6.66E-04	7.473	513.713	41.867	39.0962
150	850	8.91E-05	8.03E-04	9.011	512.214	43.366	44.0476
180	880	8.91E-05	9.31E-04	10.445	508.936	46.644	48.0994
220	920	8.91E-05	1.09E-03	12.211	504.988	50.592	52.4776
260	960	8.91E-05	1.23E-03	13.830	497.261	58.319	55.9979
300	1000	8.91E-05	1.36E-03	15.319	497.562	58.018	58.8887





K_a [M^{-1}] = 855 ± 20%

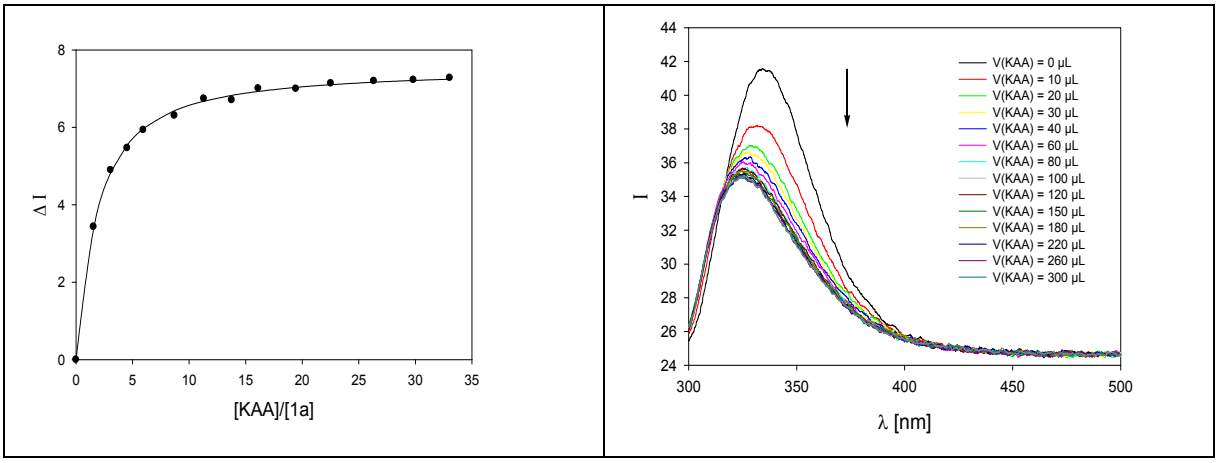
K_d[µM] = 1170 ± 20%

Fluorescence titration for peptide KAA

Titration of **KAA** and tweezer **1a** in phosphate buffer (200 mM, pH 7.6)

λ_{exc}= 285 nm	**Tweezer 1a**	**KAA**
Amount [mg]: Volume [mL]: Concentration [mol/L]:	0.164 ($2.18 \cdot 10^{-4}$mmol) 10 $2.18 \cdot 10^{-5}$	0.347 ($1.2 \cdot 10^{-3}$mmol) 0.5 $2.4 \cdot 10^{-3}$

V_{Guest} [µL]	V_{total} [µL]	[1a] [mol/L]	[KAA] [mol/L]	[KAA]/ [1a]	I 334 nm	ΔI_{obs}	ΔI_{calc}
0	700	$2.19 \cdot 10^{-5}$	0	0	41.6	0.0	0
10	710	$2.19 \cdot 10^{-5}$	$3.39 \cdot 10^{-5}$	1.55	38.1	3.4	3.4
20	720	$2.19 \cdot 10^{-5}$	$6.69 \cdot 10^{-5}$	3.06	36.7	4.9	4.8
30	730	$2.19 \cdot 10^{-5}$	$9.89 \cdot 10^{-5}$	4.53	36.1	5.5	5.5
40	740	$2.19 \cdot 10^{-5}$	$1.30 \cdot 10^{-4}$	5.95	35.6	5.9	5.9
60	760	$2.19 \cdot 10^{-5}$	$1.90 \cdot 10^{-4}$	8.69	35.3	6.3	6.4
80	780	$2.19 \cdot 10^{-5}$	$2.47 \cdot 10^{-4}$	11.29	34.8	6.7	6.7
100	800	$2.19 \cdot 10^{-5}$	$3.01 \cdot 10^{-4}$	13.77	34.9	6.7	6.8
120	820	$2.19 \cdot 10^{-5}$	$3.52 \cdot 10^{-4}$	16.12	34.6	7.0	6.9
150	850	$2.19 \cdot 10^{-5}$	$4.25 \cdot 10^{-4}$	19.43	34.6	6.9	7.0
180	880	$2.19 \cdot 10^{-5}$	$4.92 \cdot 10^{-4}$	22.53	34.4	7.1	7.1
220	920	$2.19 \cdot 10^{-5}$	$5.76 \cdot 10^{-4}$	26.33	34.4	7.2	7.2
260	960	$2.19 \cdot 10^{-5}$	$6.52 \cdot 10^{-4}$	29.82	34.3	7.2	7.2
300	1000	$2.19 \cdot 10^{-5}$	$7.22 \cdot 10^{-4}$	33.04	34.3	7.3	7.2



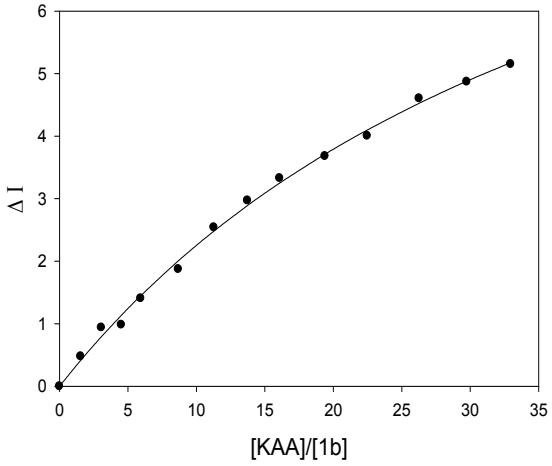
K_a [M^{-1}] = 33340 ± 3 %

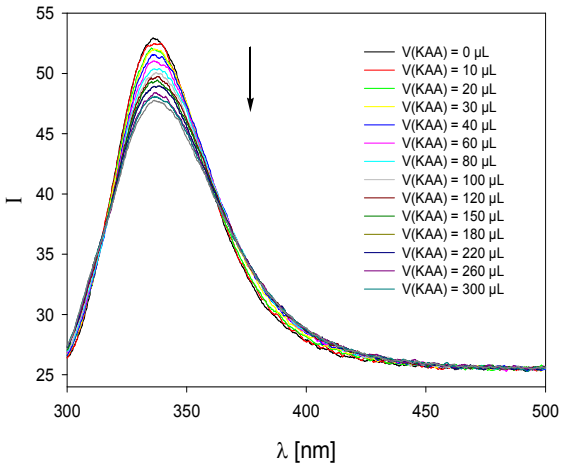
K_d[µM] = 30 ± 3 %

Titration of **KAA** and tweezer **1b** in phosphate buffer (200 mM, pH 7.6)

λ_{exc}= 280 nm	Receptor **1b**	Guest KAA
Amount [mg]:	0.165	0.360
Volume [mL]:	10.277	0.52
Concentration [mol/L]:	$2.18 \cdot 10^{-5}$	$2.4 \cdot 10^{-3}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{334})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.19E-05	0.00E+00	0.00	52.9	0.0	0.0
10	710	2.19E-05	3.38E-05	1.55	52.4	0.5	0.4
20	720	2.19E-05	6.67E-05	3.05	51.9	0.9	0.8
30	730	2.19E-05	9.87E-05	4.51	51.9	0.9	1.1
40	740	2.19E-05	1.30E-04	5.94	51.5	1.4	1.4
60	760	2.19E-05	1.90E-04	8.67	51.0	1.9	2.0
80	780	2.19E-05	2.46E-04	11.27	50.4	2.5	2.5
100	800	2.19E-05	3.00E-04	13.73	49.9	2.9	2.9
120	820	2.19E-05	3.51E-04	16.08	49.6	3.3	3.3
150	850	2.19E-05	4.24E-04	19.38	49.2	3.7	3.7
180	880	2.19E-05	4.91E-04	22.47	48.9	4.0	4.1
220	920	2.19E-05	5.74E-04	26.27	48.3	4.6	4.5
260	960	2.19E-05	6.50E-04	29.75	48.0	4.9	4.9
300	1000	2.19E-05	7.20E-04	32.95	47.7	5.2	5.2





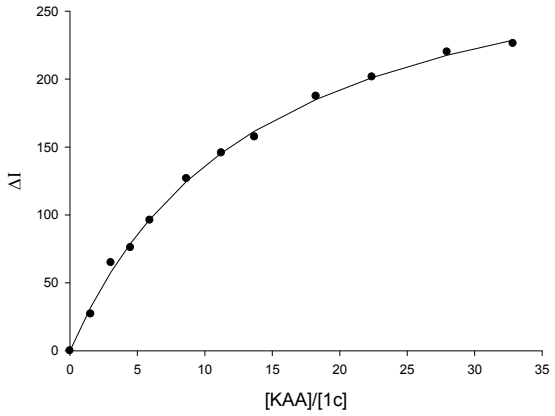
K_a [M^{-1}] = 1105 ± 1%

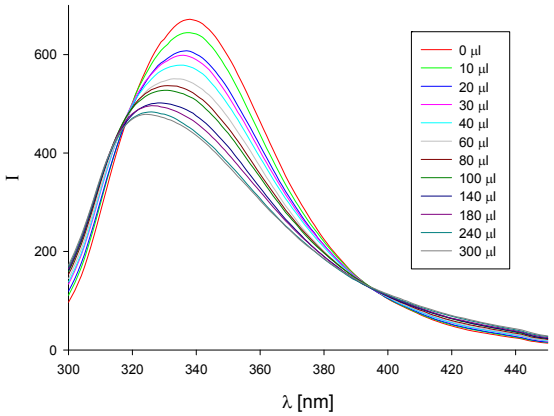
K_d[µM] = 905 ± 1%

Titration of **KAA** and tweezer**1c** in phosphate buffer (10 mM, pH 7.6)

λ_{exc}= 285 nm λ_{em}= 338 nm	Receptor **1c**	Guest KAA
Amount [mg]:	0.154	0.37
Volume [mL]:	8.58	0.503
Concentration [mol/L]:	$2.33 \cdot 10^{-05}$	$2.55 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{338})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.33E-05	0.00E+00	0.00	671.428	0.000	0.000
10	710	2.33E-05	3.59E-05	1.54	644.313	27.115	32.063
20	720	2.33E-05	7.09E-05	3.04	606.546	64.882	57.917
30	730	2.33E-05	1.05E-04	4.50	595.503	75.925	79.153
40	740	2.33E-05	1.38E-04	5.92	575.253	96.175	96.878
60	760	2.33E-05	2.01E-04	8.64	544.662	126.766	124.722
80	780	2.33E-05	2.62E-04	11.23	525.733	145.695	145.552
100	800	2.33E-05	3.19E-04	13.69	514.004	157.424	1c.693
140	840	2.33E-05	4.25E-04	18.25	484.077	187.351	185.041
180	880	2.33E-05	5.22E-04	22.39	469.864	201.564	201.088
240	940	2.33E-05	6.51E-04	27.95	451.425	220.003	217.517
300	1000	2.33E-05	7.65E-04	32.85	445.244	226.184	228.679





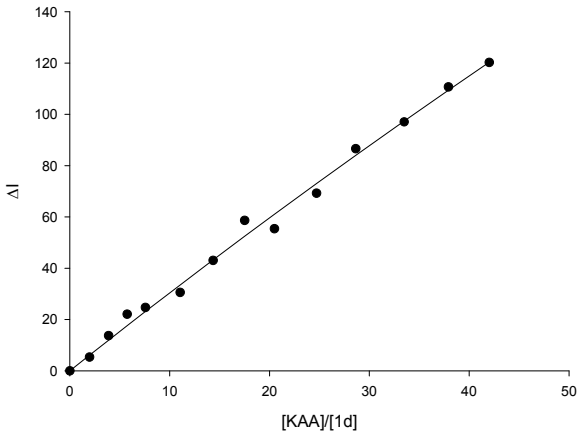
K_a [M^{-1}] = 3300 ± 5 %

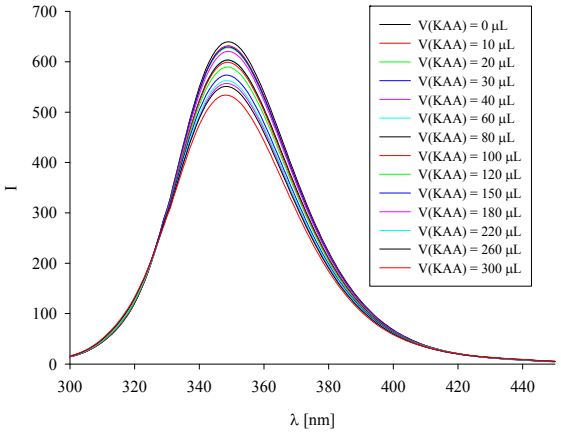
K_d[µM] = 303 ± 5 %

Titration of **KAA** and tweezer **1d** in phosphate buffer (10 mM, pH 7.2)

λ_{exc}= 285 nm	Receptor **1d**	Guest KAA
Amount [mg]:	0.215	1.349
Volume [mL]:	4.50	0.80
Concentration [mol/L]:	$6.65 \cdot 10^{-05}$	$9.2 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{348})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	6.57E-05	0.00E+00	0.000	476.535	0.000	0.0000
10	710	6.57E-05	1.30E-04	1.973	471.176	5.359	6.0899
20	720	6.57E-05	2.56E-04	3.891	462.806	13.729	11.9661
30	730	6.57E-05	3.78E-04	5.756	454.449	22.086	17.6395
40	740	6.57E-05	4.98E-04	7.572	451.804	24.731	23.1205
60	760	6.57E-05	7.27E-04	11.058	445.960	30.575	33.5432
80	780	6.57E-05	9.45E-04	14.367	433.475	43.060	43.3038
100	800	6.57E-05	1.15E-03	17.509	417.927	58.608	52.4635
120	820	6.57E-05	1.35E-03	20.499	421.166	55.369	61.0761
150	850	6.57E-05	1.63E-03	24.719	407.293	69.242	73.0718
180	880	6.57E-05	1.88E-03	28.652	389.996	86.539	84.0812
220	920	6.57E-05	2.20E-03	33.496	379.260	97.275	97.4253
260	960	6.57E-05	2.49E-03	37.937	365.539	110.996	109.451
300	1000	6.57E-05	2.76E-03	42.022	355.788	120.747	120.344





K_a [M^{-1}] = 30 ± 83%

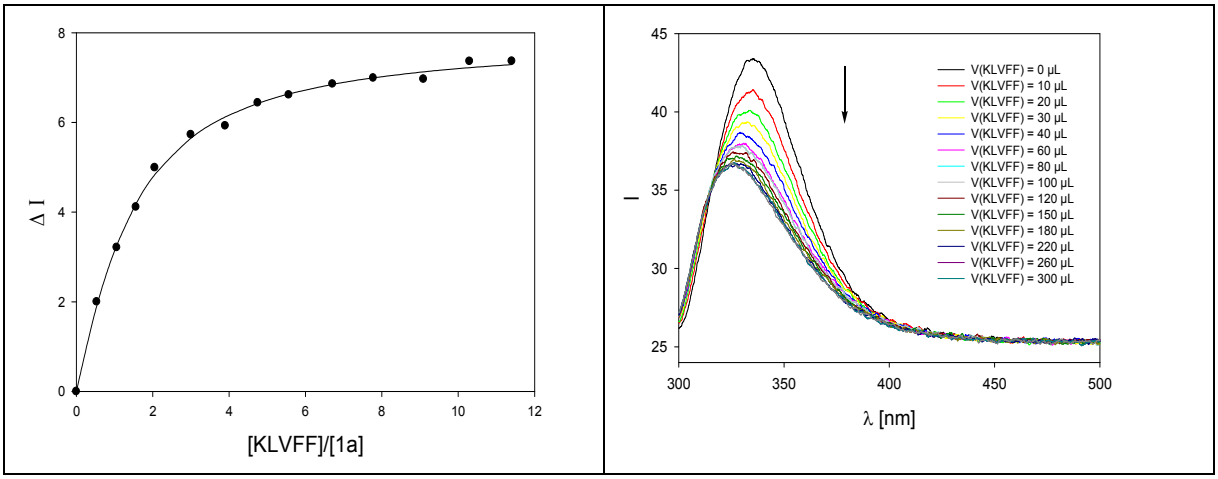
K_d[µM] = 33333 ± 83%

Fluorescence titrations for KLVFF

Titration of **KLVFF** and tweezer**1a** in phosphate buffer (200 mM, pH 7.6)

λ_{exc}= 280 nm	**Tweezer 1a**	**KLVFF**
Amount [mg]:	0.172 ($2.29 \cdot 10^{-4}$mmol)	0.217 ($3.32 \cdot 10^{-4}$ mmol)
Volume [mL]:	10.487	0.4
Concentration [mol/L]:	$2.18 \cdot 10^{-5}$	$8.3 \cdot 10^{-4}$

V_{Gast} [µL]	V_{gesamt} [µL]	[**750**] [mol/L]	[KLVFF] [mol/L]	[KLVFF]/ [**1a**]	I 334 nm	ΔI_{obs}	ΔI_{calc}
0	700	$2.19 \cdot 10^{-5}$	0.00	0.00	43.3	0.0	0.0
10	710	$2.19 \cdot 10^{-5}$	$1.17 \cdot 10^{-5}$	0.54	41.3	2.0	1.9
20	720	$2.19 \cdot 10^{-5}$	$2.31 \cdot 10^{-5}$	1.06	40.1	3.2	3.3
30	730	$2.19 \cdot 10^{-5}$	$3.42 \cdot 10^{-5}$	1.56	39.2	4.1	4.2
40	740	$2.19 \cdot 10^{-5}$	$4.49 \cdot 10^{-5}$	2.06	38.3	4.9	4.8
60	760	$2.19 \cdot 10^{-5}$	$6.56 \cdot 10^{-5}$	3.00	37.6	5.7	5.7
80	780	$2.19 \cdot 10^{-5}$	$8.52 \cdot 10^{-5}$	3.90	37.4	5.9	6.1
100	800	$2.19 \cdot 10^{-5}$	$1.04 \cdot 10^{-4}$	4.75	36.9	6.4	6.4
120	820	$2.19 \cdot 10^{-5}$	$1.22 \cdot 10^{-4}$	5.56	36.7	6.6	6.6
150	850	$2.19 \cdot 10^{-5}$	$1.47 \cdot 10^{-4}$	6.71	36.4	6.6	6.8
180	880	$2.19 \cdot 10^{-5}$	$1.70 \cdot 10^{-4}$	7.78	36.3	6.9	6.9
220	920	$2.19 \cdot 10^{-5}$	$1.99 \cdot 10^{-4}$	9.09	36.3	6.9	7.1
260	960	$2.19 \cdot 10^{-5}$	$2.25 \cdot 10^{-4}$	10.30	35.9	7.4	7.2
300	1000	$2.19 \cdot 10^{-5}$	$2.49 \cdot 10^{-4}$	11.41	35.9	7.4	7.3



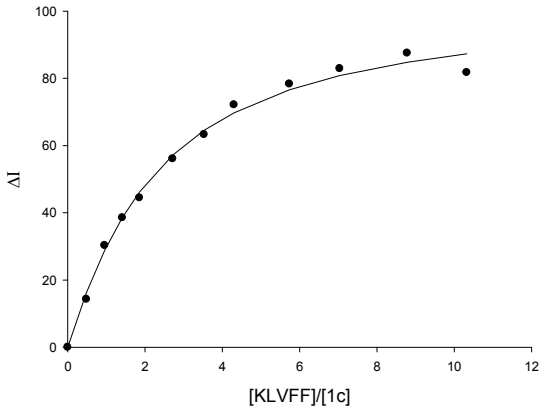
K_a [M^{-1}] = 49481 ± 5 %

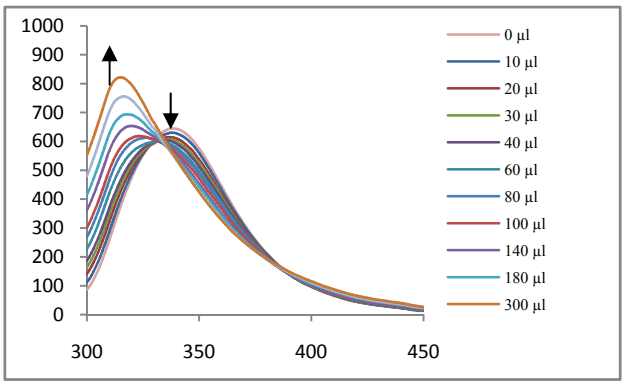
K_d[µM] =20 ± 5 %

Titration of **KLVFF** and tweezer **1c** in phosphate buffer (10 mM, pH 7.6)

λ_{exc}= 285 nm λ_{em}= 338 nm	Receptor **1c**	Guest KLVFF
Amount [mg]:	0.113	0.355
Volume [mL]:	6.724	0.725
Concentration [mol/L]:	$2.18 \cdot 10^{-05}$	$7.5 \cdot 10^{-04}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{338})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.18E-05	0.00E+00	0.00	644.084	0.000	0.000
10	710	2.18E-05	1.06E-05	0.48	629.776	14.308	16.276
20	720	2.18E-05	2.08E-05	0.96	613.787	30.297	28.826
30	730	2.18E-05	3.08E-05	1.41	605.562	38.522	38.553
40	740	2.18E-05	4.05E-05	1.86	599.635	44.449	46.180
60	760	2.18E-05	5.92E-05	2.72	588.012	56.072	57.153
80	780	2.18E-05	7.69E-05	3.53	580.781	63.303	64.522
100	800	2.18E-05	9.38E-05	4.30	571.938	72.146	69.743
140	840	2.18E-05	1.25E-04	5.73	565.785	78.299	76.576
180	880	2.18E-05	1.53E-04	7.04	561.215	82.869	80.811
240	940	2.18E-05	1.92E-04	8.78	556.559	87.525	84.792
300	1000	2.18E-05	2.25E-04	10.32	562.350	81.1b	87.306





K_a [M^{-1}] = 26200 ± 11 %

K_d[µM] =38 ± 11%

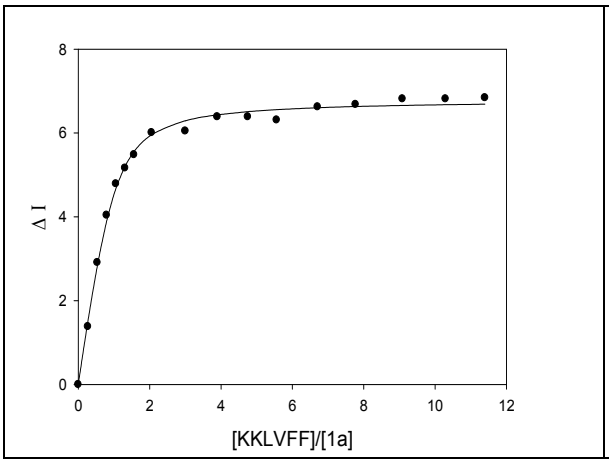
Δλ ~ 20 nm,blue shift

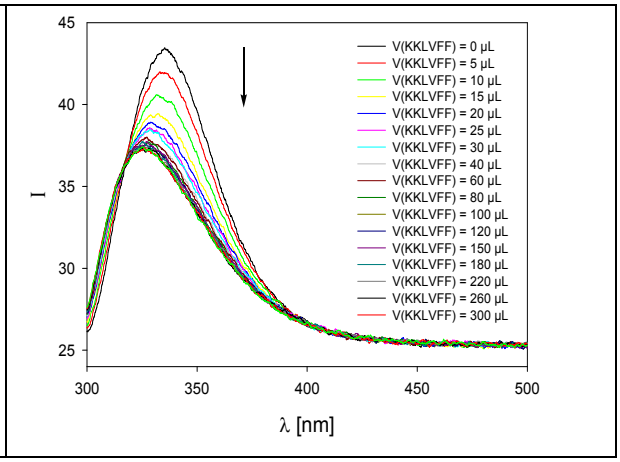
Fluorescence titrations for KKLVFF

Titration of **KKLVFF**and tweezer **1a** in phosphate buffer (200 mM, pH 7.64)

λ_{exc}= 280 nm	**Tweezer1a**	**KKLVFF**
Amount [mg]:	0.172 ($2.29 \cdot 10^{-4}$mmol)	0.26 ($3.32 \cdot 10^{-4}$mmol)
Volume [mL]:	10.487	0.45
Concentration [mol/L]:	$2.18 \cdot 10^{-5}$	$8.3 \cdot 10^{-4}$

V_{Guest} [µL]	V_{total} [µL]	[1a] [mol/L]	[KKLVFF] [mol/L]	[KKLVFF]/ [1a]	I 334 nm	ΔI_{obs}	ΔI_{calc}
0	700	$2.19 \cdot 10^{-5}$	0	0	43.3	0	0
5	705	$2.19 \cdot 10^{-5}$	$5.89 \cdot 10^{-6}$	0.27	41.9	1.4	1.5
10	710	$2.19 \cdot 10^{-5}$	$1.17 \cdot 10^{-5}$	0.54	40.4	2.9	2.8
15	715	$2.19 \cdot 10^{-5}$	$1.74 \cdot 10^{-5}$	0.80	39.3	4.0	3.9
20	720	$2.19 \cdot 10^{-5}$	$2.31 \cdot 10^{-5}$	1.06	38.5	4.8	4.7
25	725	$2.19 \cdot 10^{-5}$	$2.86 \cdot 10^{-5}$	1.31	38.1	5.2	5.2
30	730	$2.19 \cdot 10^{-5}$	$3.41 \cdot 10^{-5}$	1.56	37.8	5.5	5.6
40	740	$2.19 \cdot 10^{-5}$	$4.49 \cdot 10^{-5}$	2.05	37.3	6.0	5.9
60	760	$2.19 \cdot 10^{-5}$	$6.56 \cdot 10^{-5}$	3.00	37.3	6.0	6.3
80	780	$2.19 \cdot 10^{-5}$	$8.52 \cdot 10^{-5}$	3.90	36.9	6.4	6.4
100	800	$2.19 \cdot 10^{-5}$	$1.04 \cdot 10^{-4}$	4.75	36.9	6.4	6.5
120	820	$2.19 \cdot 10^{-5}$	$1.22 \cdot 10^{-4}$	5.56	36.9	6.3	6.6
150	850	$2.19 \cdot 10^{-5}$	$1.47 \cdot 10^{-4}$	6.70	36.7	6.6	6.6
180	880	$2.19 \cdot 10^{-5}$	$1.70 \cdot 10^{-4}$	7.77	36.6	6.7	6.6
220	920	$2.19 \cdot 10^{-5}$	$1.99 \cdot 10^{-4}$	9.08	36.5	6.8	6.7
260	960	$2.19 \cdot 10^{-5}$	$2.25 \cdot 10^{-4}$	10.29	36.5	6.8	6.7
300	1000	$2.19 \cdot 10^{-5}$	$2.49 \cdot 10^{-4}$	11.40	36.5	6.8	6.7





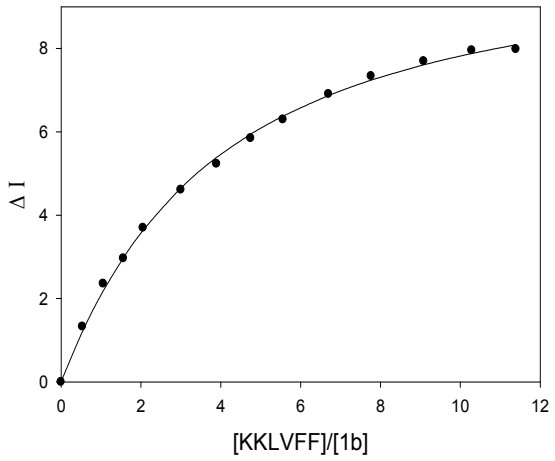
K_a [M^{-1}] = 277310 ± 1 %

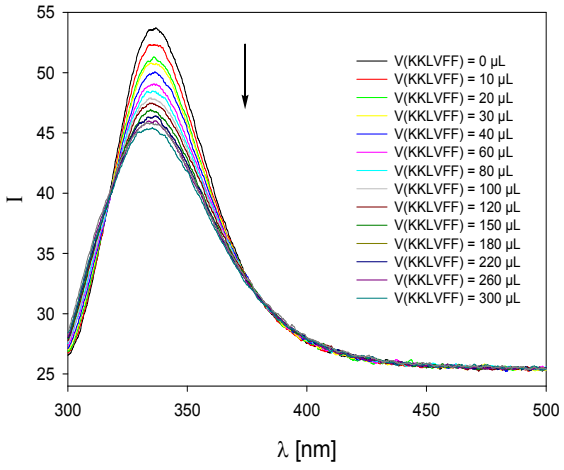
K_d[µM] =4 ± 1 %

Titration of **KKLVFF** and tweezer **1b** in phosphate buffer (200 mM, pH 7.64)

λ_{exc}= 280 nm	Receptor **1b**	Guest KKLVFF
Amount [mg]:	0.165	0.497
Volume [mL]:	10.277	0.765
Concentration [mol/L]:	$2.18 \cdot 10^{-05}$	$8.0 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{336})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.19E-05	0.00E+00	0.00	53.7	0.0	0.0
10	710	2.19E-05	1.17E-05	0.35	52.3	1.3	1.2
20	720	2.19E-05	2.31E-05	1.05	51.3	2.4	2.2
30	730	2.19E-05	3.41E-05	1.56	50.7	2.9	2.9
40	740	2.19E-05	4.49E-05	2.05	49.9	3.7	3.6
60	760	2.19E-05	6.55E-05	3.00	49.1	4.6	4.6
80	780	2.19E-05	8.51E-05	3.89	48.4	5.2	5.4
100	800	2.19E-05	1.04E-04	4.75	47.8	5.9	5.9
120	820	2.19E-05	1.21E-04	5.56	47.4	6.3	6.4
150	850	2.19E-05	1.46E-04	6.70	46.8	6.9	6.9
180	880	2.19E-05	1.70E-04	7.77	46.3	7.3	7.2
220	920	2.19E-05	1.98E-04	9.08	45.9	7.7	7.6
260	960	2.19E-05	2.25E-04	10.28	45.7	7.9	7.9
300	1000	2.19E-05	2.49E-04	11.39	45.7	7.9	8.1





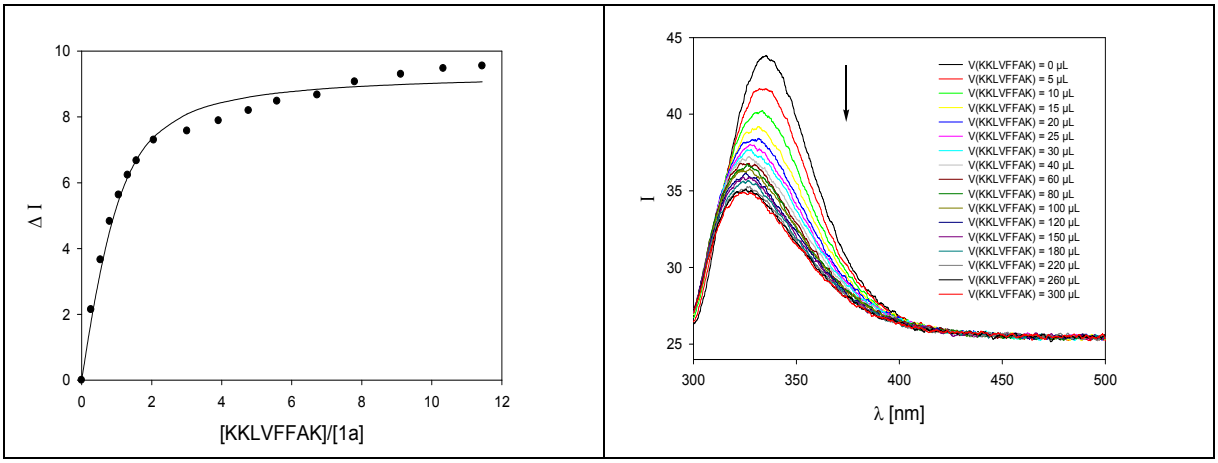
K_a [M^{-1}] = 14048 ± 1%

K_d[µM] = 71 ± 1

Fluorescence titration of **KKLVFFAK** and tweezer **1a** in phosphate buffer (200 mM, pH 7.64)

λ_{exc}= 280 nm	**Tweezer1a**	**KKLVFFAK**
Amount [mg]:	0.172 ($2.29 \cdot 10^{-4}$mmol)	0.394 ($4.00 \cdot 10^{-4}$mmol)
Volume [mL]:	10.487	0.48
Concentration [mol/L]:	$2.18 \cdot 10^{-5}$	$8.3 \cdot 10^{-4}$

V_{Guest} [µL]	V_{total} [µL]	[1a] [mol/L]	[KKLVFFAK] [mol/L]	[KKLVFFAK]/ [1a]	I 334 nm	ΔI_{obs}	ΔI_{calc}
0	700	$2.19 \cdot 10^{-5}$	0.00	0.00	43.8	0.0	0.0
10	710	$2.19 \cdot 10^{-5}$	$1.17 \cdot 10^{-5}$	0.54	40.1	3.7	3.3
20	720	$2.19 \cdot 10^{-5}$	$2.32 \cdot 10^{-5}$	1.06	38.1	5.6	5.5
30	730	$2.19 \cdot 10^{-5}$	$3.43 \cdot 10^{-5}$	1.57	37.1	6.7	6.7
40	740	$2.19 \cdot 10^{-5}$	$4.51 \cdot 10^{-5}$	2.06	36.5	7.3	7.4
60	760	$2.19 \cdot 10^{-5}$	$6.58 \cdot 10^{-5}$	3.01	36.2	7.6	8.1
80	780	$2.19 \cdot 10^{-5}$	$8.55 \cdot 10^{-5}$	3.91	35.9	7.9	8.4
100	800	$2.19 \cdot 10^{-5}$	$1.04 \cdot 10^{-4}$	4.77	35.6	8.2	8.6
120	820	$2.19 \cdot 10^{-5}$	$1.22 \cdot 10^{-4}$	5.58	35.3	8.5	8.7
150	850	$2.19 \cdot 10^{-5}$	$1.47 \cdot 10^{-4}$	6.73	35.1	8.7	8.8
180	880	$2.19 \cdot 10^{-5}$	$1.70 \cdot 10^{-4}$	7.80	34.7	9.1	8.9
220	920	$2.19 \cdot 10^{-5}$	$1.99 \cdot 10^{-4}$	9.12	34.5	9.3	8.9
260	960	$2.19 \cdot 10^{-5}$	$2.26 \cdot 10^{-4}$	10.33	34.3	9.5	9.0
300	1000	$2.19 \cdot 10^{-5}$	$2.50 \cdot 10^{-4}$	11.44	34.2	9.6	9.1



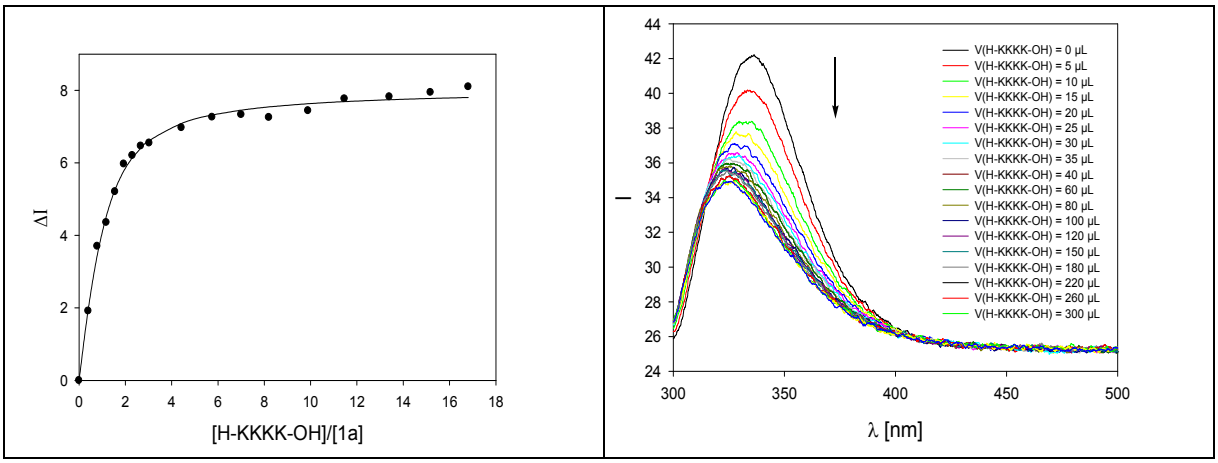
K_a [M^{-1}] = 135848 ± 1 %

K_d[µM] = 7 ± 1 %

Fluorescence titration of **H-KKKK-OH** and tweezer **1a** in phosphate buffer (200 mM, pH 7.64)

λ_{exc}= 280 nm	**Tweezer1a**	**H-KKKK-OH**
Amount [mg]:	0.172 ($2.29 \cdot 10^{-4}$mmol)	0.26 ($4.89 \cdot 10^{-4}$mmol)
Volume [mL]:	10.487	0.45
Concentration [mol/L]:	$2.18 \cdot 10^{-5}$	$1.2 \cdot 10^{-3}$

V_{Guest} [µL]	V_{total} [µL]	[1a] [mol/L]	[KKKK] [mol/L]	[KKKK]/ [1a]	I 334 nm	ΔI_{obs}	ΔI_{calc}
0	700	$2.19 \cdot 10^{-5}$	0.00	0.00	42.0	0.0	0.0
10	710	$2.19 \cdot 10^{-5}$	$1.73 \cdot 10^{-5}$	0.79	38.3	3.7	3.5
20	720	$2.19 \cdot 10^{-5}$	$3.40 \cdot 10^{-5}$	1.56	36.8	5.2	5.3
30	730	$2.19 \cdot 10^{-5}$	$5.03 \cdot 10^{-5}$	2.30	35.8	6.2	6.1
40	740	$2.19 \cdot 10^{-5}$	$5.83 \cdot 10^{-5}$	2.67	35.6	6.5	6.4
60	760	$2.19 \cdot 10^{-5}$	$6.62 \cdot 10^{-5}$	3.03	35.5	6.5	6.6
80	780	$2.19 \cdot 10^{-5}$	$9.67 \cdot 10^{-5}$	4.42	35.1	6.9	7.1
100	800	$2.19 \cdot 10^{-5}$	$1.26 \cdot 10^{-4}$	5.75	34.8	7.3	7.3
120	820	$2.19 \cdot 10^{-5}$	$1.53 \cdot 10^{-4}$	7.00	34.7	7.3	7.5
150	850	$2.19 \cdot 10^{-5}$	$1.79 \cdot 10^{-4}$	8.20	34.8	7.3	7.5
180	880	$2.19 \cdot 10^{-5}$	$2.16 \cdot 10^{-4}$	9.89	34.6	7.4	7.6
220	920	$2.19 \cdot 10^{-5}$	$2.51 \cdot 10^{-4}$	11.46	34.3	7.8	7.7
260	960	$2.19 \cdot 10^{-5}$	$2.93 \cdot 10^{-4}$	13.40	34.2	7.8	7.7
300	1000	$2.19 \cdot 10^{-5}$	$3.32 \cdot 10^{-4}$	15.18	34.1	7.9	7.8



K_a [M^{-1}] = 96610 ± 7 %

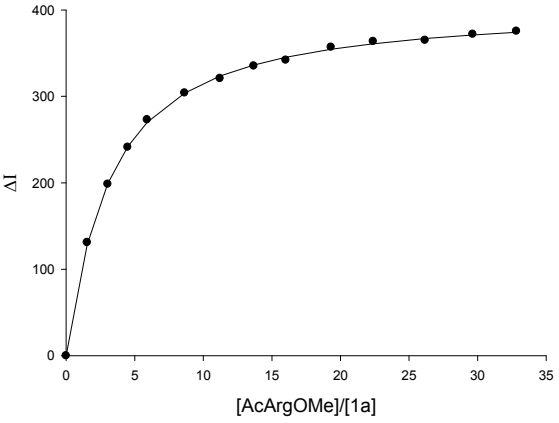
K_d[µM] = 10 ± 7 %

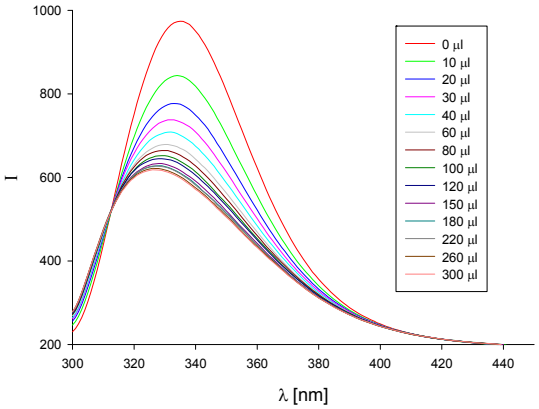
Fluorescence titrations for Ac ArgOMe

Titration of **AcArgOMe** and tweezer **1a** in phosphate buffer (200mM, pH 7.6)

λ_{exc}= 285 nm λ_{em}= 335 nm	Receptor **1a**	Guest AcArgOMe ·HCl
Amount [mg]:	0.170	0.364
Volume [mL]:	8.96	0.535
Concentration [mol/L]:	$2.33 \cdot 10^{-05}$	$2.55 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. ($I_{335\ nm}$)**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.33E-05	0.00E+00	0.00	973.832	0.000	0.000
10	710	2.33E-05	3.59E-05	1.54	842.941	130.891	128.837
20	720	2.33E-05	7.09E-05	3.04	775.363	198.469	199.554
30	730	2.33E-05	1.05E-04	4.50	732.780	241.052	242.139
40	740	2.33E-05	1.38E-04	5.92	700.879	272.953	270.041
60	760	2.33E-05	2.01E-04	8.64	669.874	303.958	303.919
80	780	2.33E-05	2.62E-04	11.23	653.089	320.743	323.546
100	800	2.33E-05	3.19E-04	13.68	638.677	335.155	336.290
120	820	2.33E-05	3.73E-04	16.02	631.899	341.933	345.214
150	850	2.33E-05	4.50E-04	19.32	616.878	356.954	354.492
180	880	2.33E-05	5.22E-04	22.39	610.332	363.500	360.880
220	920	2.33E-05	6.10E-04	26.18	608.956	364.876	366.829
260	960	2.33E-05	6.91E-04	29.65	602.008	371.824	371.029
300	1000	2.33E-05	7.65E-04	32.84	598.502	375.330	374.151





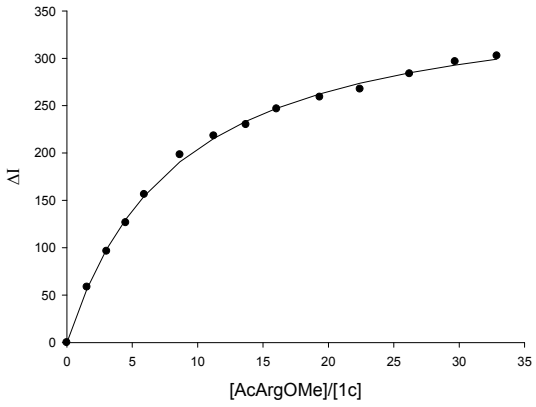
K_a [M^{-1}] = 16400 ± 2 %

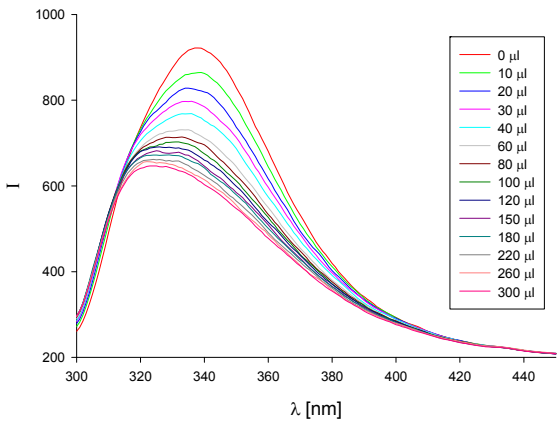
K_d[µM] = 60± 2 %

Titration of **AcArgOMe**and tweezer **1c** in phosphate buffer (200mM, pH 7.6)

λ_{exc}= 285 nm	Receptor **1c**	Guest Ac ArgOMe ·HCl
Amount [mg]:	0.156	0.340
Volume [mL]:	8.69	0.499
Concentration [mol/L]:	$2.33 \cdot 10^{-05}$	$2.55 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{337})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.33E-05	0.00E+00	0.00	921.704	0.000	0.000
10	710	2.33E-05	3.60E-05	1.54	863.162	58.542	56.863
20	720	2.33E-05	7.10E-05	3.05	825.328	96.376	98.541
30	730	2.33E-05	1.05E-04	4.51	795.250	126.454	130.157
40	740	2.33E-05	1.38E-04	5.93	765.497	156.207	154.846
60	760	2.33E-05	2.02E-04	8.66	723.468	198.236	190.741
80	780	2.33E-05	2.62E-04	11.24	703.545	218.159	215.465
100	800	2.33E-05	3.19E-04	13.70	691.642	230.062	233.478
120	820	2.33E-05	3.74E-04	16.04	675.124	246.580	247.162
150	850	2.33E-05	4.51E-04	19.35	662.666	259.038	262.445
180	880	2.33E-05	5.23E-04	22.42	654.232	267.472	273.656
220	920	2.33E-05	6.11E-04	26.22	638.021	283.683	284.648
260	960	2.33E-05	6.92E-04	29.69	625.181	296.523	292.749
300	1000	2.33E-05	7.66E-04	32.89	619.139	302.565	298.964





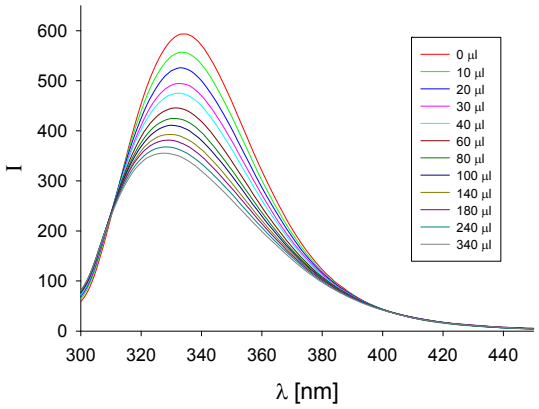
K_a [M^{-1}] = 5600 ± 4 %

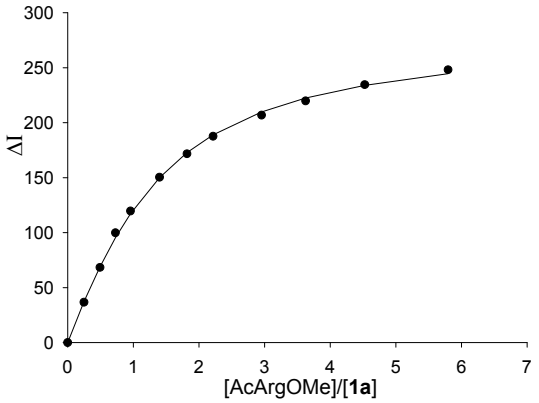
K_d[µM] = 178 ± 4 %

Titration of **AcArgOMe** and tweezer **1a** in phosphate buffer (10mM, pH 7.6)

λ_{exc}= 285 nm λ_{em}= 334 nm	Receptor **1a**	Guest AcArgOMe ·HCl
Amount [mg]:	0.225	0.101
Volume [mL]:	10.710	0.828
Concentration [mol/L]:	$2.579 \cdot 10^{-05}$	$4.573 \cdot 10^{-04}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. ($I_{334\ nm}$)**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.58E-05	0.00E+00	0.00	593.577	0.000	0.000
10	710	2.58E-05	6.44E-06	0.25	556.958	36.619	37.456
20	720	2.58E-05	1.27E-05	0.49	525.313	68.264	69.073
30	730	2.58E-05	1.88E-05	0.73	493.808	99.769	95.421
40	740	2.58E-05	2.47E-05	0.96	473.990	119.587	117.216
60	760	2.58E-05	3.61E-05	1.40	443.240	150.337	150.075
80	780	2.58E-05	4.69E-05	1.82	421.906	171.671	172.777
100	800	2.58E-05	5.72E-05	2.22	405.990	187.587	188.925
140	840	2.58E-05	7.62E-05	2.96	386.727	206.850	209.801
180	880	2.58E-05	9.35E-05	3.63	373.825	219.752	222.433
240	940	2.58E-05	1.17E-04	4.53	359.004	234.573	233.984
340	1040	2.58E-05	1.50E-04	5.80	345.525	248.052	244.467





K_a [M^{-1}] = 50600 ± 5 %

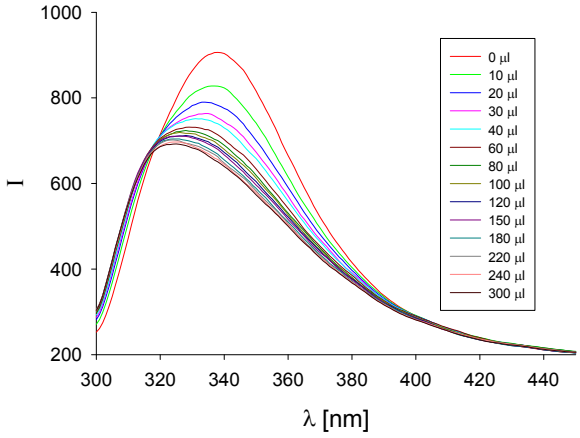
K_d[µM] = 20 ± 5 %

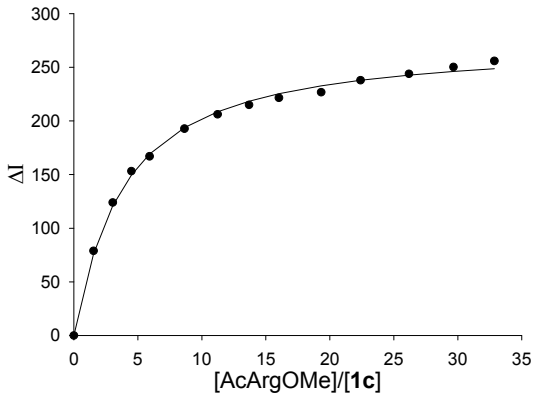
ΔI_{max} = 282 (47 %)

Titration of **AcArgOMe** and tweezer **1c** in phosphate buffer (10mM, pH 7.2)

λ_{exc}= 285 nm	Receptor **1c**	Guest Ac ArgOMe·HCl
Amount [mg]:	0.100	0.354
Volume [mL]:	5.568	0.520
Concentration [mol/L]:	$2.33 \cdot 10^{-05}$	$2.55 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{338})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.33E-05	0.00E+00	0.00	906.244	0.000	0.000
10	710	2.33E-05	3.59E-05	1.54	827.374	78.870	76.058
20	720	2.33E-05	7.09E-05	3.04	782.379	123.865	120.955
30	730	2.33E-05	1.05E-04	4.50	753.140	153.104	149.585
40	740	2.33E-05	1.38E-04	5.92	739.276	166.968	169.129
60	760	2.33E-05	2.01E-04	8.65	713.500	192.744	193.803
80	780	2.33E-05	2.62E-04	11.23	700.130	206.114	208.608
100	800	2.33E-05	3.19E-04	13.69	691.374	214.870	218.432
120	820	2.33E-05	3.74E-04	16.03	684.805	221.439	225.413
150	850	2.33E-05	4.50E-04	19.33	679.489	226.755	232.761
180	880	2.33E-05	5.22E-04	22.41	668.375	237.869	237.873
220	920	2.33E-05	6.10E-04	26.19	662.402	243.842	242.675
260	960	2.33E-05	6.91E-04	29.67	656.113	250.131	246.088
300	1000	2.33E-05	7.66E-04	32.86	650.395	255.849	248.638





K_a [M^{-1}] = 13000 ± 5 %

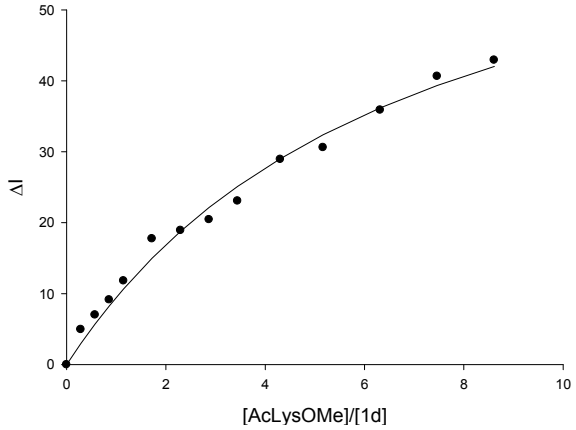
K_d[µM] = 77 ± 5 %

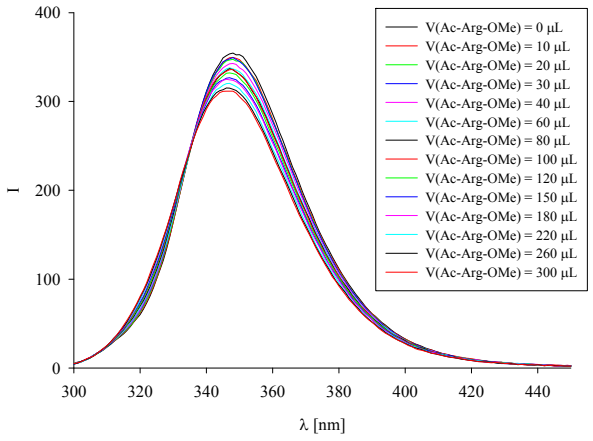
ΔI_{max} = 274 (30 %)

Titration of **AcArgOMe** and tweezer **1d** in phosphate buffer (200mM, pH 7.6)

λ_{exc}= 285 nm	Receptor **1d**	Guest Ac ArgOMe·HCl
Amount [mg]:	0.141	0.208
Volume [mL]:	2.00	0.40
Concentration [mol/L]:	$9.70 \cdot 10^{-05}$	$1.95 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{348})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	9.70E-05	0.00E+00	0.000	354.492	0.000	0.0000
10	710	9.70E-05	2.75E-05	0.283	349.540	4.952	2.9700
20	720	9.70E-05	5.42E-05	0.558	347.493	6.999	5.7261
30	730	9.70E-05	8.01E-05	0.826	345.364	9.128	8.2892
40	740	9.70E-05	1.05E-04	1.086	342.694	11.798	10.6780
60	760	9.70E-05	1.54E-04	1.587	336.766	17.726	14.9956
80	780	9.70E-05	2.00E-04	2.061	335.593	18.899	18.7888
100	800	9.70E-05	2.44E-04	2.512	334.062	20.430	22.1443
120	820	9.70E-05	2.85E-04	2.941	331.431	23.061	25.1314
150	850	9.70E-05	3.44E-04	3.546	325.565	28.927	29.0404
180	880	9.70E-05	3.99E-04	4.111	323.905	30.587	32.3905
220	920	9.70E-05	4.66E-04	4.806	318.624	35.868	36.1733
260	960	9.70E-05	5.28E-04	5.443	313.851	40.641	39.3446
300	1000	9.70E-05	5.85E-04	6.029	311.581	42.911	42.0394





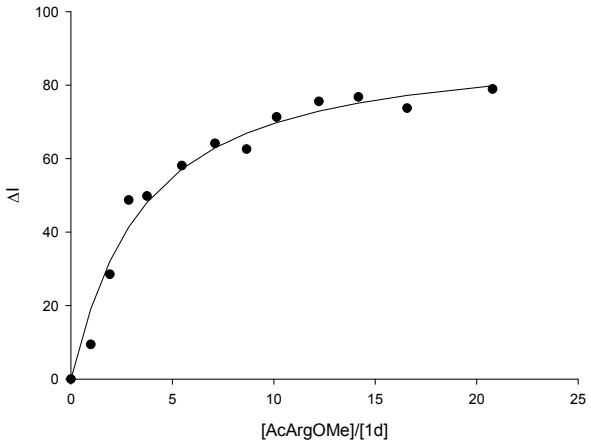
K_a [M^{-1}] = 1134 ± 26%

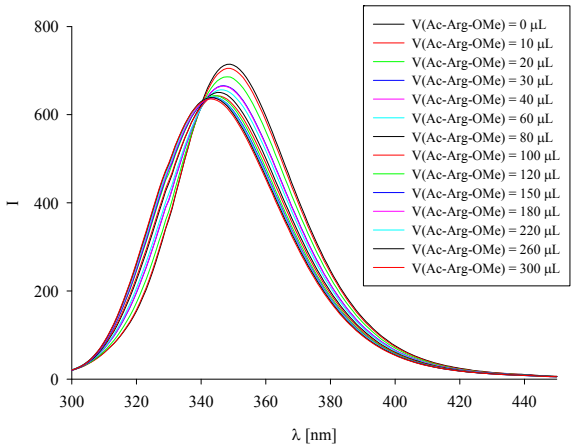
K_d[µM] = 882 ± 26%

Titration of **AcArgOMe** and tweezer **1d** in phosphate buffer (10mM, pH 7.2)

λ_{exc}= 285 nm	Receptor **1d**	Guest Ac ArgOMe· HCl
Amount [mg]:	0.492	1.43
Volume [mL]:	7.00	0.8
Concentration [mol/L]:	$9.67 \cdot 10^{-05}$	$6.70 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{348})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	9.67E-05	0.00E+00	0.00	714.662	0.000	0.0000
10	710	9.67E-05	9.44E-05	0.976	705.219	9.443	19.7970
20	720	9.67E-05	1.86E-04	1.925	686.177	28.485	32.9222
30	730	9.67E-05	2.75E-04	2.848	665.925	48.737	41.9554
40	740	9.67E-05	3.62E-04	3.745	664.865	49.797	48.4348
60	760	9.67E-05	5.29E-04	5.470	656.591	58.071	56.9735
80	780	9.67E-05	6.87E-04	7.107	650.534	64.128	62.2789
100	800	9.67E-05	8.38E-04	8.661	642.645	62.574	65.8686
120	820	9.67E-05	9.81E-04	10.140	643.352	71.310	68.4499
150	850	9.67E-05	1.18E-03	12.228	639.091	75.571	71.1925
180	880	9.67E-05	1.37E-03	14.173	637.916	76.746	73.1148
220	920	9.67E-05	1.60E-03	16.569	640.940	73.722	74.9300
300	1000	9.67E-05	2.01E-03	20.787	635.733	78.929	77.1957





K_a [M^{-1}] = 3558 ± 18%

K_d[µM] = 281 ± 18%

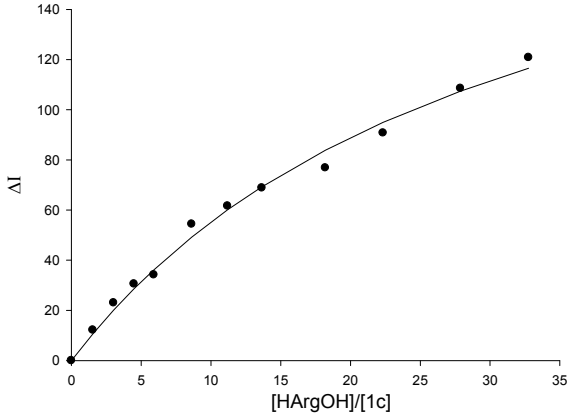
ΔI_{max} = 91 (13 %)

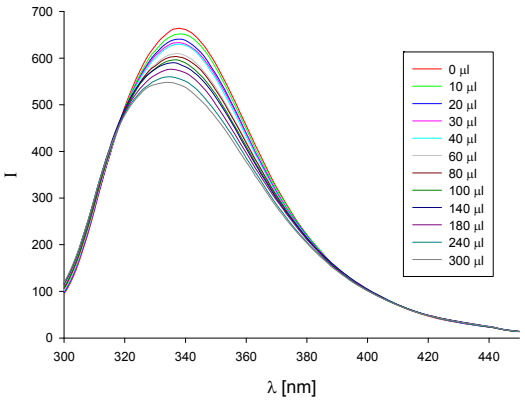
Fluorescence titrations for HArgOH

Titration of **HArgOH** and tweezer **1c** in phosphate buffer (10mM, pH 7.6)

λ_{exc}= 285 nm λ_{em}= 338 nm	Receptor **1c**	Guest H Arg OH · HCl
Amount [mg]:	0.154	0.282
Volume [mL]:	8.58	0.607
Concentration [mol/L]:	$2.33 \cdot 10^{-05}$	$2.54 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{338})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.33E-05	0.00E+00	0.00	663.928	0.000	0.000
10	710	2.33E-05	3.58E-05	1.54	651.777	12.151	10.660
20	720	2.33E-05	7.07E-05	3.03	640.915	23.013	20.121
30	730	2.33E-05	1.05E-04	4.49	633.350	30.578	28.573
40	740	2.33E-05	1.38E-04	5.90	629.736	34.192	36.168
60	760	2.33E-05	2.01E-04	8.62	609.553	54.375	49.252
80	780	2.33E-05	2.61E-04	11.20	602.310	61.618	60.118
100	800	2.33E-05	3.18E-04	13.65	595.105	68.823	69.282
140	840	2.33E-05	4.24E-04	18.20	587.086	76.842	83.879
180	880	2.33E-05	5.21E-04	22.34	573.167	90.761	94.982
240	940	2.33E-05	6.50E-04	27.88	555.393	108.535	107.403
300	1000	2.33E-05	7.63E-04	32.76	543.114	120.814	116.533





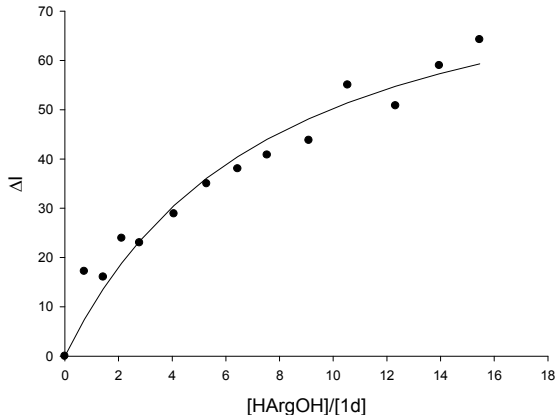
K_a [M^{-1}] = 1430 ± 15 %

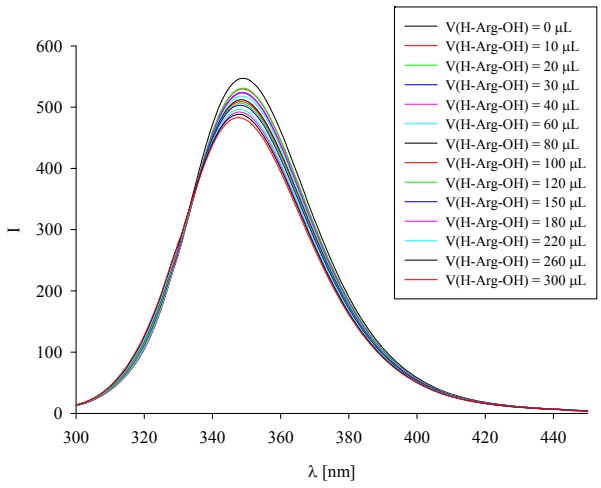
K_d[µM] = 699 ± 15 %

Titration of **HArgOH** and tweezer **1d** in phosphate buffer (10mM, pH 7.2)

λ_{exc}= 285 nm λ_{em}= 348 nm	Receptor **1d**	Guest H Arg OH · HCl
Amount [mg]:	0.259	0.774
Volume [mL]:	4.00	0.80
Concentration [mol/L]:	$8.91 \cdot 10^{-05}$	$4.59 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{338})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	8.91E-05	0.00E+00	0.00	547.049	0.000	0.0000
10	710	8.91E-05	6.47E-05	0.726	529.854	17.195	7.4316
20	720	8.91E-05	1.28E-04	1.432	531.017	16.032	13.6360
30	730	8.91E-05	1.89E-04	2.118	523.134	23.915	18.8764
40	740	8.91E-05	2.48E-04	2.786	524.054	22.995	23.3500
60	760	8.91E-05	3.63E-04	4.069	518.176	28.873	30.5603
80	780	8.91E-05	4.71E-04	5.286	512.063	34.986	36.0975
100	800	8.91E-05	5.74E-04	6.442	509.052	37.997	40.4704
120	820	8.91E-05	6.72E-04	7.542	506.257	40.792	44.0047
150	850	8.91E-05	8.10E-04	9.095	503.272	43.777	48.1879
180	880	8.91E-05	9.39E-04	10.542	492.028	55.021	51.4265
220	920	8.91E-05	1.10E-03	12.324	496.235	50.814	54.7516
260	960	8.91E-05	1.24E-03	13.958	488.097	58.952	57.3016
300	1000	8.91E-05	1.38E-03	15.461	482.845	64.204	59.3180





K_a [M^{-1}] = 1643 ± 27%

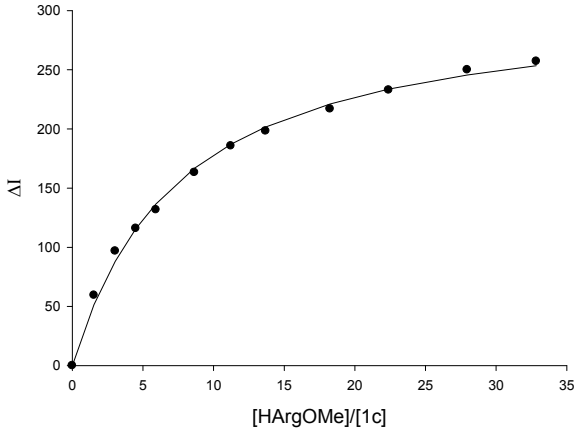
K_d[µM] = 609 ± 27%

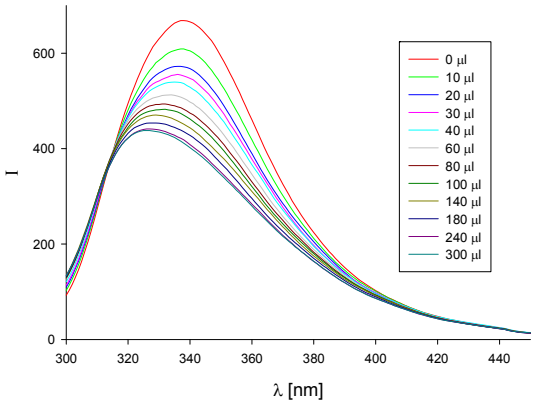
Fluorescence titrations for HArgOMe

Titration of **HArgOMe** and tweezer **1c** in phosphate buffer (10mM, pH 7.6)

λ_{exc}= 285 nm λ_{em}= 338 nm	Receptor **1c**	Guest H ArgOMe ·2HCl
Amount [mg]:	0.154	0.429
Volume [mL]:	8.575	0.644
Concentration [mol/L]:	$2.33 \cdot 10^{-05}$	$2.55 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. ($I_{338\ nm}$)**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2,33E-05	0,00E+00	0,00	668,334	0,000	0,000
10	710	2,33E-05	3,59E-05	1,54	608,912	59,422	51,408
20	720	2,33E-05	7,09E-05	3,04	571,524	96,810	88,201
30	730	2,33E-05	1,05E-04	4,50	552,344	115,990	115,571
40	740	2,33E-05	1,38E-04	5,92	536,594	131,740	136,610
60	760	2,33E-05	2,01E-04	8,64	505,163	163,171	166,659
80	780	2,33E-05	2,62E-04	11,23	482,611	185,723	186,984
100	800	2,33E-05	3,19E-04	13,68	470,043	198,291	201,600
140	840	2,33E-05	4,25E-04	18,25	451,324	217,010	221,160
180	880	2,33E-05	5,22E-04	22,39	435,475	232,859	233,623
240	940	2,33E-05	6,51E-04	27,95	418,363	249,971	245,633
300	1000	2,33E-05	7,65E-04	32,84	411,150	257,184	253,393





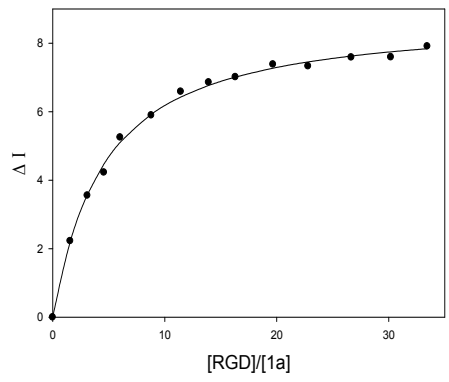
K_a = 6260 ± 6 %

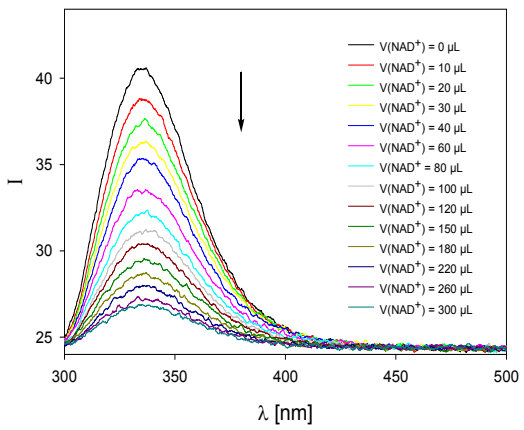
K_d[µM] = 160 ± 6 %

Titration of **RGD** and tweezer **1a** in phosphate buffer (200mM, pH 7.6)

λ_{exc}= 280 nm	**Tweezer 1a**	**H ArgGly Asp OH**
Amount [mg]: Volume [mL]: Concentration [mol/L]:	0.164 ($2.18 \cdot 10^{-4}$mmol) 10 $2.18 \cdot 10^{-5}$	0.696 ($2.01 \cdot 10^{-3}$mmol) 0.825 $2.4 \cdot 10^{-3}$

V_{Guest} [µL]	V_t [µL]	[**750**] [mol/L]	[RGD] [mol/L]	[RGD]/ [**1a**]	I 334 nm	ΔI_{obs}	ΔI_{calc}
0	700	$2.19 \cdot 10^{-5}$	0.00	0.00	42.7	0.0	0.0
10	710	$2.19 \cdot 10^{-5}$	$3.43 \cdot 10^{-5}$	1.57	40.4	2.2	2.2
20	720	$2.19 \cdot 10^{-5}$	$6.77 \cdot 10^{-5}$	3.10	39.1	3.6	3.6
30	730	$2.19 \cdot 10^{-5}$	$1.00 \cdot 10^{-4}$	4.58	38.4	4.2	4.5
40	740	$2.19 \cdot 10^{-5}$	$1.32 \cdot 10^{-4}$	6.02	37.4	5.3	5.1
60	760	$2.19 \cdot 10^{-5}$	$1.92 \cdot 10^{-4}$	8.80	36.8	5.9	5.9
80	780	$2.19 \cdot 10^{-5}$	$2.50 \cdot 10^{-4}$	11.43	36.1	6.6	6.4
100	800	$2.19 \cdot 10^{-5}$	$3.04 \cdot 10^{-4}$	13.93	35.8	6.9	6.8
120	820	$2.19 \cdot 10^{-5}$	$3.56 \cdot 10^{-4}$	16.31	35.7	7.0	7.0
150	850	$2.19 \cdot 10^{-5}$	$4.30 \cdot 10^{-4}$	19.67	35.3	7.4	7.3
180	880	$2.19 \cdot 10^{-5}$	$4.98 \cdot 10^{-4}$	22.80	35.3	7.3	7.5
220	920	$2.19 \cdot 10^{-5}$	$5.82 \cdot 10^{-4}$	26.65	35.1	7.6	7.6
260	960	$2.19 \cdot 10^{-5}$	$6.60 \cdot 10^{-4}$	30.19	35.1	7.6	7.7
300	1000	$2.19 \cdot 10^{-5}$	$7.31 \cdot 10^{-4}$	33.44	34.8	7.9	7.8





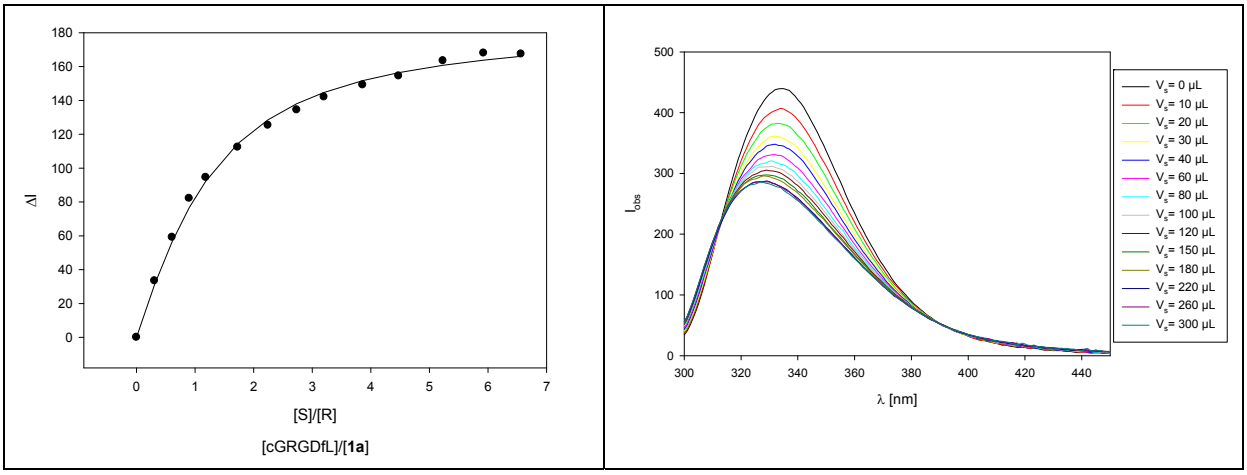
K_a [M^{-1}] = 11660 ± 1 %

K_d[µM] = 86 ± 1 %

Titration of **cRGDfL** and tweezer **1a** in phosphate buffer (10 mM, pH 7.4)

Receptor	Tweezer**1a**
Solvent	Phosphate buffer pH 7.4
***T* [°C]**	25
Substrate	cGRGDfL
m_R [mg]	0.12
m_S [mg]	0.25
$[R]_0$ [M]	$3.7 \cdot 10^{-5}$
$[S]_0$ [M]	$0.8 \cdot 10^{-3}$
V_{0R} [mL]	4.0
V_{0S} [mL]	0.4

V_{Guest} [µL]	V_{Total}[µL]	[R][mol/L]	[S][mol/L]	[S]/[R]	I335 nm	ΔI_{obs}
0	700	3.68E-05	0.00E+00	0.00	439.525	0.000
10	710	3.68E-05	1.13E-05	0.31	406.075	33.450
20	720	3.68E-05	2.24E-05	0.61	380.365	59.160
30	730	3.68E-05	3.31E-05	0.90	357.329	82.196
40	740	3.68E-05	4.36E-05	1.18	344.975	94.550
60	760	3.68E-05	6.36E-05	1.73	327.138	112.387
80	780	3.68E-05	8.26E-05	2.24	314.131	125.394
100	800	3.68E-05	1.01E-04	2.73	305.119	134.406
120	820	3.68E-05	1.18E-04	3.20	297.448	142.077
150	850	3.68E-05	1.42E-04	3.86	290.326	149.199
180	880	3.68E-05	1.65E-04	4.48	285.031	154.494
220	920	3.68E-05	1.93E-04	5.23	276.013	163.512
260	960	3.68E-05	2.18E-04	5.93	271.499	168.026
300	1000	3.68E-05	2.42E-04	6.56	272.071	167.454



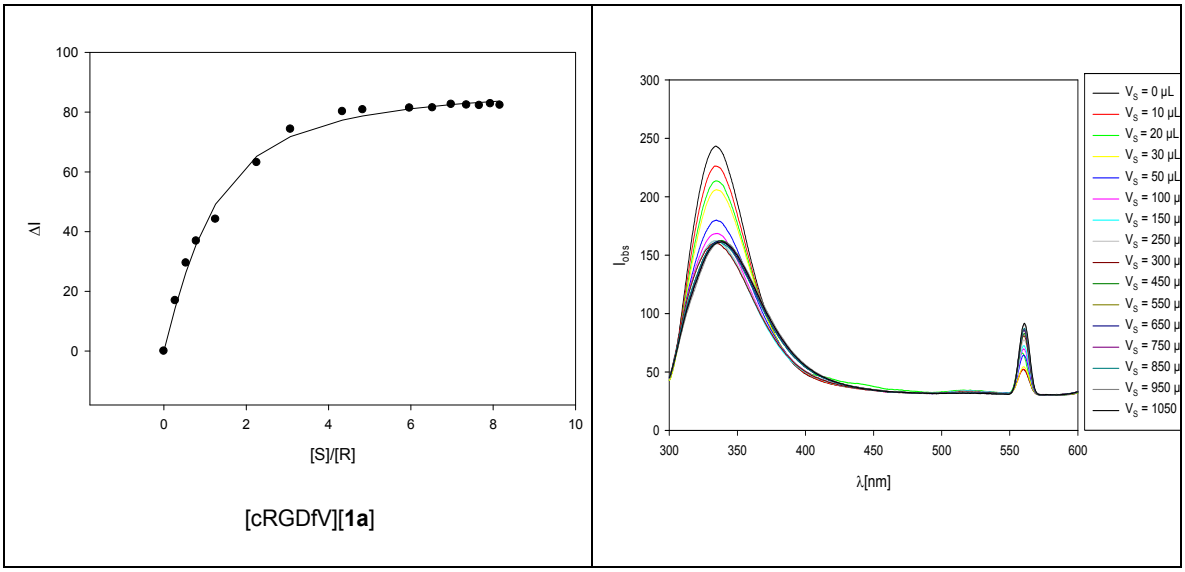
K_a= 38706 ±3125

K_d[µM] =26 ± 8 %

Titration of **cRGDfV** and tweezer **1a**in phosphate buffer (10mM, pH 7.4)

Receptor	**1a**
Solvent	Phosphate buffer pH 7.4
T **[°C]**	25
Substrate	cRGDfV
m_R **[mg]**	0.892
m_S **[mg]**	4.907
$[R]_0$ **[M]**	$9.95 \cdot 10^{-5}$
$[S]_0$ **[M]**	$1.12 \cdot 10^{-3}$
V_{0R} **[mL]**	11.0
V_{0S} **[mL]**	7.60

V_{Guest} **[µL]**	V_{Total}[µL]	[R][mol/L]	[S][mol/L]	[S]/[R]	I334 nm	ΔI_{obs}
0	400	$9.95 \cdot 10^{-5}$	0	0.000	242.896	0.000
10	410	$9.95 \cdot 10^{-5}$	$2.74 \cdot 10^{-5}$	0.275	226.009	16.887
20	420	$9.95 \cdot 10^{-5}$	$5.34 \cdot 10^{-5}$	0.537	213.434	29.462
30	430	$9.95 \cdot 10^{-5}$	$7.83 \cdot 10^{-5}$	0.787	206.067	36.829
50	450	$9.95 \cdot 10^{-5}$	$1.24 \cdot 10^{-6}$	1.253	198.764	44.132
100	500	$9.95 \cdot 10^{-5}$	$2.24 \cdot 10^{-6}$	2.255	179.812	63.084
150	550	$9.95 \cdot 10^{-5}$	$3.10 \cdot 10^{-6}$	3.075	168.613	74.283
250	650	$9.95 \cdot 10^{-5}$	$4.31 \cdot 10^{-6}$	4.336	162.722	80.174
300	700	$9.95 \cdot 10^{-5}$	$4.81 \cdot 10^{-6}$	4.832	162.128	80.768
450	850	$9.95 \cdot 10^{-5}$	$5.94 \cdot 10^{-6}$	5.969	161.568	81.328
550	950	$9.95 \cdot 10^{-5}$	$6.50 \cdot 10^{-6}$	6.527	161.500	81.396
650	1050	$9.95 \cdot 10^{-5}$	$6.95 \cdot 10^{-6}$	6.980	160.293	82.603
750	1150	$9.95 \cdot 10^{-5}$	$7.31 \cdot 10^{-6}$	7.353	160.532	82.364
850	1250	$9.95 \cdot 10^{-5}$	$7.63 \cdot 10^{-6}$	7.667	160.693	82.203
950	1350	$9.95 \cdot 10^{-5}$	$7.90 \cdot 10^{-6}$	7.934	160.107	82.789
1050	1450	$9.95 \cdot 10^{-5}$	$8.13 \cdot 10^{-6}$	8.164	160.624	82.272



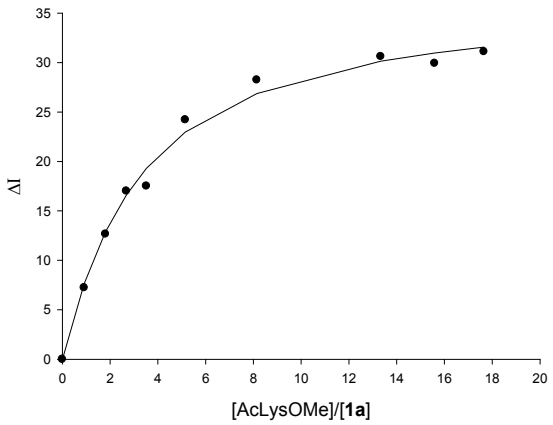
K_a= 16791 ± 1817, K_d[µM] = 59 ± 11 %

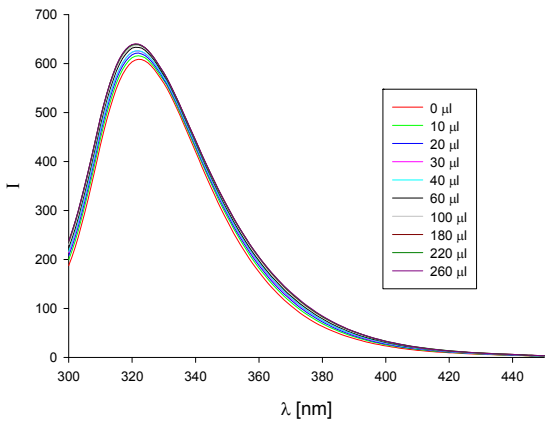
Fluorescence titrations of the tweezers and the amino acid guests in methanol and mixture of methanol-buffer

Fluorescence titration of the tweezer **1a** with AcLysOMe in methanol

λ_{exc}= 285 nm λ_{em}= 322 nm	Receptor **1a**	Guest Ac Lys OMe ·HCl
Amount [mg]:	0.120	0.382
Volume [mL]:	6.00	1.00
Concentration [mol/L]:	$2.46 \cdot 10^{-05}$	$1.60 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{322})**	**$-\Delta I_{obs}$**	**$-\Delta I_{calc}$**
0	700	2.46E-05	0.00E+00	0.00	608.731	0.000	0.000
10	710	2.46E-05	2.25E-05	0.92	615.971	7.240	7.651
20	720	2.46E-05	4.45E-05	1.81	621.386	12.655	12.889
30	730	2.46E-05	6.58E-05	2.68	625.740	17.009	16.594
40	740	2.46E-05	8.65E-05	3.52	626.250	17.519	19.308
60	760	2.46E-05	1.26E-04	5.15	632.937	24.206	22.964
100	800	2.46E-05	2.00E-04	8.15	636.981	28.250	26.873
180	880	2.46E-05	3.27E-04	13.33	639.343	30.612	30.135
220	920	2.46E-05	3.83E-04	15.59	638.661	29.930	30.962
260	960	2.46E-05	4.33E-04	17.65	639.838	31.107	31.555





K_a [M^{-1}] = 15200 ± 11 %

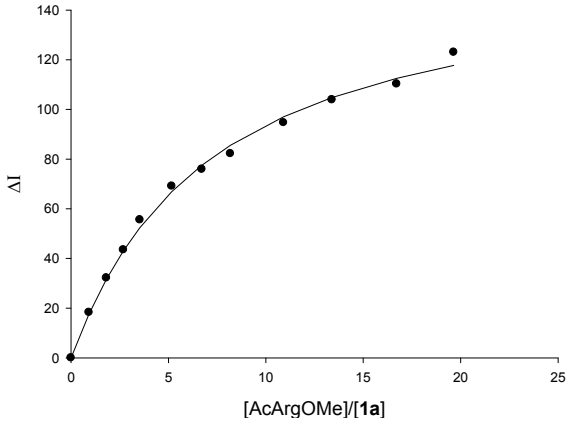
K_d [µM] = 66 ± 11 %

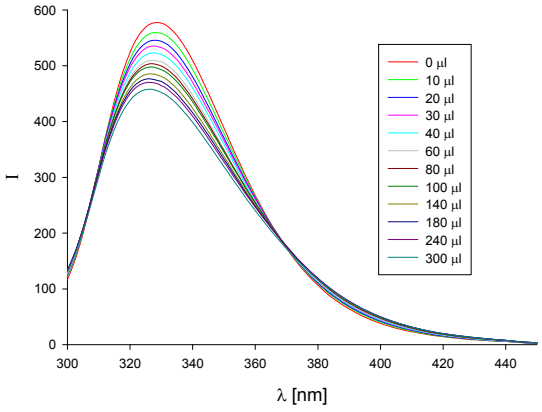
ΔI_{max}= -37 (6 %)

Fluorescence titration of the tweezer **1a** with AcArgOMe in 1:9 mixture of methanol/buffer (10 mM, pH 7.6)

λ_{exc}= 285 nm λ_{em}= 322 nm	Receptor **1a**	Guest Ac ArgOMe ·HCl
Amount [mg]:	0.178	0.318
Volume [mL]:	9.00	0.75
Concentration [mol/L]:	$2.43 \cdot 10^{-05}$	$1.59 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{329})**	**ΔI_{obs}**	**ΔI_{calc}**
0	700	2.43E-05	0.00E+00	0.00	577.521	0.000	0.000
10	710	2.43E-05	2.24E-05	0.92	559.216	18.305	17.616
20	720	2.43E-05	4.42E-05	1.82	545.347	32.174	31.650
30	730	2.43E-05	6.53E-05	2.69	534.020	43.501	43.031
40	740	2.43E-05	8.59E-05	3.54	521.926	55.595	52.412
60	760	2.43E-05	1.25E-04	5.17	508.400	69.121	66.898
80	780	2.43E-05	1.63E-04	6.72	501.594	75.927	77.513
100	800	2.43E-05	1.99E-04	8.18	495.321	82.200	85.598
140	840	2.43E-05	2.65E-04	10.91	482.860	94.661	97.059
180	880	2.43E-05	3.25E-04	13.39	473.636	103.885	104.770
240	940	2.43E-05	4.06E-04	16.72	467.250	110.271	112.518
300	1000	2.43E-05	4.77E-04	19.64	454.493	123.028	117.696





K_a [M^{-1}] = 6380 ± 8 %

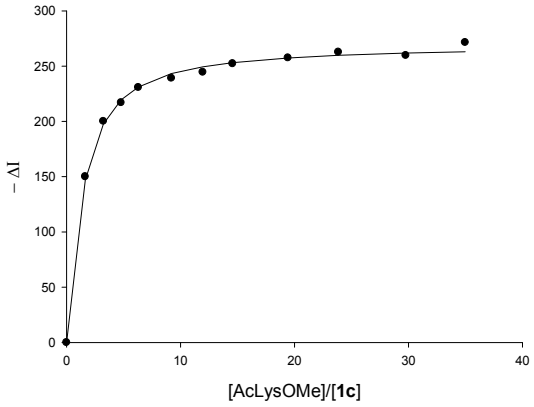
K_d [µM] = 157 ± 8 %

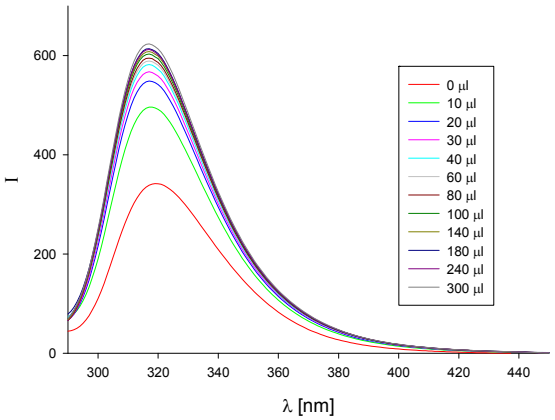
ΔI_{max}= 158 (27 %)

Fluorescence titration of the tweezer **1c** with AcLysOMe in methanol

λ_{exc}= 285 nm λ_{em}= 320 nm	Receptor **1c**	Guest Ac Lys OMe
Amount [mg]:	0.118	0.459
Volume [mL]:	7.000	0.754
Concentration [mol/L]:	$2.19 \cdot 10^{-05}$	$2.55 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{320})**	**- ΔI_{obs}**	**- ΔI_{calc}**
0	700	2.19E-05	0.00E+00	0.00	341.665	0.000	0.000
10	710	2.19E-05	3.59E-05	1.64	491.668	150.003	147.138
20	720	2.19E-05	7.08E-05	3.24	541.670	200.005	197.765
30	730	2.19E-05	1.05E-04	4.79	558.559	216.894	219.535
40	740	2.19E-05	1.38E-04	6.30	572.238	230.573	231.212
60	760	2.19E-05	2.01E-04	9.21	580.712	239.047	243.285
80	780	2.19E-05	2.62E-04	11.96	586.192	244.527	249.429
100	800	2.19E-05	3.19E-04	14.58	593.864	252.199	253.137
140	840	2.19E-05	4.25E-04	19.43	599.100	257.435	257.390
180	880	2.19E-05	5.22E-04	23.85	604.290	262.625	259.757
240	940	2.19E-05	6.51E-04	29.77	601.297	259.632	261.830
300	1000	2.19E-05	7.65E-04	34.98	613.000	271.335	263.074





K_a [M^{-1}] = 49800 ± 6 %

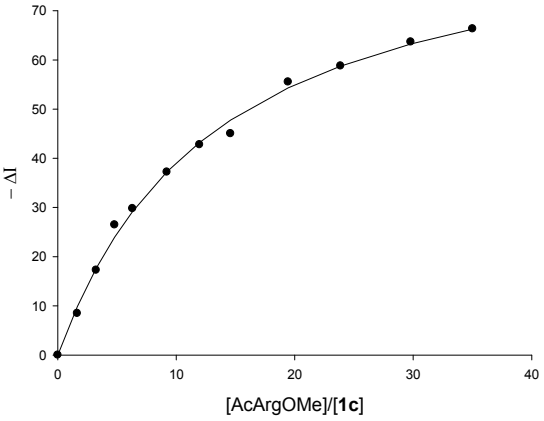
K_d [µM] = 20 ± 6 %

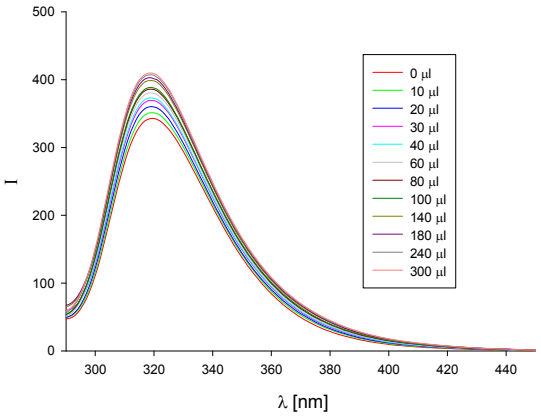
ΔI_{max} = -270 (44 %)

Fluorescence titration of the tweezer **1c** with AcArgOMe in methanol

λ_{exc}= 285 nm λ_{em}= 320 nm	Receptor **1c**	Guest Ac ArgOMe
Amount [mg]:	0.118	0.484
Volume [mL]:	7.000	0.711
Concentration [mol/L]:	$2.19 \cdot 10^{-05}$	$2.55 \cdot 10^{-03}$

Guest V (µL)	**Receptor V (µL)**	**[Receptor] [mol/L]**	**[Guest] [mol/L]**	**[Guest]/ [Receptor]**	**F.I. (I_{320})**	**- ΔI_{obs}**	**- ΔI_{calc}**
0	700	2.19E-05	0.00E+00	0.00	342.695	0.000	0.000
10	710	2.19E-05	3.59E-05	1.64	351.154	8.459	9.834
20	720	2.19E-05	7.09E-05	3.24	359.956	17.261	17.635
30	730	2.19E-05	1.05E-04	4.80	369.160	26.465	23.956
40	740	2.19E-05	1.38E-04	6.31	372.464	29.769	29.172
60	760	2.19E-05	2.02E-04	9.21	379.892	37.197	37.254
80	780	2.19E-05	2.62E-04	11.97	385.463	42.768	43.213
100	800	2.19E-05	3.19E-04	14.59	387.707	45.012	47.780
140	840	2.19E-05	4.25E-04	19.45	398.203	55.508	54.306
180	880	2.19E-05	5.22E-04	23.87	401.469	58.774	58.740
240	940	2.19E-05	6.52E-04	29.80	406.335	63.640	63.235
300	1000	2.19E-05	7.66E-04	35.01	409.009	66.314	66.264





K_a [M^{-1}] = 3620 ± 7 %

K_d [µM] = 276 ± 7 %

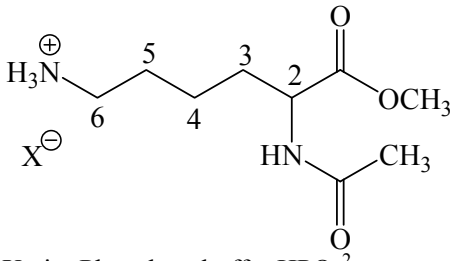
ΔI_{max} = -91 (22 %)

1.4 ^{1}H NMR titrations

NMR titrations of the phosphate tweezer 1a

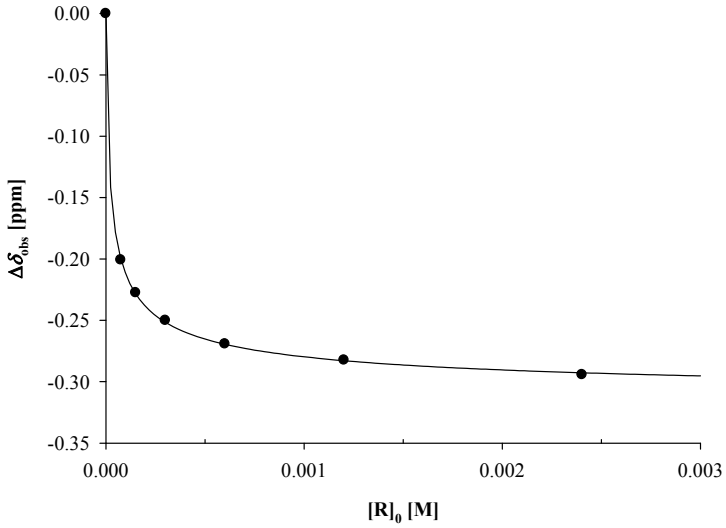
Titration of tweezer **1a** and**AcLysOMe** in phosphate buffer (70 mM, pH 7.2)

Receptor	**1a**	M_R [g/mol]	1a.19
Solvent	Phosphate buffer	M_S [g/mol]	238.11
T [°C]	25	m_R [mg]	3.61
Substrat	**Ac Lys OMe**	m_S [mg]	1.39
	δ_0 (2-H) [ppm] = 4.379	V_0 [mL]	2
	δ_0 (6-H) [ppm] = 2.980	$[R]_0$ [mM]	2.41
	δ_0 (-*N*Ac) [ppm] = 2.031	$[S]_0$ [mM]	2.49
	δ_0 (-COOMe) [ppm] = 3.752		



X^-: im Phosphate buffer HPO_3^{2-}

$[R]_0$ [mM]	$[S]_0$ [mM]	δ_{obs} (*N*Ac-H)	$\Delta\delta_{obs}$	$\Delta\delta_{calc}$
2.41	2.49	2.325	- 0.294	- 0.293
1.20	1.24	2.313	- 0.282	- 0.283
0.60	0.62	2.300	- 0.269	- 0.269
0.30	0.31	2.281	- 0.250	- 0.252
0.15	0.16	2.258	- 0.228	- 0.228
0.08	0.08	2.232	- 0.201	- 0.199



K_a [M^{-1}] = 58350 ± 0*

$\Delta\delta_{max}$(2-H) [ppm] = 0.51

$\Delta\delta_{max}$(6-H) [ppm] = 3.91

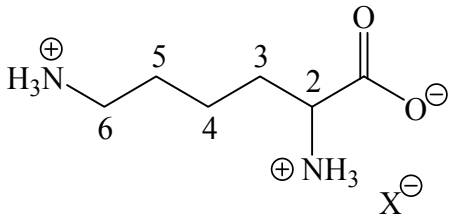
$\Delta\delta_{max}$(-*N*Ac) [ppm] = - 0.32

$\Delta\delta_{max}$ (-COOMe) [ppm]= - 0.23

* Limit of 95% - confidence interval from the nonlinear regression of the signals of the Protons *N*Ac-H.

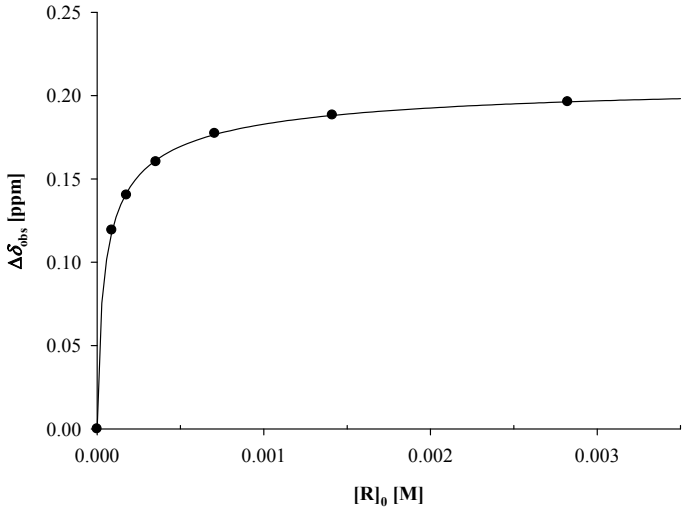
Titration of tweezer **1a** and **HLysOH** in phosphate buffer (70 mM, pH 7.2)

Receptor	**1a**	M_R [g/mol]	1a.19
Solvent	Phosphate buffer	M_S [g/mol]	182.08
T [°C]	25	m_R [mg]	5.00
Substrat	**H Lys OH**	m_S [mg]	1.39
	δ_0 (2-H) [ppm] = 3.741	V_0 [mL]	2
	δ_0 (3-H) [ppm] = 1.713	$[R]_0$ [mM]	2.82
	δ_0 (5-H) [ppm] = 1.891	$[S]_0$ [mM]	3.24
	δ_0 (6-H) [ppm] = 3.009		



X^-: in Phosphate buffer HPO_3^{2-}

$[R]_0$ [mM]	$[S]_0$ [mM]	δ_{obs} (2-H)	$\Delta\delta_{obs}$	$\Delta\delta_{calc}$
2.82	3.24	3.545	0.196	0.196
1.41	1.62	3.553	0.188	0.188
0.71	0.81	3.564	0.177	0.177
0.35	0.41	3.581	0.160	0.1c
0.18	0.20	3.601	0.140	0.142
0.09	0.10	3.622	0.119	0.118



K_a [M^{-1}] = 25006 ± 1890*

$\Delta\delta_{max}$(2-H) [ppm] = 0.24

$\Delta\delta_{max}$(3-H) [ppm] = 0.76

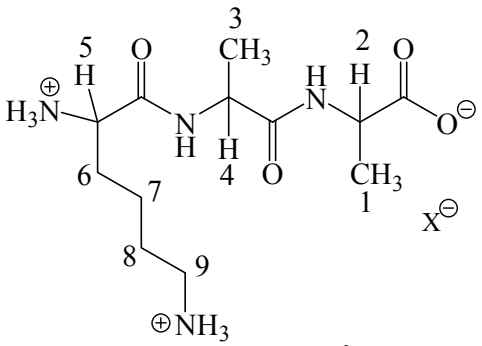
$\Delta\delta_{max}$(5-H) [ppm] = 4.47

$\Delta\delta_{max}$ (6-H) [ppm] = 4.51

* Limit of 95% - confidence interval from the nonlinear regression of the signals of the Protons 2-H.

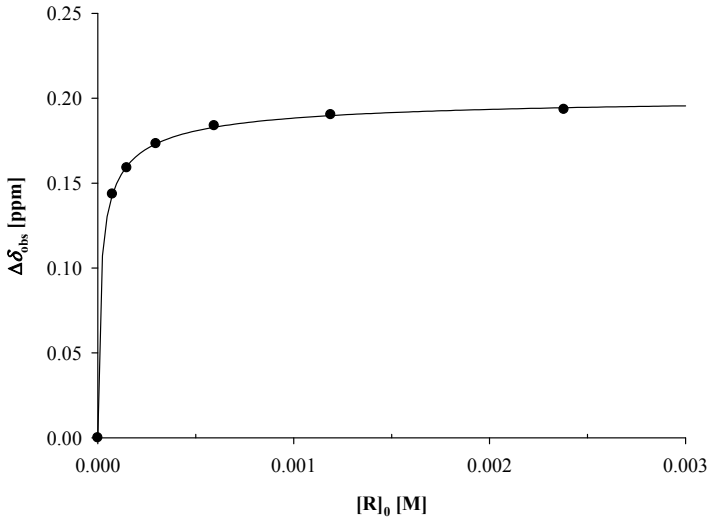
Titration of tweezer **1a** and **KAA** in phosphate buffer (70 mM, pH 7.2)

Receptor	**1a**	M_R [g/mol]	1a.19
Solvent	Phosphate buffer	M_S [g/mol]	288.35
T [°C]	25	m_R [mg]	3.57
Substrat	**KAA**	m_S [mg]	1.75
	δ_0 (1-H) [ppm] = 1.414	V_0 [mL]	2
	δ_0 (3-H) [ppm] = 1.336	$[R]_0$ [mM]	2.38
	δ_0 (4-H) [ppm] = 4.097	$[S]_0$ [mM]	2.13
	δ_0 (5-H) [ppm] = 3.966		
	δ_0 (6-H) [ppm] = 1.905		
	δ_0 (7-H) [ppm] = 1.463		
	δ_0 (8-H) [ppm] = 1.713		
	δ_0 (9-H, 9´-H) [ppm] = 3.013		



X^-: im Phosphate buffer HPO_3^{2-}

$[R]_0$ [mM]	$[S]_0$ [mM]	δ_{obs} (5-H)	$\Delta\delta_{obs}$	$\Delta\delta_{calc}$
2.38	2.13	3.773	0.193	0.194
1.19	1.06	3.776	0.190	0.190
0.59	0.53	3.782	0.184	0.183
0.30	0.27	3.793	0.173	0.173
0.15	0.13	3.807	0.159	0.160
0.07	0.07	3.823	0.144	0.143



K_a [M^{-1}] = 90803 ± 8423

$\Delta\delta_{max}$(1-H) [ppm] = - 0.13

$\Delta\delta_{max}$(3-H) [ppm] = - 0.00

$\Delta\delta_{max}$(4-H) [ppm] = - 0.17

$\Delta\delta_{max}$(5-H) [ppm] = 0.20

$\Delta\delta_{max}$(6-H) [ppm] = 1.09

$\Delta\delta_{max}$(7-H) [ppm] = 2.28

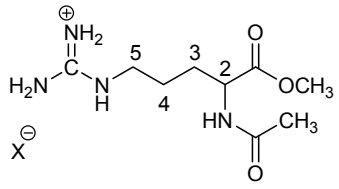
$\Delta\delta_{max}$(8-H) [ppm] = 3.22

$\Delta\delta_{max}$ (9-H, 9´-H) [ppm] = 5.82, 5.92

* Limit of 95% - confidence interval from the nonlinear regression of the signals of the Protons 5-H.

Titration of tweezer **1a** and AcArgOMe in phosphate buffer (10 mM, pH 7.2)

Receptor	**1a**	M_R [g/mol]	770.78
Solvent	Phosphate buffer	M_S [g/mol]	266.7
T[°C]	25	m_R[mg]	0.800
Substrate	**Ac ArgOMe**	m_S[mg]	0.511



X^-: HPO_4^{2-}

δ_0 (2-H) [ppm] = 4.421

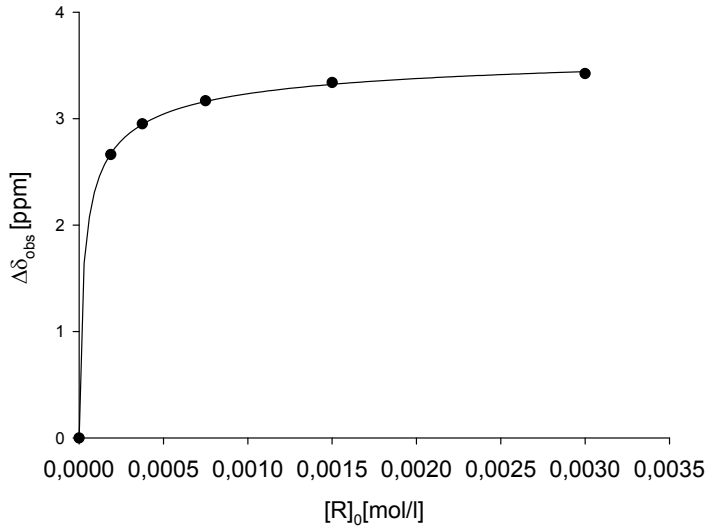
δ_0 (5-H) [ppm] = 3.226

δ_0 (4-H) [ppm] = 1.663

δ_0 (-NAc) [ppm] = 2.052

δ_0 (-CO_2Me) [ppm] = 3.775

$[R]_0$[mM]	$[S]_0$[mM]	δ (5-H) [ppm]	$\Delta\delta_{obs}$[ppm]	$\Delta\delta_{calc}$[ppm]
3.0	3.0	-0.198	3.424	3.442
1.5	1.5	-0.113	3.338	3.323
0.75	0.75	0.058	3.168	3.162
0.375	0.375	0.274	2.952	2.947
0.188	1.88	0.563	2.663	2.671



$K_a[M^{-1}]$ = 45939 ± 2065

$K_d[\mu M]$ = 22 ± 4 %

$\Delta\delta_{max}$ (5-H) [ppm] = 3.748 ± 0.16

$\Delta\delta_{max}$ (4-H) [ppm] = 2.540 ± 0.005

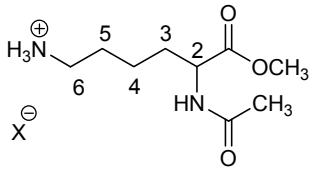
$\Delta\delta_{max}$ (3-H) [ppm] = 1.229 ± 0.007

$\Delta\delta_{max}$ (2-H) [ppm] = 0.630 ± 0.002

* Limit of 95% - confidence interval from the nonlinear regression of the signals of the Protons 5-H.

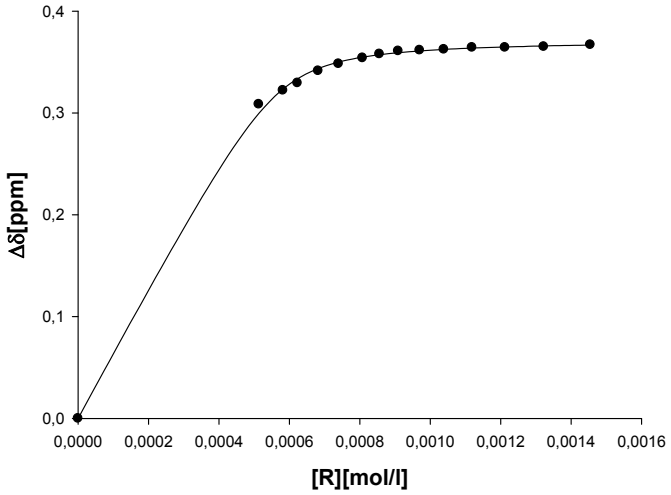
NMR titrations of sulfate tweezer 1c

Titration of tweezer **1c** and**AcLysOMe** in phosphate buffer (10 mM, pH 7.2)

Receptor	**1c**	M_R[g/mol]	770.78
Solvent	Phosphate buffer	M_S[g/mol]	238.7
T[°C]	25	m_R[mg]	0.672
Substrate	**AcLysOMe**	m_S[mg]	0.410
	δ_0 (2-H) [ppm] = 4.398	V_0 [ml]	3.0
	δ_0 (6-H) [ppm] = 2.999	$[S_0]$[mM]	0.5725
	δ_0 (-*NAc*) [ppm] = 2.050		
	δ_0 (-CO_2Me) [ppm] = 3.770		

X^-: HPO_4^{2-}

V [ml]	[R][mM]	δ (2-H) [ppm]	$\Delta\delta_{obs}$[ppm]	$\Delta\delta_{calc}$[ppm]
0.60	1.4548	4.0313	0.3670	0.3667
0.66	1.3225	4.0332	0.3651	0.3658
0.72	1.2123	4.0340	0.3643	0.3648
0.78	1.1191	4.0340	0.3643	0.3637
0.84	1.0391	4.0359	0.3624	0.3624
0.90	0.9699	4.0367	0.3616	0.3609
0.96	0.9093	4.0374	0.3609	0.3592
1.02	0.8558	4.0405	0.3578	0.3572
1.08	0.8082	4.0443	0.3540	0.3549
1.18	0.7397	4.0501	0.3482	0.3500
1.28	0.6819	4.0570	0.3413	0.3436
1.40	0.6235	4.0689	0.3294	0.3337
1.50	0.5819	4.0761	0.3222	0.3235
1.70	0.5135	4.0898	0.3085	0.2997
0.00	0.0000	4.3983	0.0000	0.0000



$K_a[M^{-1}]$ = 79536 ± 8889

K_d[µM] = 12 ± 11 %

$\Delta\delta_{max}$ (2-H) [ppm] = 0.37

$\Delta\delta_{max}$ (3-H) [ppm] = 1.29

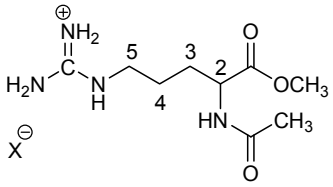
$\Delta\delta_{max}$ (4-H) [ppm] = 2.64

$\Delta\delta_{max}$ (6-H) [ppm] = 3.75

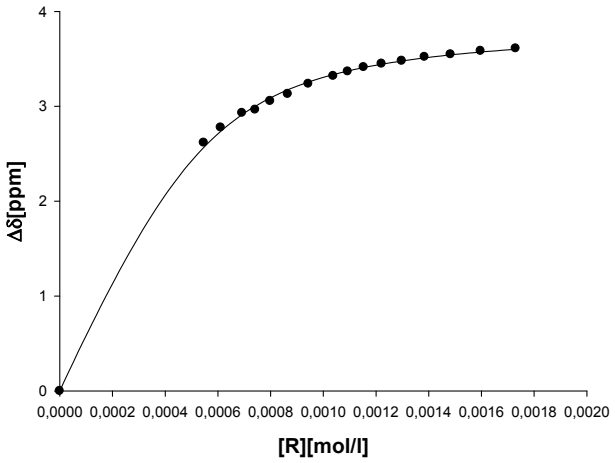
$\Delta\delta_{max}$ (5-H) [ppm] = 4.41

* Limit of 95% - confidence interval from the nonlinear regression of the signals of the Protons 2-H.

Titration of tweezer **1c** and **AcArgOMe** in phosphate buffer (10 mM, pH 7.2)

Receptor	**1c**	M_R[g/mol]	770.78
Solvent	Phosphate buffer	M_S[g/mol]	266.7
T[°C]	25	m_R[mg]	0.800
Substrate	**AcArgOMe**	m_S[mg]	0.511
	δ_0 (2-H) [ppm] = 4.421	V_0 [ml]	3.42
	δ_0 (5-H) [ppm] = 3.226	[S]$_0$[mM]	0.5602
	δ_0 (4-H) [ppm] = 1.663		
	δ_0 (-NAc) [ppm] = 2.052		
X^-: HPO_4^{2-}	δ_0 (-CO_2Me) [ppm] = 3.775		

V [ml]	[R] [mM]	δ (5-H) [ppm]	$\Delta\delta_{obs}$[ppm]	$\Delta\delta_{calc}$[ppm]
0.60	1.7298	-0.3837	3.6096	3.6009
0.65	1.5968	-0.3578	3.5837	3.5719
0.70	1.4827	-0.3216	3.5475	3.5416
0.75	1.3839	-0.2950	3.5209	3.5101
0.80	1.2974	-0.2534	3.4793	3.4773
0.85	1.2211	-0.2227	3.4486	3.4433
0.90	1.1532	-0.1865	3.4124	3.4079
0.95	1.0925	-0.1410	3.3669	3.3714
1.00	1.0379	-0.0926	3.3185	3.3338
1.10	0.9436	-0.0113	3.2372	3.2553
1.20	0.8649	0.0957	3.1302	3.1729
1.30	0.7984	0.1700	3.0559	3.0876
1.40	0.7414	0.2620	2.9639	3.0004
1.50	0.6919	0.2955	2.9304	2.9119
1.70	0.6105	0.4491	2.7768	2.7358
1.90	0.5463	0.6097	2.6162	2.5658
0.00	0.0000	3.2259	0.0000	0.0000



$K_a[M^{-1}]$ = 11342 ± 561

$K_d[\mu M]$ = 88 ± 5 %

$\Delta\delta_{max}$ (2-H) [ppm] = 0.42

$\Delta\delta_{max}$ (3-H) [ppm] = 1.32

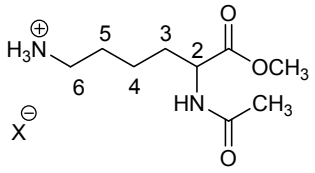
$\Delta\delta_{max}$ (4-H) [ppm] = 2.51

$\Delta\delta_{max}$ (5-H) [ppm] = 3.86

* Limit of 95% - confidence interval from the nonlinear regression of the signals of the Protons 5-H.

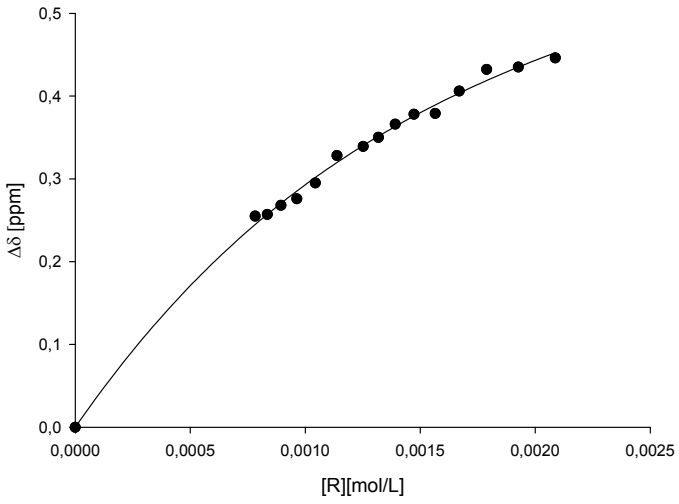
NMR titrations of the carboxymethyl tweezer 1d

Titration of tweezer **1d** and**AcLysOMe** in phosphate buffer (10 mM, pH 7.2)

Receptor	**1d**	M_R[g/mol]	726.72
Solvent	Phosphate buffer (74 mM)	M_S[g/mol]	238.7
T[°C]	25	m_R[mg]	0.910
Substrate	**AcLysOMe**	m_S[mg]	0.552
	δ_0 (3b-H) [ppm] = 1.682	V_0 [ml]	3.00
	δ_0 (6-H) [ppm] = 2.984	[S_0][mM]	0.771
	δ_0 (-*NAc*) [ppm] = 2.038		
	δ_0 (-CO_2Me) [ppm] = 3.763		

X^-: HPO_4^{2-}

V **[ml]**	**[R][mM]**	**δ (3b-H) [ppm]**	**$\Delta\delta_{obs}$[ppm]**	**$\Delta\delta_{calc}$[ppm]**
0.60	2.0870	1.2360	0.4460	0.4524
0.65	1.9265	1.2470	0.4350	0.4351
0.70	1.7889	1.2500	0.4320	0.4188
0.75	1.6696	1.2760	0.4060	0.4036
0.80	1.5653	1.3030	0.3790	0.3893
0.85	1.4732	1.3040	0.3780	0.3759
0.90	1.3913	1.3160	0.3660	0.3634
0.95	1.3181	1.3320	0.3500	0.3515
1.00	1.2522	1.3430	0.3390	0.3404
1.10	1.1384	1.3540	0.3280	0.3199
1.20	1.0435	1.3870	0.2950	0.3016
1.30	0.9632	1.4060	0.2760	0.2853
1.40	0.8944	1.4140	0.2680	0.2705
1.50	0.8348	1.4250	0.2570	0.2571
1.60	0.7826	1.4270	0.2550	0.2449
0.00	0.0000	1.6820	0.0000	0.0000



$K_a[M^{-1}]$ = 859 ± 11%

$\Delta\delta_{max}$ (3a-H) [ppm] = 0.52

$\Delta\delta_{max}$ (3b-H) [ppm] = 0.77

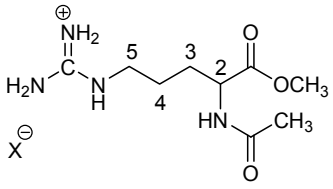
$\Delta\delta_{max}$ (4-H) [ppm] = 0.40

$\Delta\delta_{max}$ (5-H) [ppm] = 0.54

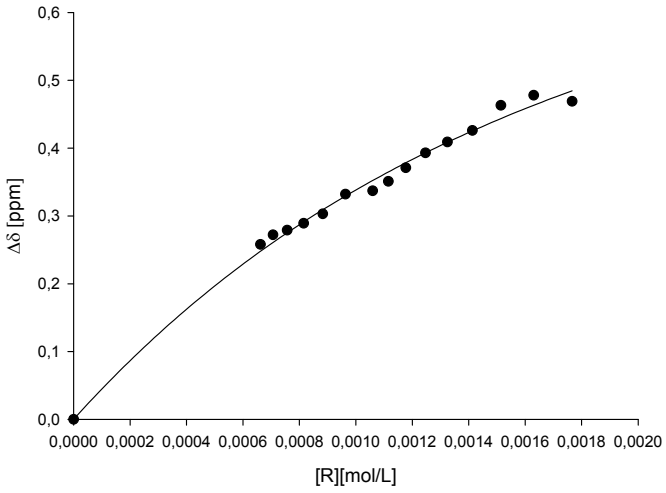
$\Delta\delta_{max}$ (6-H) [ppm] = 0.94

***** Limit of 95% - confidence interval from the nonlinear regression of the signals of the Protons 3b-H.

Titration of tweezer **1d** and **AcArgOMe** in phosphate buffer (10 mM, pH 7.2)

Receptor	**1d**	M_R[g/mol]	726.72
Solvent	Phosphate buffer (74 mM)	M_S[g/mol]	266.7
T[°C]	25	m_R[mg]	0.770
Substrate	**AcArgOMe**	m_S[mg]	0.552
	δ_0 (2-H) [ppm] = 4.414	V_0 [ml]	3.00
	δ_0 (5-H) [ppm] = 3.213	$[S]_0$[mM]	0.6898
	δ_0 (3-H) [ppm] = 1.656		
	δ_0 (-NAc) [ppm] = 2.041		
X^-: HPO_4^{2-}	δ_0 (-CO_2Me) [ppm] = 3.762		

V [ml]	[R] [mM]	δ (5-H) [ppm]	$\Delta\delta_{obs}$[ppm]	$\Delta\delta_{calc}$[ppm]
0.60	1.7659	2.744	0.4690	0.4846
0.65	1.6301	2.735	0.4780	0.4632
0.70	1.1514	2.750	0.4630	0.4436
0.75	1.4127	2.787	0.4260	0.4254
0.80	1.3244	2.804	0.4090	0.4086
0.85	1.2466	2.820	0.3930	0.3930
0.90	1.1773	2.842	0.3710	0.3784
0.95	1.1153	2.862	0.3510	0.3649
1.00	1.0596	2.876	0.3370	0.3522
1.10	0.9632	2.881	0.3320	0.3293
1.20	0.8829	2.910	0.3030	0.3091
1.30	0.8150	2.924	0.2890	0.2912
1.40	0.7568	2.934	0.2790	0.2752
1.50	0.7064	2.941	0.2720	0.2608
1.60	0.6622	2.955	0.2580	0.2478
0.00	0.0000	3.213	0.0000	0.0000



$K_a[M^{-1}]$ = 718 ± 18%

$\Delta\delta_{max}$ (5-H) [ppm] = 0.96

$\Delta\delta_{max}$ (4b-H) [ppm] = 0.62

$\Delta\delta_{max}$ (4a-H) [ppm] = 0.48

$\Delta\delta_{max}$ (3-H) [ppm] = 0.52

* Limit of 95% - confidence interval from the nonlinear regression of the signals of the Protons 5-H.

1.5 Solvent-dependent ^{1}H NMR spectra of the complexes

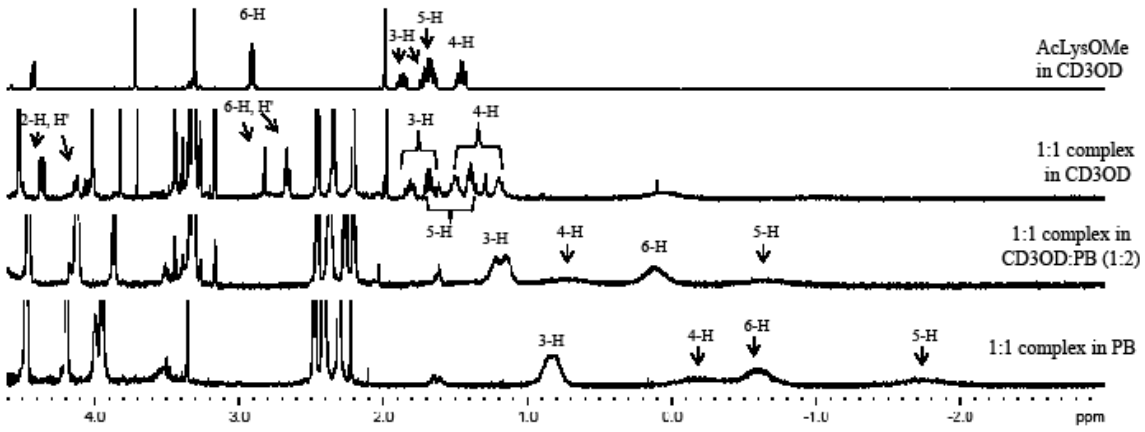


Figure S2. ^{1}H-NMR spectra of 1:1 mixture of the phosphate tweezer **1a** and **AcLysOMe** in different polarity medium methanol/phosphate buffer (10mM, pH 7.2) mixture. Lysine side-chain protons are assigned by numbers.

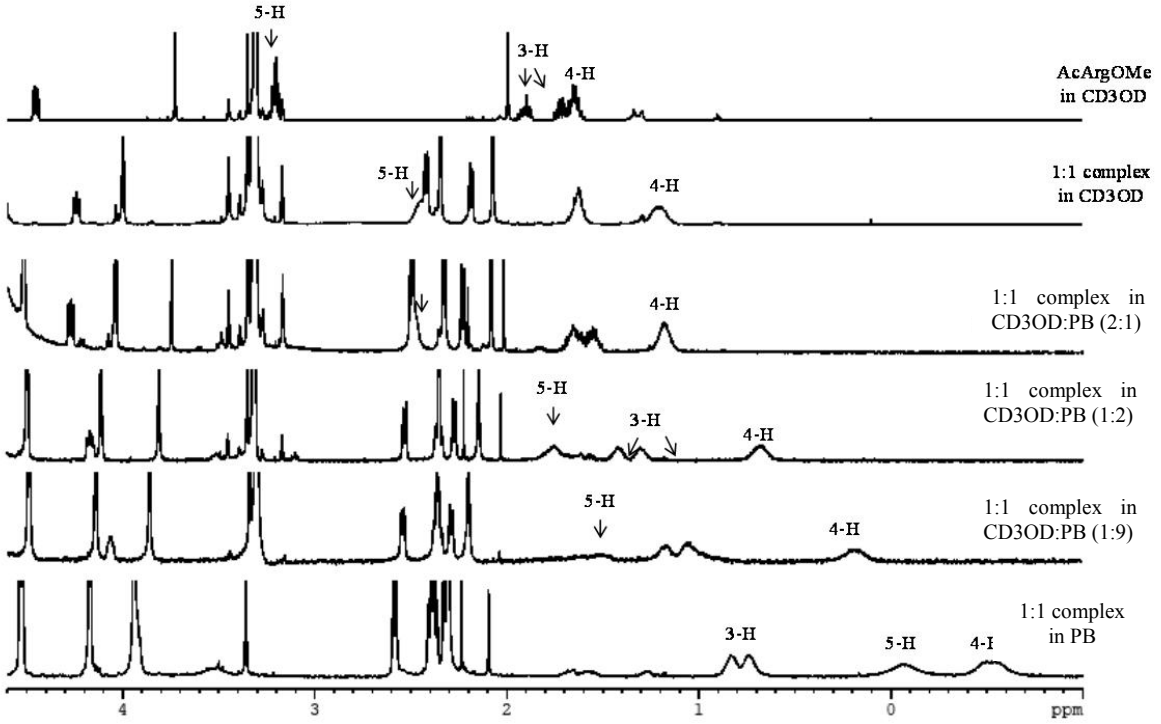


Figure S3. ^{1}H-NMR spectra of 1:1 mixture of the phosphate tweezer **1a** and **AcArgOMe**each at 1.0 mM concentration in different polarity medium methanol/phosphate buffer (PB, 10mM, pH 7.2) mixture. The spectrum in methanol/buffer (1:9) was measured at 0.5 mM concentration of both host and guest. Arginine side chain protons are assigned by numbers.

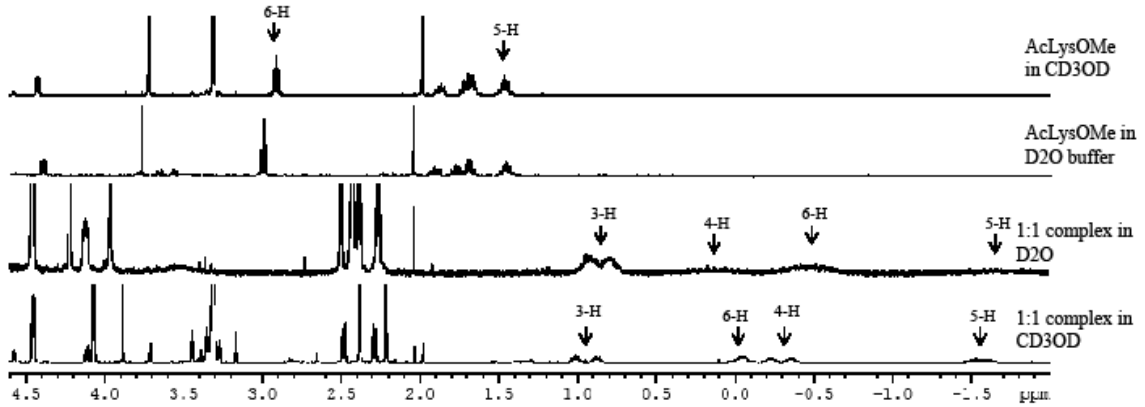


Figure S4. [1]H-NMR spectra of 1:1 mixture of the sulfate tweezer **1c** and **AcLysOMe**, each at 1.0 mM concentration.Signals of lysine side-chain are shifted upfieldin the similar range both in buffer and in methanol. 6-H protons of lysine shifted upfield by ~ 3.40 ppm in phosphate buffer (10 mM, pH 7.2) and by ~ 3.00 ppm in methanol.

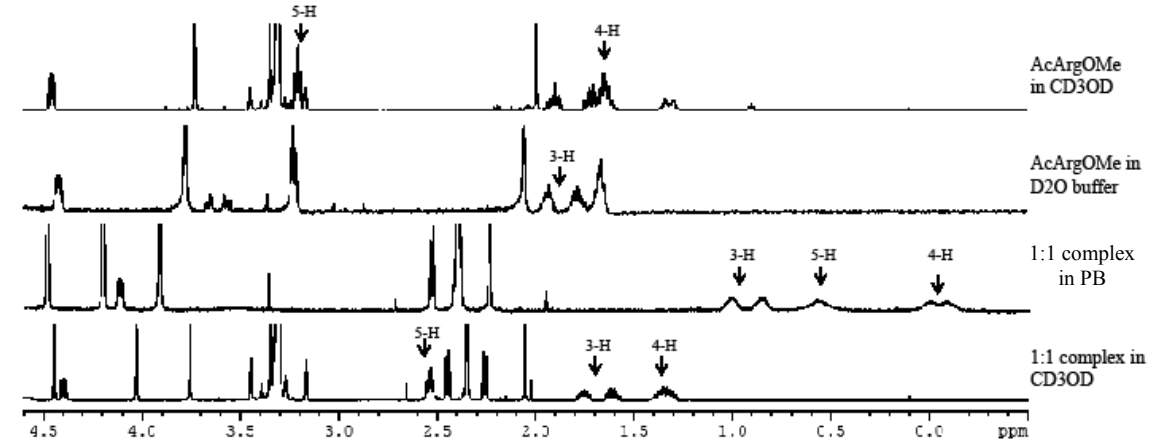


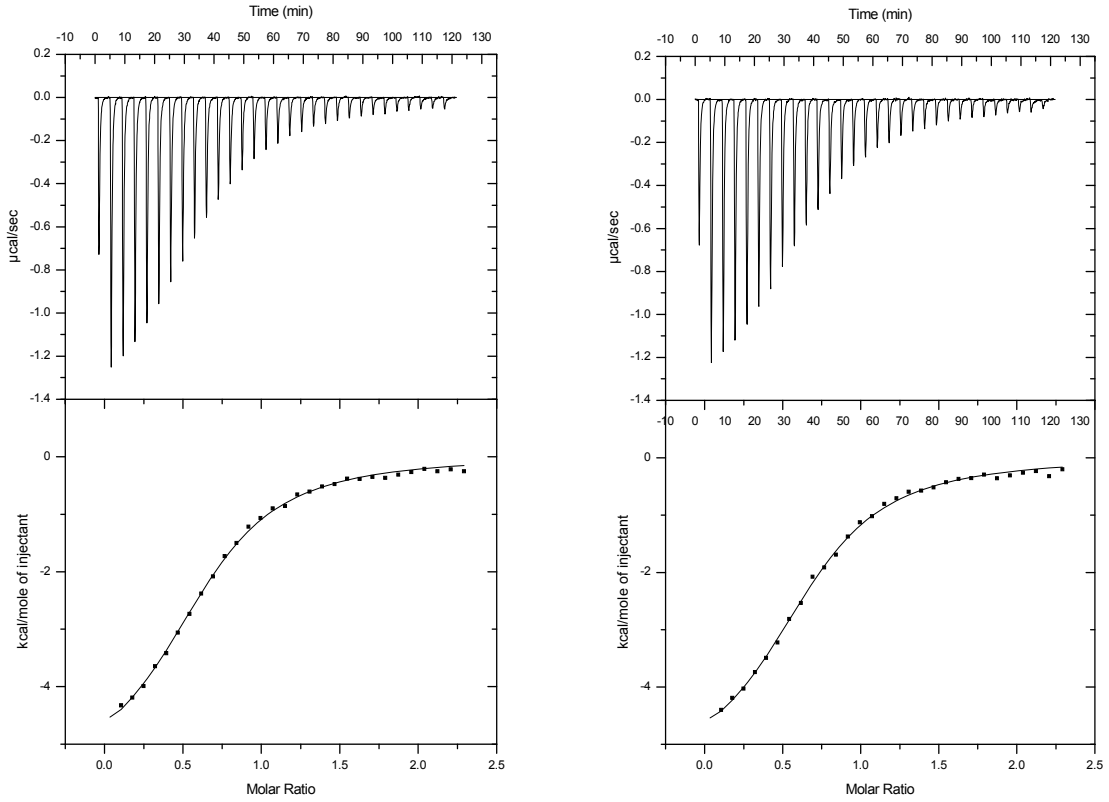
Figure S5. [1]H-NMR spectra of 1:1 ratio of the sulfate tweezer **1c** and **AcArgOMe**, each at 1.0 mM concentration.Signals of the arginine side chain protons areshifted upfield strongly in buffer but only weakly in methanol. The signal of the arginine protons 5-H is shifted upfield by ~ 2.70 ppm in buffer and by ~ 0.70 ppm in methanol.

1.6 Isothermal titration calorimetry (ITC) studies of thehost-guest complex formation of tweezers 1a and 1c.

ITC experiments of the phosphate tweezer 1a complexes

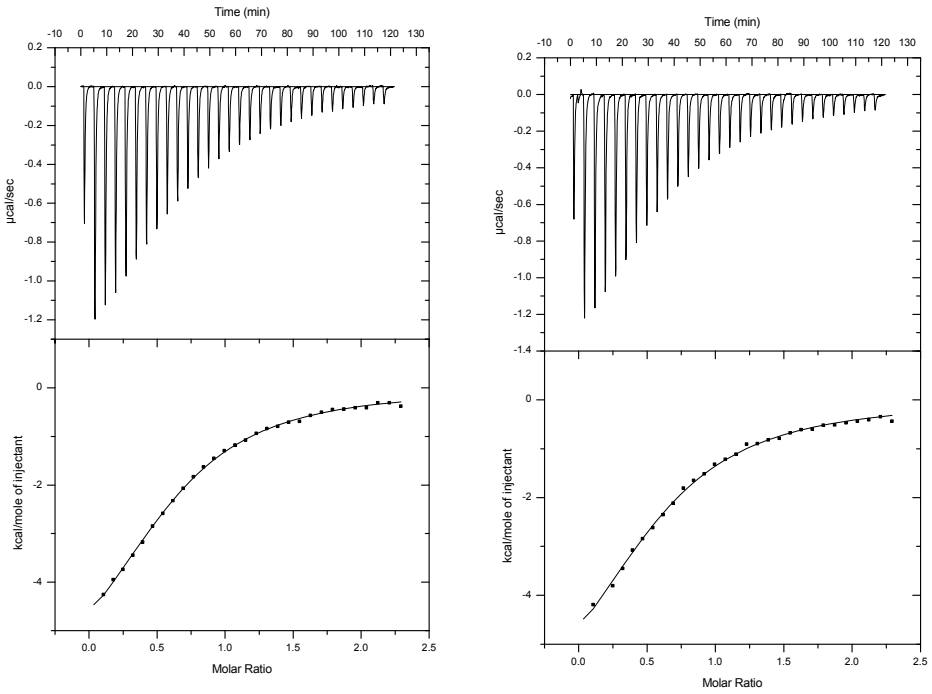
ITC titration of the tweezer **1a** (0.1 mM) with AcLysOMe (1.0 mM) in phosphate buffer (10 mM, pH 7.6)

Nr.	K_a [M^{-1}]	n	ΔH[kcal/mol]	-TΔS[kcal/mol]	ΔG[kcal/mol]
1	69300 ± 3700	0.679 ± 0.009	-5.552 ± 0.101	-1.05	-6.60
2	67900 ± 3200	0.648 ± 0.008	-5.609 ± 0.095	-0.99	-6.60



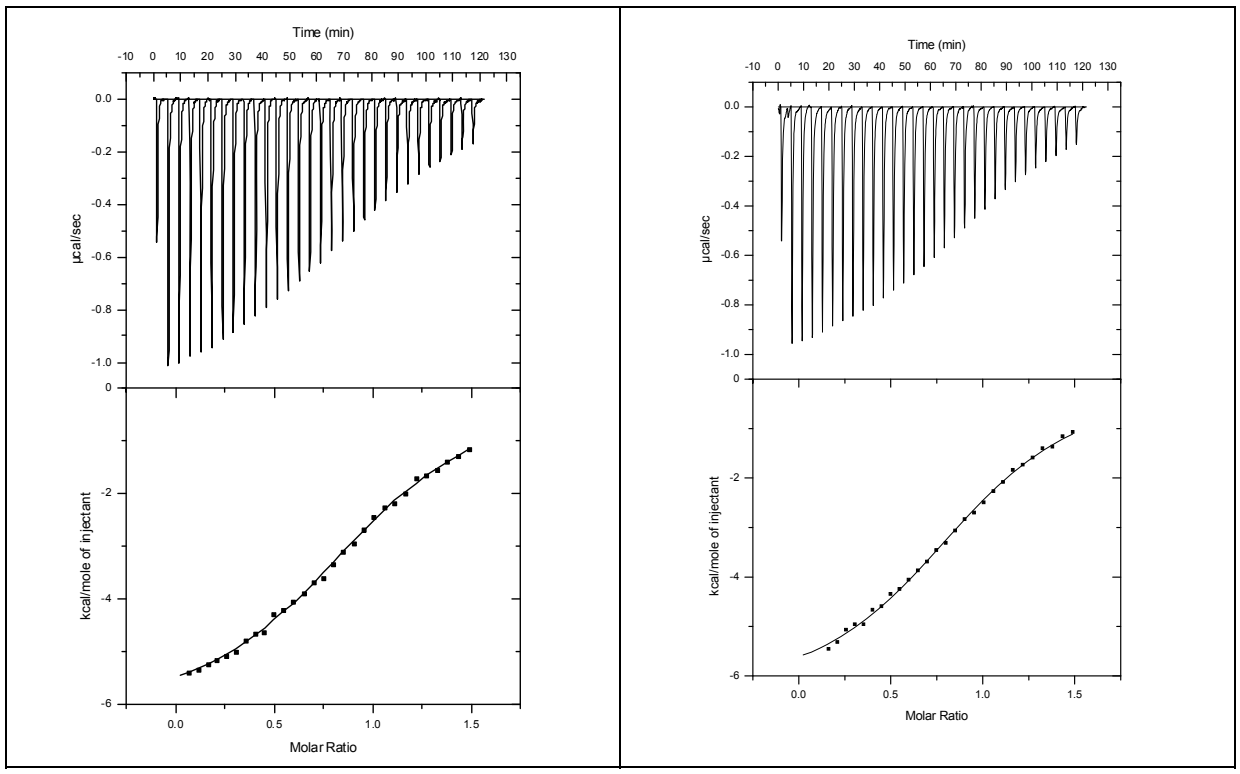
ITC titration of the tweezer **1a** (0.1 mM) with AcArgOMe (1.0 mM) in phosphate buffer (10 mM, pH 7.6)

Nr.	K_a [M^{-1}]	n	ΔH[kcal/mol]	-TΔS[kcal/mol]	ΔG[kcal/mol]
1	31700 ± 1100	0.625 ± 0.010	-6.805 ± 0.145	0.67	-6.14
2	27500 ± 1700	0.613 ± 0.020	-7.249 ± 0.305	1.19	-6.06



ITC titration of the tweezer **1a** (0.1 mM) with KLVFF (0.65 mM) in phosphate buffer (10 mM, pH 7.6)

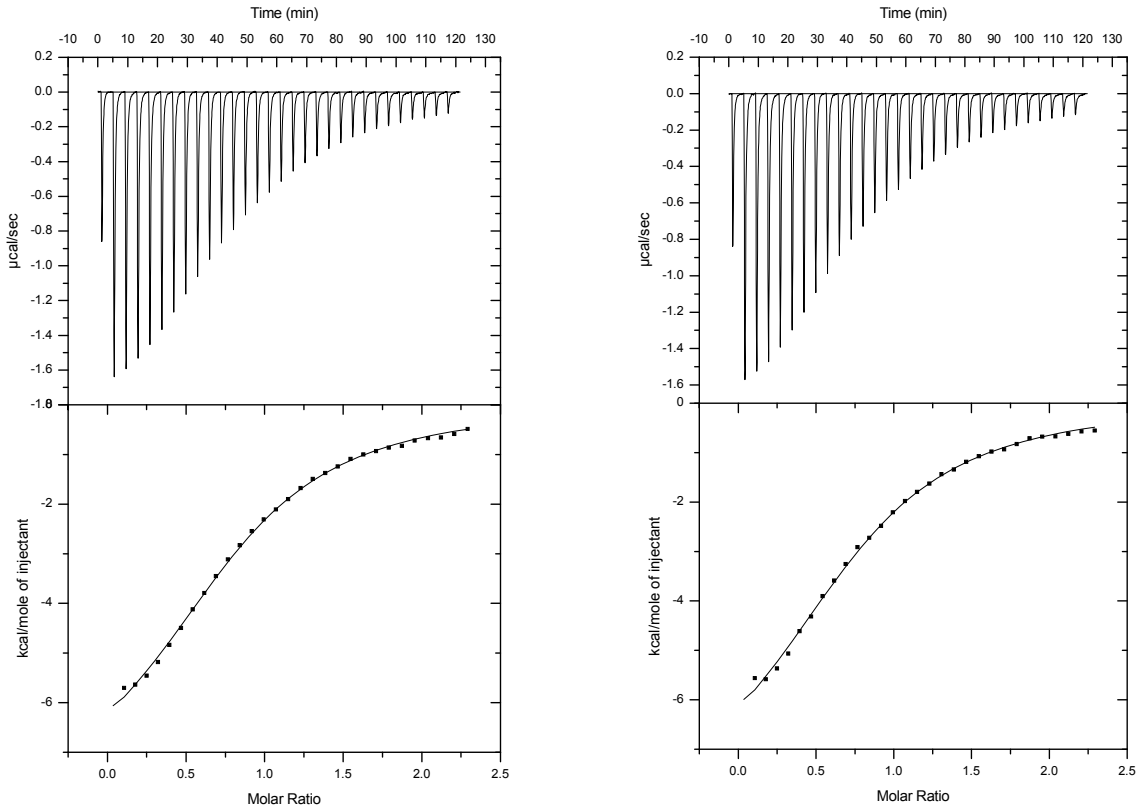
Nr.	K_a [M^{-1}]	n	ΔH[kcal/mol]	-TΔS[kcal/mol]	ΔG[kcal/mol]
1	65800 ± 2600	1.02 ± 0.005	-6.293 ± 0.055	-0.28	-6.57
2	65300 ± 3300	0.983 ± 0.007	-6.466 ± 0.084	-0.10	-6.57



ITC experiments of the sulfate tweezer 1c complexes

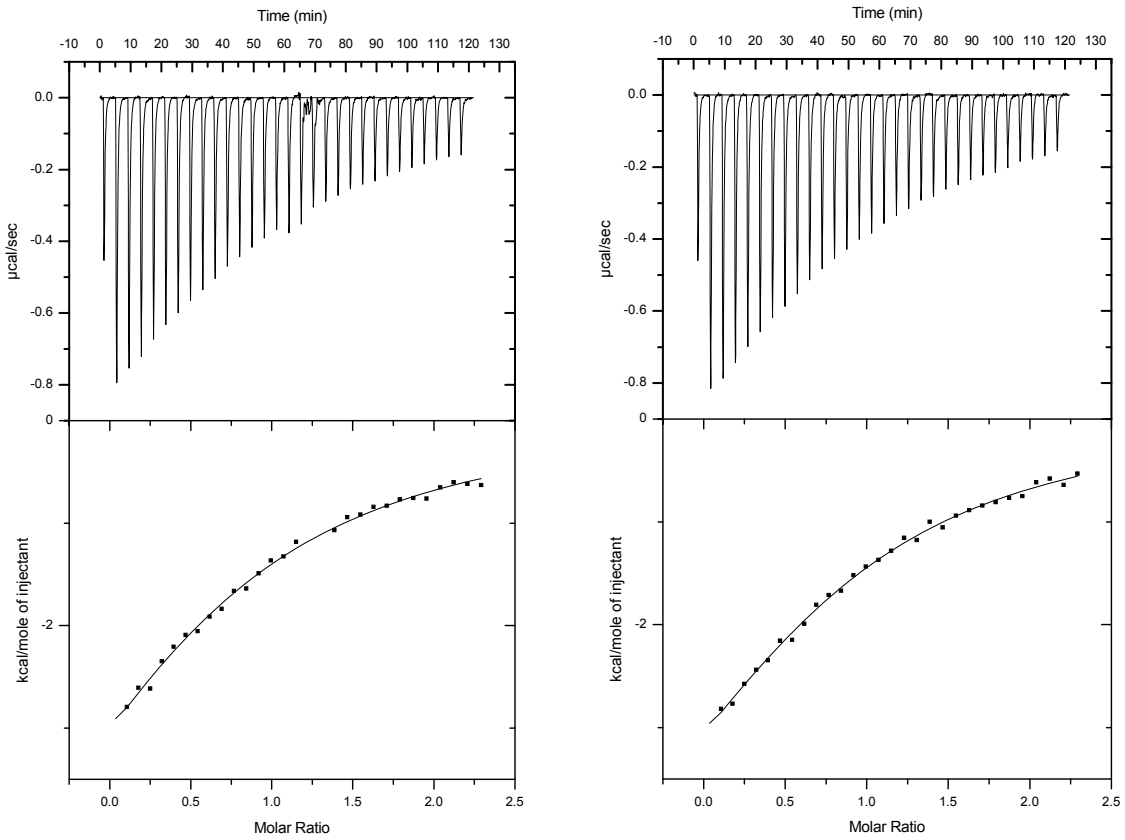
ITC titration of the tweezer **1c** (0.1 mM) with AcLysOMe (1.0 mM) in phosphate buffer (10 mM, pH 7.6)

Nr.	K_a [M^{-1}]	n	ΔH[kcal/mol]	-TΔS[kcal/mol]	ΔG[kcal/mol]
1	36200 ± 1600	0.823 ± 0.011	-8.171 ± 0.159	1.96	-6.21
2	33000 ± 1800	0.782 ± 0.015	-8.403 ± 0.226	2.24	-6.16



The ITC titration of the tweezer **1c** (0.1 mM) with AcArgOMe (1.0 mM) in phosphate buffer (10 mM, pH 7.6)

Nr.	K_a [M^{-1}]	n	ΔH[kcal/mol]	-TΔS[kcal/mol]	ΔG[kcal/mol]
1.	11300 ± 1000	0.904 ± 0.048	-5.92 ± 0.045	0.387	-5.53
2.	9490 ± 1100	0.816 ± 0.071	-6.75 ± 0.796	1.317	-5.43



2. Computational Section:

2.1 **Calculation of host-guest complex structures by QM/MM: Material and Methods**

The models of the inclusion complexes between the anionic tweezers **1a'-d'** and amino acids or short peptides were built by using the VMD program.[1] Since the phosphate tweezers **1a** is partially protonated in buffered aqueous solution at almost neutral pH value, we also used the mono- and diprotonated structures **1a'** and **1a''** for the calculations (Figure 7). The neutralized initial structures were then submitted to energy minimizations with the CHARMM c33b1 program.[2] After that, the system was placed in a water sphere of 30 Å of radii centered on one of the central carbon atoms of the tweezers. To ensure a correct water distribution twelve hydration-minimization cycles were performed. To prevent the water molecules from vaporing off, a four order polynomial potential was applied to all water oxygen atoms. After this, the hydrated systems were submitted to 1 ns MD simulations at 300 K for which the program CHARMM c33b1 with the CHARMM22 force field and the TIP3P model for water were used.[3,4] The parameters for the tweezers and tosyl terminal group were generated using the Swissparam server and tested by us (unpublished data).[5] Randomly selected snapshots from the MD simulations were then submitted to QM/MM optimization. The QM/MM optimizations were performed with the program ChemShell v3.2.[6] The Turbomole 5.10 program was used to handle the QM region and DL_POLY, as driver of the

CHARMM22force field, to treat the MM part.[7,8] The QM part which includes all atoms of the tweezers and part of the lateral chain of Lys or Arg (see Figure S) was described using the B3LYP density functional with empirical dispersive energy correction (B3LYP-D2) and the SVP basis set from the Turbomole basis set library.[9,10,11] Open valencies at the QM/MM border were saturated using hydrogen link atoms.[12] An electrostatic embedding scheme was used for the interactions between QM and MM regions.[13] To avoid overpolarization of the QM region at the boundary a charge shift scheme was applied.[14] No electrostatic cutoffs were used. The optimization was performed with the HDLC optimizer.[15] The active region consisted of a water sphere of 13 Å of radii centered on one of the central carbon atoms of the tweezers. All atoms within the active region were allowed to move in each optimization step. The optimization was finished when the maximum gradient component was below 0.00045 a.u.

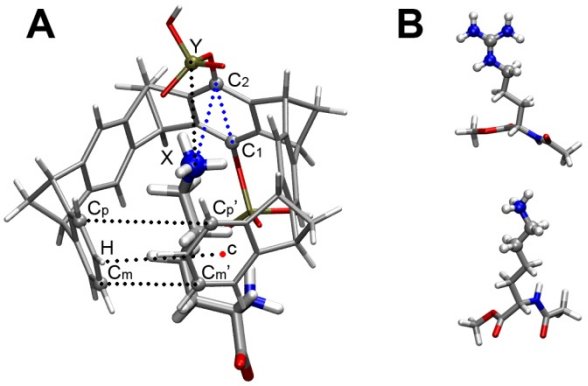


Figure S6. **A** Distances (black dotted lines) and angle (blue dotted line) used to describe the interaction between the molecular tweezers and the amino acid and peptides models (Y = P, S, or C atom of the $OCH_2CO_2^-$ group of the tweezers, X = the N atom or the central C atom of the guanidinium moiety in the lateral chain of Lys or Arg respectively). **B** Atoms of the lateral chains of Arg and Lys included in the QM region used for the QM/MM optimizations are highlighted with a sphere representation.

Table S1. Representative distances and the C_1-C_2-X angle for the isolated tweezers and the inclusion complexes between the tweezers and different Lys/Arg/peptide models (*o* stands for the guest not inserted in the tweezers cavity and *i* when the guest is threaded inside the tweezers). Depending on the systems X is the P, S or the C atom of the carboxylate group of the tweezers, while Y is the N or the central C atom of the guanidinium moiety in the lateral chain of Lys or Arg respectively. π…H-cis the distance between the orto hydrogen atom of the last benzene ring and the center of the opposite benzene ring (see Figure 6). Values in

parentheses are for QM/MM optimized structures. All distances are in Å and the angle in degrees.

System	C_p-C'$_p$	C_m-C'$_m$	X-Y	C_1-C_2-X	π…H-c
1a"	5.51 ± 0.20 (*5.24*)	3.92 ± 0.20 (*3.51*)	-	-	4.49 ± 0.25 (3.81)
1a'	5.71 ± 0.21 (*5.43*)	3.91 ± 0.20 (*3.80*)	-	-	4.07 ± 0.24 (4.13)
1a' •H Lys OH'	5.51 ± 0.21 (*5.24*)	4.11 ± 0.20 (*3.71*)	3.57 ± 0.15 (*3.39*)	85 ± 3 (*88*)	-
1a' •KAA'	5.80 ± 0.21 (*5.32*)	4.67 ± 0.22 (*3.85*)	3.32 ± 0.10 (*3.29*)	92 ± 3 (*89*)	-
1a' •Ac Lys OMe'	6.24 ± 0.22 (*5.63*)	4.98 ± 0.22 (*4.24*)	3.82 ± 0.10 (*3.91*)	95 ± 3 (*98*)	-
1a' •Ac ArgOMe'	5.62 ± 0.18 (*5.52*)	3.96 ± 0.18 (*3.76*)	3.91 ± 0.07 (*4.00*)	91 ± 3 (*89*)	-
1b'	6.49 ± 0.24 (*5.94*)	4.96 ± 0.26 (*4.33*)	-	-	5.66 ± 0.31 (4.76)
1b' •Ac Lys OMe'	7.23 ± 0.22 (*7.83*)	6.29 ± 0.21 (*6.82*)	3.90 ± 0.12 (*4.06*)	65 ± 3 (*65*)	-
1b' •TsArgOMe'	5.53 ± 0.18 (5.33)	3.86 ± 0.17 (3.83)	3.88 ± 0.10 (3.95)	86 ± 3 (82)	-
1c'	5.81 ± 0.22 (*5.49*)	3.96 ± 0.20 (*3.89*)	-	-	4.14 ± 0.25 (4.05)
1c' •Ac Lys OMe'	5.69 ± 0.22 (*5.48*)	4.82 ± 0.22 (*4.52*)	4.12 ± 0.10 (*4.06*)	64 ± 3 (*62*)	-
1c' •Ac ArgOMe'	5.58 ± 0.17 (*5.16*)	3.72 ± 0.15 (*3.48*)	4.10 ± 0.10 (*4.28*)	82 ± 3 (*78*)	-
1d'	5.54 ± 0.20 (*5.25*)	3.73 ± 0.17 (*3.51*)	-	-	4.38 ± 0.25 (3.87)
1d' •Ac Lys OMe' (i)	5.30 ± 0.19 (*4.97*)	3.77 ± 0.16 (*3.53*)	3.20 ± 0.19 (*3.48*)	74 ± 3 (72)	-
1d' •Ac Lys OMe' (o)	5.48 ± 0.19 (*5.54*)	3.78 ± 0.18 (*3.68*)	3.32 ± 0.14 (*3.20*)	64 ± 3 (*62*)	-
1d' • Ac ArgOMe' (i)	5.55 ± 0.18 (*5.20*)	3.79 ± 0.16 (*3.42*)	3.64 ± 0.10 (*3.60*)	77 ± 3 (*77*)	-
1d' • Ac Arg OMe' (o)	5.67 ± 0.22 (*5.40*)	3.97 ± 0.21 (*3.67*)	3.84 ± 0.10 (*3.90*)	69 ± 3 (*65*)	-

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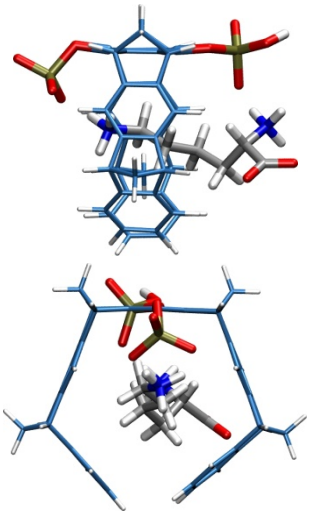
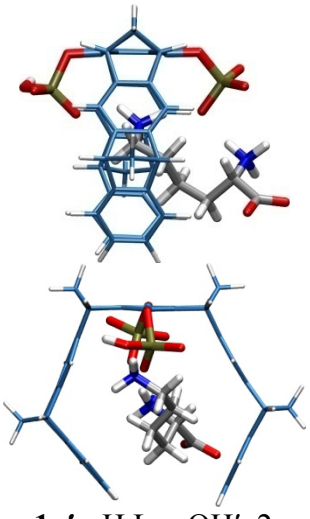
2.2 **Calculation of ^{1}H NMR shifts of the guest signals by ab initio methods**

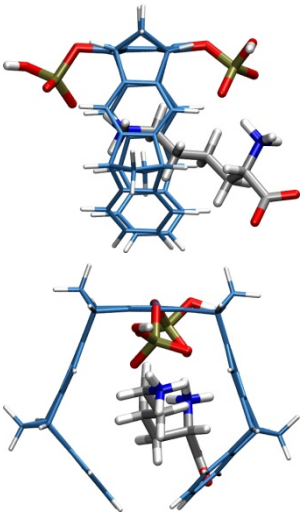
The solvent effects were modelled using optimized QM/MM structures with an explicit, static 4-Å water layer around both (the host-guest complex and the pure guest molecule as well). Figure S7 shows the compexstructures used for the computation of ^{1}H NMR shifts without the water layer:



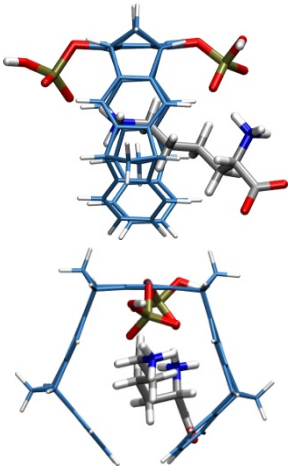
1a′ • H Lys OH′, 1



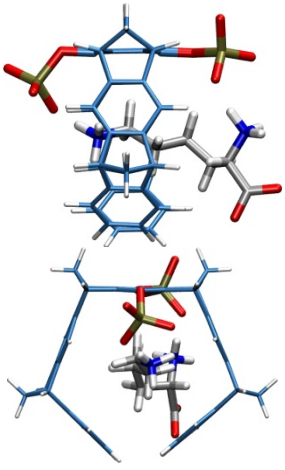
1a′ • H Lys OH′, 2



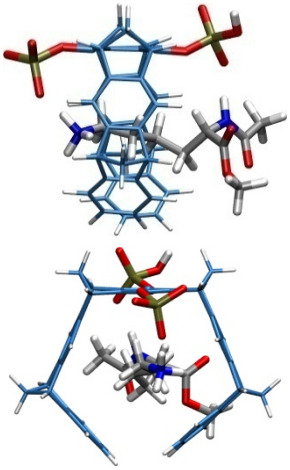
1a″ • H Lys OH′



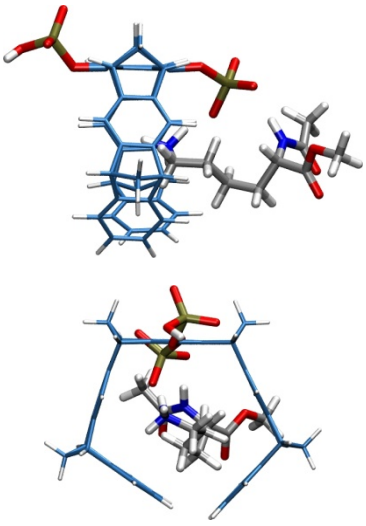
1a″ • H Lys OH′



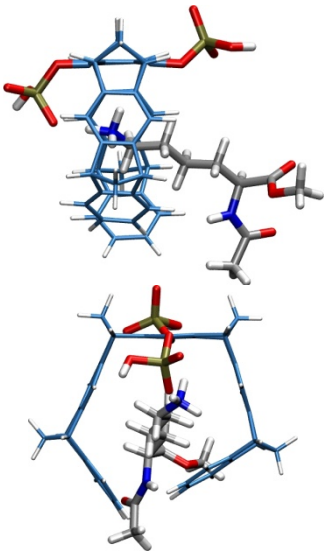
1a‴ • H Lys OH′



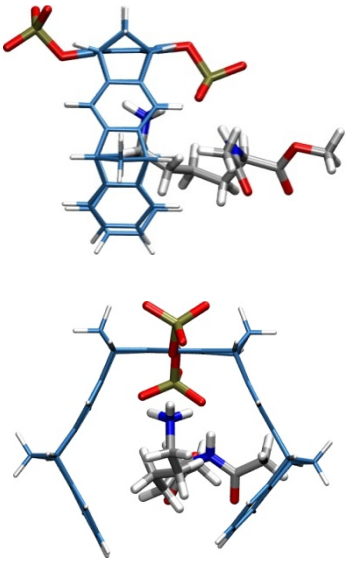
1a′ • Ac Lys OMe′, 1



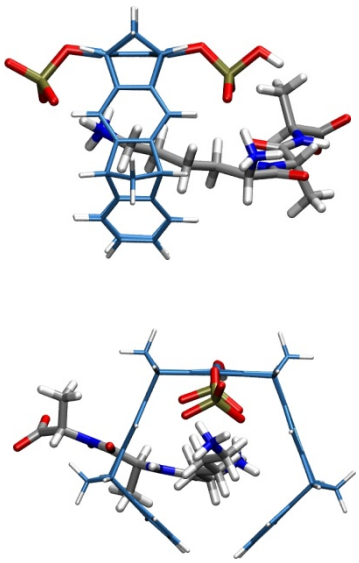
1a′ • Ac Lys OMe′, 2



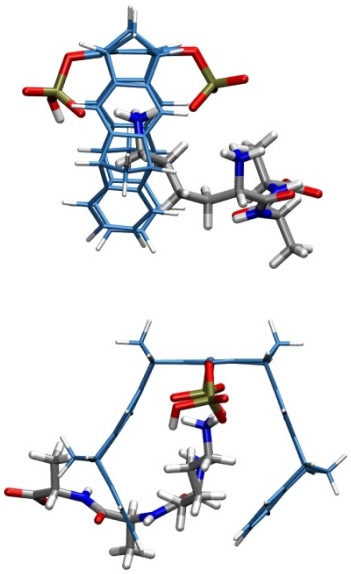
1a″ • Ac Lys OMe′



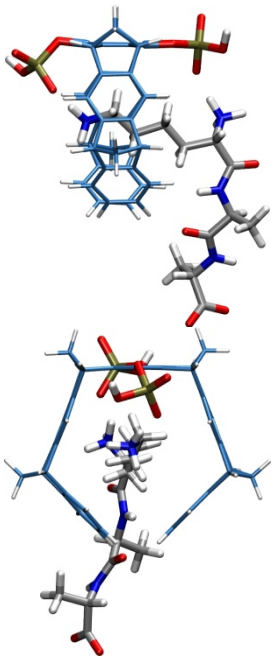
1a‴ • Ac Lys OMe′



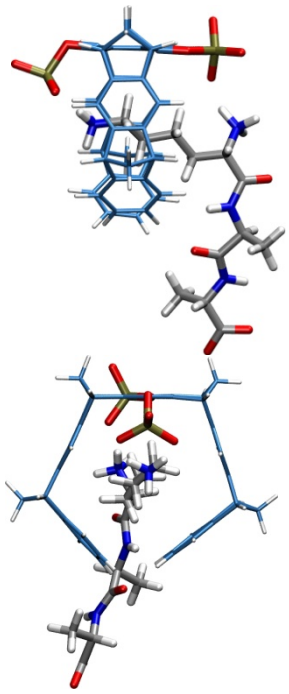
1a′ • KAA′, 1



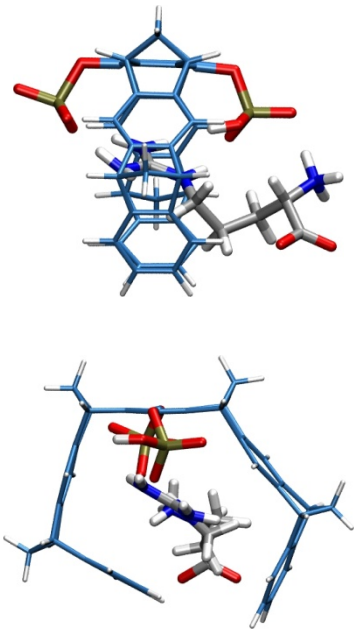
1a′ • KAA′, 2



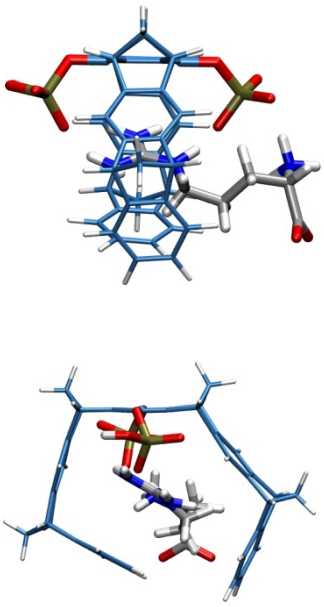
1a″ • KAA′



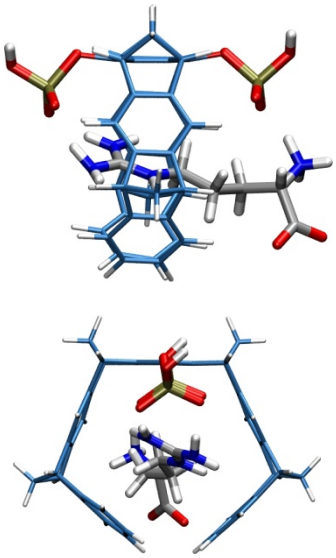
1a‴ • KAA′



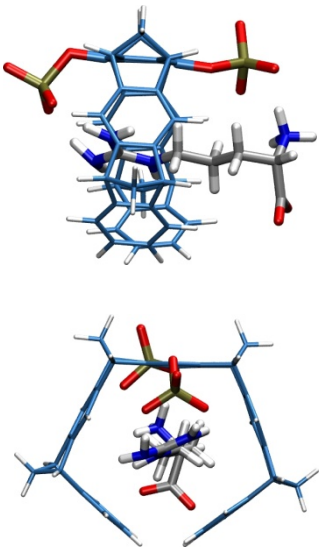
1a′ • H Arg OH′, 1



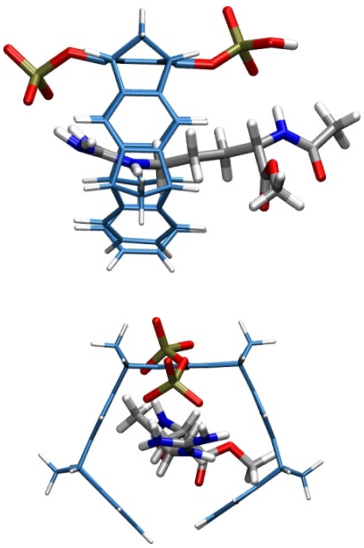
1a′ • H Arg OH′, 2



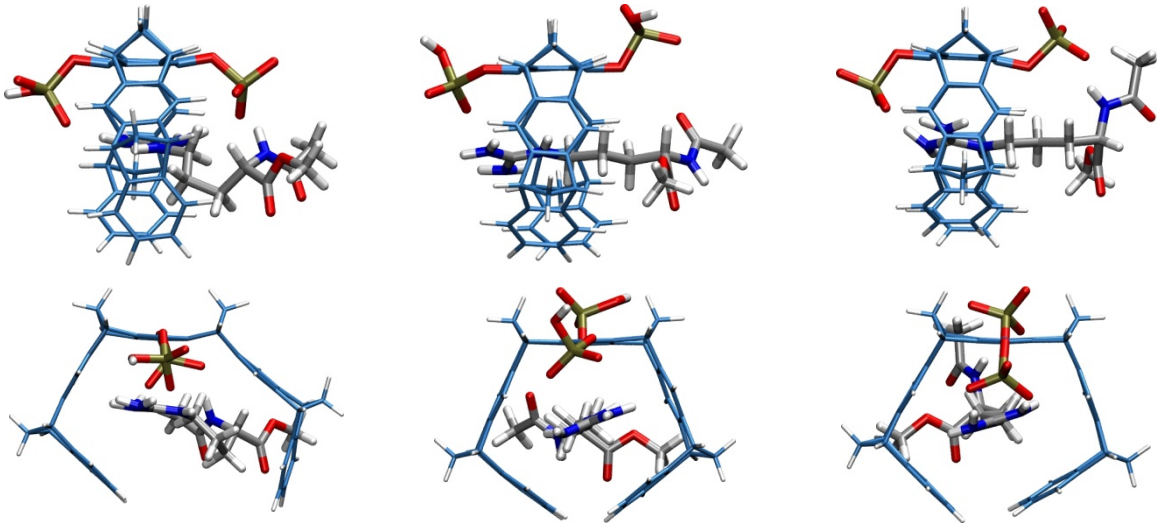
1a″ • H Arg OH′



1a‴ • H Arg OH′



1a′ • Ac ArgOMe′, 1



1a′ • Ac ArgOMe′, 2 **1a″** • Ac ArgOMe′ **1a‴** • Ac ArgOMe′

Figure S7. Host-guest complex structures of the differently protonated phosphate tweezers **1a'** (≡ **1**: $R^1 = OPO_3^{2-}$, $R^2 = OP(OH)O_2^-$), **1a"**(≡ **1**: $R^1 = R^2 = OP(OH)O_2^-$), **1a"'**(≡ **1**: $R^1 = R^2 = OPO_3^{2-}$) with lysine and arginine derivatives (without counterions) optimized by QM/MM calculations, each structure contains a 4Å water layer. In each host-guest complex of the tweezer**1a'** there are two conformers, one with the positively charged lysine ammonium or arginine guanidinium end group pointing toward the doubly negatively charged phosphate group (1) and the other one pointing away from the doubly negatively charged phosphate group (2).

Table S2. Comparison of experimental and computational (HF/SVP) complexation-induced chemical ^{1}H NMR shifts $\Delta\delta_{max}$ for the guest protons in the host-guest complexes of the phosphate tweezer**1a** with lysine and arginine derivatives. The ^{1}H NMR data were calculated for the differently protonated complex structures of **1a'** (≡ **1**: $R^1 = OPO_3^{2-}$, $R^2 = OP(OH)O_2^-$), **1a"**(≡ **1**: $R^1 = R^2 = OP(OH)O_2^-$), **1a"'**(≡ **1**: $R^1 = R^2 = OPO_3^{2-}$) as shown in Figure S7.

host-guest complex	$\Delta\delta_{max}$ [ppm]				
	6-H	**5-H**	**4-H**	**3-H**	**2-H**
exp.: **1a** • H Lys OH	4.51	4.47	-	0.76	0.24
calc.: **1a′** • H Lys OH′, 1	5.44	4.78	1.88	0.57	0.91
calc.: **1a′** • H Lys OH′, 2	3.95	2.77	2.42	0.27	0.99
calc.: **1a″** • H Lys OH′	5.22	4.00	1.68	0.55	0.81
calc.: **1a‴** • H Lys OH′	6.04	4.11	1.99	0.38	0.37
exp.: **1a** • Ac Lys OMe	3.91	-	-	-	0.51[a]
calc.: **1a′** • Ac Lys OMe′, 1	3.62	5.51	4.62	1.24	
calc.: **1a′** • Ac Lys OMe′, 2	2.20	3.39	0.72	0.52	-0.53
calc.: **1a″** • Ac Lys OMe′		0.92	5.17	2.64	1.69
calc.: **1a‴** • Ac Lys OMe′	0.28	0.53	3.53	1.95	0.83 -
	0.07	1.68			
exp.: **1a** • KAA	5.92	3.22	2.28	1.09	
calc.: **1a′** • KAA′, 1	0.20[b]	5.71	5.08	2.55	0.36
calc.: **1a′** • KAA′, 2		0.06[b]	4.06	2.59	1.19
calc.: **1a″** • KAA′	0.09	0.19[b]	6.18	4.89	1.73
calc.: **1a‴** • KAA′	0.86	0.20[b]	6.92	5.45	2.21
	1.20	0.26[b]			
	5-H	**4-H**	**3-H**	**2-H**	
exp.: **1a** • H Arg OH	-	-	-	-	
calc.: **1a′** • H Arg OH′, 1	3.00	0.75	0.44	0.17	
calc.: **1a′** • H Arg OH′, 2	2.75	1.18	0.11	-0.57	3.69
calc.: **1a″** • H Arg OH′		0.88	0.12	-0.38	
calc.: **1a‴** • H Arg OH′	3.07	1.55	-0.07	-1.05	
exp.: **1a** • Ac ArgOMe	3.75	2.54	1.23	0.63	
calc.: **1a′** • Ac ArgOMe′, 1	5.46	2.46	0.56	1.07	1.21
calc.: **1a′** • Ac ArgOMe′, 2	2.58	0.11	2.17	5.64	
calc.: **1a″** • Ac ArgOMe′	2.46	0.56	1.07	2.30	
calc.: **1a‴** • Ac ArgOMe′	0.97	0.04	0.86		

[a] $\Delta\delta_{max}$: -0.32 (exp.), -0.36,-0.28,-0.24,-0.77,(calc. **1a′**,1, **1a′**,2, **1a″**,**1a‴**), NCOCH_3; -0.23 (exp.), -0.17,-0.16,0.13,0.38, (calc. **1a′**,1, **1a′**,2, **1a″**,**1a‴**), CO_2CH_3. [b] 6-,5-,4-,3-,2-H ≡ 9-,8-,7-,6-,5-H in KAA