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Fluoride binding in water with the use of micellar nanodevices based on salophen complexes

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S1. Simulation of the PRE effect for two superimposed signals

Figure S1. UV-vis titration of a $3.46.10^{-5}$ M solution of receptor 1 in CH_2Cl_2 with TBAF

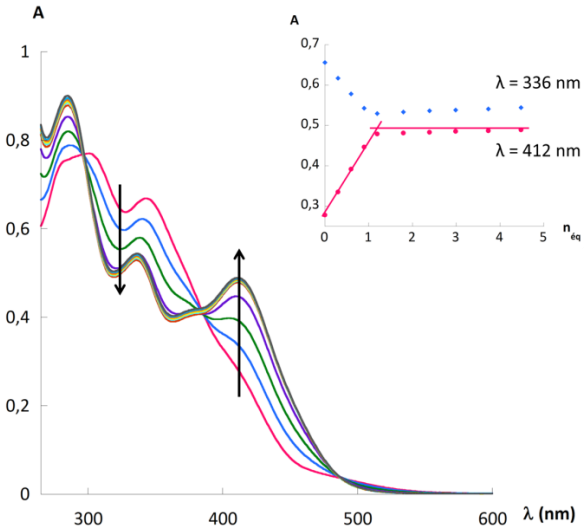

Figure S2. UV-vis titration of a $3.06.10^{-5}$ M solution of receptor **2** in CH_2Cl_2 with TBAF

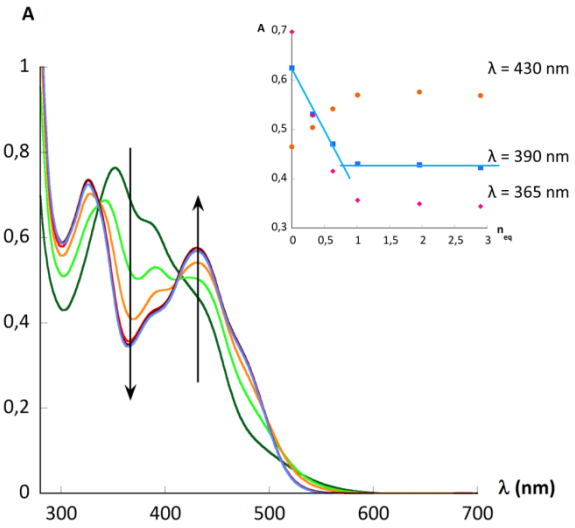

Figure S3. ^{1}H NMR spectrum of a 1.5 mM solution of receptor **1** in 50 mM Triton X-100 (D_20). Receptors signals are amplified and shown for different additions of KF. (●) surfactant signals. The assignment of the receptor signals was made by comparison with the spectrum of the receptor in CTAX micelles.

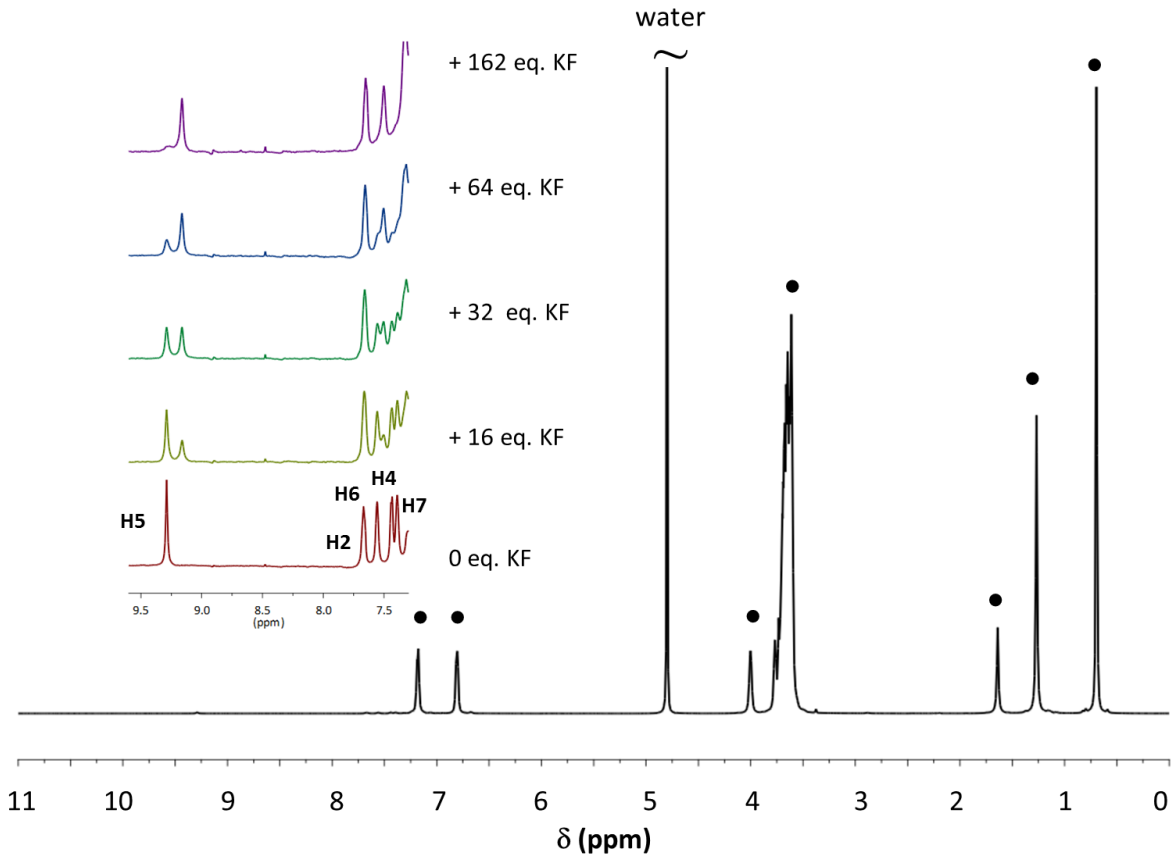

Table S1. Normalized relaxivity (ϕ ; $mM^{-1}s^{-1}$) values for the nuclei of CTABr (50 mM) and receptor **1** (1 mM) solubilized in the micelles (D_20) before and after the addition of 4 equivalents of KF. 2σ ≤ 15%. Values normalized to the relaxivity value obtained for the head protons of the surfactant**.**

	Surfactant protons				Receptor protons						
	$^{+}N(CH_3)_3$	α	β	ω	H1	H2	H3	H4	H5	H6	H7
0 eq KF	1,00	0.89	0.58	0.05	1,7	0.69	0.33	0.17	0.12	0.13	0.14
4 eq KF	1,00	0.9	0.65	0.05	0.18	0.31	0.20	0.10	0.08	0.08	0.10

Table S2. Normalized relaxivity (ϕ ; $mM^{-1}s^{-1}$) values for the nuclei of CTACl (50 mM) and receptor **1** (1 mM) solubilized in the micelles before and after the addition of 4 equivalents of KF. 2σ ≤ 15%. Values normalized to the relaxivity value obtained for the head protons of the surfactant.

	Surfactant protons				Receptor protons						
	$^{+}N(CH_3)_3$	α	β	ω	H1	H2	H3	H4	H5	H6	H7
0 eq KF	1,00	0.94	0.62	0.06	0.88	0.57	0.27	0.15	0.11	0.14	0.13
4 eq KF	1,00	1.00	0.68	0.06	0.14	0.28	0.19	0.10	0.07	0.10	0.12

Table S3. Normalized relaxivity (ϕ $mM^{-1}s^{-1}$) values for the nuclei of TX100 (50mM) and receptor **1** (1 mM) solubilized in TX100 micelles (D_20). 2σ ≤ 15%. Values normalized to the relaxivity value obtained for the hydrophilic part of the surfactant.

	Surfactant protons						Receptor protons						
HP	a	b	c	d	e	f	H1	H2	H3	H4	H5	H6	H7
1,00	0.29	0.09	0.07	0.05	0.04	0.03	/[a]	0.44	0.25	0.19	0.16	0.17	0.19

[a] H1 is not present (under surfactant signals)

Table S4. Normalized relaxivity (ϕ $mM^{-1}s^{-1}$) values for the nuclei of DPC (20 mM) and receptor **1** (1 mM) nuclei solubilized in DPC micelles (D_20). 2σ ≤ 15%. Values normalized to the relaxivity value obtained for the alpha protons of the surfactant.

	Surfactant protons					Receptor protons						
Head	α	β	γ	δ	ω	H1	H2	H3	H4	H5	H6	H7
0.90	1	0.50	0.24	0.18	0.09	0.29	/[a]	0.36	/[a]	0.27	/[a]	/[a]

[a]H2, H4, H6 and H7 are superimposed

Table S5. Normalized relaxivity (ϕ $mM^{-1}s^{-1}$) values for the nuclei of CTABr (50mM) and receptor **2** (1mM) solubilized in CTABr micelles before and after the addition of 4 equivalents of KF. 2σ ≤ 15%.Values normalized to the relaxivity value obtained for the head protons of the surfactant.

	Surfactant protons				Receptor protons								
	$^{+}N(CH_3)_3$	α	β	ω	H1	H2	H3	H4	H5	H6	H7	H8	H9
0 eq KF	1	0,83	0,51	0,04	0,14[a]	0,23	0,19	0,13	0,07[b]	0,08	0,06	/[a]	/[b]
4 eq KF	1	0,89	0,56	0,05	0,12[a]	0,25	0,20	0,15	0,07[b]	0,08	0,04	/[a]	/[b]

[a]H1 and H8 are superimposed
[b]H5 and H9 are superimposed

Table S6. Normalized relaxivity (ϕ $mM^{-1}s^{-1}$) values for the nuclei of CTACl (50mM) and receptor **2** (1mM) solubilized in CTACl micelles before and after the addition of 4 equivalents of KF. 2σ ≤ 15%.Values normalized to the relaxivity value obtained for the head protons of the surfactant.

	Surfactant protons				Receptor protons								
	$^{+}N(CH_3)_3$	α	β	ω	H1	H2	H3	H4	H5	H6	H7	H8	H9
0 eq KF	1	0,98	0,61	0,06	0,07[a]	0,09	0,07[b]	0,08	0,05[c]	/[b]	0,04	/[a]	/[c]
4 eq KF	1	1,02	0,62	0,07	0,08[a]	0,13	0,08[b]	0,10	0,06[c]	/[b]	0,04	/[a]	/[c]

[a]H1 and H8 are superimposed
[b]H3 and H6 are superimposed
[c]H5 and H9 are superimposed

Table S7. Normalized relaxivities (ϕ $mM^{-1}s^{-1}$) values for the nuclei of TX100 (50mM) and receptor **2** (1mM) solubilized in TX100 micelles. 2σ ≤ 15%.Values normalized to the value obtained for the protons of the hydrophilic part of the surfactant.

	Surfactant protons						Receptor protons								
HP	a	b	c	d	e	f	H1	H2	H3	H4	H5	H6	H7	H8	H9
1,00	0.27	0.09	0.07	0.06	0.04	0.04	0.36[a]	0.58	0.28[b]	/[c]	/[c]	/[b]	0.06	/[a]	/[c]

[a]H1 and H8 are superimposed
[b]H3 and H6 are superimposed
[c]H4, H5 and H9 are not present (under surfactant signals)

Table S8. Hydrodynamic diameter (nm) of CTABr micelles (50 mM surfactant in the presence of 50 mMKBr) and of CTACl micelles (50 mM surfactant in the presence of 100mM KCl) in H_2O upon addition of receptors 1 or 2.

		CTABr	CTACl
	[Receptor]	Diameter (polydispersity)	Diameter (polydispersity)
	0	4.62 (0.310)	4.39 (0.228)
Receptor**1**	0.25	5.22 (0.229)	4.44 (0.267)
	1	6.02 (0.461)	4.40 (0.238)
	2	7.70 (0.573)	4.74 (0.238)
Receptor**2**	0.25	5.00 (0.334)	4.26 (0.265)
	1	6.29 (0.471)	4.35 (0.256)
	2	8.15 (0.557)	4.72 (0.213)

S1. Simulation of the PRE effect for two superimposed signals

Simulations were carried out in order to evaluate the possibility of gaining qualitative information via Paramagnetic Relaxation Enhancement experiments for superimposed NMR signals (i.e. protons 1 and 8 of Receptor 2 in CTABr micelles).

Protons 1 and 6 of receptor **1**, which have non superimposed signals in the ^{1}H NMR spectrum, were used as a basis for this simulation (they are comparable to protons 1 and 8 of Receptor 2). The measured longitudinal relaxation times of these two protons, for the different additions of paramagnetic agent, are given in the table below. The corresponding relaxation rates of the two protons are plotted as a function of paramagnetic agent concentration in the figure.

For each paramagnetic agent concentration, the analytical expression for the Inversion-Recovery relaxation curves of the two protons derived using the T_1(H1) and T_1(H6) values given in the table were first summed. A monoexponenial Inversion-Recovery relaxation curve was then fitted to this simulated curve. The T1 derived from these simulations are given in the table (T_1(H1+H6)) and the corresponding relaxation rates are plotted in the figure. The relaxivities are derived from the slopes.

From this simulation, it can be concluded that the relaxivity value of two superimposed signals is weighted towards the smallest relaxivity value of the two individual signals.

T1 Measurements of receptor 1 (H1 and H6) upon addition of $K_3(Cr(CN)_6)$ and T1 of the simulated superposition of signals

$[K_3(Cr(CN)_6)]$ mM	T_1(H1) s	T_1(H6) s	T_1(H1+H6) s
0	1.5636	0.8368	1.1774
0.029	0.26155	0.70912	0.48421
0.058	0.12396	0.58665	0.37297
0.097	0.090149	0.51735	0.33358
0.116	0.069324	0.48105	0.31658

PRE curves for protons 1 and 6 of receptor 1 and simulated PRE curves for the superimposition of the two proton and the derived relaxivities ($mM^{-1}s^{-1}$ ±2σ).