Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

8-Hydroxyquinoline as a Building Block for Artificial Receptors: Binding Preferences in the Recognition of Glycopyranosides

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1 Description of the binding studies in homogeneous solution

1.1 ^{1}H NMR titrations

^{1}H NMR titrations were carried out in $CDCl_3$ or DMSO-d_6/$CDCl_3$ mixtures at 25°C ($CDCl_3$ was stored over activated molecular sieves and deacidified). The titration data were analyzed by non-linear regression analysis, using the program HOSTEST 5.6 and EQNMR. Dilution experiments show that the receptors do not self-aggregate in the used concentration range.

Stock solutions in $CDCl_3$ or DMSO-d_6/$CDCl_3$ mixture were prepared for the receptor and sugar. These solutions and the corresponding solvent were combined in a manner so that the concentration of the receptor was kept constant and that of the sugar varied (in the case of inverse titrations the concentration of sugar was kept constant and that of the receptor was varied). For each titration 20 samples were prepared and the ^{1}H NMR spectra were recorded. For each receptor-sugar system at least two ^{1}H NMR titrations were carried out. Examples are given in Tables S1-S3.

Table S1. ^{1}H NMR titration of receptor **2** with octyl β-D-galactopyranoside (**7a**) in $CDCl_3$.

	[Sugar] mol/L	[Receptor] mol/L	Ratio [Receptor]	[Sugar]
1	0,00000000	0,00088175	1	0,0000
2	0,00009098	0,00088175	1	0,1032
3	0,00018195	0,00088175	1	0,2064
4	0,00027293	0,00088175	1	0,3095
5	0,00036391	0,00088175	1	0,4127
6	0,00045489	0,00088175	1	0,5159
7	0,00054586	0,00088175	1	0,6191
8	0,00063684	0,00088175	1	0,7222
9	0,00072782	0,00088175	1	0,8254
10	0,00081880	0,00088175	1	0,9286
11	0,00090977	0,00088175	1	1,0318
12	0,00109173	0,00088175	1	1,2381
13	0,00127368	0,00088175	1	1,4445
14	0,00145564	0,00088175	1	1,6508
15	0,00163759	0,00088175	1	1,8572
16	0,00181955	0,00088175	1	2,0636
17	0,00218346	0,00088175	1	2,4763
18	0,00291128	0,00088175	1	3,3017
19	0,00327519	0,00088175	1	3,7144
20	0,00363910	0,00088175	1	4,1271

Table S2. ^{1}H NMR titration of receptor **3** with octyl β-D-glucopyranoside (**5a**) in $CDCl_3$.

	[Sugar] mol/L	[Receptor] mol/L	Ratio [Receptor]	[Sugar]
1	0,00000000	0,00100224	1	0,0000
2	0,00014395	0,00100224	1	0,1436
3	0,00028791	0,00100224	1	0,2873
4	0,00043186	0,00100224	1	0,4309
5	0,00057581	0,00100224	1	0,5745
6	0,00071976	0,00100224	1	0,7182
7	0,00086372	0,00100224	1	0,8618
8	0,00100767	0,00100224	1	1,0054
9	0,00115162	0,00100224	1	1,1490
10	0,00129557	0,00100224	1	1,2927
11	0,00143953	0,00100224	1	1,4363
12	0,00158348	0,00100224	1	1,5799
13	0,00172743	0,00100224	1	1,7236
14	0,00194336	0,00100224	1	1,9390
15	0,00215929	0,00100224	1	2,1545
16	0,00244720	0,00100224	1	2,4417
17	0,00259115	0,00100224	1	2,5854
18	0,00287905	0,00100224	1	2,8726
19	0,00316696	0,00100224	1	3,1599
20	0,00345486	0,00100224	1	3,4471

Table S3. ^{1}H NMR titration of octyl β-D-glucopyranoside (**5a**) with receptor **3** in $CDCl_3$ (inverse titration).

	[Receptor mol/L	[Sugar] mol/L	Ratio [Sugar]	[Receptor]
1	0,00000000	0,00078665	1	0,0000
2	0,00009477	0,00078665	1	0,1205
3	0,00018955	0,00078665	1	0,2410
4	0,00028432	0,00078665	1	0,3614
5	0,00037910	0,00078665	1	0,4819
6	0,00047387	0,00078665	1	0,6024
7	0,00056865	0,00078665	1	0,7229
8	0,00066342	0,00078665	1	0,8434
9	0,00075820	0,00078665	1	0,9638
10	0,00085297	0,00078665	1	1,0843
11	0,00094774	0,00078665	1	1,2048
12	0,00108991	0,00078665	1	1,3855
13	0,00123207	0,00078665	1	1,5662
14	0,00137423	0,00078665	1	1,7469
15	0,00151639	0,00078665	1	1,9277
16	0,00165855	0,00078665	1	2,1084
17	0,00189549	0,00078665	1	2,4096
18	0,00213242	0,00078665	1	2,7108
19	0,00236936	0,00078665	1	3,0120
20	0,00284323	0,00078665	1	3,6144

1.2 Fluorescence titrations

Fluorescence titrations were carried out in $CHCl_3$ at 25°C and the titration data were analysed on the base of Hyperquad 2006 program. Stock solutions in $CHCl_3$ were prepared for receptor and sugar. These solutions and the corresponding solvent were combined in a manner so that the concentration of the receptor was kept constant and that of the sugar varied. For each titration 20 samples were prepared; for each receptor-sugar system at least two titrations were carried out. Examples are given in Tables S4-S5 and Figure S1.

Table S4. Fluorescence titration of receptor **3** with octyl β-D-glucopyranoside (**5a**) in $CHCl_3$ (Excitation wavelength 327 nm).

	[Sugar] mol/L	[Receptor] mol/L	Ratio [Receptor]	[Sugar]
1	0,00000000	0,00014003	1	0,0000
2	0,00001379	0,00014003	1	0,0985
3	0,00002759	0,00014003	1	0,1970
4	0,00004138	0,00014003	1	0,2955
5	0,00005517	0,00014003	1	0,3940
6	0,00006896	0,00014003	1	0,4925
7	0,00008276	0,00014003	1	0,5910
8	0,00009655	0,00014003	1	0,6895
9	0,00011034	0,00014003	1	0,7880
10	0,00012413	0,00014003	1	0,8865
11	0,00013793	0,00014003	1	0,9850
12	0,00016091	0,00014003	1	1,1492
13	0,00018390	0,00014003	1	1,3133
14	0,00022988	0,00014003	1	1,6417
15	0,00027585	0,00014003	1	1,9700
16	0,00032183	0,00014003	1	2,2983
17	0,00036780	0,00014003	1	2,6266
18	0,00041378	0,00014003	1	2,9550
19	0,00045975	0,00014003	1	3,2833
20	0,00050573	0,00014003	1	3,6116

Table S5. Fluorescence titration of receptor **4** with octyl β-D-glucopyranoside (**5a**) in $CHCl_3$ (Excitation wavelength 324 nm).

	[Sugar] mol/L	[Receptor] mol/L	Ratio [Receptor]	[Sugar]
1	0,00000000	0,00011378	1	0,0000
2	0,00001839	0,00011378	1	0,1616
3	0,00003678	0,00011378	1	0,3233
4	0,00005517	0,00011378	1	0,4849
5	0,00007356	0,00011378	1	0,6465
6	0,00009195	0,00011378	1	0,8081
7	0,00011034	0,00011378	1	0,9698
8	0,00012873	0,00011378	1	1,1314
9	0,00014712	0,00011378	1	1,2930

10	0,00016551	0,00011378	1	1,4546
11	0,00018390	0,00011378	1	1,6163
12	0,00020689	0,00011378	1	1,8183
13	0,00022988	0,00011378	1	2,0203
14	0,00027585	0,00011378	1	2,4244
15	0,00032183	0,00011378	1	2,8284
16	0,00036780	0,00011378	1	3,2325
17	0,00041378	0,00011378	1	3,6366
18	0,00045975	0,00011378	1	4,0406
19	0,00055171	0,00011378	1	4,8488
20	0,00064366	0,00011378	1	5,6569

2 Changes in chemical shift observed during ^{1}H NMR titrations

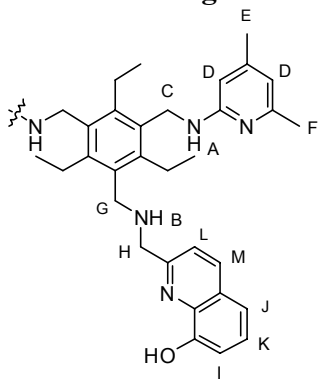

Table S6. Change in chemical shift[a] (selected signals) observed during ^{1}H NMR titrations of compounds **2** and **3** with sugar **5a**, **6a** or **7a** in $CDCl_3$.

Receptor-sugar complex	Δδ [ppm][a,b]
2•5a	NH^A: 2.45; CH_2^C: -0.17; pyr-CHs: -0.03, 0.05; CH_3^E: 0.03; CH_3^F: -0.05; CH_2^G: -0.04; CH_2^H: c; CH^J: -0.03; CH^L: -0.13; CH^M: -0.01
2•6a	NH^A: 2.13; CH_2^C: -0.08; pyr-CHs: -0.02, 0.08; CH_3^E: 0.04; CH_3^F: -0.04; CH_2^G: c; CH^J: -0.02; CH^L: -0.08; CH^M : 0.01
2•7a	NH^A: 1.52; CH_2^C: c; pyr-CHs: -0.03, 0.10; CH_3^E: 0.05; CH_3^F: -0.09; CH_2^G: c; CH_2^H: 0.08, c; CH^I: -0.04; CH^J: -0.05; CH^K: -0.02; CH^L: -0.17; CH^M : -0.05
3•5a	NH^A: 2.20; CH_2^C: -0.18; pyr-CHs: -0.03, 0.06; CH_3^E: 0.03; CH_3^F: -0.08; CH_2^H: 0.11; CH^I: -0.03; CH^J: -0.05; CH^L: -0.20; CH^M :- 0.04
3•6a	NH^A: 1.40; CH_2^C: -0.14; pyr-CHs: -0.01, 0.08; CH_3^E: 0.03; CH_3^F: -0.05; CH_2^G: c; CH_2^H: 0.04; CH^I: -0.02; CH^J: -0.03; CH^L: -0.18; CH^M :- 0.03
3•7a	NH^A: 1.50; CH_2^C: -0.09; pyr-CHs: -0.04, 0.11; CH_3^E: 0.02; CH_3^F: -0.05; CH_2^G: c; CH_2^H: 0.07, c; CH^I: -0.04; CH^K: -0.02; CH^L: -0.21; CH^M :- 0.04

[a]Limiting change in chemical shift observed during the titration for receptor signals (the concentration of receptor was kept constant and that of the sugar varied). [b](-) Δδ = upfield shift. [c]Shift with splitting.

3 Fluorescence titration of receptor **4** with β-glucopyranoside **5a**.

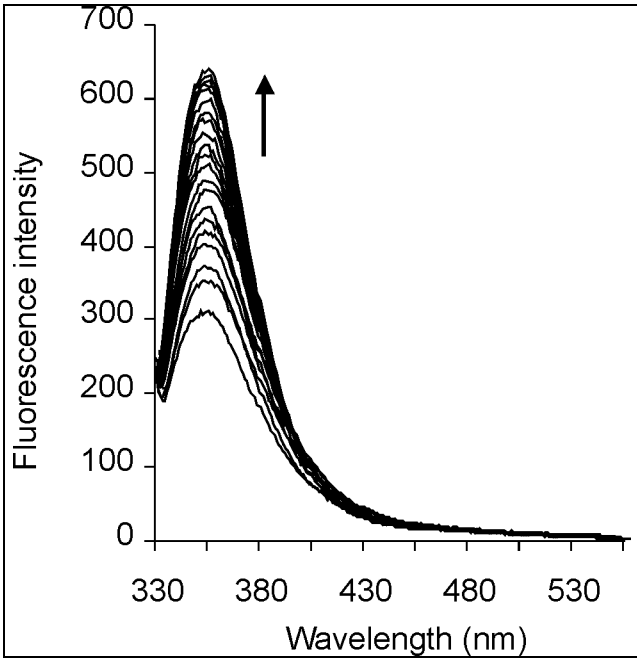

Figure S1. Fluorescence titration of receptor **4** ([**4**] = 0.11 mM) with β-glucopyranoside **5a** (0.00 – 5.80 equiv.) in $CHCl_3$. Excitation wavelength 324 nm.