Supporting Information for

Synthesis of modified cyclic and acyclic dextrins and comparison of their complexation ability

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Additional NMR and HPLC data
Characterization of the ionic derivatives by NMR

All the NMR spectra including $^1$H, HSQC-DEPT (Heteronuclear Single Quantum Coherence - Distortionless Enhancement by Polarization Transfer) were recorded in D$_2$O on a Varian VXR-300 instrument at 300 MHz.

Scheme S1: General scheme of substituted maltooligomers for NMR assignment.
Table S1: Proton assignments of 1-\textit{O}-benzylated and (2-hydroxy)propylated maltooligosaccharides (chemical shifts are in ppm).

|                  | 1-OBn                        | 1-OH                        |
|------------------|------------------------------|-----------------------------|
|                  | G6                          | G7                          | G8                          | G6                          | G7                          | G8                          |
| Benzyl, Aromatic | 7.38-7.45, br m             | 7.42-7.47, br m             | 7.40-7.60, br m             | -                           | -                           | -                           |
| Benzyl, CH\textsubscript{2}\textalpha | 4.93, d (J 11 Hz)           | 4.93, d (J 12 Hz)           | 4.93, d (J 12 Hz)           | -                           | -                           | -                           |
| Benzyl, CH\textsubscript{2}\textbeta | 4.75, d (J 11 Hz)           | 4.76, d (J 12 Hz)           | 4.75, d (J 12 Hz)           | -                           | -                           | -                           |
| (2-Hydroxy)prop-yl CH\textsubscript{2} | -                           | -                           | -                           | 3.45-3.55, 3.63-68, 3.79-3.84, br | 3.43-3.53, 3.61-3.66, 3.76-3.82, br | 3.45-3.54, 3.62-3.66, 3.78-3.82, br |
| (2-Hydroxy)prop-yl CH | -                           | -                           | -                           | 3.92-4.04, br               | 3.91-4.02, br               | 3.89-4.02, br               |
| (2-Hydroxy)prop-yl CH\textsubscript{3} | -                           | -                           | -                           | 1.14, 1.16, br             | 1.13, 1.15, br             | 1.13, 1.15, br             |
| H\textsubscript{1}\textalpha | 5.38, br                    | 5.38, br                    | 5.39, br                    | 5.21, 5.52, br             | 5.20, 5.51, br             | 5.19, 5.50, br             |
| H\textsubscript{1}\textbeta | 4.52, d (J\textsubscript{1,2} 7.7 Hz) | 4.54, d (J\textsubscript{1,2} 8 Hz) | 4.53, d (J\textsubscript{1,2} 7.6 Hz) | 4.63, d (J\textsubscript{1,2} 7.6 Hz) | 4.62, d (J\textsubscript{1,2} 7.8 Hz) | 4.62, d (J\textsubscript{1,2} 7.4 Hz) |
| H\textsubscript{2}\textalpha | 3.55, br m                  | 3.55, br m                  | 3.55, br m                  | 3.55-3.72, br, unsubst 3.69, br, subst | 3.54-3.68, br, unsubst 3.67, br, subst | 3.54-3.68, br, unsubst 3.67, br, subst |
| H\textsubscript{3}\textalpha | 3.82, br m                  | 3.84, br m                  | 3.84, br m                  | 3.76-3.87, br, unsubst 3.71-3.78, br, subst | 3.75-3.85, br, unsubst 3.68-3.77, br, subst | 3.74-3.86, br, unsubst 3.69-3.76, br, subst |
| H\textsubscript{4}\textalpha | 3.64-3.76, br m             | 3.58-3.74, br m             | 3.57-3.75, br m             | 3.44, br                    | 3.42, br                    | 3.43, br                    |
| H\textsubscript{5}\textalpha | 3.69-3.71, br m             | 3.68-3.74, br m             | 3.89-4.00, br m             | 4.03, br                    | 4.01, br                    | 4.01, br                    |
| H\textsubscript{6}\textalpha | 3.73-3.94, br m             | 3.75-3.96, br m             | 3.70-3.95, br m             | 3.74-3.93, br, unsubst 3.78-3.82, br, subst | 3.74-3.93, br, unsubst 3.78-3.82, br, subst | 3.74-3.93, br, unsubst 3.78-3.82, br, subst |
| H\textsubscript{1}\textsuperscript{2-(n-1)} | 5.38, br d                  | 5.38, br                    | 5.39, br                    | 5.39, 5.67, br             | 5.37, 5.65, br             | 5.37, 5.65, br             |
| H\textsubscript{2}\textsuperscript{2-(n-1)} | 3.60-3.63, br m             | 3.57-3.67, br m             | 3.50-3.67, br m             | 3.55-3.72, br, unsubst 3.69, br, subst | 3.54-3.68, br, unsubst 3.67, br,subst | 3.54-3.68, br, unsubst 3.67, br, subst |
|       | 1-OBn |       | 1-OH  |
|-------|-------|-------|-------|
|       | G6    | G7    | G8    | G6    | G7    | G8    |
| H₃² darm (n-1) | 3.82, br m | 3.84, br m | 3.84, br m | 3.76-3.87, br, unsubst | 3.71-3.78, br, subst | 3.74-3.86, br, unsubst |
|        | 3.64-3.76, br m | 3.58-3.74, br m | 3.57-3.75, br m | 3.71-3.78, br, subst | 3.68-3.77, br, subst | 3.69-3.76, br, subst |
| H₄² darm (n-1) | 3.92-3.97, br m | 3.91-4.02, br m | 3.62-3.73, br m | 3.76-3.87, br, unsubst | 3.71-3.78, br, subst | 3.74-3.86, br, unsubst |
|        | 3.73-3.94, br m | 3.75-3.96, br m | 3.70-3.95, br m | 3.74-3.93, br, unsubst | 3.78-3.82, br, subst | 3.74-3.93, br, unsubst |
| H₁ⁿ    | 5.38, br d | 5.38, br | 5.39, br | 5.39, 5.67, br | 5.37, 5.65, br | 5.37, 5.65, br |
| H₂ⁿ    | 3.60-3.63, br m | 3.57-3.67, br m | 3.50-3.67, br m | 3.55-3.72, br, unsubst | 3.69, br, subst | 3.54-3.68, br, unsubst |
|        | 3.82, br m | 3.84, br m | 3.84, br m | 3.76-3.87, br, unsubst | 3.71-3.78, br, subst | 3.74-3.86, br, unsubst |
| H₃ⁿ    | 3.41, t (J₁, 2 9.1 Hz) | 3.39, t (overlapped) | 3.40, t (overlapped) | 3.44, br | 3.42, br | 3.42, br |
| H₄ⁿ    | 3.33, t (J₁, 2 8.7 Hz) | 3.35, t (overlapped) | 3.33, t (overlapped) | 3.27, br | 3.25, br | 3.25, br |
| H₆ⁿ    | 3.73-3.94, br m | 3.75-3.96, br m | 3.70-3.95, br m | 3.74-3.93, br, unsubst | 3.78-3.82, br, subst | 3.74-3.93, br, unsubst |
| 1,2-Propylene-glycol CH₂ | - | - | - | 3.80, br | 3.81, br |
| 1,2-Propylene-glycol CH | - | - | - | 3.83, br | 3.84, br |
| 1,2-Propylene-glycol CH₃ | - | - | - | 1.13, 1.15, br | 1.13, 1.15, br |
**Table S2**: Carbon assignments of 1-\(O\)-benzylated and (2-hydroxy)propylated maltooligosaccharides (chemical shifts are in ppm, based on DEPT-ed-HSQC experiments).

|                  | 1-OBn |                | 1-OH |                |
|------------------|-------|----------------|------|----------------|
|                  | G6    | G7             | G8   | G6             | G7             | G8             |
| Benzyl, Aromatic | 128.8, br | 128.9          | 128.8, br | -          | -              | -              |
| Benzyl, \(\text{CH}_\alpha\) | 71.4, 71.7 | 71.6, 71.7      | 71.5, 71.7 | -          | -              | -              |
| Benzyl, \(\text{CH}_\beta\) | 71.6 | 71.6           | 71.5, 71.7 | -          | -              | -              |
| (2-Hydroxy)prop-yl \(\text{CH}_2\) | - | -              | - | 76.1, 76.3, 76.4 | 76.1, 76.2, 76.4 | 76.1, 76.3 |
| (2-Hydroxy)prop-yl \(\text{CH}\) | - | -              | - | 72.6, 73.1      | 73.1, 73.2      | 72.7, 73.1 |
| (2-Hydroxy)prop-yl \(\text{CH}_3\) | - | -              | - | 18.2           | 18.2           | 18.2           |
| \(\text{C}_1\)\(\alpha\) | 99.8, br | 99.7, br       | 99.6-99.7, br | 91.8, 98.4 | 91.7, 98.3 | 91.9, 98.3 |
| \(\text{C}_1\)\(\beta\) | 101.2 | 101.2          | 101.2 | 95.6          | 95.7           | 95.8           |
| \(\text{C}_2\) | 74.7 | 74.7           | 74.6 | 71.5, 72.8, unsubst | 71.5, 72.6, unsubst | 71.4, 72.6, unsubst |
| \(\text{C}_3\) | 71.3 | 71.3           | 71.3 | 70.9 unsubst 74.7, subst | 70.8 unsubst 74.8, subst | 70.7, 71.1 unsubst 74.7, subst |
| \(\text{C}_4\) | 76.3-77.1, br | 76.3-77.0, br | 76.4-77.0, br | 79.9           | 79.9           | 79.9           |
| \(\text{C}_5\) | 72.9 | 72.9           | 73.4 | 66.3           | 66.6           | 66.1           |
| \(\text{C}_6\) | 60.5-60.9, br | 60.5-60.9, br | 60.5-60.9, br | 60.5, unsubst 69.3, subst | 60.5, unsubst 69.2, subst | 60.4, unsubst 69.3, subst |
| \(\text{C}_1^{2-\(n-1\)}\) | 99.8 | 99.7           | 99.6-99.7, br | 96.7, 99.6 | 96.7, 99.5 | 96.7, 99.6 |
| \(\text{C}_2^{2-\(n-1\)}\) | 71.6-71.7 | 71.6-71.7      | 71.6-71.7 | 71.5, 72.8, unsubst 77.4, subst | 71.5, 72.6, unsubst 77.2, subst | 71.4, 72.6, unsubst 76.9, subst |
|                  | 1-OBn |       | 1-OH  |       |       |       |
|------------------|-------|-------|-------|-------|-------|-------|
|                  | G6    | G7    | G8    | G6    | G7    | G8    |
| C3^2-(n-1)       | 71.3  | 71.3  | 71.3  | 70.9 unsubst 74.7, subst | 70.8 unsubst 74.8, subst | 70.7, 71.1 unsubst 74.7, subst |
| C4^2-(n-1)       | 76.3-77.1, br | 76.3-77.0, br | 76.4-77.0, br | 79.9 | 79.9 | 79.9 |
| C5^2-(n-1)       | 73.4  | 73.5  | 73.0, 73.6 | 66.3 | 66.6 | 66.1 |
| C6^2-(n-1)       | 60.5-60.9, br | 60.5-60.9, br | 60.5-60.9, br | 60.4, 60.6, unsubst 69.3, subst | 60.5, unsubst 69.2, subst | 60.4, unsubst 69.3, subst |
| C1^1             | 99.8  | 99.7  | 99.6-99.7, br | 96.7, 99.6 | 96.7, 99.5 | 96.7, 99.6 |
| C2^1             | 71.6-71.7 | 71.6-71.7 | 71.6-71.7 | 71.5, 72.8, unsubst 77.4, subst | 71.5, 72.6, unsubst 77.2, subst | 71.4, 72.6, unsubst 76.9, subst |
| C3^1             | 71.3  | 71.3  | 71.3  | 70.9 unsubst 74.7, subst | 70.8 unsubst 74.8, subst | 70.7, 71.1 unsubst 74.7, subst |
| C4^1             | 69.4  | 69.4  | 69.4  | 69.4 | 69.3 | 69.2 |
| C5^1             | 73.1  | 73.1  | 73.1  | 69.4 | 69.3 | 69.2 |
| C6^1             | 60.5-60.9, br | 60.5-60.9, br | 60.5-60.9, br | 60.4, 60.6, unsubst 69.3, subst | 60.5, unsubst 69.2, subst | 60.4, unsubst 69.3, subst |
| 1,2-Propylene-glycol CH2 | -    | -     | -     | -     | 64.5 | 65.6 |
| 1,2-Propylene-glycol CH | -    | -     | -     | -     | 64.7 | 65.6 |
| 1,2-Propylene-glycol CH3 | -    | -     | -     | -     | 18.2 | 18.2 |
**Figure S1:** 300 MHz proton spectrum of 1-O-benzylmaltohexose.

**Figure S2:** DEPT-ed-HSQC spectrum of 1-O-benzylmaltohexose.
Figure S3: 300 MHz proton spectrum of 1-O-benzylmaltoheptaose.

Figure S4: DEPT-ed-HSQC spectrum of 1-O-benzylmaltoheptaose.
Figure S5: 300 MHz proton spectrum of 1-O-benzylmaltooctaose.

Figure S6: DEPT-ed-HSQC spectrum of 1-O-benzylmaltooctaose.
Figure S7: 300 MHz proton spectrum of (2-hydroxy)propylated maltohexaose.

Figure S8: DEPT-ed-HSQC spectrum of (2-hydroxy)propylated maltohexaose.
**Figure S9:** 300 MHz proton spectrum of (2-hydroxy)propylated maltoheptaose.

**Figure S10:** DEPT-ed-HSQC spectrum of (2-hydroxy)propylated maltoheptaose.
**Figure S11**: 300 MHz proton spectrum of (2-hydroxy)propylated maltooctaose.

**Figure S12**: DEPT-ed-HSQC spectrum of (2-hydroxy)propylated maltooctaose.
Characterization of the benzylated maltooligomers with HPLC

Agilent HPLC measuring system with Refractive Index Detector and/or DAD detector was used.
The used HPLC column was Inertsil HILIC, 150 × 4.6 mm, particle size 5 μm (GL Sciences Inc.)
The most appropriate mobile phase contained acetonitrile:water = 69:31.
The flow rate was 1.0 mL/min. The column temperature was set to 30 °C; the injection volume from the sample solution (concentration: 2 mg/mL mobile phase) was 100 μL.

Figure S13: HPLC chromatogram of 1-O-benzylmaltotriose and maltotriose using refractive index detector (a) and DAD detector (b).
Table S3: Area percentage of the peaks detected by HPLC.

| sample                      | Composition (in area %) | Retention time of peak (min.) |
|-----------------------------|-------------------------|-----------------------------|
|                             |                         | 2.6 | 2.9 | 3.3 | 3.6 | 4.1 | 4.6 | 5.1/5.3 | 5.9 | 6.6 |
| Benzyl-Maltohexaose         | 0.6                     | 1.9 | 3.3 | **86.5** | 1.9 | 2.0 | 3.9 |
| Benzyl-Maltoheptaose        | 0.2                     | 1.0 | 3.2 | 7.5 | **79.0** | 2.5 | 2.7 | 3.8 |
| Benzyl-Maltooctaose         | 0.4                     | 1.1 | 2.6 | 4.8 | 5.5 | **75.6** | 2.9 | 2.2 | 5.1 |

Figure S14: HPLC chromatogram of HP-maltohexaose compared to maltohexaose and O-benzyl-maltohexaose.