Electronic Supporting Information

# Lyotropic liquid crystals and linear supramolecular polymers of end-functionalized oligosaccharides

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## 1. Measurements and instrumentation

### 1.1. Nuclear magnetic resonance (NMR)

$^1$H NMR spectra were recorded at 25 °C on a Bruker Avance DRX400 (400 MHz). The solvent residual peak of $CDCl_3$ was used as internal standard and calibrated at 7.26 ppm.

### 1.2. Fourier-transform infrared spectroscopy (FTIR)

Infrared spectra were recorded using a PerkinElmer spectrometer. The samples were analysed by transmission from 400 to 4000 $cm^{-1}$ (16 scans, resolution 4 $cm^{-1}$).

### 1.3. Mass spectrometry (MS)

Mass spectra were recorded with a Bruker Daltonics Autoflex for MALDI-TOF measurements and with a Waters Micromass ZQ spectrometer for ESI experiments.

### 1.4. Transmission electron microscopy (TEM)

TEM images were collected using a FEI Tecnai G2 operated at 120 kV in bright-field mode. TEM samples were prepared by drop casting 1 mg/mL dispersion (5 µL) of the sample on Quantifoil R 2/1 Holey carbon film (Cu 200 Mesh) and the excess solvent was blotted with filter paper and let to evaporate to dry.

### 1.5. Polarized optical microscopy (POM)

POM studies were performed with a LEICA DM4500P microscope under the transmitted light (TL) mode. A λ-wave filter was used.

### 1.6. X-ray scattering

The WAXS measurements (X-ray diffraction, XRD) were performed on a Rigaku SmartLab X-ray diffractometer with a rotating anode x-ray source (9 kW, Cu Kα,β) in transmission mode of the dry sample in bulk, trapped in between two Kapton films at room temperature.

WAXS shows no sharp crystalline peaks, which is in agreement with the liquid crystalline behavior of UPy-$C_6$-MeMH-$C_6$-UPy in HFIP and the formation of supramolecular fibers in bulk.

The samples were sealed between Kapton foils during the SAXS measurement. The sample environment was evacuated to reduce scattering from air. The SAXS was measured using a rotating anode Bruker Microstar microfocus X-ray source (Cu $K_\alpha$ radiation, $\lambda$ = 1.54 Å). The beam was monochromated and focused by a Montel multilayer focusing monochromator (Incoatec). The X-ray beam was further collimated by a set of four slits (JJ X-ray). The size of the X-ray beam at the sample position was < 1 mm. The scattered intensity was collected using a Hi-Star 2D area detector (Bruker). Sample-to-detector distance was 1.59 m. A silver behenate standard sample was used for calibration of the length of the scattering vector $q$. One-dimensional SAXS data were obtained by azimuthally averaging the 2D scattering data. The magnitude of the scattering vector $q$ is given by $q = 4\pi \sin\theta / \lambda$, where $2\theta$ is the scattering angle.

### 1.7. Scanning electron microscopy (SEM)

SEM imaging was performed on a Zeiss Sigma VP microscope at 2 kV voltage. A drop of dispersion (10 µL) was added on a carbon tape fixed on sample stub and allowed to dry at ambient conditions for 18 h. The sample was subjected for sputter coating with Au/Pd under vacuum at 20 mA for 3 minutes prior to imaging.

### 1.8. Thermogravimetric analysis (TGA)

The TGA was measured with a TA Instruments Q500 TGA device using a heating rate of 10 °C/min and nitrogen as the gas carrier. A 10 mg sample size was used and after each run the gas was exchanged to oxygen to burn any leftover organics.

### 1.9. Differential scanning calorimetry (DSC)

DSC was measured with a TA Instruments Q200 MT-DSC device. A 10 mg sample size was used. Before each run, the heat history was removed by heating the sample close to degradation temperature (determined by TGA). The heating/cooling rates were set to 10 °C/min.

## 2. Experimental

### 2.1. General methods and materials

All the syntheses were performed in clean and dry glassware. Reagents and solvents were purchased from commercial sources. 1,6-diisocyanatohexane (98 % purity), dibutyltin dilaurate (DBTDL, 95 % purity) were obtained from Sigma-Aldrich and used without further purification. Technical/Analytical grade solvents (chloroform, toluene, 1,1,1,3,3,3-hexafluoro-2-propanol) were purchased from Sigma-Aldrich. Deuterated solvents for NMR measurements were obtained from Sigma-Aldrich and used as received. (2,3,6-Tri-*O*-methyl)-*β*-cyclodextrin (TM-βCD) was purchased from Carbosynth (Berkshire, United Kingdom).

### 2.2. Synthesis of (2,3,6-tri-*O*-methyl)-$\alpha,\beta$-maltoheptaose (MeMH)

The controlled cleavage of a single glycosidic bond of TM-βCD was carried out according to a slightly modified procedure reported by Kikuzawa *et al.*[1] TM-βCD (4.6 g, 3.2 mmol) was dissolved in 30% aq. $HClO_4$ (150 mL) at 0 °C, and the solution was stirred for 6 hours at room temperature. After neutralization at 0 °C with aq. NaOH (5 M), the mixture was extracted with 2 x 150 mL of dichloromethane (DCM) and dried over sodium sulfate ($Na_2SO_4$). After filtration and concentration in vacuo, the crude product was purified by flash chromatography on silica gel (DCM/MeOH 95/5, v/v) to afford the expected compound (2,3,6-tri-*O*-methyl)-$\alpha,\beta$-maltoheptaose (MeMH) (2.66 g, 60% yield) as a white solid, which was characterized by $^1$H-NMR, FTIR and MALDI-TOF MS.

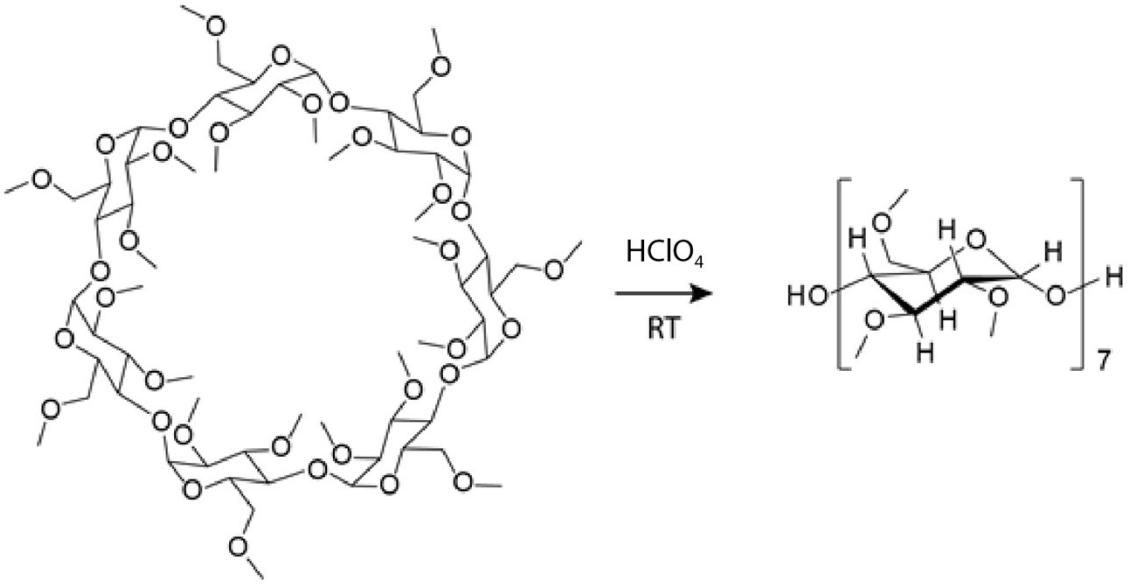


**Fig. S1:** $HClO_4$-mediated ring opening of TM-βCD yielding the targeted MeMH.

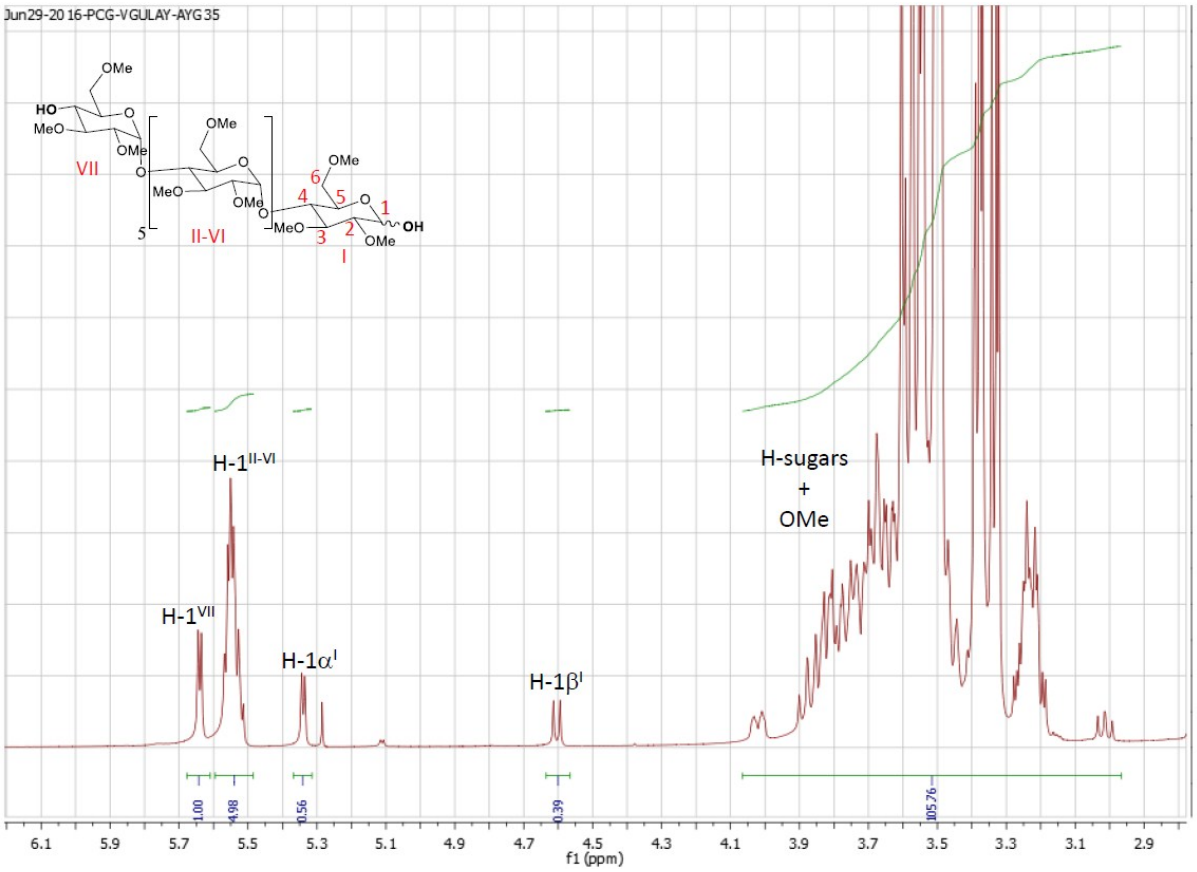


**Figure S2:** $^{1}$H-NMR of MeMH.

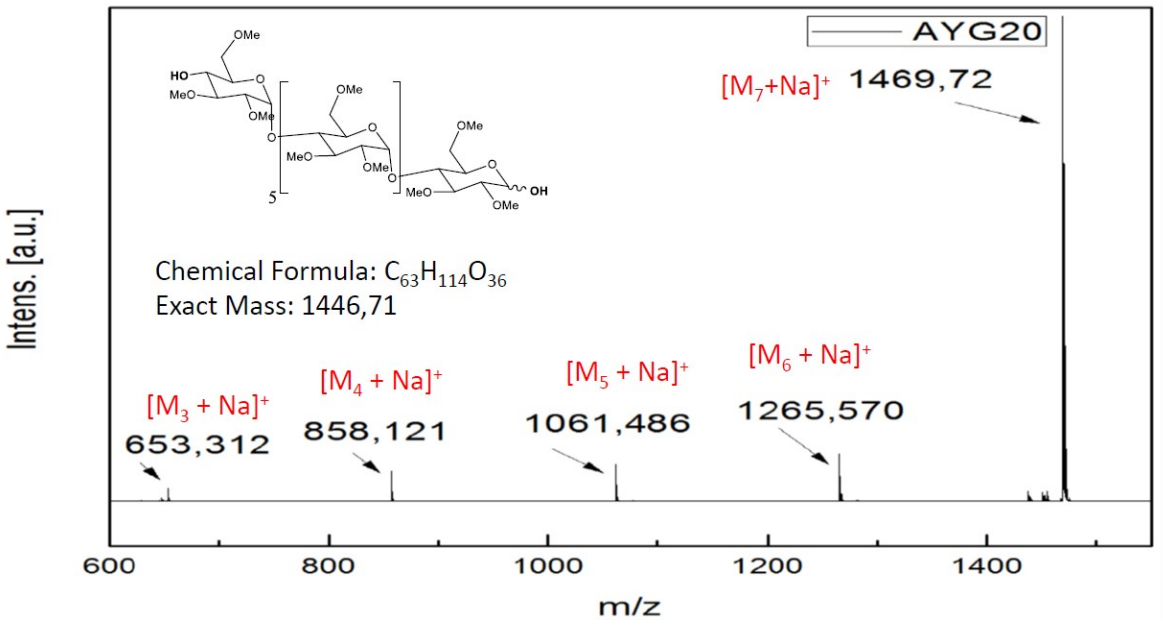


**Fig. S3:** MALDI-TOF-MS of MeMH.

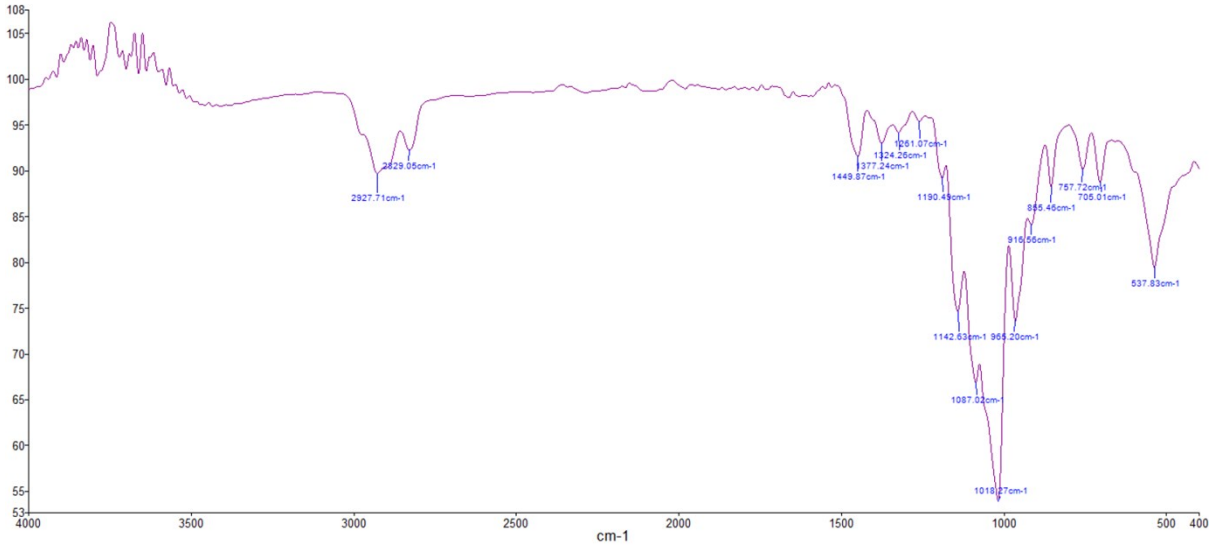


**Fig. S4:** FTIR spectrum of MeMH.

### 2.3. Synthesis of $C_6$-MeMH-$C_6$

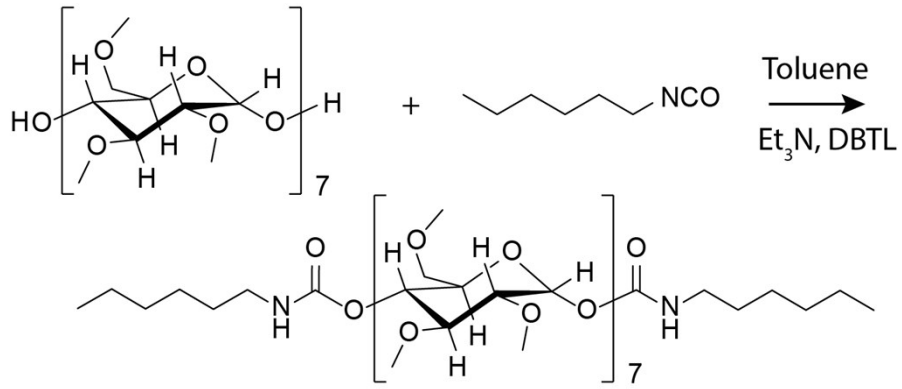


**Fig. S5:** Synthesis of $C_6$-MeMH-$C_6$.

A solution of MeMH (145 mg, 0.1 mmol), hexyl isocyanate (584 µL, 4 mmol), triethylamine (104 µL, 0.7 mmol), and 2 drops of dibutyltin dilaurate (DBTL) in dry toluene (6 mL) were stirred at 80 °C for 2 hours. The reaction mixture was extracted with water (10 mL) and the organic layer was dried over $Na_2SO_4$, filtered, and evaporated to dryness. A flash chromatography on silica gel (acetone/toluene 4/6, v/v) yielded $C_6$-(MeMH)-$C_6$ (166 mg, 97% yield) as a white solid.

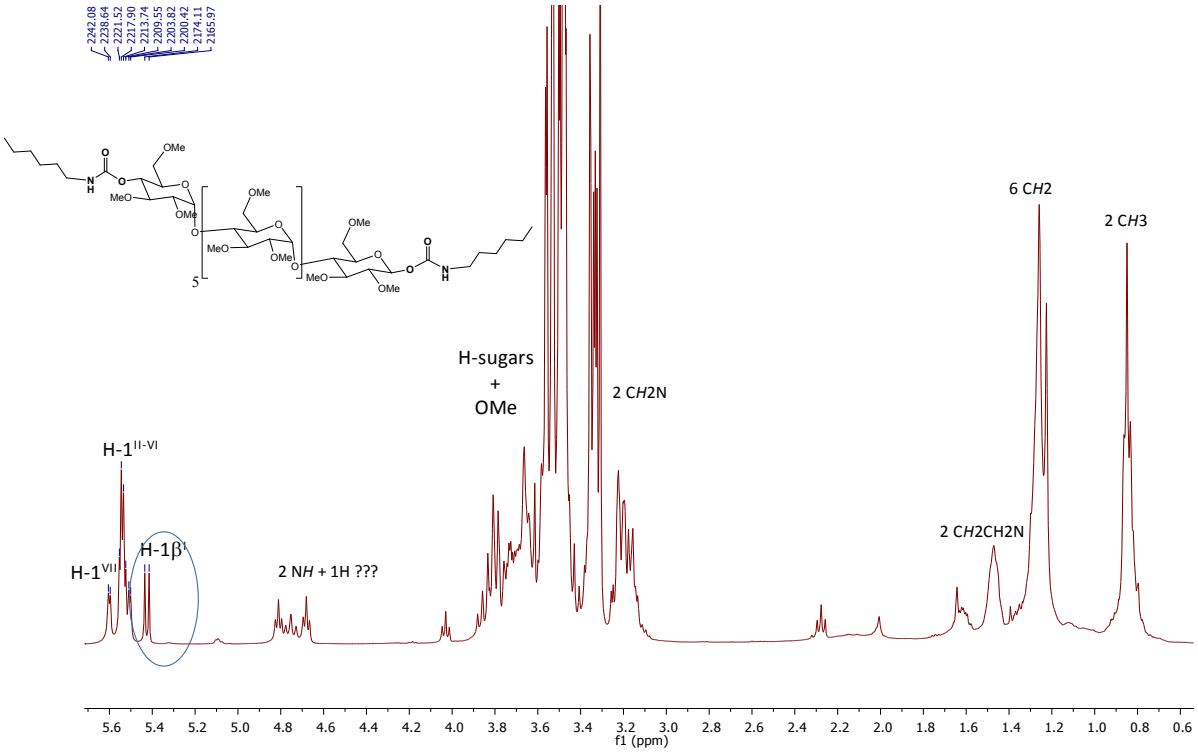


**Fig. S6:** $^{1}$H-NMR spectrum of $C_6$-MeMH-$C_6$ with $\beta$-stereoselectivity (H-1$^{I}$ $J_{1\text{-}2}$ = 8.1 Hz) at the anomeric position.

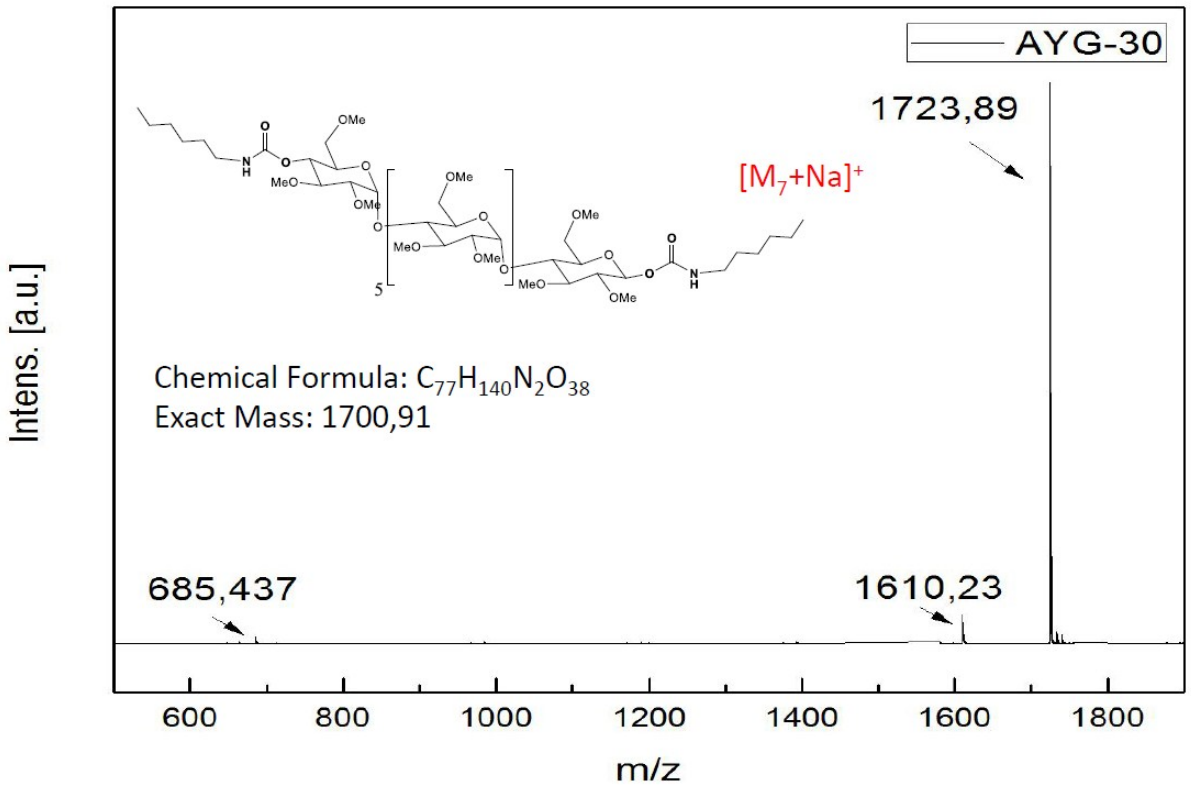


**Fig. S7:** MALDI-TOF-MS of $C_6$-MeMH-$C_6$.

## 2.4. Synthesis of UPy-$C_6$-MeMH-$C_6$-UPy

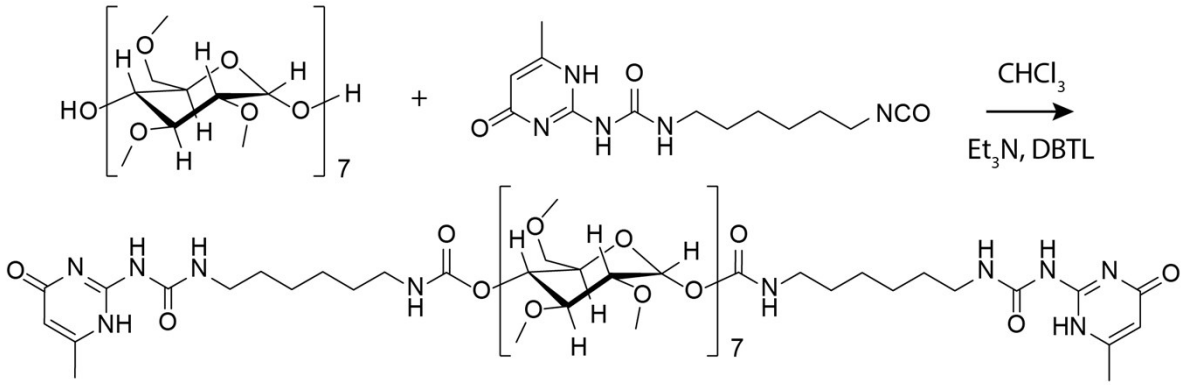


**Fig. S8:** Synthesis of UPy-$C_6$-MeMH-$C_6$-UPy.

A solution of MeMH (300 mg, 207 µmol), UPy-$C_6$-isocyanate (608 mg, 2.07 mmol), triethylamine (289 µL, 2.07 mmol,) and 2 drops of dibutyltin dilaurate (DBTL) in dry chloroform ($CHCl_3$) (25 mL) were stirred for 19 hours under reflux. The reaction mixture was first cooled down to room temperature, then diluted with $CHCl_3$ up to 250 mL and finally filtered. The filtrate was reduced to dryness in vacuo and purified by flash chromatography on silica gel (DCM/MeOH 95/5 to 90/10, v/v) yielding UPy-$C_6$-MeMH-$C_6$-UPy (223 mg, 53% yield) as a white solid.

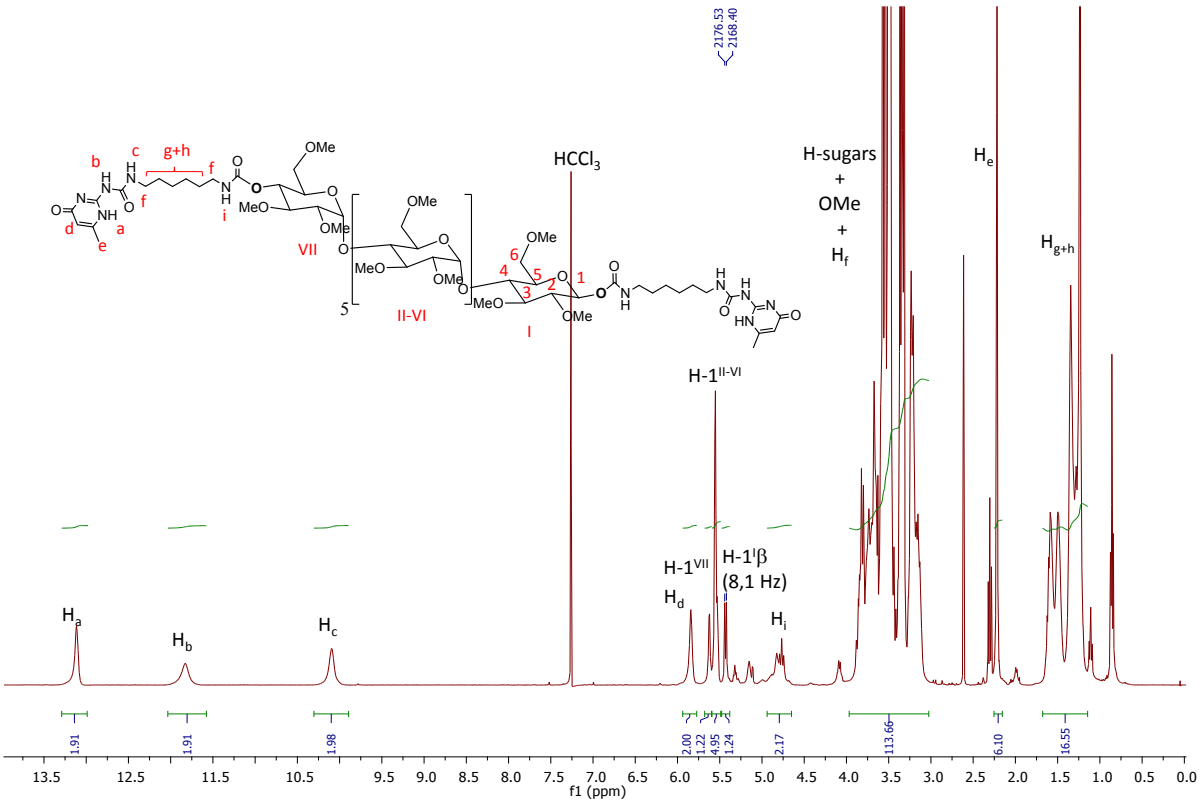


**Fig. S9:** $^1$H-NMR spectrum in dry $CDCl_3$ of UPy-$C_6$-MeMH-$C_6$-UPy which confirms that both ends have been equipped with UPy with a $\beta$-stereoselectivity (H-$1^I$; $J_{1\text{-}2}$ = 8.1 Hz) at the anomeric position and the positions of the NH signals at 13.3 ($NH_a$), 11.8 ($NH_b$), and 10.2 ($NH_c$) ppm, along with a pyrimidyl resonance at 5.8 ppm ($H_d$), indicate that the functional groups are dimerized and that the molecules are exclusively present in the keto tautomeric form.

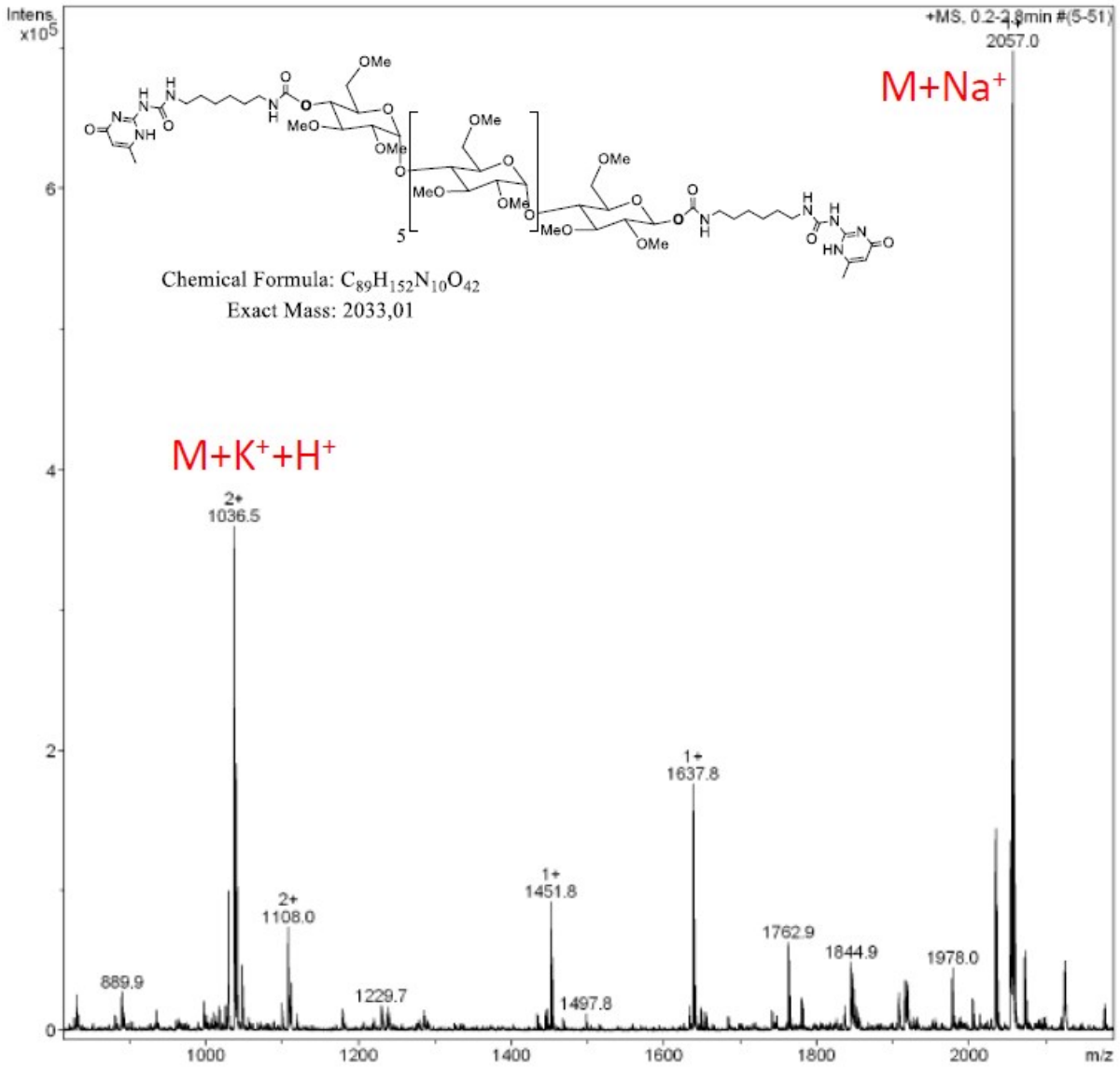


**Fig. S10:** ESI-MS spectra of the methylated maltoheptaose, where both ends have been appended with UPy (UPy-$C_6$-MeMH-$C_6$-UPy).

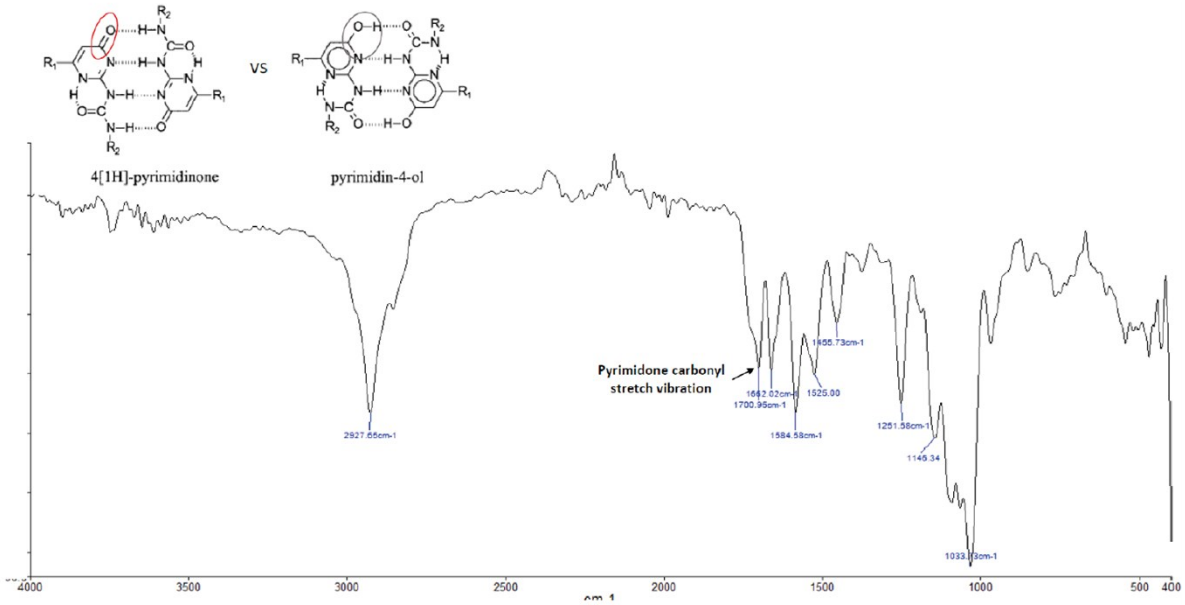


**Fig. S11:** FTIR spectra of the UPy-$C_6$-MeMH-$C_6$-UPy showing no isocyanate band at $\nu$ = 2268 $cm^{-1}$ and characteristic band at $\nu$ = 1700 $cm^{-1}$ of the pyrimidinone carbonyl stretch vibration, which is absent in the enol tautomer (UPy functionalities remain dimerized in the solid-state under the keto tautomer form).

### 3. TGA measurements

The TGA measurements were conducted to determine the point where the thermal degradation begins. This information was used to determine the DSC heating ranges.

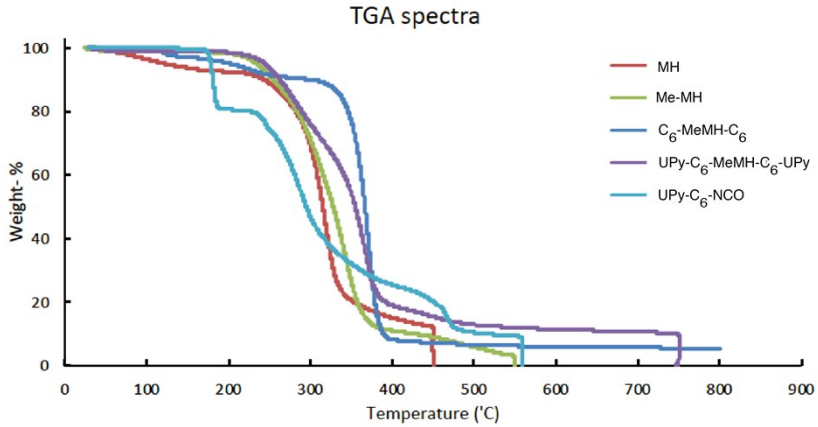


**Fig. S12:** The TGA spectra of maltoheptaose (MH) and its derivatives (MeMH, $C_6$-MeMH-$C_6$, UPy-$C_6$-MeMH-$C_6$-UPy) and UPy-$C_6$-NCO

**Table S1:** Temperatures of the first to fourth degradation steps observed in the TGA thermograms of the synthesized sugars and used synthons

| | 1st | 2nd | 3rd | 4th | Temp 95% |
|---|---|---|---|---|---|
| MH | 236 | | | | 125 |
| MeMH | 222 | | | | 235 |
| $C_6$-MeMH-$C_6$ | 116 | 201 | 329 | | 204 |
| UPy-$C_6$-MeMH-$C_6$-UPy | 235 | | | | 245 |
| UPy-$C_6$-NCO | 173 | 237 | 256 | 463 | 179 |

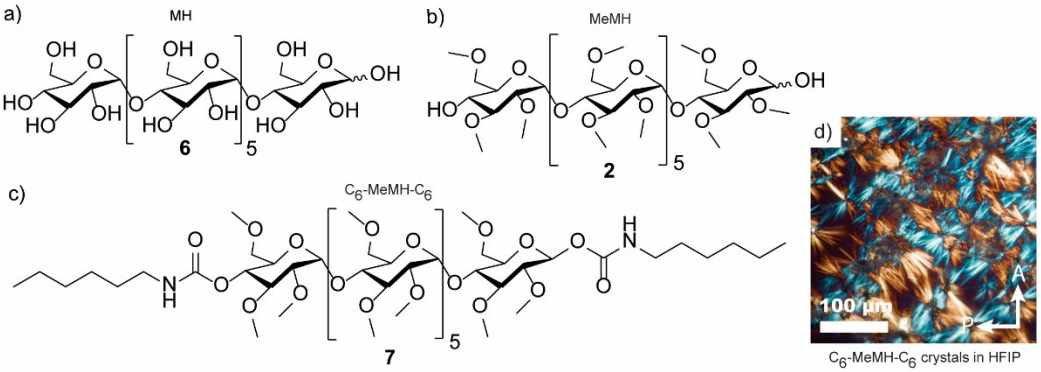


**Fig. S13**. Reference compounds, identifying the relevance of the self-associating UPy terminal moieties for the lyotropic LC behavior in HFIP. a) Linear maltoheptaose (MH) with free OH groups in the reducing and non-reducing ends (**6**). b) Permethylated linear maltoheptaose (MeMH) with free OH groups in the reducing and non-reducing ends (**2**). c) Permethylated linear maltoheptaose with telechelic hexyl end-functionalizations $C_6$-MeMH-$C_6$ (**7)**. Neither MH, MeMH, nor $C_6$-MeMH-$C_6$ showed lyotropic liquid crystallinity in any tried solvents (or combination of solvents). d) POM image of the crystals formed by $C_6$-MeMH-$C_6$ (**7)** in HFIP (initially 500 mg/mL) after 24 h of incubation

## 4. References

A. Kikuzawa, T. Kida, Y. Nakatsuji, and M. Akashi. “Short Synthesis of Skeleton-Modified Cyclodextrin Derivatives with Unique Inclusion Ability.” *J. Org. Chem.,* 2005, **70**, 1253–1261.