Supporting Information for

Controlled Synthesis of Polyglucose in One-Dimensional Coordination Nanochannels

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Materials

All the reagents and solvents were commercially available and used as received without further purification. [La(1,3,5-benzenetrisbenzoate)(H_2O)]$_n$ (**1**) was prepared according to previously described methods.[1]

Measurements

The X-ray powder diffraction (XRPD) data were collected using a Rigaku RINT 2000 Ultima diffractometer employing CuKα radiation using a flat-bed sample holder. The IR spectra were measured using a Thermo Scientific Nicolet iS5. MALDI–TOF MS spectra were recorded in the linear positive mode on a mass spectrometer (BRUKER DALTONICS, Ultraflex III). 2,5-Dihydroxybenzoic acid was used as a matrix. ESI MS spectra were obtained using a Thermo Scientific Exactive. The ^{1}H and ^{13}C NMR spectra were obtained using a JEOL A-500 and 600, respectively. The thermogravimetric analysis was carried out from room temperature to 500 °C at a heating rate of 10 °C min^{-1} using a Rigaku Instrument Thermo Plus TG8120 in a N_2 atmosphere. Differential scanning calorimetry (DSC) was carried out with a Seiko Instruments DSC 6220 under a N_2 atmosphere and 10 K min^{-1} heating rate. Gel permeation chromatography (GPC) measurements on the resulting polysaccharides were performed in DMF at 60 °C on two linear-type poly(vinylidene fluoride) KD-806M that were connected to a JASCO DU-H2130 precision pump and a JASCO RI-71S refractive index detector. The columns were calibrated against standard polystyrene samples.

Polymerization of glucose in the nanochannels of 1

The host compound **1** (0.30 g) was dried by heating at 130 °C under vacuum (0.31 kPa) for 4 h. Dried **1** was immersed in an aqueous solution (1.0 mL) of glucose (Glc**,** 0.12 g, 0.64 mmol) and phosphoric acid (3.0 mg, 31 μmol) at room temperature to incorporate Glc and the acid into the pores. Excess water was removed by evaporation under vacuum (0.31 kPa) at room temperature (**1**⊃Glc). **1**⊃Glc was heated at 110 °C for 48 h under vacuum (0.31 kPa). The resulting product was stirred in 0.5 M aqueous sodium ethylenediaminetetraacetate solution (Na-EDTA, 3.0 mL) for 20 min to decompose the porous framework of **1**. Addition of MeOH (30 mL) gave a clear solution that did not contain any polymeric product, as was evidenced by MALDI–TOF MS measurement.

Polymerization of AGlc in the nanochannels of 1

After drying **1** (0.30 g) in the same procedure as the above glucose polymerization, it was immersed in a dry MeOH solution (1.0 mL) of 1,6-anhydro-β-D-glucose (AGlc, 0.12

g, 0.65 mmol) and 1-benzyltetrahydrothiophenium bromide[2] (8.2 mg, 31 μmol) at room temperature to incorporate AGlc and the initiator into the pores to give an adduct (**1**⊃AGlc). The MeOH was evaporated under vacuum (10 kPa) at room temperature. Subsequently, **1**⊃AGlc was heated to the appropriate temperature for a predetermined time under a N_2 atmosphere to promote the cationic ring-opening polymerization of AGlc.

The resulting product was washed with MeOH repeatedly, and was dried under reduced pressure at room temperature to give a composite (**1**⊃PGlc). Treatment of **1**⊃PGlc with 0.5 M aqueous Na-EDTA solution (3.0 mL) for 20 min released the polymeric product by decomposition of **1**. The obtained clear solution was added to MeOH (30 mL) to give a precipitate that was washed several times with MeOH and dried under reduced pressure at room temperature, providing PGlc.

Bulk polymerization of AGlc

AGlc (1.0 g, 6.3 mmol) and 1-benzyltetrahydrothiophenium bromide (82 mg, 0.31 mmol) were heated at 150 °C for 48 h under a N_2 atmosphere. The resulting black-colored product was washed with MeOH repeatedly, and was dried under reduced pressure at room temperature (0.79 g, yield = 79%).

Solution polymerization of AGlc

AGlc (1.0 g, 6.3 mmol) and 1-benzyltetrahydrothiophenium bromide (82 mg, 0.31 mmol) were dissolved in dry DMF (30 mL) and then the solution was heated at 150 °C under a N_2 atmosphere. After addition of MeOH to the reaction mixture, the resulting precipitate was washed with MeOH and dried under reduced pressure at room temperature (0.70 g, yield = 70%).

Solubility test of PGlc

To determine whether cross-linked polymer was contained in the product, we examined the solubility of PGlc (10 mg) in water (1.0 mL). After filtering the insoluble product, the filtrate was evaporated to give PGlc, which was weighed to determine the solubility.

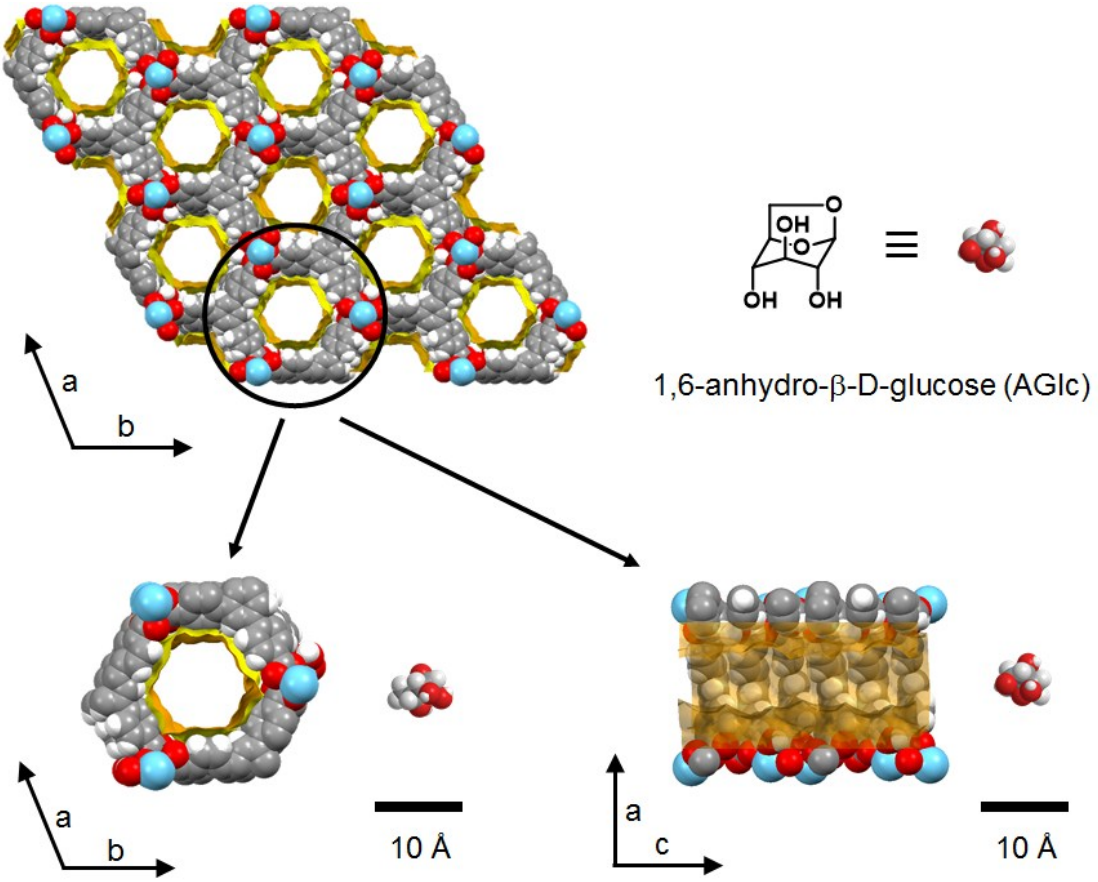


Figure S1. Size relationship between **1** and AGlc displayed by space filling model (La, blue; O, red; C, gray; H, white; inner surface, yellow).

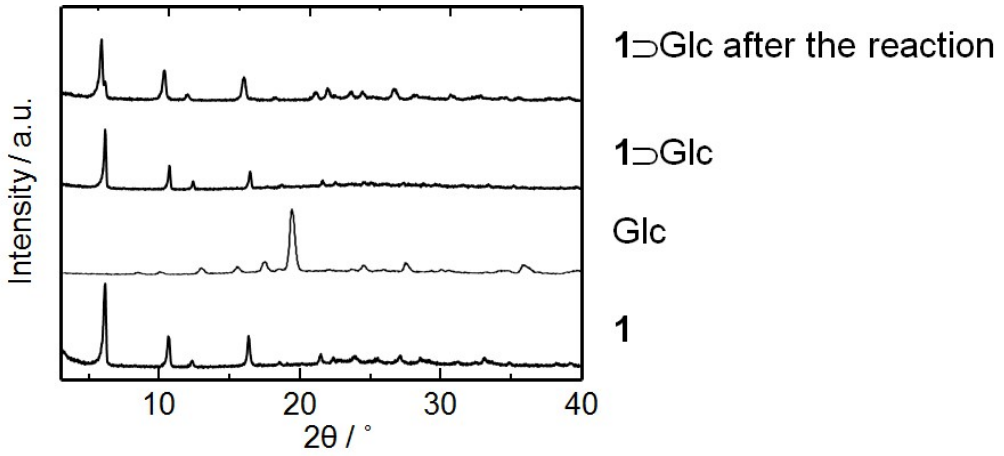


Figure S2. XRPD patterns of **1**, Glc, and **1**⊃Glc before and after the heat treatment with phosphoric acid. A characteristic peak for crystalline Glc appears at $2\theta = 19.2°$. This peak was not observed in the XRPD patterns of **1**⊃Glc, indicating no leakage of Glc from the nanochannels.

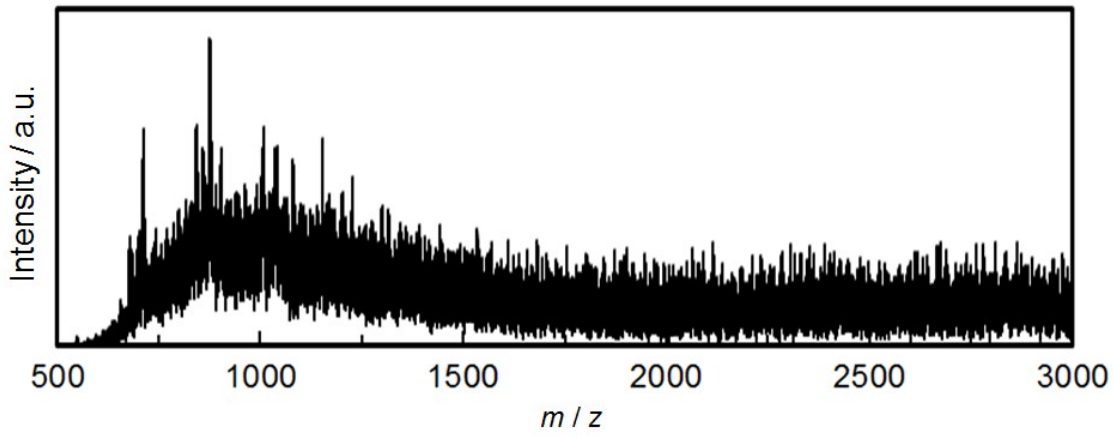


Figure S3. MALDI–TOF MS spectrum of the product obtained from **1**⊃Glc after reaction in the presence of phosphoric acid. Characteristic peaks for PGlc were not detectable.

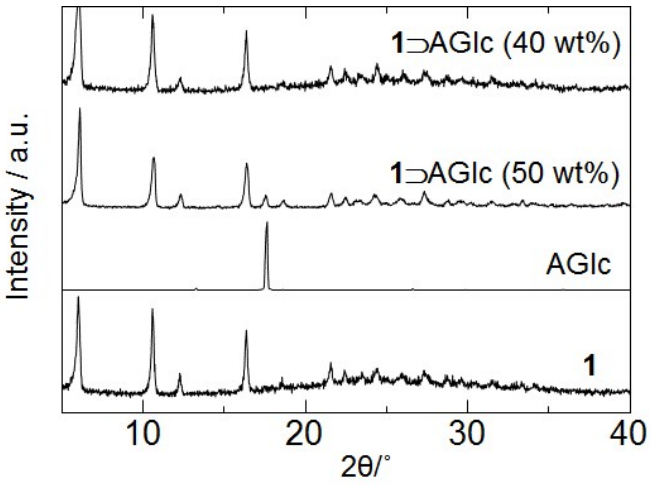


Figure S4. XRPD patterns of **1**, AGlc, and **1**⊃AGlc with different guest loading amounts. A characteristic peak for crystalline AGlc is observed at $2\theta = 17.3°$. The loading amount of AGlc could be optimized by the appearance of this diffraction peak. In the case of **1**⊃AGlc with 50 wt% of guest loading, a small peak for crystalline AGlc assembly was recognized because of the leakage of AGlc outside the host channels. In contrast, this peak did not appear in the XRPD pattern of **1**⊃AGlc with 40 wt% AGlc, representing the full accommodation of AGlc inside the nanochannels of **1**. Thus, in our experiments, polymerization of AGlc was carried out with a loading of 40 wt% AGlc in **1**.

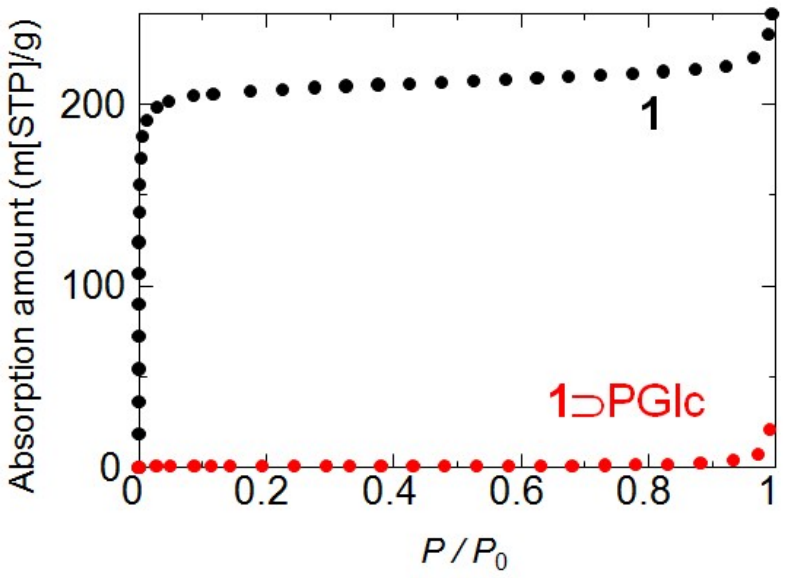
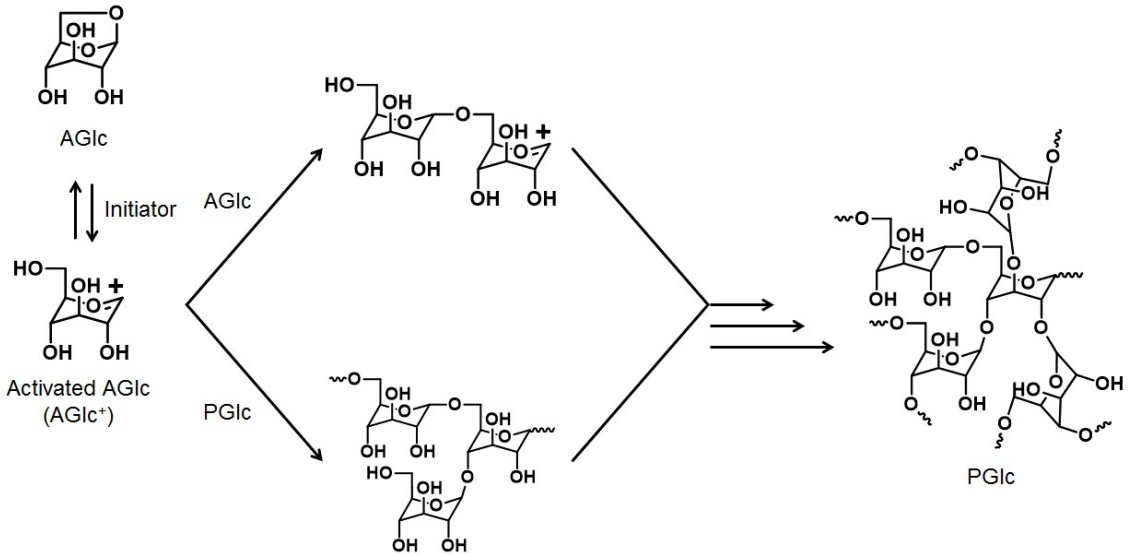


Figure S5. Nitrogen adsorption isotherms of **1** (black) and **1**⊃PGlc (red) at 77 K.



Scheme S1. Mechanism of cationic ring-opening polymerization of AGlc. In the presence of cationic initiator, AGlc is rapidly protonated at the 1,6-ether oxygen atom, resulting in the ring-opening reaction to afford the carbonium ion ($AGlc^+$). This active $AGlc^+$ attacks the 1,6-ether oxygen atom of the remaining monomer to form a 1,6-glycosidic linkage, where a reactive end group is continuously regenerated to provide PGlc during the propagation step. However, in this polymerization process, the reactive species often react with other hydroxyl groups of AGlc as well as another PGlc chain to form 1,2-, 1,3-, and 1,4-glycosidic linkages, leading to termination reactions and unfavorable cross-linking of PGlc.[3]

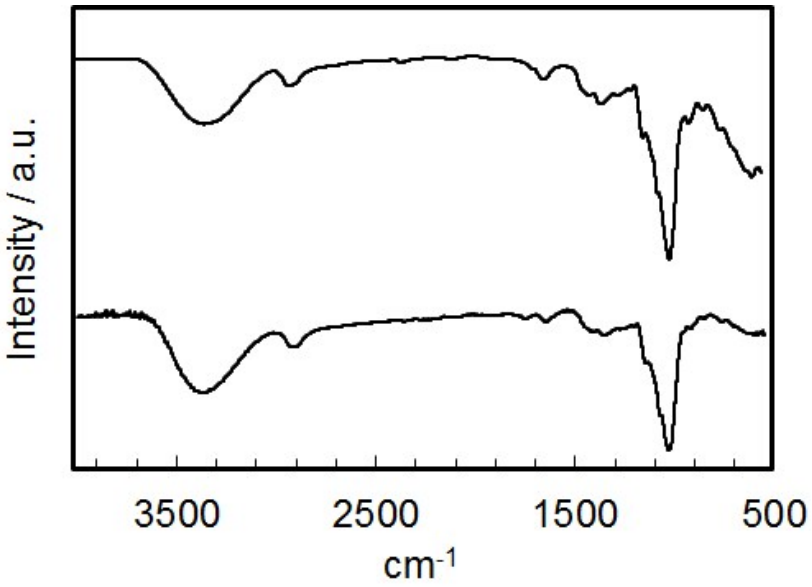


Figure S6. IR spectra of PGlc synthesized in DMF solution (top) and prepared using **1** (bottom). The IR spectrum of the PGlc from **1** was almost the same as that obtained from solution polymerization. The representative peaks appearing at 1032 and 3353 cm^{-1} were attributed to the C–O–C stretching of the glycosidic linkages and O–H stretching of PGlc, respectively.[4]

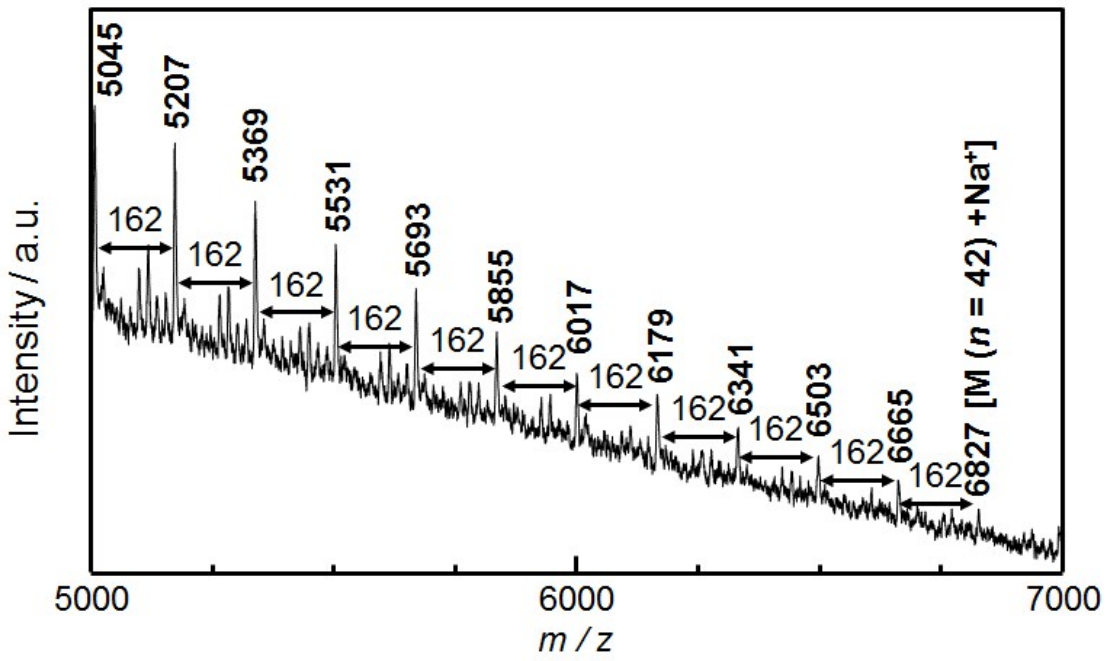


Figure S7. MALDI–TOF MS spectrum of PGlc synthesized using **1**. Peaks for a number of polymers with the repeating unit of glucose (*m*/*z* 162) could be detected.

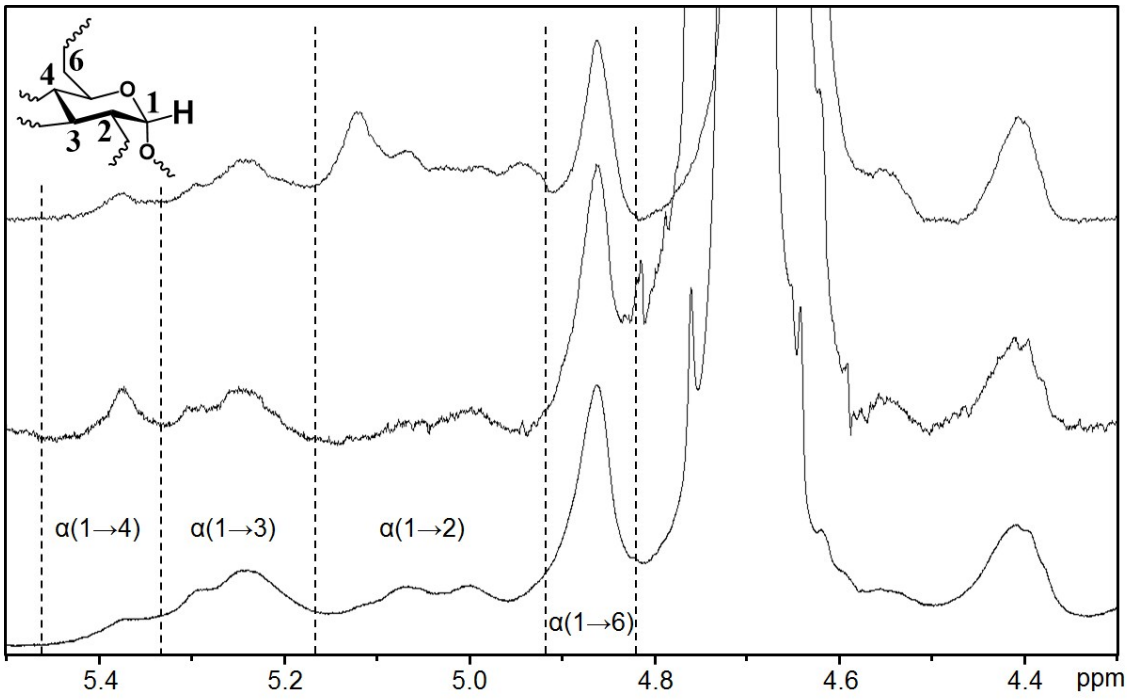


Figure S8. ^{1}H NMR spectra (D_2O) of PGlc synthesized in bulk (top), DMF solution (middle), and using **1** (bottom). The enclosed structure shows the α-D-glucose unit structure in PGlc. The peaks at 4.83–4.93, 4.93–5.18, 5.18–5.33, and 5.33–5.47 ppm were attributed to the H-1 protons of α1→6, α1→2, α1→3, and α1→4 glyosidic bonds, respectively.[5-9] The signals corresponding to β1→*n* glycosidic bonds were overlapped with a large peak for H_2O at 4.68 ppm.

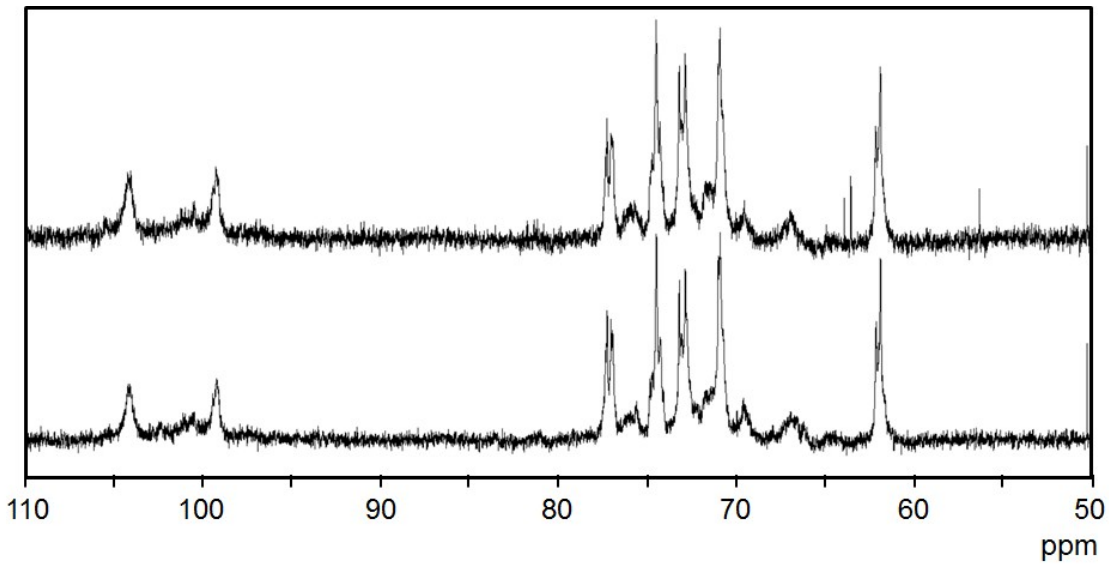
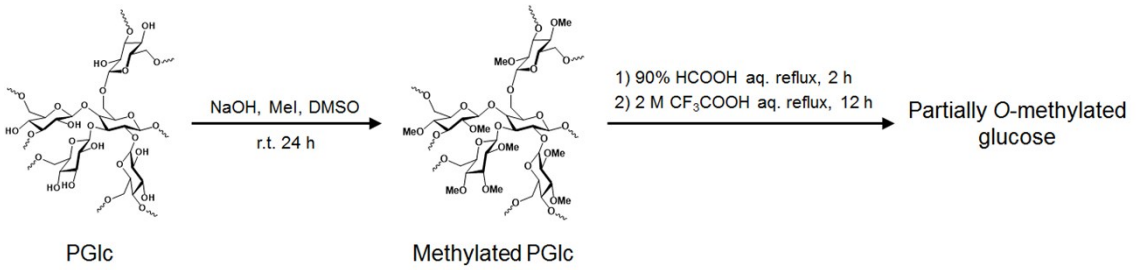


Figure S9. ^{13}C NMR spectra (D_2O) of PGlc synthesized in DMF solution (top) and using **1** (bottom). The spectrum of the PGlc from **1** was almost the same as that obtained from solution polymerization.[5-8] ^{13}C NMR: δ(ppm) 104.18, 98.47, 77.52, 77.20, 76.63, 76.31, 74.90, 73.57, 73.26, 70.89, 68.81, 66.87, 61.41, 61.17.

Methylation analysis of PGlc[6, 10]



Scheme S2. Per-*O*-methylation and subsequent hydrolysis of PGlc.

After PGlc (0.19 g) was dissolved in dry DMSO (5 mL), sodium hydroxide (0.64 g, 16 mmol) and methyl iodide (0.64 mL, 10 μmol) were added to the solution and then stirred at room temperature for 24 h under a N_2 atmosphere. The resultant mixture was poured into water (20 mL) and extracted five times with CH_2Cl_2 (20 mL). The combined extract was washed three times with water (20 mL), and then dried over sodium sulfate. After evaporation of the solvent, the obtained solid was dissolved in ethyl acetate and poured into hexane to give per-*O*-methylated PGlc. If the reaction did not progress quantitatively, the resulting product underwent the same methylation process to provide a fully methylated PGlc. In this regard, methylation of all of the hydroxyl groups was demonstrated by the complete disappearance of the broad peak corresponding to the hydroxyl groups of PGlc (3000–3600 cm^{-1}) in the IR spectrum of the methylated PGlc (Fig. S9).

For the subsequent hydrolysis of the methylated PGlc, it was refluxed in 90% aqueous solution of formic acid (2 mL) for 2 h. Then, the reaction mixture was refluxed with 2 M trifluoroacetic acid in water (2 mL) for 12 h. The solvent was removed under reduced pressure, and the mixtures of partially *O*-methylated glucoses (0.18 g) were separated using silica column chromatography (CH_2Cl_2, then CH_2Cl_2/MeOH 90:10), which were identified by ESI MS spectrometry.

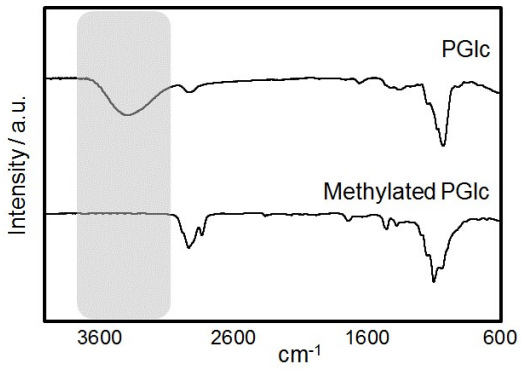


Figure S10. IR spectra of the PGlc and methylated PGlc.

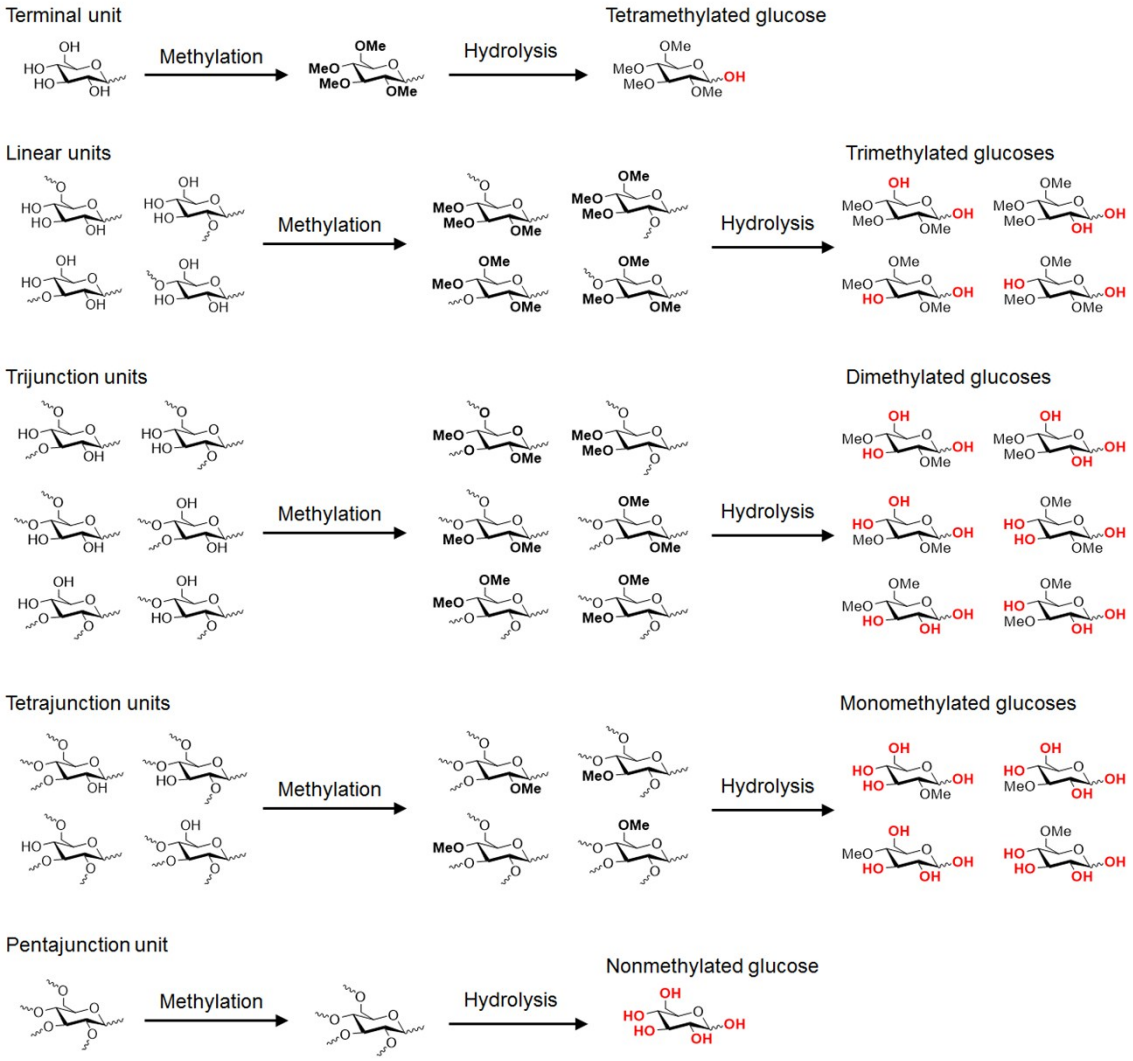


Figure S11. Structures of tetra-, tri-, di-, mono-, and nonmethylated glucoses. The derivatization of a polysaccharide for methylation analysis includes conversion of all free hydroxyl groups into methoxy groups followed by acid hydrolysis. Acidic hydrolysis of the resulting polysaccharides only cleaves the interglycosidic linkages and leaves the methyl–ether bonds intact. The hydrolyzed monomers can be separated and identified by ESI MS spectrometry.

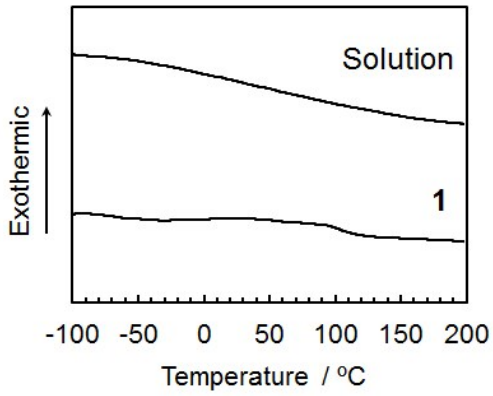


Figure S12. DSC profiles of PGlc synthesized in DMF solution and using nanochannels of **1**. To remove structural water in the PGlc, PGlc was heated at 100 °C under vacuum before DSC measurement.

References

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