Supporting Information for

Grafted Cellulose Strands on the Surface of Silica: Effect of Environment on Reactivity

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Synthesis

General and Cellulose Dissolution. Synthesis was performed on a Schlenk line equipped with argon and vacuum (vacuum was kept below 0.5 mTorr). Figure S1 describes synthesis steps for grafting poly(1-4-β-glucon) (β-Glu) on silica. The challenge of grafting single strands of β-Glu derived from recalcitrant cellulose requires use of an aprotic, acid stable, highly anhydrous solvent, which is able to solvate cellulose, such as 8% wt LiCl in Dimethylacetamide (LiCl/DMAc).1-3 LiCl (Sigma Aldrich > 99.0%) was dried in a Schlenk tube under vacuum at 190 °C overnight. A fresh batch of absolute DMAc (DMAc, Sigma Aldrich > 99.5%) was refluxed for a minimum of 2 h and subsequently distilled over CaH₂. The freshly distilled DMAc was mixed with dried with LiCl to yield an 8% wt LiCl in DMAc solution.² The solution was allowed to stir for at least 12 h to ensure complete dissolution of the salt. Avicel PH-101 (Sigma Aldrich, DP 230 to 280, Rg was reported to be ~56 nm)⁴ was activated for dissolution by solvent exchange (sequential treatment with H₂O, methanol, and dried DMAc)¹⁻²⁻⁵ followed by drying under vacuum at 50 °C overnight, to remove traces of water, while keeping the cellulose surface wetted with DMAc. Dried LiCl/DMAc solution was transferred to dried cellulose via dry syringe to form a ~1.5% wt cellulose solution. The resulting mixture was allowed to stir for 48 h to ensure complete dissolution of the microcrystalline cellulose.
Silica Hydroxylation. 0.8 g of silica support (SiO$_2$, Cab-o-sil M5, Cabot Corporation) consisting of a 200 nm – 300 nm aggregates with a primary particle size of 14 nm in diameter [$^6$] was fully hydroxylated by dispersing the support in a 1:1:5 (by volume) solution of 31% H$_2$O$_2$, 30% ammonium hydroxide, and water, respectively, for a period of 15 min. It was subsequently centrifuged to remove excess aqueous solution.$^7$

Chlorination (Step 1). Hydroxylated silica (see above) or as-received Cab-o-sil silica was dried under vacuum at 200 °C overnight. 20 mL of freshly dried dichloromethane (DCM) was refluxed for at least 2 h and freshly distilled over CaH$_2$, and was added to the dried silica. The resulting slurry was vigorously mixed to achieve a homogeneous mixture. A solution of SiCl$_4$ in DCM (1 M, 5 mL, Sigma Aldrich) was added via dry syringe to the silica slurry, and the resulting cloudy solution was allowed to stir for at least 12 h. Residual DCM was subsequently evaporated under vacuum (for at least 4 h) at 65 °C.

Grafting (Step 2). To prevent any possible degradation of the dissolved β-Glu strands due to HCl released upon reaction of β-Glu R-OH group with surface Si-Cl groups, grafting was performed in an ice bath. 20 mL of the 1.5% wt cellulose solution in LiCl/DMAc was transferred via dry syringe into the dried chlorinated silica and sonicated for 1 h in ice cold water and subsequently stirred for at least 12 h.

Redispersing and Washing (Step 3). The final synthesis slurry was extensively washed with four different solvents, using the following wash sequence, which was repeated twice for each solvent. The wash sequence consisted of: (i) centrifugation to recover solids, (ii) resuspension of solids in a solvent by vortexing at 3000 rpm for 5 min, and, finally, (iii) stirring for an additional equilibrating period of 12 h. This sequence was repeated using the solvent series: (i) 20 mL of
fresh LiCl/DMAc, (ii) 20 mL fresh DMAc, (iii) 20 mL methanol, and (iv) 20 mL water (doubly distilled and deionized). The final washed material was dried under vacuum at 120 °C overnight.

**Figure S1** Synthesis procedure for grafted cellulose on silica material.
**Characterization**

*Thermal gravimetric Analysis (TGA).* Measurement was performed on a Netzsch 449C Jupiter TGA equipped with a QMS 403 Aëolos quadrapole mass spectrometer (MS). A carrier gas of 20% O₂ and 80% argon was used, and volatiles were sent through a heated (300 °C) fused silica capillary. Approximately 3 mg – 10 mg of sample was placed in an aluminum oxide crucible and was allowed to equilibrate at RT for 30 min prior to measurement. The temperature program consisted of: (i) heating to 40 °C and holding for 30 min and (ii) heating at 5 °C/min up to a final temperature of 800 °C. Results were analyzed using Proteus thermal analysis software.

*N₂ Physisorption.* BET specific surface areas were calculated directly from nitrogen adsorption-desorption isotherms, which were measured at 77 K on a Micrometrics ASAP 2020 instrument. All samples were degassed at 105 °C for 4 h prior to analysis.

*NMR Spectroscopy.* Solid-state ¹³C CP/MAS NMR spectra were obtained using a Bruker DSX-500 spectrometer and a 4 mm Bruker CPMAS probe. Powder samples (~80 mg) were packed in ZrO2 rotors and were spun at 8 kHz. Typical CP contact time was 1 ms and signal was averaged with a recycle delay time of 6 sec. The chemical shift was referenced to TMS.

*Catalysis Procedure.* Catalysis experiments involving β-Glu hydrolysis were conducted in a batch reactor (model 8648, 9 mL, Ace Glass) at 105 °C, under autogeneous pressure. The individual masses of SGH and SGL materials were chosen such that the amount of grafted β-Glu in each catalysis experiment was 3.5 mg. Materials were dispersed in 3 g of pH 4 aqueous solution, consisting of dilute HCl (37%, ACS reagent Sigma). Samples were stirred at room temperature at 350 rpm for 12 h prior to the start of reaction. The first sample was taken after the initial stirring at room temperature, and remaining samples were taken by temporarily cooling the tubes to reduce pressure prior to sampling. Approximately 150 μL of the reaction solution
was withdrawn for analysis. Samples were centrifuged for 15 min to remove solids before soluble \( \beta \)-Glu fragments were analyzed by High Pressure Liquid Chromatography (HPLC) at 4 \( ^\circ \)C on a Dionex HPAEC-PAD system Model ICS-3000 (High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection).

**Supplementary Discussion and Results**

*Thermal Gravimetric Analysis.* Figure S2(B) represents thermal gravimetric analysis data for as-made materials. This data yields (4.5 ± 0.03) % wt and (7.7 ± 0.03) % wt of grafted \( \beta \)-Glu strands for materials SGL and SGH, respectively. The surface coverages in Table 1 were calculated from these mass loss percentages by normalizing to the measured surface area and cellobiose molecular mass. The lack of any significant mass loss for SG0 means that the series of intensive washes removes all weakly (physically) adsorbed \( \beta \)-Glu strands from the surface of the silica, and demonstrates that activation of the silica surface via chlorination is required for \( \beta \)-Glu grafting. The square root of the reciprocal \( \beta \)-Glu surface coverage represents the average distance between two adjacent cellobiose groups. These values ((1.50 ± 0.02) nm for SGL and (1.10 ± 0.02) nm for SGH) are useful to compare to 0.78 nm and 1.034 nm, the unit cell dimension of crystalline cellulose (polymorph I) and the distance between cellobiose repeat units on a single strand, respectively.\(^9\)
Figure S2 Thermal gravimetric analysis of as made materials. Analysis was performed using a 20% oxygen/argon mixture and at 5 °C/min for: SG0, SGL and SGH.
Calculation of coverages, packing density, and respective error values as appearing in the manuscript are detailed as followed.

To calculate coverages of $\beta$-Glu strands on the surface of Cab-o-sil, equation 1 was used where $m_{\text{cellulose}}$ and $m_{\text{SiO}_2}$ are defined as the mass of cellulose and silica in the sample, respectively. Masses were measured using thermal gravimetric analysis as discussed above. Available silica surface area per gram of silica, denoted as $S$, was taken from the BET surface area measured for the respective control material, which was synthesized under identical conditions except in the absence of cellulose.

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(1) \quad \text{Cellobiose Coverage} = C = \frac{m_{\text{cellulose}}}{m_{\text{SiO}_2} \times S} = \frac{m_r}{m \times S}
\]

Packing density is calculated according to equation 2. As a basis, the magnitude of the cellobiose footprint for a close-packed solid, denoted as $A_{\text{cellobiose}}$, was taken from the crystal structure of cellulose. Such a procedure can be used to demonstrate random, irreversible adsorption corresponding to a packing density of 0.49 when analyzing surface coverages for grafted calixarene-Ti$^{IV}$ sites,\textsuperscript{10} by taking the footprint to be $1.4 \text{ nm} \times 1.4 \text{ nm}$ and using the measured grafting density of 0.25 calixarene per nm$^2$.\textsuperscript{10}

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(2) \quad \text{Packing Density} = A_{\text{cellobiose}} \times C = (1.034 \times 0.78) \times C_{CEL}
\]

Error values for cellobiose coverages and adjacent cellobiose distances were calculated by using a 3% error with respect to both physisorption and thermal gravimetric analysis results. Error values were calculated according to the standard method for calculating absolute errors, as detailed in equations 3 for a specific case.
The parametric representation allows a rapid assessment of the effect of environment on amount of $\beta$-Glu strand hydrolysis by quantifying how much more of a particular $\beta$-Glu fragment is released for each retention time (representing a particular $\beta$-Glu fragment). Normalized peak heights relative to the amorphous cellulose control vary between 0-fold to 25-fold for SGH while for SGL values vary between 5-fold to 150-fold.

Figure S3 Parametric plot of relative amount of soluble poly(1→4-$\beta$-glucan) fragments after 5 h hydrolysis at 105 °C and pH 4 for SGH and SGL plotted against the values extracted for amorphous cellulose.
References