Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting information

Efficiency of superacid HF/SbF_5 for the selective decrystallization/depolymerization of cellulose to glucose

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Chemicals:
MCC PH AVICEL 101, 102, 105 and 200 were kindly provided by FMC BIOPOLYMERS. Granular cellulose was purchased to sigma Aldrich.

Optimized experimental procedure:
In the optimized experiment, 0.4g of cellulose was stirred with 3mL of HF at 20°C for 30 min in a sealed Teflon® flask. Then SbF_5 (1 mL) was added to the reaction medium, and the reaction was maintained under stirring for 10 min at 0 °C. The hydrolysis was obtained by the addition of 20 mL of water and the stirring was performed during 10 min at 0°C. After the hydrolysis, 40 g of amberlyst A26 -OH was added to neutralize the solution. After filtration to remove the resin and distillation of water under vacuum the products were analyzed by GPC and HPLC chromatography.

Analytical methods:
Low-temperature ^1H NMR spectra were recorded at -20 °C in a Teflon® NMR tube on a 400 MHz Bruker Advance DPX spectrometer using HF/SbF_5 as solvent and CD_3COCD_3 as external reference.

SEC analyses were performed on a Shimadzu Prominence LC equipped with a degasser DGU-20A3, a pump system (LC-20AQ), a thermostated autosamplor SIL-20AC (samples were maintained at 15°C) and an oven CTO-20AC maintained at 40°C. Oligo- and fructooligosaccharides were separated on a Shodex KS-802 column, using water as eluent, and quantified by a refractor indice detector. Note that external calibration of the LC was performed using fructose, glucose, cellobiose, cellotriose, cellotetraose,cellopentose and cellohexose as standard.
Glucose was analyzed on a Shimadzu HPLC equipped with a pump system (LC-20AD), an autosamplor SIL-10A and a controller CBM 20A. Products were separated on a Varian 100-5 amino S 250 x 4.6 mm (NH2) column using a mixture water/acetonitrile (2/8) as eluent, a flow rate of 0.8 mL/min and quantified by a refractor indice detector (Waters 2410). External calibration of the LC was performed using standards of glucose.

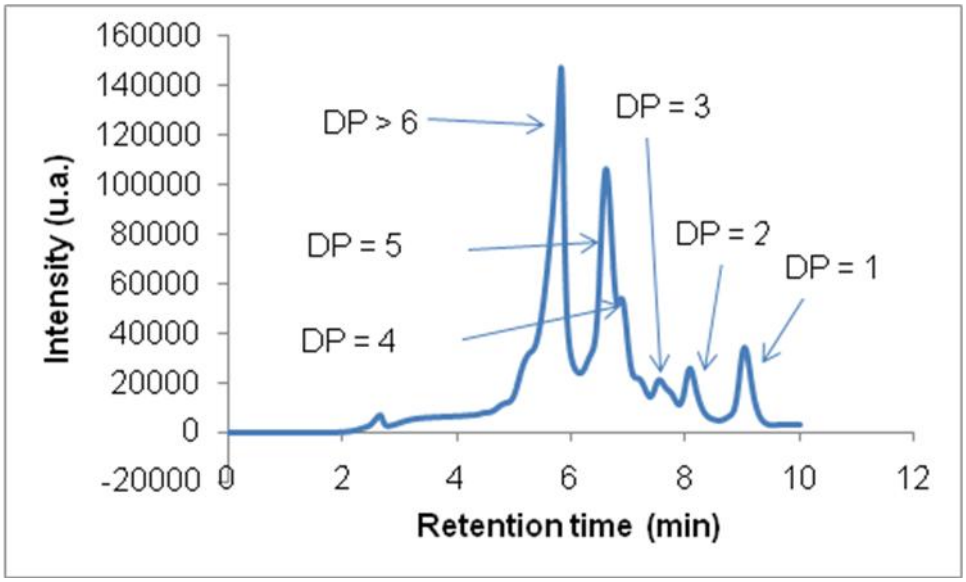

Figure S1 : GPC analysis of the solution after neutralization with resin Amberlyst A26-OH

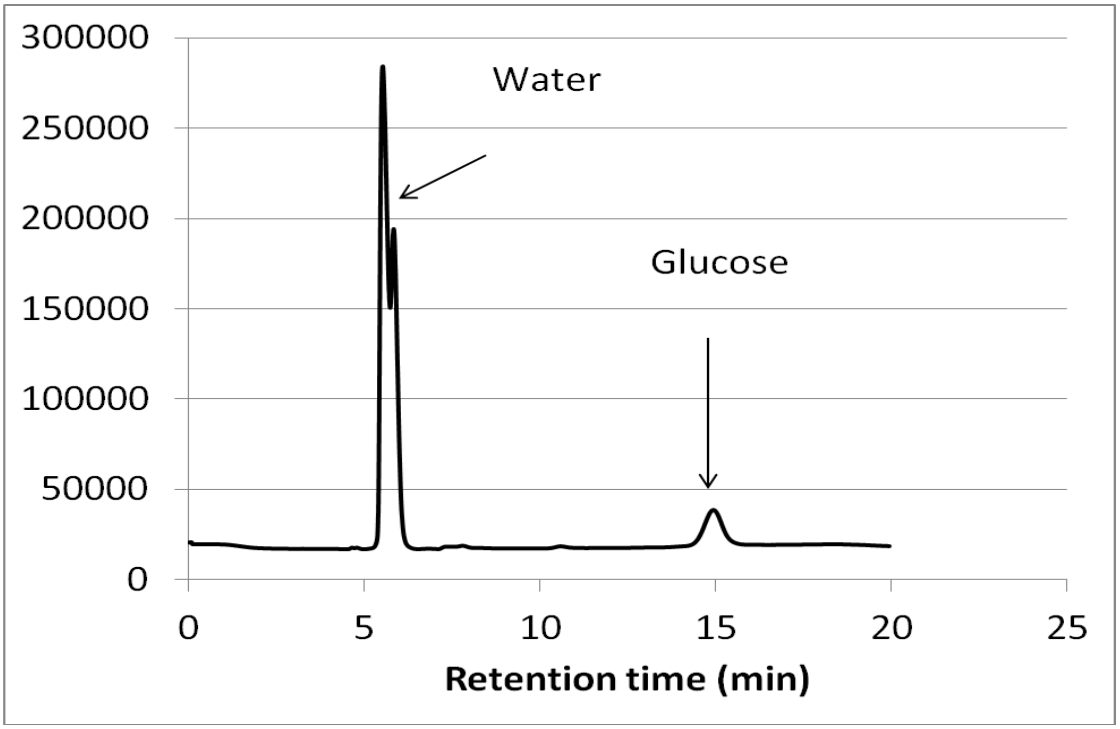

Figure S2 : HPLC analysis of the solution after neutralization with resin Amberlyst A26-OH

XRD analysis:

A blank was first realized by mixing HF and water. Then NaOH was added to obtain the neutralized crude. After, the same procedure was performed in the presence of cellulose. The XRD shows that all the cellulose was decrystallized after this reaction. The same reaction was performed in CF_3SO_3H.

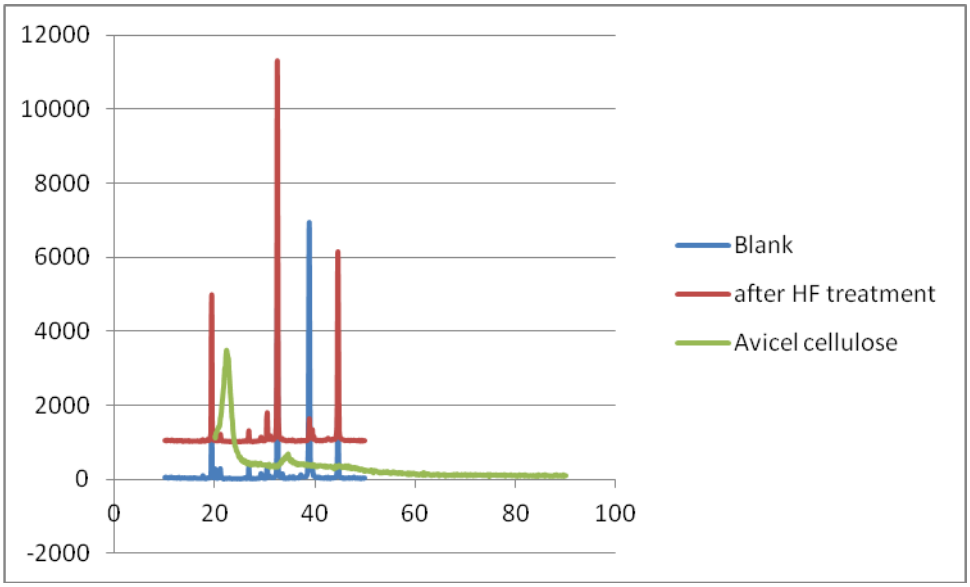

Figure S3 : XRD analyses of the cellulose before and after HF treatment; Comparison with the blank without cellulose

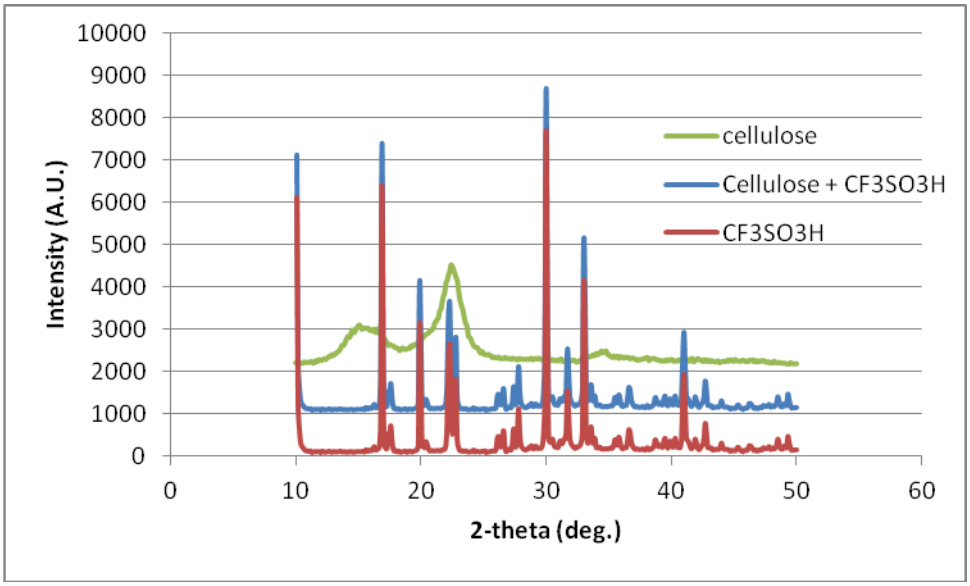

Figure S4 : XRD analyses of the cellulose before and after CF_3SO_3H treatment; Comparison with the blank without cellulose.

^{1}H NMR analysis :

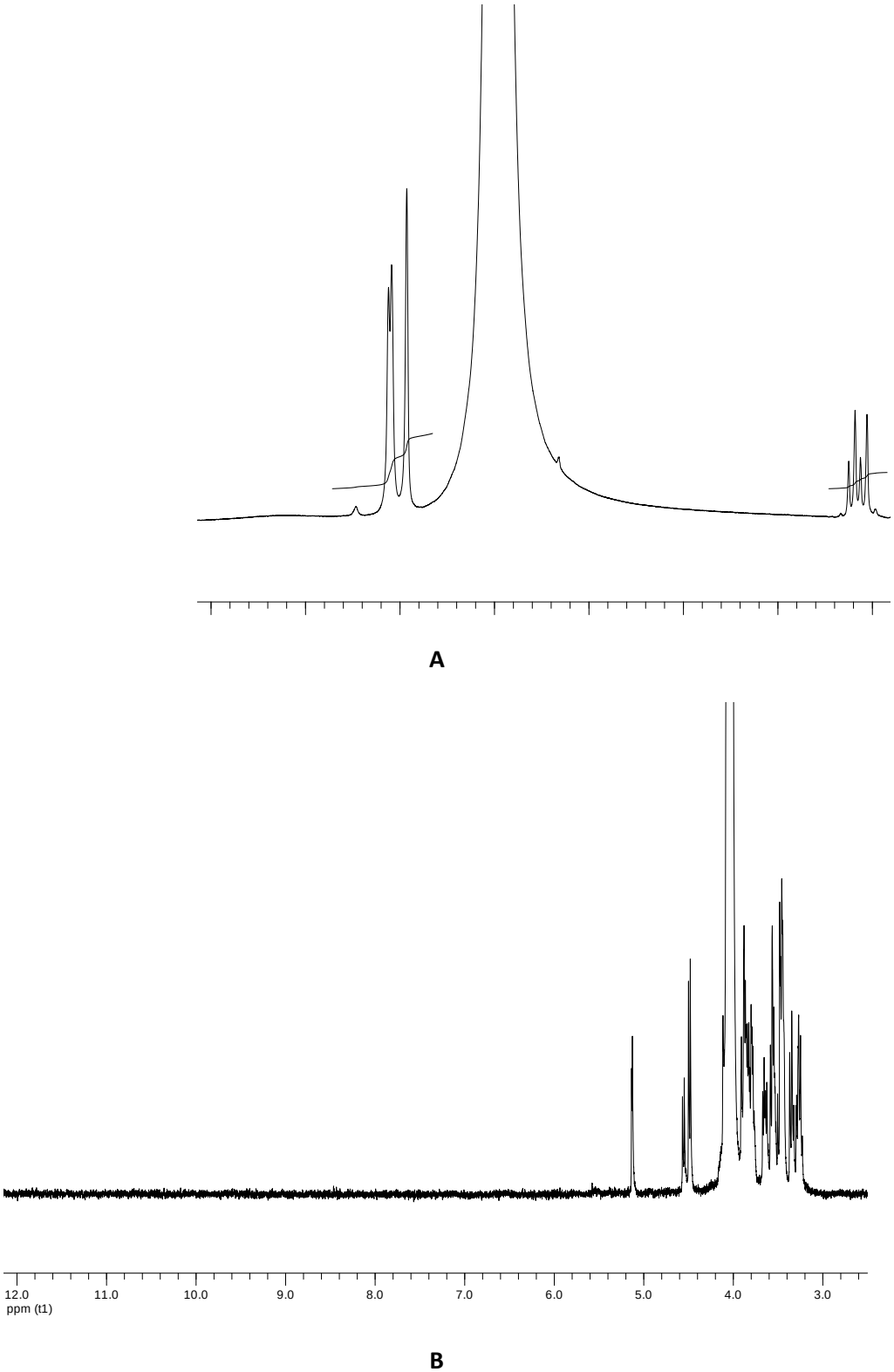

Figure S5 : Low-temperature ^{1}H NMR spectrum of (poly)protonated cellobiose in superacid HF/SbF_5 (A) compared to cellobiose ^{1}H NMR spectrum (B).