Base-free trifluoroacetylation: From methyl glucopyranoside to cellulose nanofibers

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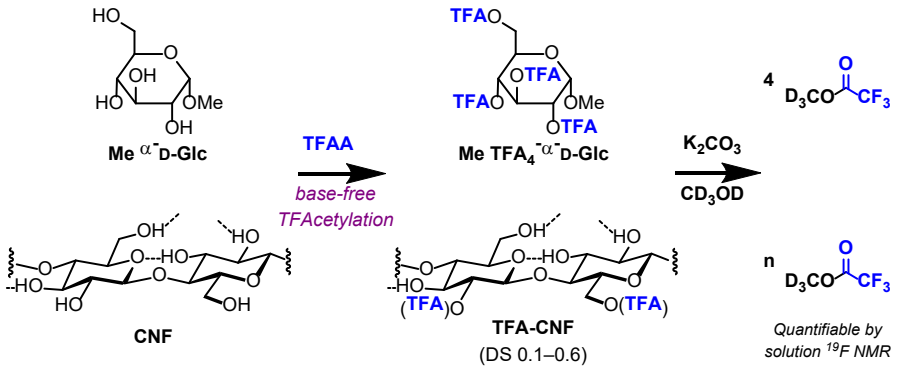
Abstract

Trifluoroacetic anhydride (TFAA) reacts smoothly with low molecular weight carbohydrates and cellulose nanofibers (CNFs) under base-free conditions. Methyl α-D-glucopyranoside was used as a model compound to optimize reaction conditions, which were then applied to lyophilized CNFs for surface modification. ATR-IR spectroscopy and powder X-ray diffraction were employed to characterize the modified CNFs. Trifluoroacetylation for 4 h yields a degree of substitution (DS) of 0.4 acyl groups per anhydroglucose unit while maintaining a crystallinity index near 50%. DS values were quantified by gravimetry, acid–base titration after saponification, and a novel approach utilizing solution ^{19}F NMR spectroscopy which offers greater accuracy than the other techniques. This study presents an efficient, base-free method for derivatizing carbohydrates as well as surface functionalization of CNFs with trifluoroacetyl groups, potentially expanding their application in fiber-reinforced thermoplastic composites.

Graphical Abstract



Keywords: Cellulose nanofibers, ^{19}F NMR spectroscopy, Glucopyranoside, Surface Functionalization, Trifluoroacetic

1. Introduction

Trifluoroacetylation is a valuable method of derivatizing carbohydrates and polysaccharides with application toward chromatography,[1,2,3,4,5] spectroscopic analysis,[6,7,8,9,10,11] and natural products characterization.[12,13,14,15] The trifluoroacetyl (TFA) group improves the volatility of saccharides which facilitates their separation and analysis and also provides spectroscopic handles for ^{19}F NMR spectroscopy,[6,7] and its strong electron-withdrawing nature is useful for ^{1}H NMR analysis of ring protons.[8,11–14] TFA esters are hydrophobic yet hydrolytically labile which engenders their use as protecting groups[16] or as auxiliaries for stereocontrolled glycosylation.[17,18]

TFA esters are typically prepared using trifluoroacetic anhydride (TFAA), a volatile colorless liquid with a boiling point of 40 °C, in combination with a mild base such as pyridine[15,19,20] or sodium trifluoroacetate.[1,17,20] Other methods include Fischer esterification with trifluoroacetic acid (TFA-OH)[21,22] and *N*-methylbis(trifluoroacetamide) in pyridine,[3,11,16] although the latter is more costly and requires heating. Trifluoroacetylation can also be achieved in high yields using TFAA without additional acid or base;[8,9,12–14] it can be argued that generation of TFA-OH as a byproduct makes such processes autocatalytic. This is advantageous for preserving TFA esters, which are highly sensitive to hydrolytic cleavage in the presence of weak base and even neutral protic solvents.[23]

TFAA has been used to derivatize cellulose which has long been recognized as a promising biorenewable feedstock for producing thermoplastic composites. Chemically modified cellulose has great potential to reduce the carbon footprint of petroleum-derived thermoplastics, however the intrinsic green qualities of cellulose can be compromised by process chemistry and the generation of non-recyclable waste. In this regard, trifluoroacetylation is a curious choice for cellulose modification. At first glance, this appears to step away from sustainable chemistry, as the negative impact of perfluoroalkylated (PFA) pollutants has raised safety concerns on the use of fluorochemicals in manufacturing. However, closed-loop processes that employ TFA-OH and TFAA may be practical from a process chemistry vantage: Both chemicals are volatile (bp 72 and 40 °C respectively) and can be recovered in an energy-efficient manner, and TFA-OH can be regenerated into TFAA by reactive distillation from dehydrative agents with reduced environmental impact.[24,25] Furthermore, unlike other PFAs, there is little evidence for the bioaccumulation of TFA in living organisms, and recent assessments confirm a low health

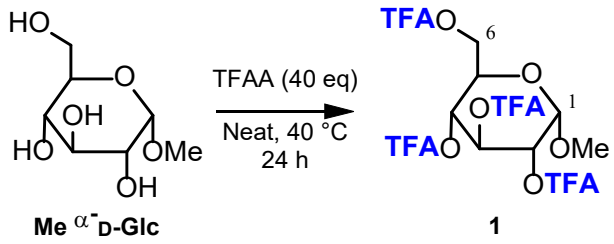
risk.[26,27] Thirdly, earlier studies indicate that the polysaccharide chains in cellulose are mostly compatible with trifluoroacetylation conditions. For example, Liebert et al. utilized TFAA/TFA-OH acid mixtures to achieve high degrees of substitution (DS) on cellulose from microcrystalline forms with a net depolymerization of 3% in the absence of water.[22] This process chemistry is in active use for converting cellulose and second-generation biowaste into functional materials.[28,29,30]

Efforts to produce biorenewable thermoplastics have gravitated toward nanostructured forms of cellulose, namely nanocrystals and nanofibers.[31] Cellulose nanofibers (CNFs) exhibit high tensile strength and a low weight fraction can significantly enhance the mechanical and barrier properties of a thermoplastic composite.[32] However, surface modification of CNFs is needed to improve their dispersion and blending in hydrophobic matrices. We have recently developed a practical approach for lyophilizing CNFs from an aqueous *tert*-butanol slurry, followed by esterification with fatty acids to enable their dispersion in nonpolar media.[33] In this study we evaluate base-free trifluoroacetylation of lyophilized CNFs with control over degree of substitution (DS) and retention of crystallinity, and introduce a novel method to quantify DS based on ^{19}F solution NMR spectroscopy of saponified TFA-CNFs in methanol-d_4.

2. Results and Discussion

*2.1 Base-free synthesis of methyl 2,3,4,6-tetra-O-trifluoroacetyl-α-D-glucopyranoside (**1**).*

We first confirmed the compatibility of glycosidic bonds with base-free trifluoroacetylation using methyl α-D-glucopyranoside as a substrate. The synthesis of **1** has been reported multiple times although its spectroscopic characterization is sporadic,[1,4,6,7,34,35] suggesting challenges in isolating **1** in analytically pure form. After surveying multiple conditions, we determined that reactions with TFAA in the presence of a base or acid scavenger could not produce **1** without spectroscopic impurities, whereas treatment with neat TFAA at 40 °C followed by concentration cleanly produced **1** without decomposition (**Scheme 1**). Auxiliary solvents were unnecessary, however dry nonpolar solvents were also compatible with base-free trifluoroacetylation. The purity of **1** post reaction (without workup) was verified by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy in dry $CDCl_3$ and by GC/MS (**Figures 1**, **S1**–**S4**), which were also in accord with previous reports.[6,7,35]



Scheme 1. Base-free synthesis of methyl 2,3,4,6-tetra-*O*-trifluoroacetyl-α-glucopyranoside (**1**).

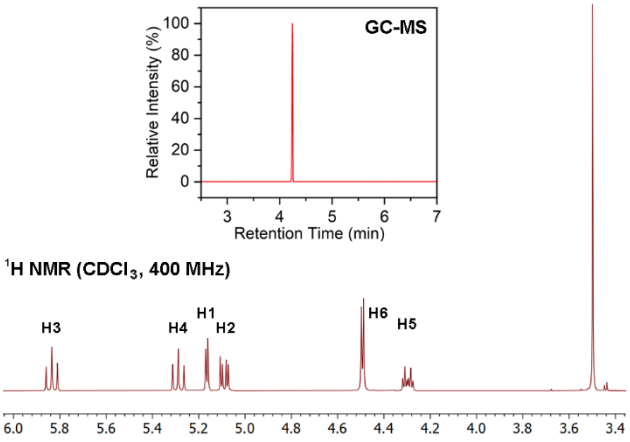


Figure 1. Post-reaction purity of peracylated glucoside **1** established by ^{1}H NMR spectroscopy and GC/MS (inset).

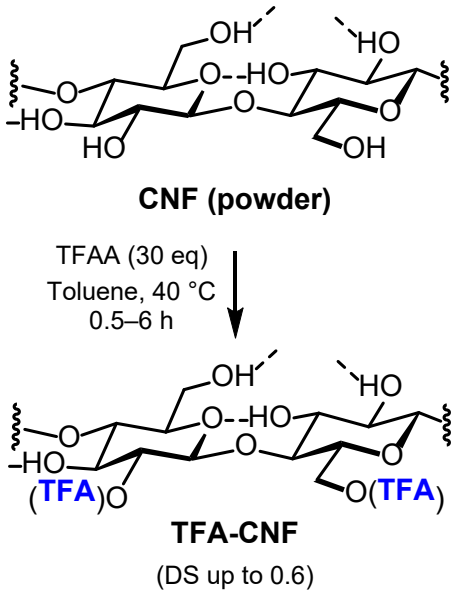
2.2 Preparation and characterization of trifluoroacetylated cellulose nanofibers.

The clean conversion of methyl α-D-glucopyranoside into **1** encouraged us to apply similar conditions toward the surface functionalization of CNFs derived from wood pulp (**Scheme 2**). Dry CNF powder was prepared by lyophilization of a frozen aqueous CNF slurry containing 10 wt% *tert*-butyl alcohol (TBA) as previously described.[33] The aqueous TBA mixture forms a eutectic that suppresses ice crystallization upon freezing and preserves the ultrafine CNF structure during lyophilization to yield a porous aerogel, which is then ground into a powder and dried under P_2O_5. Unlike the synthesis of **1** however, we found auxiliary solvent to be helpful as dispersion in neat TFAA caused the CNF suspensions to swell and interfere with magnetic stirring. Dispersing CNF in dry toluene prior to treatment with freshly distilled TFAA at 40 °C reduced swelling and provided good control over surface chemistry, with DS values increasing over time (**Table 1**).[19] TFA-CNF was collected by washing the solid with anhydrous ethyl acetate

to displace residual acid and toluene prior to drying under vacuum. Gravimetric analysis yielded DS values based on Equation 1:

$$DS_{Grav} = \frac{162 * (m_F - m_I)}{97 * m_I} \quad (1)$$

where 162 and 97 are the formula weights of anhydroglucose ($C_6H_{10}O_5$) and trifluoroacetyl (CF_3CO), and m_I and m_F are the initial and final dry masses of CNF and TFA-CNF. The DS values reported in Table 1 represent the median of multiple reactions; we note that reproducibility is affected by the dryness of the CNF and presence of TFA during treatment.



Scheme 2. Trifluoroacetylation of lyophilized CNF in TFAA/toluene with variable DS.

Table 1. Degree of substitution (DS) and crystallinity index (CI) values for TFA-CNF samples

Sample[a]	DS[b]	CI (%)[c]
CNF (lyophilized)	0	75
TFA-CNF (2 h)	0.27	59
TFA-CNF (4 h)	0.43	49
TFA-CNF (6 h)	0.60	31

[a] Based on conditions in Scheme 2. [b] Median value from multiple experiments. [c] From PXRD analysis (Fig. 2b).

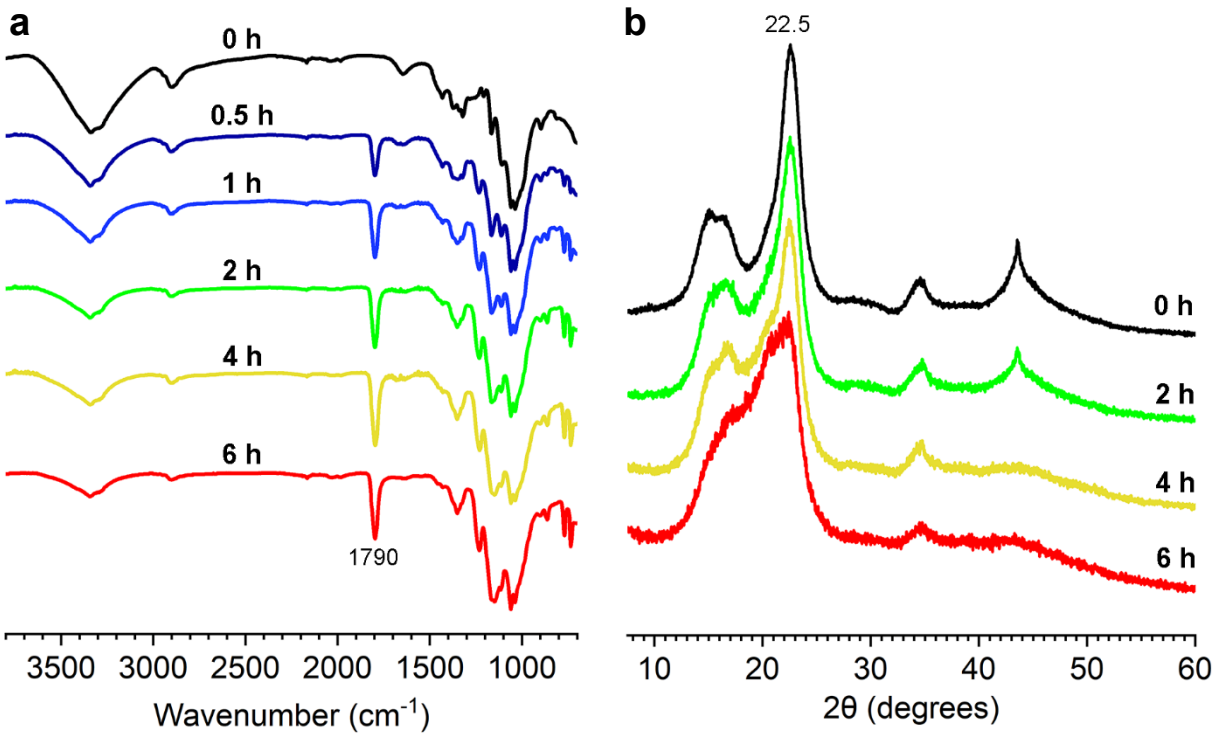


Figure 2. (a) ATR-IR spectra of CNFs treated in TFAA/toluene (0–6 h); (b) PXRD for evaluating crystallinity index (CI) of TFA-CNF samples.

As expected, the increase in DS over time correlated with the strength of the TFA carbonyl stretching frequency ($\nu_{C=O}$) obtained by attenuated total reflectance infrared spectroscopy (ATR–IR), appearing as a sharp peak at 1790 cm^{-1} (**Figure 2a**). To determine the extent to which TFAA/toluene affected CNF crystallinity, powder x-ray diffraction (PXRD) was used to evaluate changes in TFA-CNF structure based on the (002) reflection of cellulose (2θ peak at 22.5°; **Figure 2b**).[36] The crystallinity index (CI) was calculated by Segal's method as expressed in Equation 2:

$$CI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \qquad (2)$$

where I_{200} is the normalized intensity of the peak near 22.5° and I_{am} is the intensity of the relative minimum at 18–19° representing amorphous cellulose.[37] CI values declined steadily from an initial value of 75% to almost 50% within 4 hours (**Table 1**); by 6 hours, the amorphous fraction was significant enough to mask secondary reflection peaks. CNFs contain both crystalline and

amorphous regions with the latter reacting more quickly with TFAA; as trifluoroacetylation progresses, defibrillation (disentanglement) of the amorphous segments promotes the unbundling of closely packed CNFs which accelerates the dissolution of crystalline cellulose.[38] The crystalline domains in cellulose are chiefly responsible for improving the barrier properties of CNF-reinforced composites, particularly those being developed for disposable packaging.[39,40] For such applications, a high content of crystalline cellulose (CI $\geq$ 50%) can be retained by limiting TFAA treatment to four hours or less.

2.3 Quantifying degree of substitution by ^{19}F solution NMR spectroscopy.

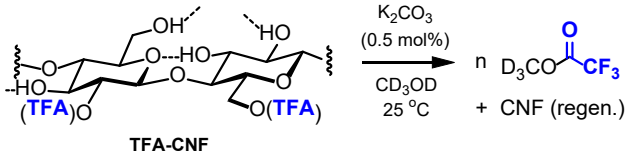
Methods for quantifying DS on CNFs are essentially the same as those used for cellulose polysaccharide. Gravimetry, the most common and traditional method, simply involves a mass difference before and after chemical derivatization (Eq. 1), however this approach has relatively high uncertainty and is susceptible to external sources of error (**Table S1**). The DS of esterified CNFs can also be measured by saponification with acid–base titration, and parameterized methods based on IR spectroscopy have been reported.[41,42] All of these are limited to bulk DS values and cannot distinguish functionalization of CNF surfaces from the interior of amorphous segments. In this regard, ^{13}C solid-state NMR spectroscopy with magic-angle spinning and dynamic nuclear polarization (MAS-DNP) arguably has the greatest potential and sensitivity for a true estimate of ligand density on CNF surfaces,[43,44] however it is a specialized technique with limited availability.

The moisture sensitivity of TFA-CNFs creates challenges for accurate gravimetry and requires extra attention to anhydrous conditions during mass analysis. To circumvent this source of error, we developed an in situ variant of the saponification method with quantitation by ^{19}F solution NMR spectroscopy. Labile TFA groups can be saponified quantitatively in methanol-d_4, enabling NMR analysis of the corresponding methyl-d_3 ester. The workflow is straightforward and obviates the need to obtain mass differences, relying instead on molar quantities measured from ^{19}F NMR signals.

In situ TFA methanolysis was tested with glucoside **1**, which was dissolved in CD_3OD with a catalytic amount of K_2CO_3 plus one molar equivalent of α,α,α-trifluorotoluene as an internal standard (TFT; δ –63.72 ppm). The ^{19}F NMR spectrum of the reaction mixture after 10 min

revealed a single peak at –76.42 ppm indicating full conversion to methyl-d_3 trifluoroacetate (CD_3OTFA), and peak integration of the ^{19}F NMR signals confirmed a 4:1 ratio of CD_3OTFA to TFT (**Figure S5**). We note that in the presence of adventitious moisture a minor upfield signal in the ^{19}F NMR spectrum may be observed that presumably belongs to TFA-OH, however the peak is transient and only the CD_3OTFA signal is sustained. ^1H NMR analysis also confirmed complete deacylation by the regeneration of methyl α-D-glucopyranoside (**Figure S6**).

Methanolysis of TFA-CNF was carried out in a similar fashion (**Scheme 3**) with an added centrifugation step to separate the liquid phase for ^{19}F NMR analysis (**Figure 3a**). Again, a single ^{19}F NMR peak for CD_3OTFA at –76.42 ppm indicates complete transesterification, which was confirmed by the absence of $\nu_{C=O}$ stretching in ATR-IR analysis of the CNF byproduct (**Figure 3b**). Transesterification was complete within minutes; the CNFs also experienced proton–deuterium exchange with CD_3OD, with ν_{C-D} stretching observed at ~2500 cm^{-1}. Again, DS could be obtained simply by ratiometric analysis of the ^{19}F NMR peak integration using a standard curve to establish a linear relationship (**Figure S7**). A slope of 0.94 was obtained, which may be attributed to the ^{19}F nuclei in TFT and CD_3OTFA having slightly different relaxation times.



Scheme 3. Methanolysis of TFA-CNF.

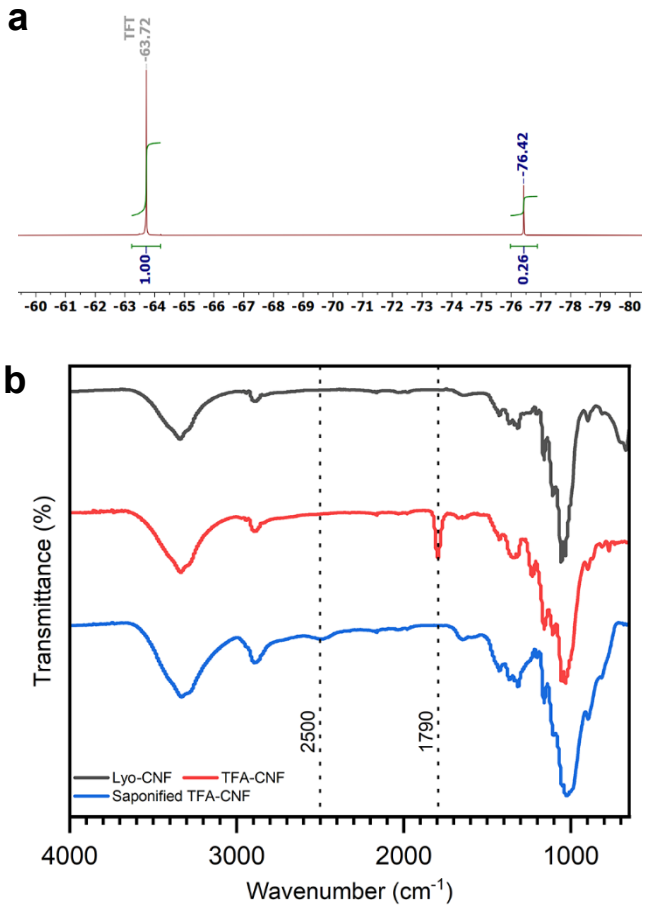


Figure 3. (a) ^{19}F NMR spectrum of CD_3OTFA with TFT as an internal standard. (b) ATR-IR spectra of CNF and TFA-CNF before and after in situ methanolysis with CD_3OD.

The ratiometric analysis of CD_3OTFA signals was further vetted by comparing degree of substitution values by gravimetry (DS_{grav}), ^{19}F NMR spectroscopy (DS_{F19}), and acid–base titration (DS_{titr}; **Table 2**). Several TFA-CNF samples with DS_{grav} values between 0.1 and 0.4 were used for comparison; acid–base titrations were performed twice in accordance with ASTM D871-96,[4242] and ^{19}F NMR analysis was performed in quadruplicate. The DS_{F19} values are very similar to DS_{grav} values whereas DS_{titr} values correlate poorly with either method, which we attribute to loss of TFA by evaporation during solution processing. The DS_{F19} values are more accurate than DS_{grav} values, which are based on single measurements and are prone to systematic error from moisture absorption. Adventitious moisture does not interfere with ^{19}F NMR analysis, and replicate trials can be performed with a low standard deviation (**Table S2**). The compact

workflow of the ^{19}F NMR-based method ensures that no material is lost during saponification, and that the signals are specific for CD_3OTFA.

Table 2. Comparison of DS values for TFA-CNF samples from three different methods

Sample	DS_{grav}[a]	DS_{F19}[b]	DS_{titr}[c]
A	0.09	0.11	0.04
B	0.16	0.17	0.05
C	0.23	0.21	0.17
D	0.31	0.27	--
E	0.38	0.32	--

[a] Based on Eq, 1; uncertainty = 0.017. [b] Based on Eq. S1–S4; mean values (*N*=4); stdev = 0.00–0.02; uncertainty = 0.026–0.037; [c] Based on Eq. S5–S6; mean values (*N*=2); stdev = 0.02–0.06.

3. Conclusions

This study demonstrates the efficacy of base-free trifluoroacetylation using TFAA as a mild yet efficient method for derivatizing both glycosides and lyophilized CNFs while preserving glycosyl bonds. TFA-CNFs were functionalized with controlled increases in DS over time, albeit with tradeoffs in cellulose crystallinity. A key contribution is the development of a method for quantifying DS based on in situ methanolysis and solution ^{19}F NMR spectroscopy, with improved accuracy over gravimetric and acid–base titration methods. Preliminary studies suggest that TFA-CNFs exhibit appreciable miscibility in several aprotic solvents, which is promising for their integration into biodegradable polymers for fiber-reinforced thermoplastic composites. Future studies should focus on scalable process chemistry and the tradeoffs between DS and crystallinity in the performance of CNF-based composites for packaging, biomedical devices, and other single-use applications where biodegradable alternatives to petroleum-based plastics are increasingly sought after.

4. Experimental Details

4.1. Materials and analytical methods

Cellulose nanofiber (CNF) pulp was obtained as a 3% slurry (100% fines) from University of Maine and converted into powder form (see Sec. 4.3) and stored in a desiccator with $CaSO_4$.

Methyl α-D-glucopyranoside and trifluoroacetic anhydride (TFAA) were obtained from Sigma–Aldrich and dried *in vacuo* or distilled over P_2O_5. Toluene and dichloromethane were received from Fisher Scientific and distilled over CaH_2. Anhydrous HPLC-grade ethyl acetate was received from Fisher Scientific and used without purification. Methanol-d_4 was supplied by Cambridge Isotope Laboratories in 0.75-mL ampules and used as received. Trifluorotoluene (TFT) was obtained from Thermo Scientific and used as received.

NMR spectra (^{1}H, ^{13}C, and ^{19}F) were acquired using a Bruker AV-III-400-HD instrument equipped with a 5 mm BBFO Z-gradient SmartProbe. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained in 8, 64, and 16 scans, respectively. Chemical shifts were referenced to $CHCl_3$ at δ_H 7.26 ppm, $CDCl_3$ at δ_C 77.16 ppm, and TFT at δ_F –63.72 ppm. Powder X-ray diffraction (PXRD) patterns were obtained using a Panalytical Empyrean powder X-ray diffractometer equipped with a high-speed PIXcel 3D Medipix detector. PXRD curves were smoothed using the Savitzky-Golay filter with a window size of 40 data points in OriginPro. ATR-IR spectra were acquired using a Thermo Nicolet 6700 FT-IR Spectrophotometer. GC-MS data were obtained using a Shimadzu GC-2010/MS-QP2010 instrument equipped with a single quadrupole EI mass spectrometer detector used in positive mode.

*4.2. Synthesis of Methyl 2,3,4,6-Tetra-O-trifluoroacetyl-α-glucopyranoside (**1**)*

Methyl α-D-glucopyranoside (0.35 g; 1.80 mmol) was added to a dry 50-mL round-bottomed flask, then charged with TFAA (10.02 mL; 72.10 mmol). The mixture was stirred at 40 °C for 24 h under an Ar atmosphere with a reflux condenser. The glucopyranoside gradually dissolved, indicating the substitution of the hydroxyl groups. After 24 h, the flask was removed from heat. Unreacted TFAA and TFA-OH byproduct were removed using a rotary evaporator and azeotroped thrice with dry dichloromethane. The product was placed under high vacuum to remove residual solvent, resulting in a clear, colorless syrup (1.03 g; 1.78 mmol, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 (t, *J* 9.8 Hz, 1H), 5.29 (t, *J* 9.8 Hz, 1H); 5.17 (d, *J* 3.6 Hz, 1H); 5.09 (dd, *J* 10.1, 3.6 Hz, 1H), 4.50 (d, *J* 3.8 Hz, 2H), 4.30 (dt, *J* 10.1, 3.6 Hz, 1H), 3.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.25, 156.82, 156.77, 156.57, 156.53, 156.33, 156.09, 118.43, 115.87, 115.60, 113.03, 112.77, 109.94, 95.90, 73.08, 72.34, 71.18, 66.09, 64.34, 56.50. ^{19}F NMR (376 MHz, $CDCl_3$): δ –75.83 (s), –75.93 (s), –75.99 (s), –76.25 (s). EI-MS: *m/z* 405 $[M–(OTFA)_2]^+$, 465 $[M–OTFA]^+$, 547 $[M–OCH_3]^+$.

4.3. Trifluoroacetylation of Cellulose Nanofibers

Lyophilized CNFs were prepared from an aqueous slurry containing 10 wt% *tert*-butyl alcohol according to our previously published procedure.[33] Anhydrous CNF (1.0 g, 6.17 mmol) was added into an oven-dried 100 mL round-bottomed flask that was tared for gravimetric analysis. In a typical reaction, dry toluene (20 mL) and freshly distilled TFAA (25.7 mL; 185.03 mmol) were added to the flask equipped with a large stirbar and condenser, with gentle stirring at 40 °C for 2 h under Ar atmosphere. The solid was removed from heat and recovered via vacuum filtration using a finely meshed fritted funnel under a nitrogen blanket. The solid was washed with 100 mL of anhydrous ethyl acetate then dried *in vacuo*. The final product was a clumped, white powder that could be loosened easily with a spatula. The range of DS values after a 2-hour reaction is 0.2–0.4, depending on the initial physical qualities of the powdered CNF.

4.4. Degree of Substitution Analysis by ^{19}F NMR spectroscopy (DS_{F19})

A 1.5-mL Eppendorf tube was tared on a high-precision balance (±0.05 mg). Approximately 50 mg of the TFA-CNF sample was added; an electrostatic gun was used on the sample and tube to minimize the impact of static electricity on solid transfer and weighing error. The tubes were centrifuged at 14,800 rpm for 1 min prior to the addition of methanol-d_4 (666.0 mg), TFT (20.0 mg), and K_2CO_3 (15.0 mg). The tube was capped, vortex mixed periodically for up to 1 h, then centrifuged at 14,800 rpm for 10 min. The supernatant was transferred into an NMR tube for solution ^{19}F NMR analysis. This procedure was repeated with replicate samples (N=4), resulting in DS_{F19} values with standard deviations at or below 0.02.

4.5. Degree of Substitution Analysis by Acid/Base Titration (DS_{titr})

This procedure was adapted from ASTM D871-96 with minor modifications,[42] using TFA-CNF dried overnight under P_2O_5. A 0.25-g sample was transferred into a 250-mL Erlenmeyer flask and suspended in 40 mL of a 75% EtOH solution; a replicate and blank sample were also prepared. The flasks were loosely capped and heated to 55 °C for 1 h to aid in swelling, then treated with 40 mL of a 0.5 M NaOH solution and heated again at 55 °C for 1 h. The alkaline mixtures were agitated on an orbital shaker at 25 °C for 48 h, then titrated with a 0.5 M HCl

solution using phenolphthalein as an indicator to achieve initial neutralization. An additional 1 mL of acid was added to neutralize residual NaOH gradually diffusing from the regenerated cellulose. The sample was kept at 25 °C for another 12 h then back-titrated with 0.5 M NaOH until a final endpoint was reached, which was used to calculate DS_{titr} (see Supplemental Information).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We gratefully acknowledge financial support from the U.S. National Science Foundation (CHE-2204206) and the National Institutes of Health (P30-CA023168).

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