International Conference on Nanotechnology for Renewable Materials

Surface Modification of Cellulose Nanofibers: Mechanochemical Esterification & Trifluoroacetylation

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PURDUE CHEMISTRY

TAPPI NANO DIVISION

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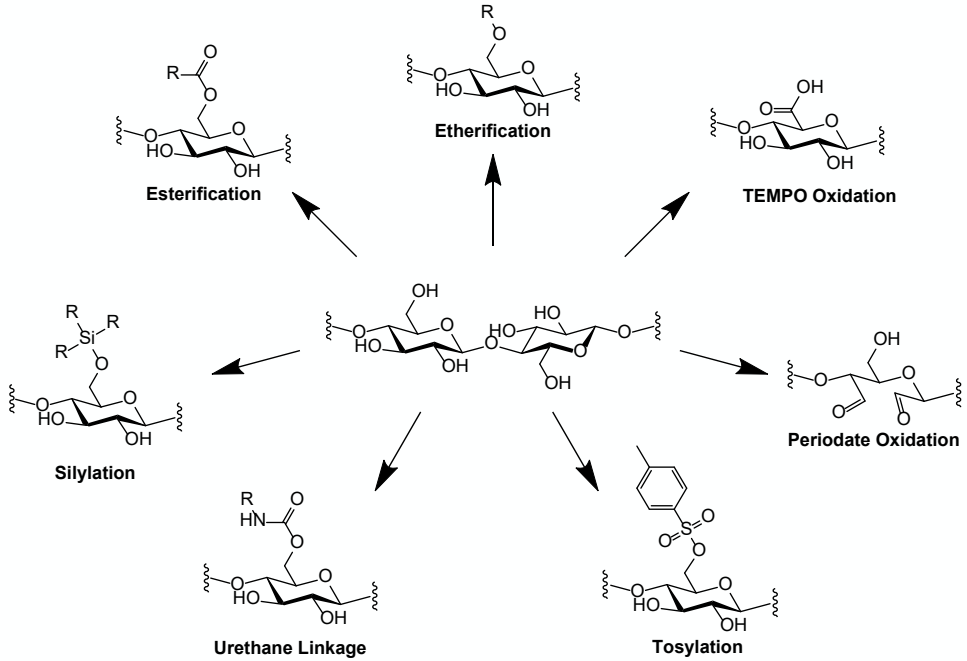
Cellulose Nanofibers (CNFs) are a Promising Scaffold for Functionalization

- Innovations in cellulose-based materials are frequently driven by surface modifications
- Cellulose nanofibers (CNFs) have a high density of surface hydroxyl (OH) groups that can be exploited for adding new functionality
- CNFs are difficult to disperse in solution and have propensity to agglomerate
- Removing bulk water while preventing hornification facilitates CNF functionalization



Possible routes for cellulose functionalization

Our group has developed a sustainable protocol to effectively functionalize CNFs and is investigating applications and further modifications of CNF-based materials

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Tavakolian, M. et al. *Nano-Micro Lett.*, **2020**, 12:73.
Thakur, V. et al. *Mater. Adv*. **2021**, *2*, 1872-1895.

CNF Dewatering Process: from Slurry to Dry Powder

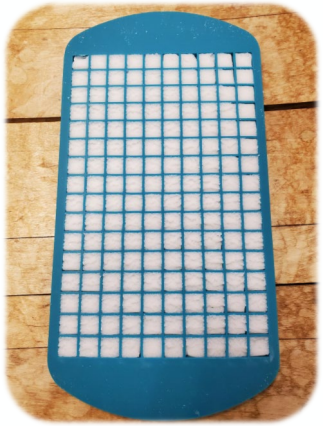
3 wt% CNF slurry (gel)

Dewatering

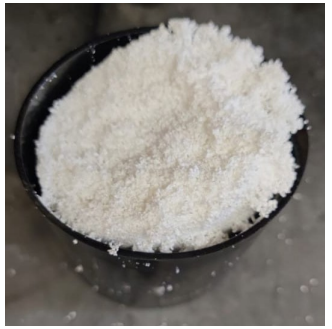
~4.5 wt% CNF (paste)

Add *t*BuOH (10 wt%)

Freeze at –20 °C (eutectic formed)



Freeze-dry



Grind CNF aerogel into processable powder

- Eutectic reduces hornification during lyophilization
- Surface-to-volume ratio increases with preservation of nanostructure
- CNF powder suitable for mechanochemical processing

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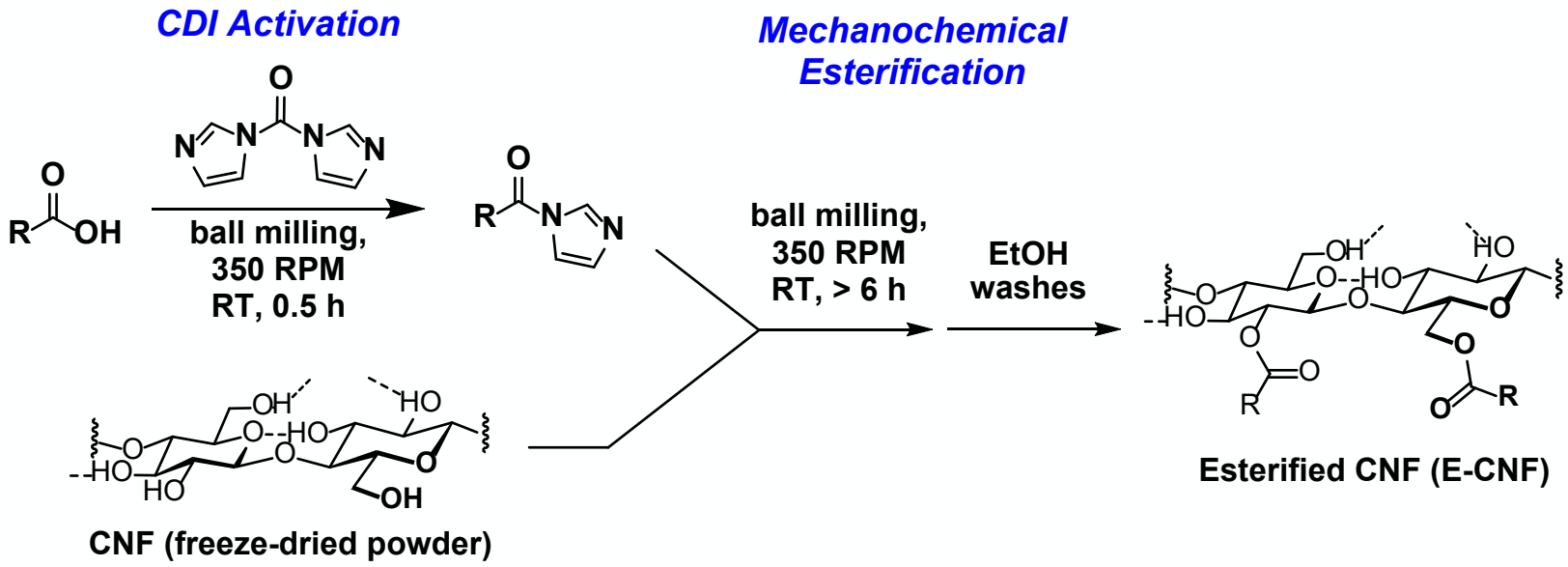
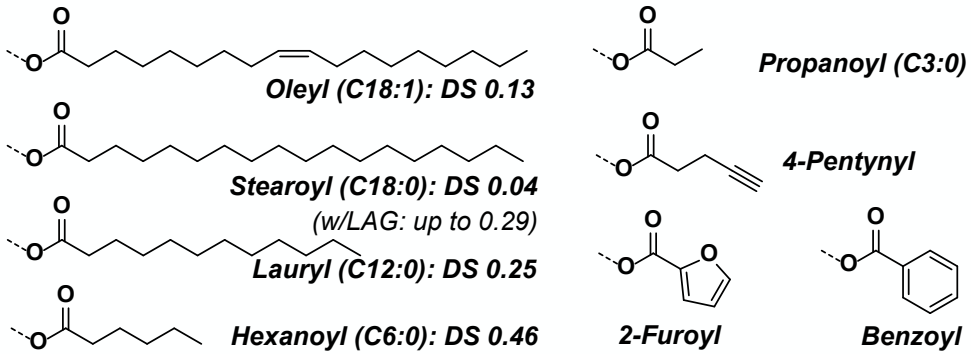
Mavlan, M.; Chang, T.; Feng, R.; Wilkinson, J. W.; Nicholas, R. J.; Idahagbon, N. B.; Youngblood, J. P.; Wei, A., "Mechanochemical Esterification of Cellulose Nanofibers Lyophilized from Eutectic Water–tert-Butanol Mixtures." *Manuscript accepted*.

Esterification of Lyophilized CNF by Mechanochemistry



Low-speed ball mill



- Solventless reaction with alcohol washes
- Purification by vacuum filtration
- Applicable to a variety of carboxylic acids
- Surface functionalization enables dispersion in aprotic solvents

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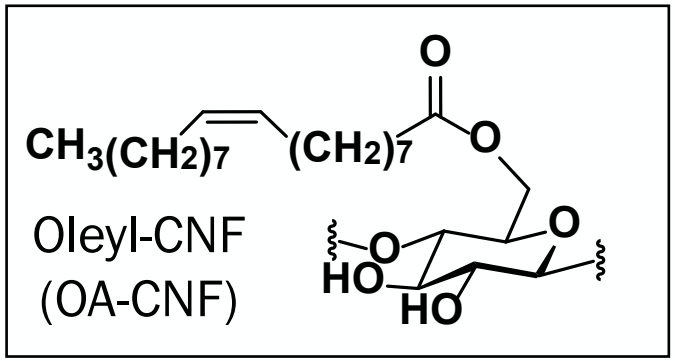
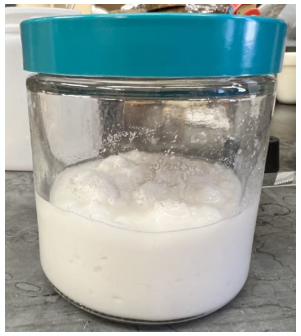
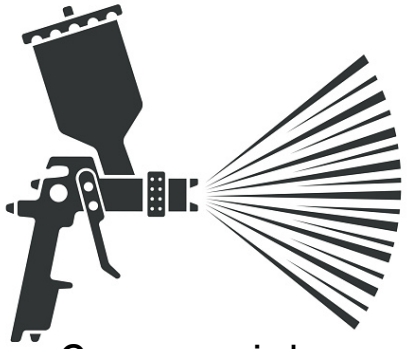
Mavlan, M.; Chang, T.; Feng, R.; Wilkinson, J. W.; Nicholas, R. J.; Idahagbon, N. B.; Youngblood, J. P.; Wei, A., "Mechanochemical Esterification of Cellulose Nanofibers Lyophilized from Eutectic Water–tert-Butanol Mixtures." *Manuscript accepted*.

Oleyl-CNF as a Functional Superhydrophobic Material



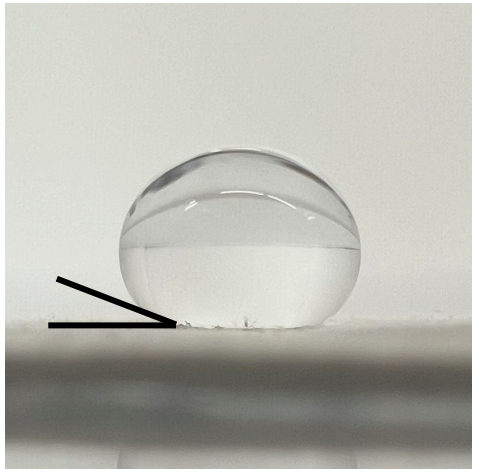


OA-CNF slurry in EtOAc



Commercial spray gun

From top to bottom: Polystyrene, cardboard, aluminum, glass



Contact angle: 159°

Forms water repelling barrier to surfaces

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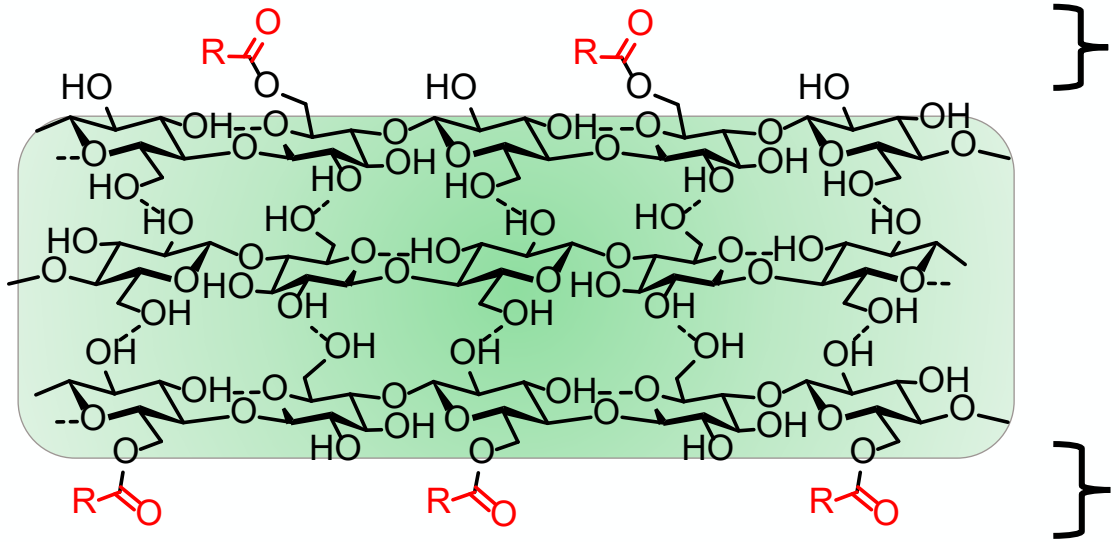
Chang, T.; Mavlan, M.; Nicholas, R. J.; Wilkinson, J.; Youngblood, J. P.; Wei, A., *Manuscript in preparation*.

Surface Characterization of Cellulose Nanofibers (CNFs)

"Degree of Substitution" (DS) as a figure of merit:

$$DS = \frac{162 \times (m_2 - m_1)}{m_1 \times M_{acyl}}$$

162 = molar mass of anhydroglucose ($C_6H_{10}O_5$)
m_2 = mass of esterified CNF
m_1 = mass of initial CNF
M_{acyl} = molar mass of acyl group (RCO)



- Facile method for quantitative DS remains a challenge in the field
- Mass-based methods ambiguous, due to CNF fiber width distributions
- Solid-state ^{13}C NMR is quantitative but time-consuming

Issues related to surface functionalization (SF):

- Are all surface OHs modified? Which ones?
- Are SF metrics reproducible?
- Can SF metrics be used to fine-tune chemical properties, such as hydrophobicity and drug loading?

SF values should correlate more precisely with physicochemical behavior

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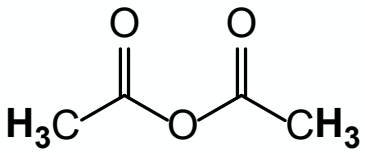
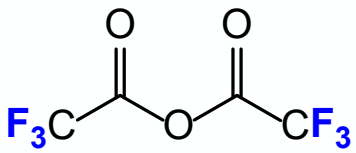
Foster, J. E. et al. *Chem. Soc. Rev.*, **2018**, *47*, 2609-2679.

Trifluoroacetate (TFA) esters for SF quantitation by solution F-19 NMR spectroscopy



Acetic Anhydride

vs.

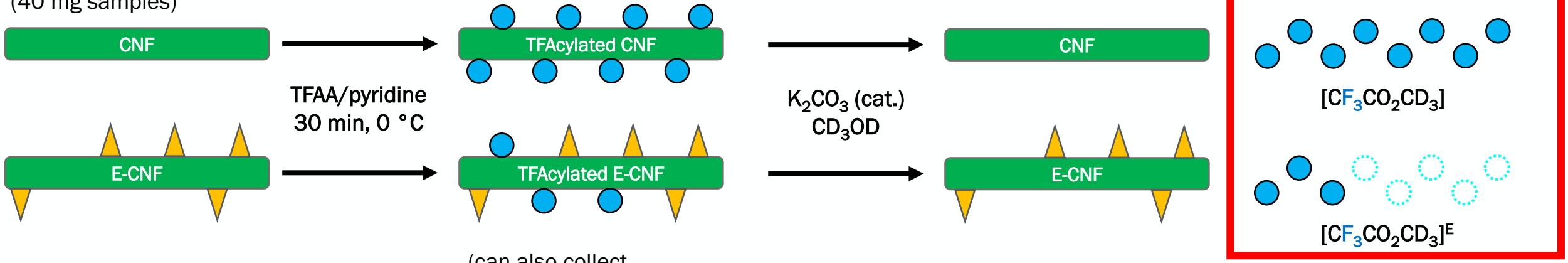


Trifluoroacetic Anhydride (TFAA)

- TFAA reacts very quickly with alcohols can be used to quantify accessible surface OH groups
- TFA esters are labile and released by mild solvolysis
- Standard esters are stable in the presence of TFAA
- **TFA molarity can be quantified by solution ^{19}F NMR**

Analytical workflow:

(40 mg samples)



(can also collect mass-based DS values)

$[CF_3CO_2CD_3]$ = total surface OH's

$[CF_3CO_2CD_3]^E$ = residual surface OH's

$[CF_3CO_2CD_3] - [CF_3CO_2CD_3]^E$ = E-density per unit mass

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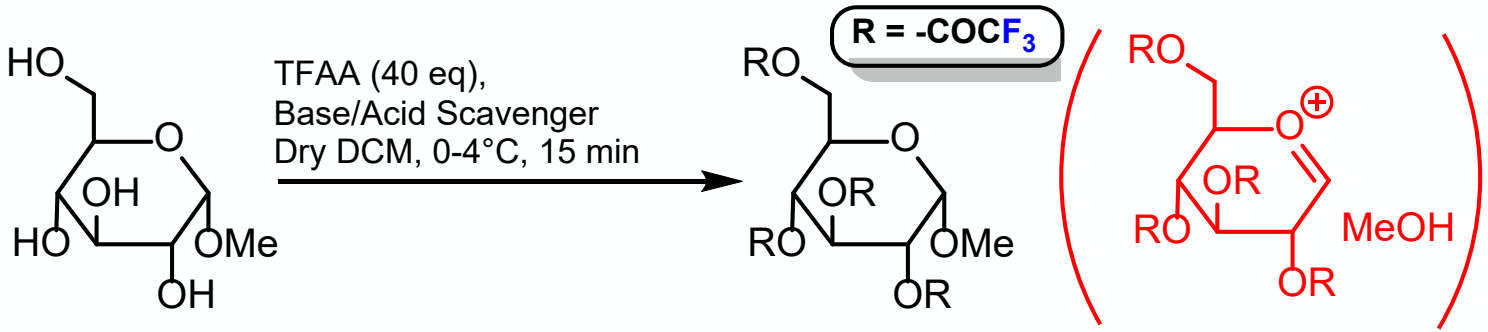
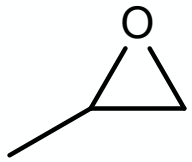
Survey of TFAcylation Conditions



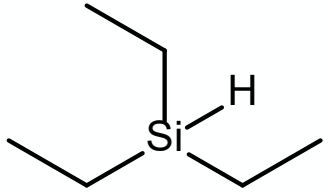
- α-Methyl glucoside (CNF surrogate)
- TFAA (10 eq per –OH)
- Acid Scavenger to neutralize CF_3CO_2H

Scavenger candidates:



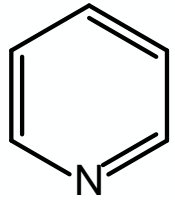
Propylene oxide

Mild
Too slow;
Many by-products

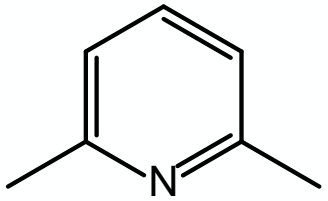


Triethylsilane

Reacts with TFA
TFA–Et_3SiH is an active reducing agent

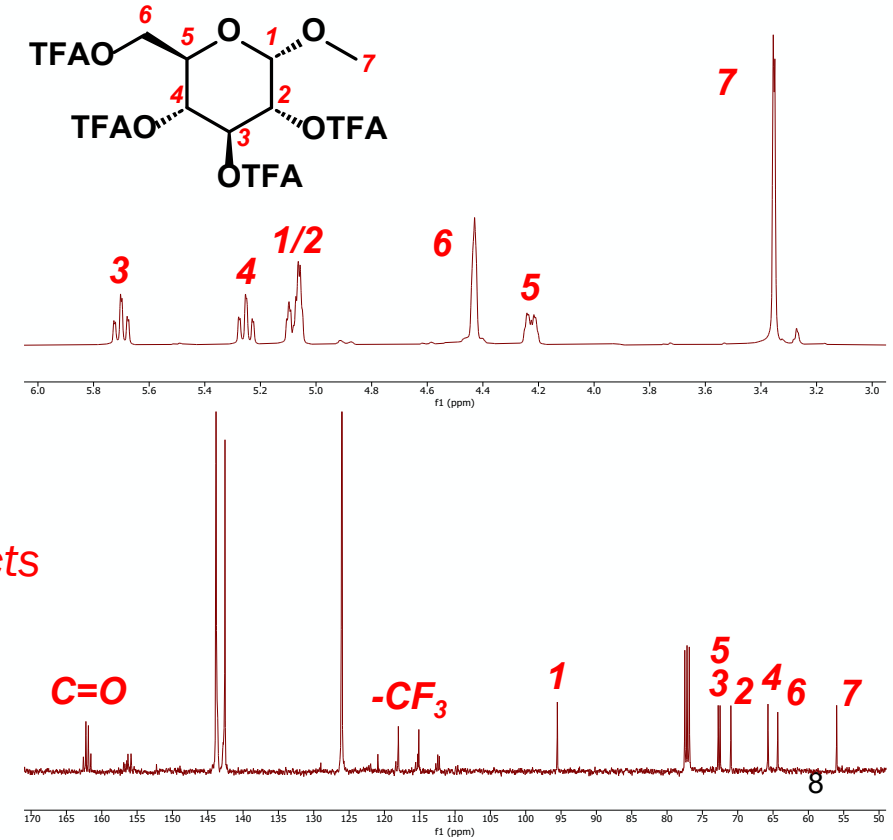


pyridine



lutidine

Quick (15 min)
Exothermic, colored by-products
(but can be removed by washing with aprotic solvents)



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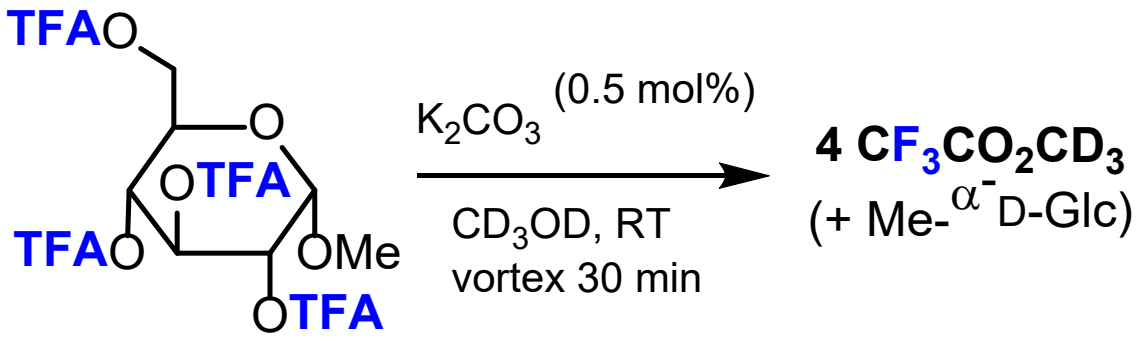
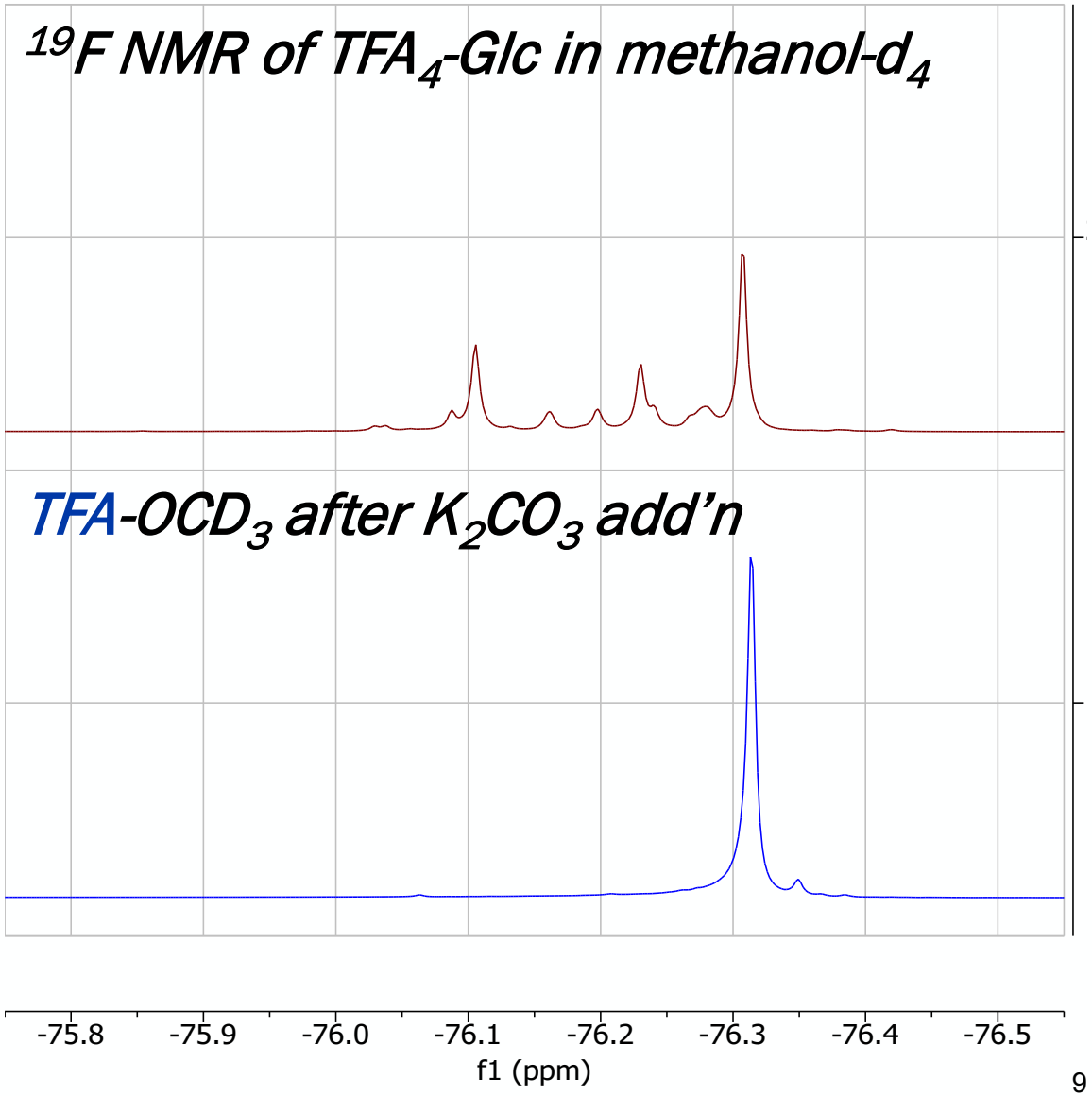
Trans-esterification of TFAcylated Methyl Glucoside



- Mild basic conditions
- TFA-CD_3 ester can be quantified by ratiometric peak integration versus CF_3Ph using solution ^{19}F NMR.
- Can be applied directly toward TFA-CNFs suspended in CD_3OD for quantitative DS
- Solution NMR-based approach has great practical advantages over SS-NMR methods with similar goals



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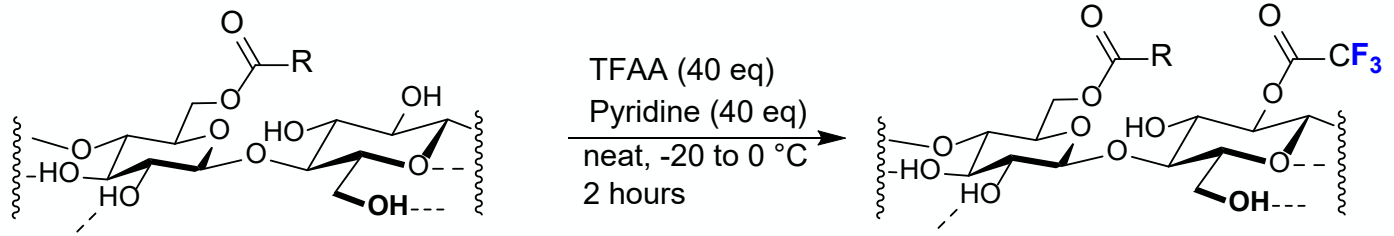
Applying TFAcylation Conditions to CNFs and E-CNFs

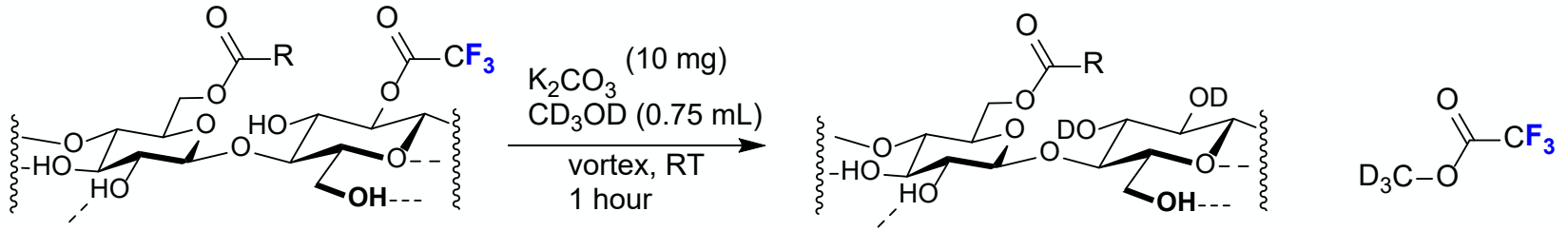
TFAcylated E-CNFs:



E-CNF

TFA-E-CNF

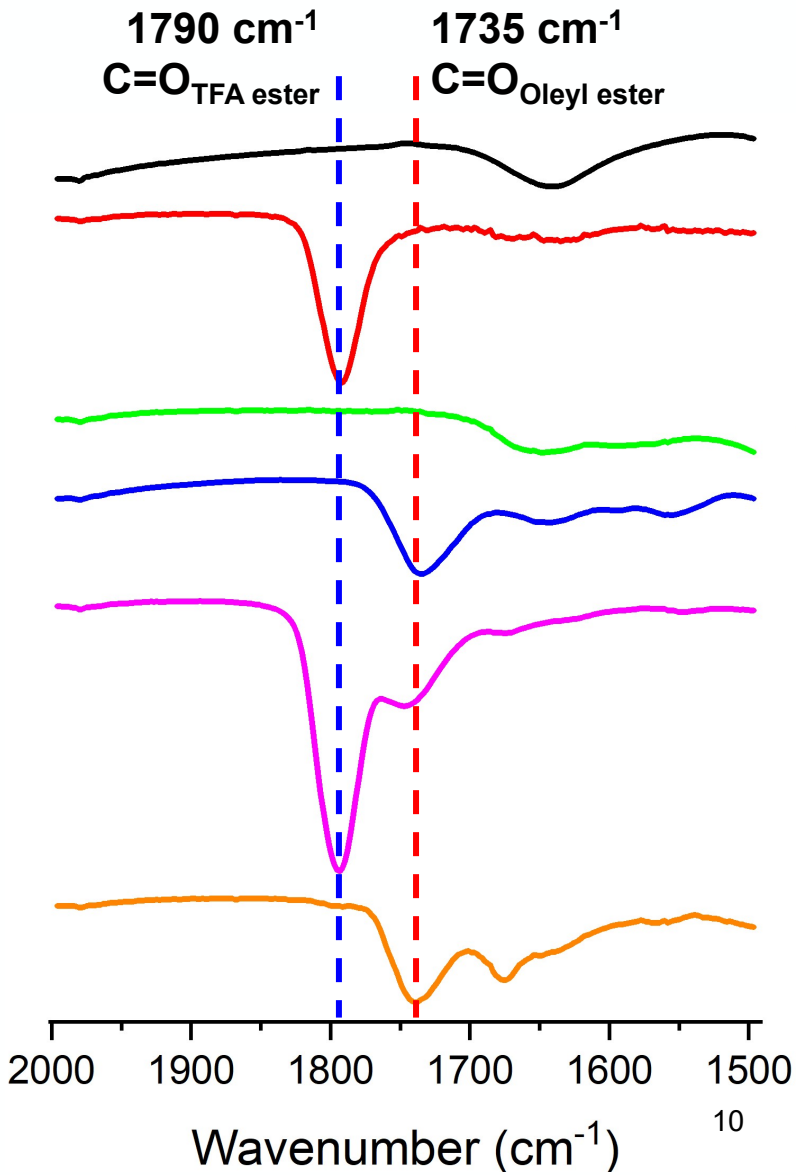
After cleavage of TFA esters:



TFA-E-CNF
(40 mg)

E-CNF

Methyl-d_3
Trifluoroacetate



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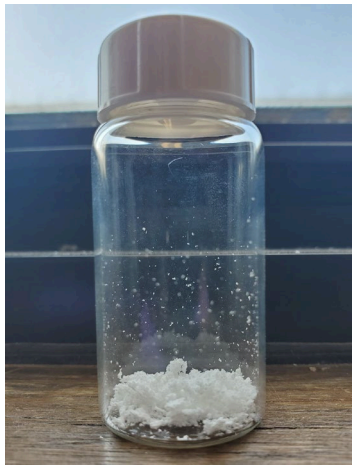
Ongoing Workflow for Preparing TFA-CNF for F-19 NMR Analysis



TFA-CNF w/salts (100 mg)

Add pyr.

T = 0 h

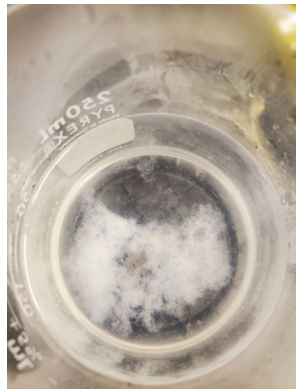
Gentle heat

Vortex

T = 1.5 h

- *Swelling TFA-CNFs in pyridine releases residual pyridinium salts*
- *Acetone precipitates TFA-CNF and enables filtration*
- *TFA-CNF is fully dried under vacuum before saponification with CD_3OD*

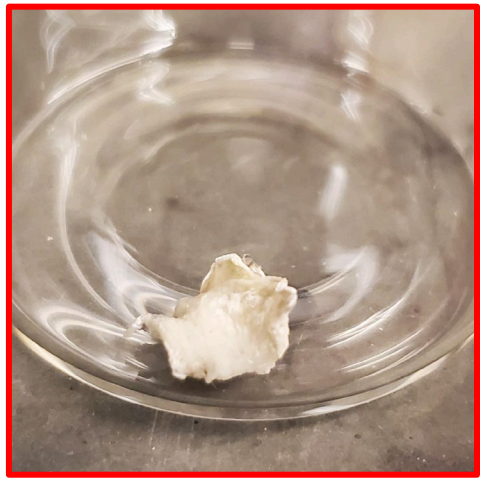
Precipitate in cold acetone



Centrifuge

CNF Sediment

Vac. filter, dry overnight



Dried TFA-CNF (~20 mg)

Add CD_3OD w/K_2CO_3

^{19}F solution NMR spectroscopy (TFA quantitation)

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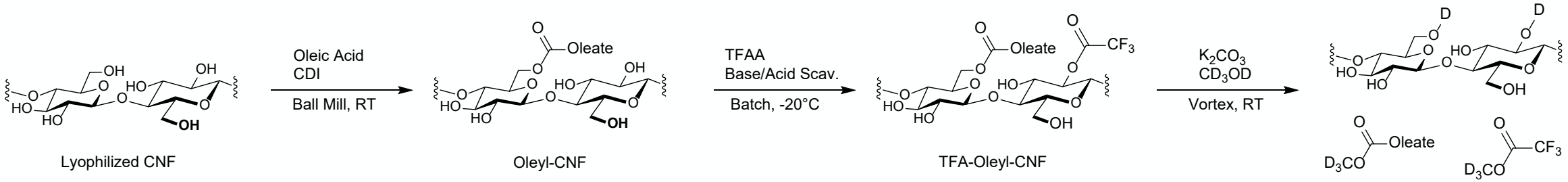
Conclusions and Future Directions



- Efficient esterification of CNFs after lyophilization from 10% TBA eutectic
- Can install TFA groups onto accessible surface OH's as handles for spectroscopic characterization
- Saponification with mild base allows for solution ^{19}F NMR analysis
- Can correlate mass-based DS and ^{19}F NMR signal of free TFA
- TFAcylation and saponification of E-CNFs is in progress

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Acknowledgements

- PI: Alexander Wei
- Wei Lab
  - Nosa Idahagbon
  - Victor Jammal
- Funding:
  - National Science Foundation (NSF)
- TAPPI Nano Conference

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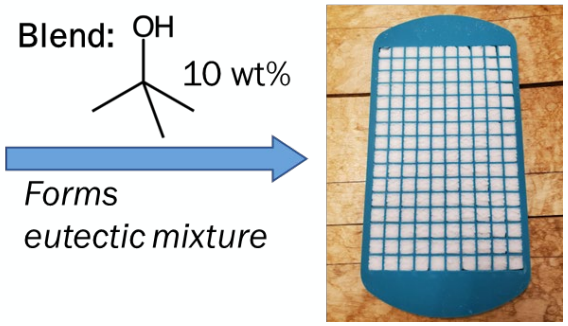
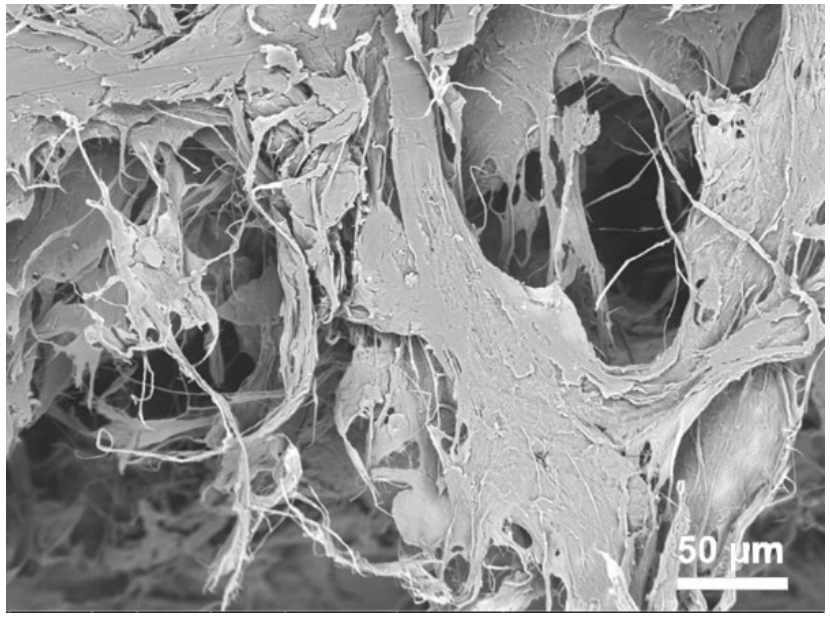
Supplemental: SEM of Freeze-Dried Eutectic



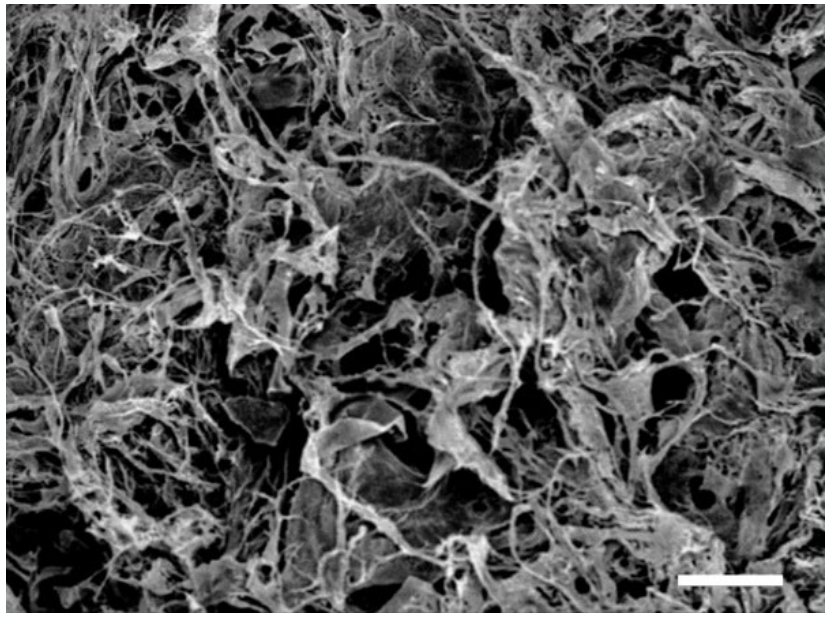
TBA (wt%)	Specific surface area (m^2/g)[a]
0	2.44 ± 0.03
10	23.47 ± 0.17
20	23.83 ± 0.17
30	20.47 ± 0.15
40	22.08 ± 0.14
50	19.57 ± 0.12

BET measurements of CNFs freeze-dried from slurries with variable amounts of TBA.

0% TBA



10% TBA



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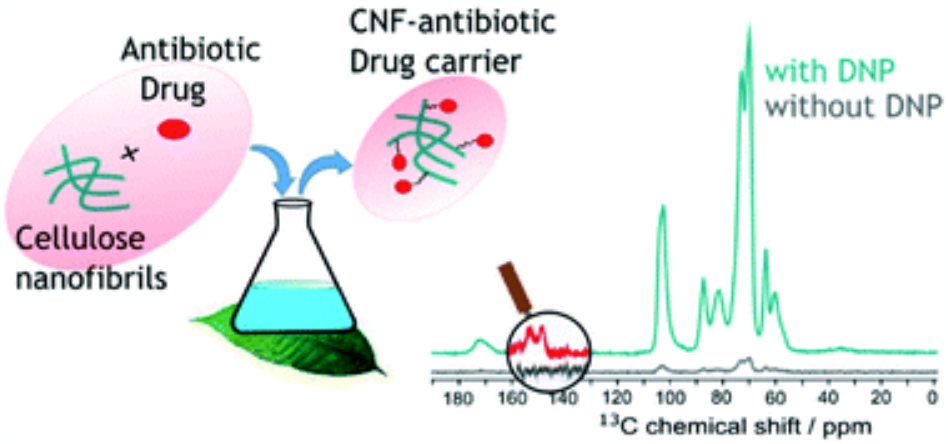
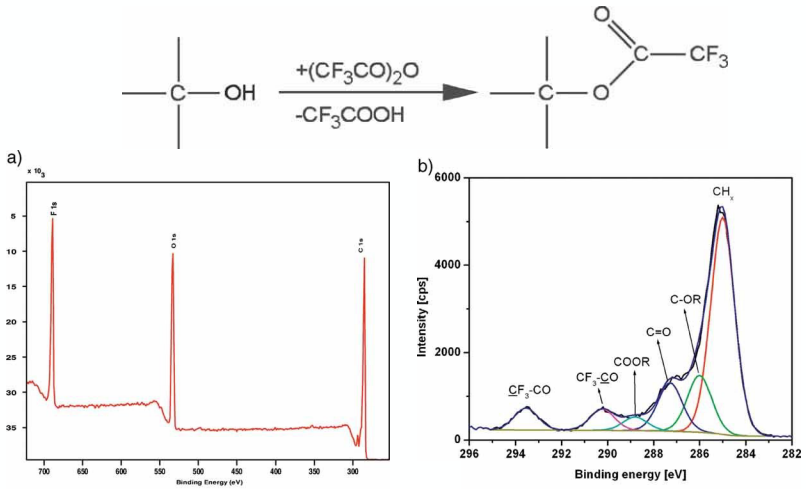
Supplemental: Current Strategies to Quantify Surface Moieties



Dynamic Nuclear Polarization (DNP) enhance NMR[1]

- Sensitive to trace amounts of TEMPO moieties
- Provides precise estimation of drug loading within ~1 wt%



Quantification of –OH groups by TFAA Derivatization[2]

- Measure amount of –OH on plasma oxidized poly(propylene) samples using TFA groups
- Quantifiable by XPS analysis with 95% confidence level

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[1] Kumar, A. et al. *Chem. Sci.*, **2020**, *11*, 3868-3877.
[2] Gross, T. et al. *Plasma Process. Polym.* ***2010****, 7, 494–503.*