Dual Ionic Liquid-Functionalized Cellulosic Materials: Thermal, Mechanical and Conductive Properties

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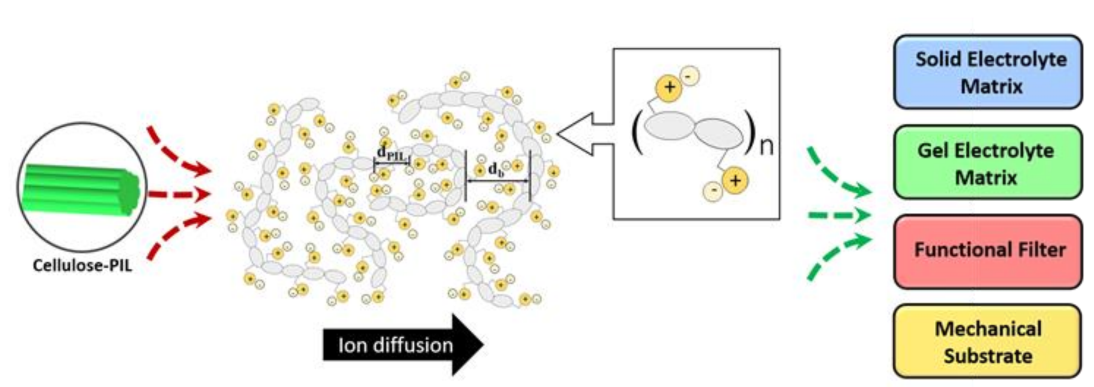
ABSTRACT

Cellulose, an inexpensive and renewable biomacromolecule, represents an intriguing synthetic foundation for new materials with task-specific properties. Here, we wish to report a synthetic route for functionalizing cellulose with a side chain containing two ionic liquid functional groups using azide-alkyne 'click' cyclization strategy, followed by quaternization of the two resulting heterocycles (1,2,3-triazole and imidazole). Through this functionalization strategy, the resulting cellulosic materials exhibited significant softening, with several glass transition (T_g) values observed below room temperature, indicating the amorphous nature of the materials, with the T_g dependent on both the length of the side chain and the counteranion used. Stress and strain at break of the materials were found by dynamic mechanical analysis to generally be in excess of 2 MPa and 250 %, respectively, indicating not only a high degree of mechanical robustness, but also elasticity. Enhancements in conductivity as high as 6-orders of magnitude were found when compared to native cellulose. In the end, cellulose can be utilized as a sustainable, foundational biopolymer in the preparation of new conductive materials.

INTRODUCTION



- Structural saccharide polymers, such as cellulose, interact through hydrophobic and electrostatic interactions, and the resulting matrices can exhibit useful and novel properties.
- First-generation IL-functionalized cellulosic materials utilized azide-alkyne click cyclization, followed by quaternization, to create 1,2,3-triazolium groups off of each sugar unit.
- The presence of the 1,2,3-triazolium group led to a 6-orders of magnitude enhancement in conductivity versus microcrystalline cellulose, with T_g values of approximately 100 °C; however, the materials lacked flexibility.

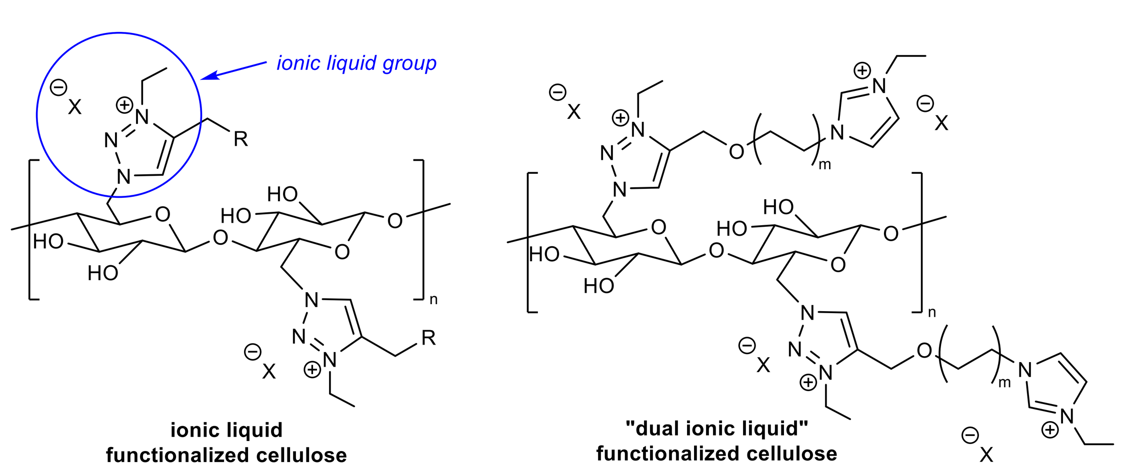
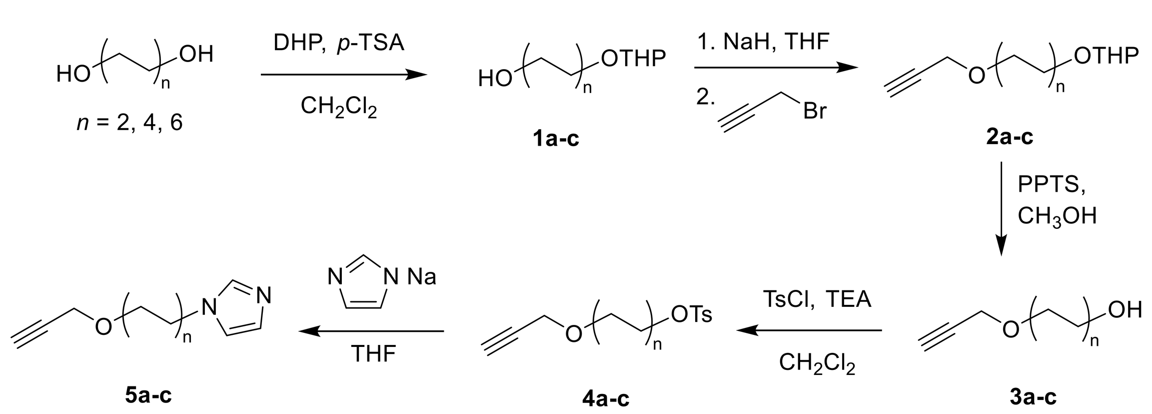


Figure 1. Structures of (left) single and (right) dual ionic liquid-functionalized cellulosic materials.

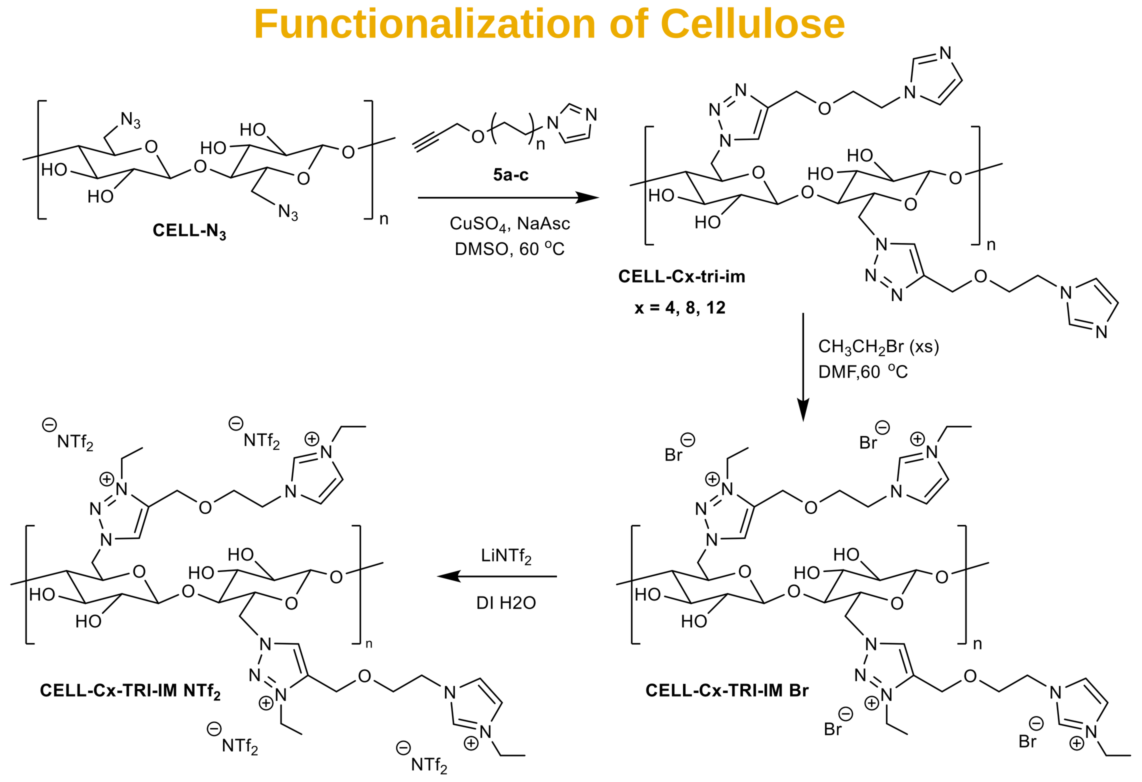
- Our hypothesis is that by introducing a second IL unit (imidazolium) via a mostly hydrocarbon tether we can further improve the conductivity and flexibility of the materials by depressing the T_g.
- Overall, IL-functionalized cellulosic materials are unique in that a renewable, sustainable, biomacromolecule in cellulose can serve as a foundational platform for novel conductive materials.

SYNTHESIS

Synthesis of Alkynyl-Substituted Imidazoles

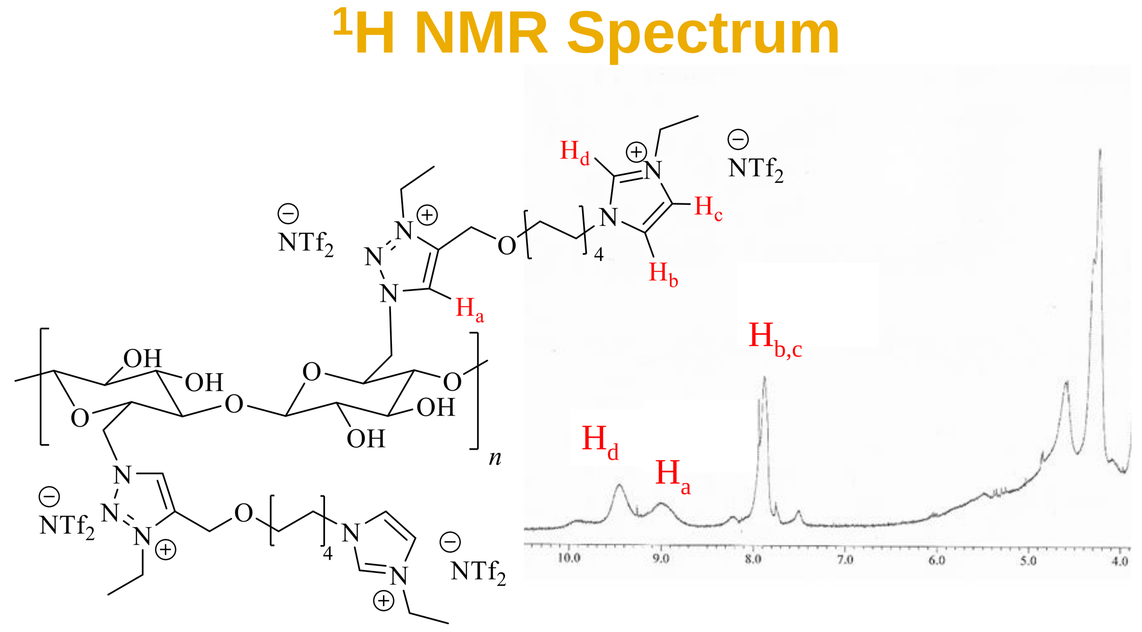


Functionalization of Cellulose



ANALYSES

^{1}H NMR Spectrum

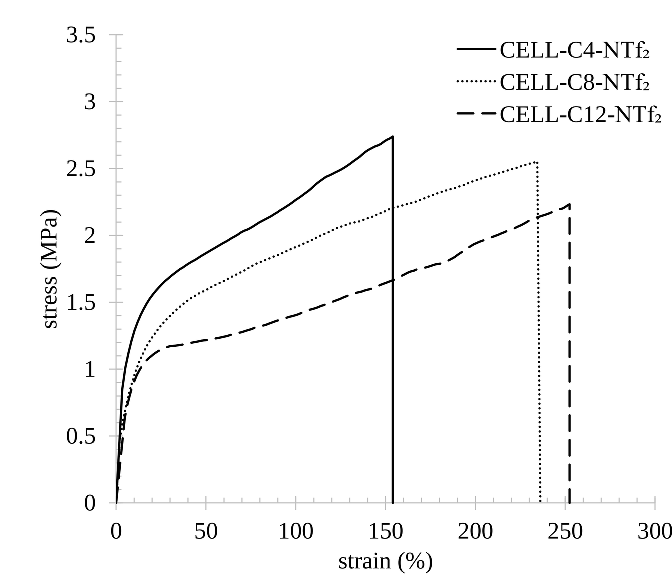


Thermal Data (DSC, TGA)

material	DSC T_g (°C)	TGA $T_{d5\%}$ (°C)
cellulose	N/A	301
CELL-TRI-NTf_2 (mono)	90	240
CELL-C4-NTf_2	-8.1	225
CELL-C8-NTf_2	-14.2	228
CELL-C12-NTf_2	-7.6	226

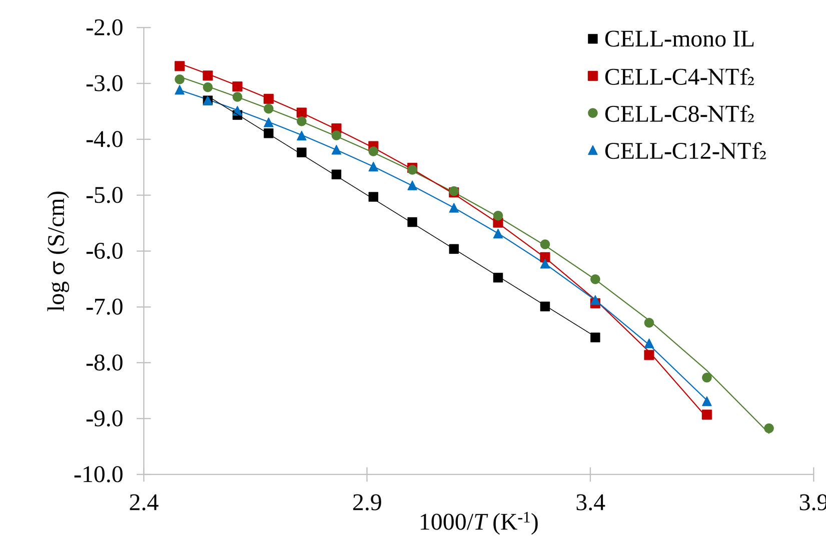
ANALYSES

Mechanical (DMA) Stress-Strain Data



- Stress and strain at break were found to be in excess of 2 MPa and 150 %, respectively
- Materials are mechanically robust and modestly elastic
- Intercalation between longer side chains is thought to increase stress at break for the C12 system.

Ionic Conductivity



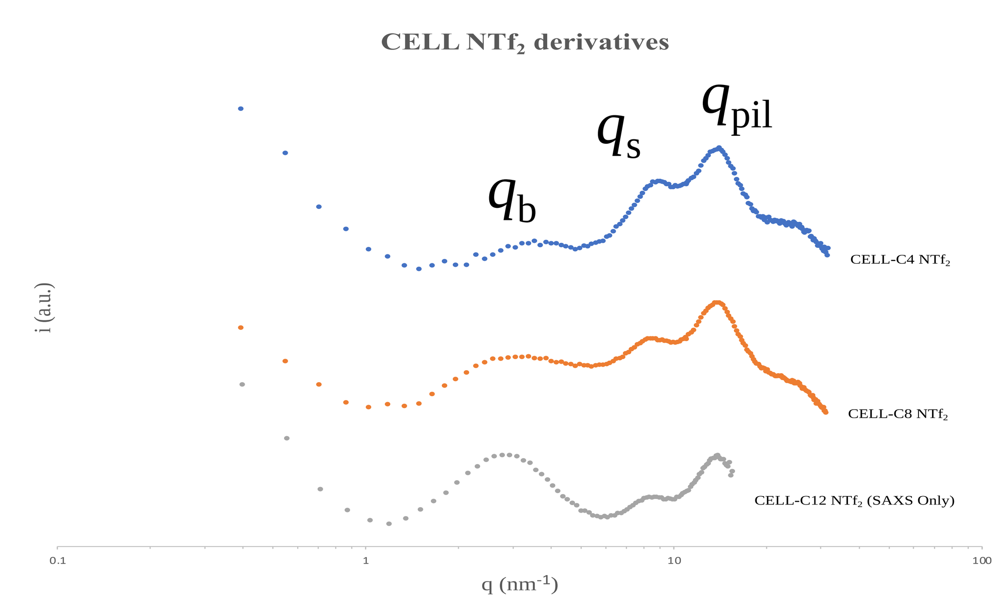
Conductivity was found to increase 1-2 orders of magnitude from a single-IL unit to two.

Conductivities of prior mono-IL functionalized cellulose followed Arrhenius (linear) behavior as the data was collected mostly below the T_g of the respective polymers.

Dual-IL functionalized cellulosic materials exhibit T_g values below room temperature, leading to VFT (non-linear) behavior.

X-ray Scattering

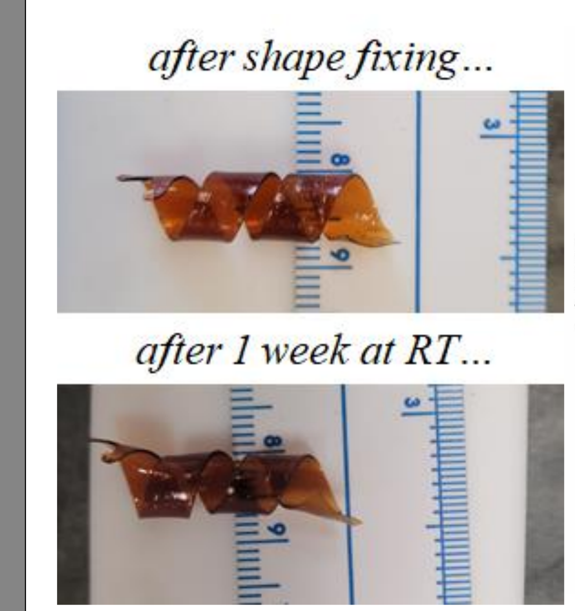
q_s: amorphous halo
q_b: backbone-to-backbone correlation distance
q_{pil}: distance between neighboring ionic groups

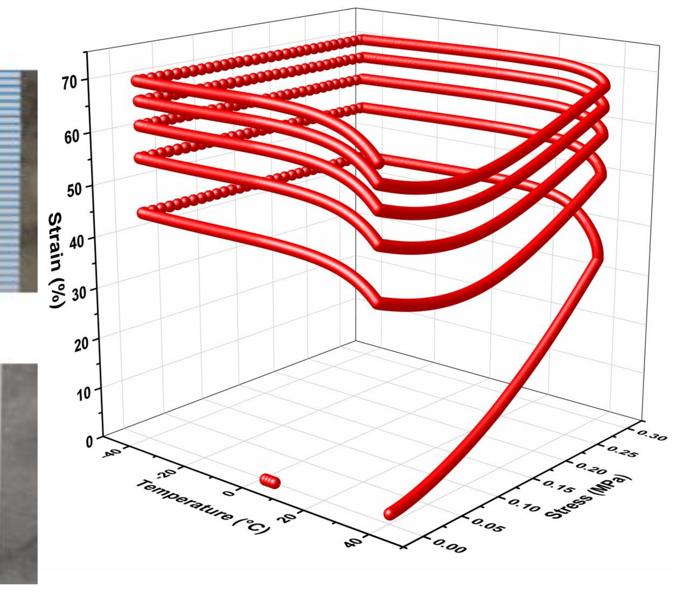


WAXS/SAXS combined X-ray scattering as a function of scattering vector dual-IL-functionalized cellulosic materials

Data indicates intercalation between side chains with C12 analog.

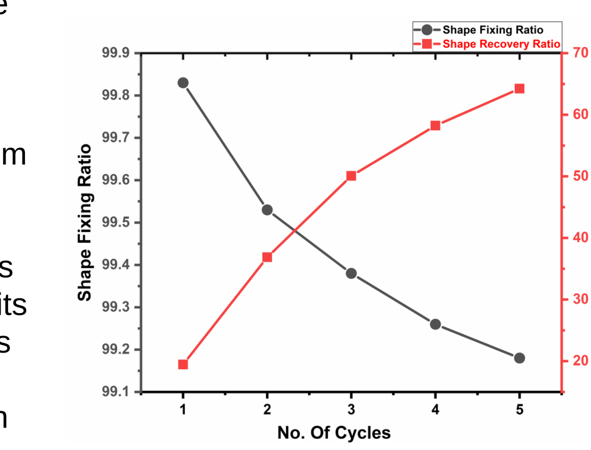
SHAPE-MEMORY BEHAVIOR





The **shape-fixity ratio** quantifies the ability of the polymer to fix the temporary shape and is the deformation after the stress was released with respect to the maximum deformation.

The **shape-recovery ratio** quantifies the ability of the polymer to recover its original shape and was calculated as the total deformation recovered with respect to the maximum deformation reached.



SUMMARY

- Cellulose is an inexpensive and sustainable raw material which, when functionalized with an ionic liquid unit, could serve as an important foundational polymer for new PILs.
- Functionalization of cellulose leads to a disruption of hydrogen bonding, an increase in free volume and segmental motion, leading to a decrease in T_g and an increase in ionic conductivity
- The additional IL (imidazolium) unit further decreased T_g while increasing flexibility and conductivity.

- **Reference**: Miller, R. J.; Smith, V. M.; Love, S. A.; Byron, S. M.; Salas-de la Cruz, D.; Miller, K. M. *ACS Appl. Polym. Mater.* **2021,** *3*, 1097-1106.

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