# Analysis of cellulose nanomaterial systems via advanced autofluorescence spectroscopy

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Session 18: Advanced Characterization Strategies for CNM Distribution and Other Properties
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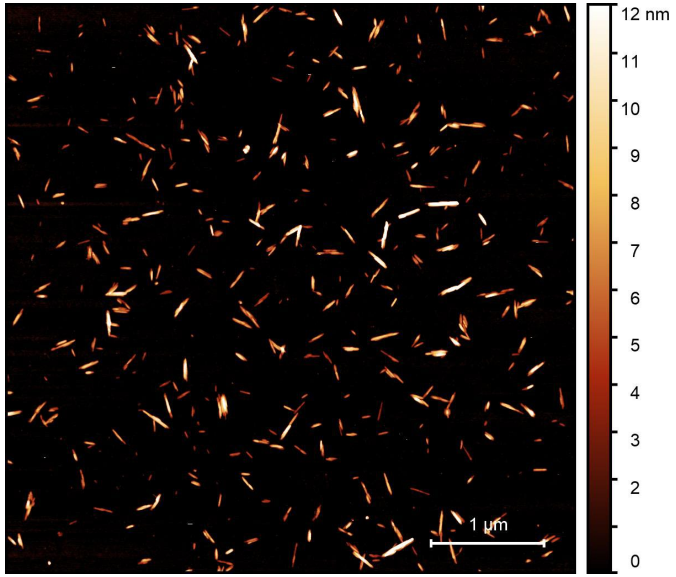
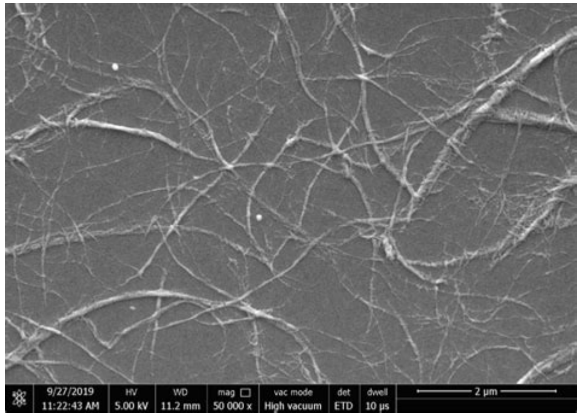
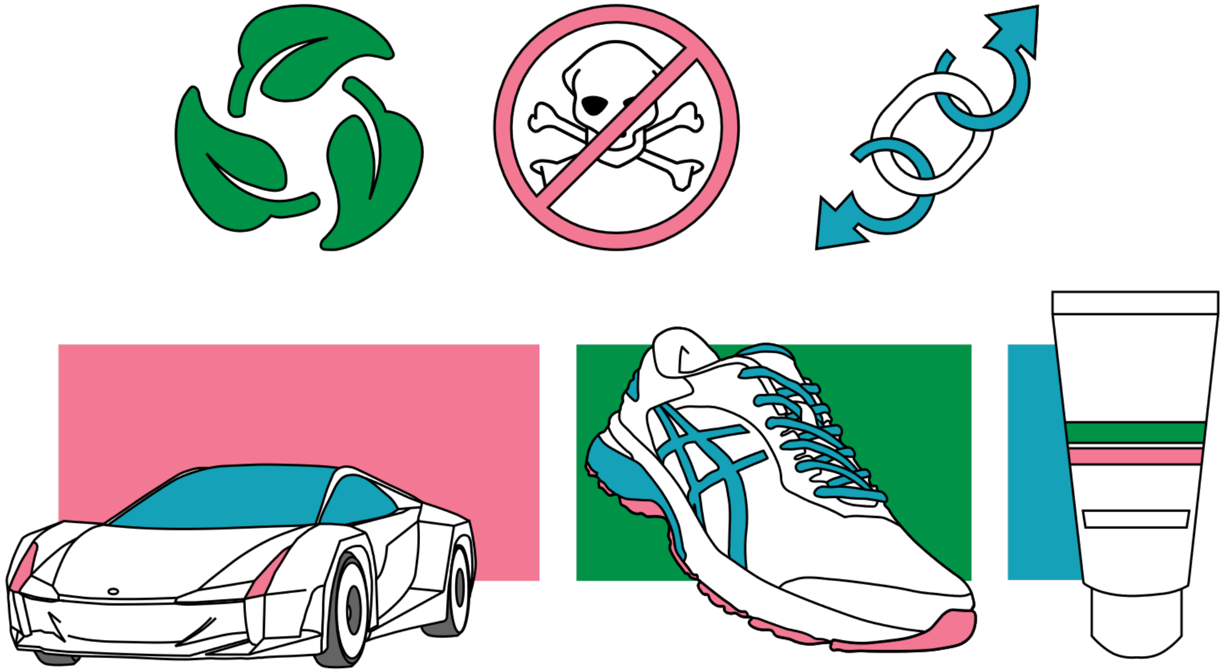
THE UNIVERSITY OF BRITISH COLUMBIA

# Cellulose nanomaterials



| Cellulose nanomaterial | Production | Length | Cross-section |
|---|---|---|---|
| Nanocrystals (CNCs) | Hydrolysis | 100-250 nm | 5-70 nm |
| Nanofibrils (CNFs) | Mechanical degradation | 0.1-2 µm | 5-60 nm |

Klemm et al. (**2018**) *Mater. Today* 21:720.
https://www.celluloselab.com/products-for-industries/jinjiahao-cnf-1000-bar/

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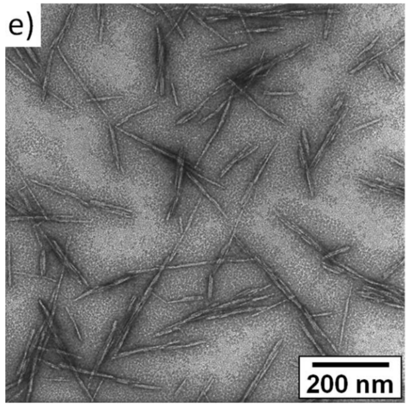
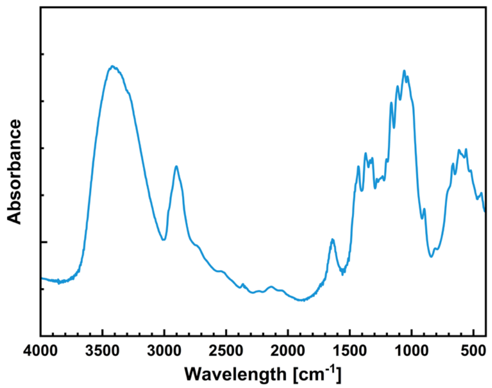
# Analysis of nanomaterials

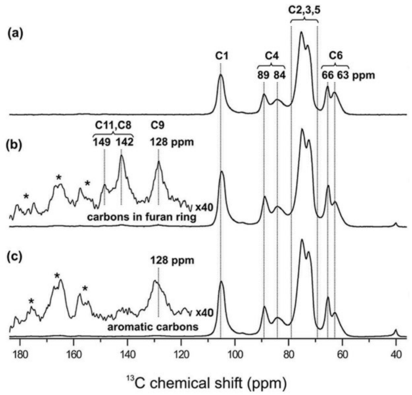
### Electron microscopy



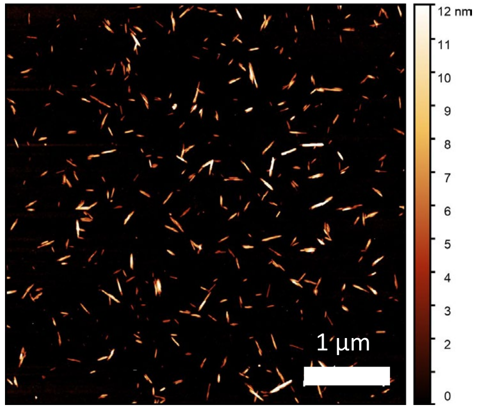

### Infrared spectroscopy



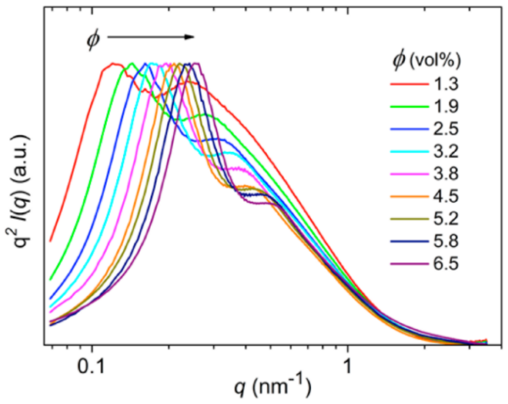

### Solid state NMR



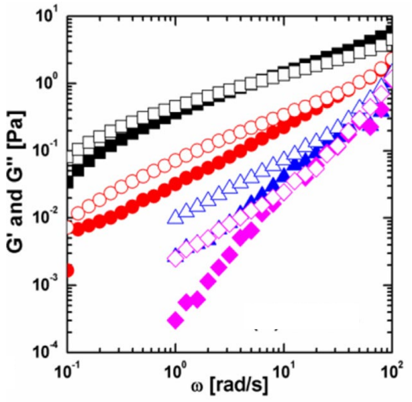

### Atomic force microscopy




### X-ray scattering

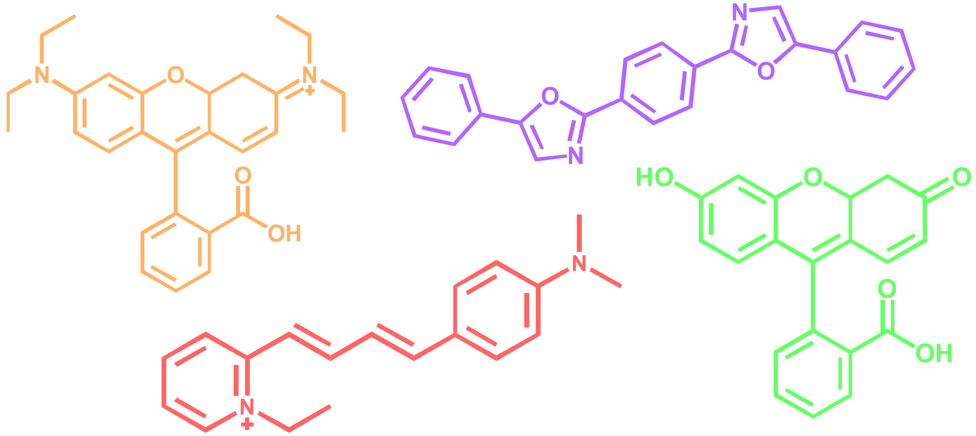


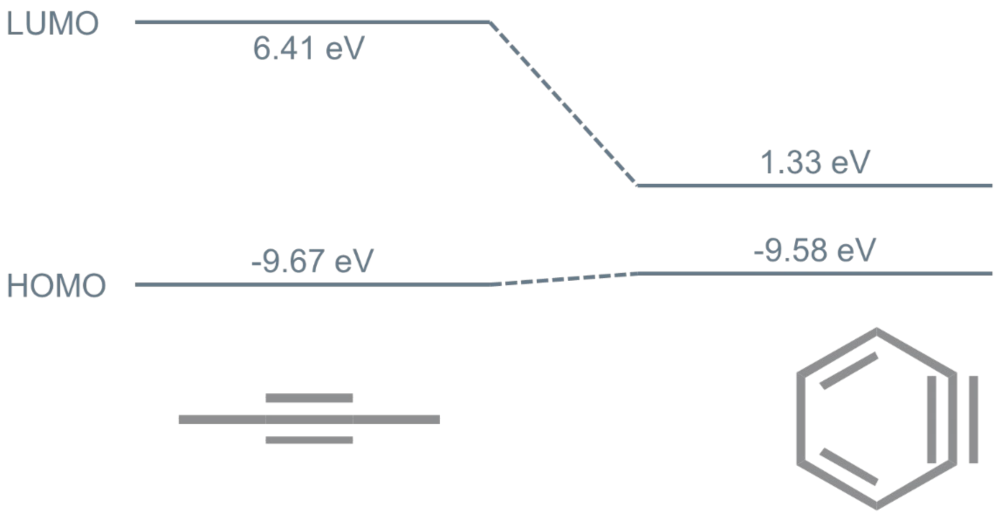

### Rheology

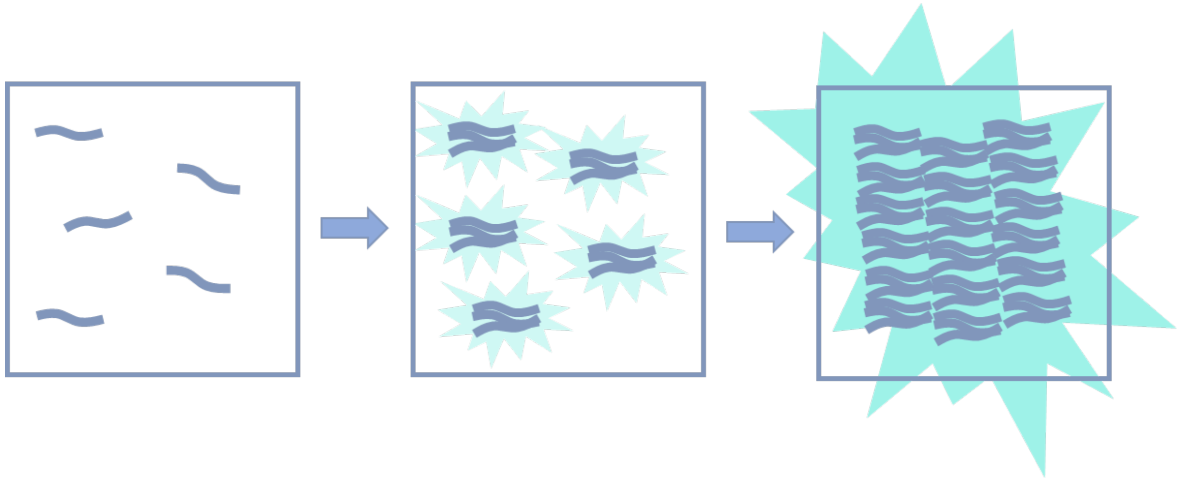



Moon et al. (**2011**) *Chem. Soc. Rev.* 40:3941.
Schütz et al. (**2015**) *Langmuir* 31:6507.
Navarro et al. (**2015**) *Biomacromolecules* 16:1293.
Li et al. (**2015**) *ACS Sustainable Chem. Eng.* 3:821.

# Cluster-triggered autofluorescence spectroscopy



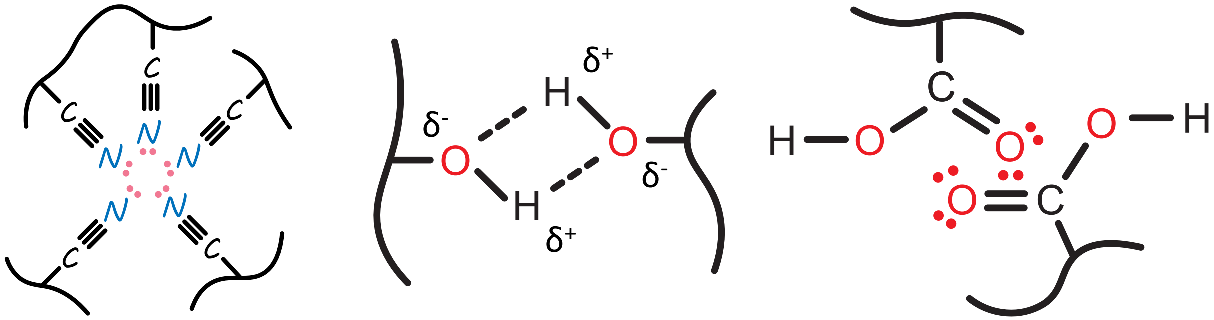


through space interactions

dipole-dipole interactions

n,π interactions



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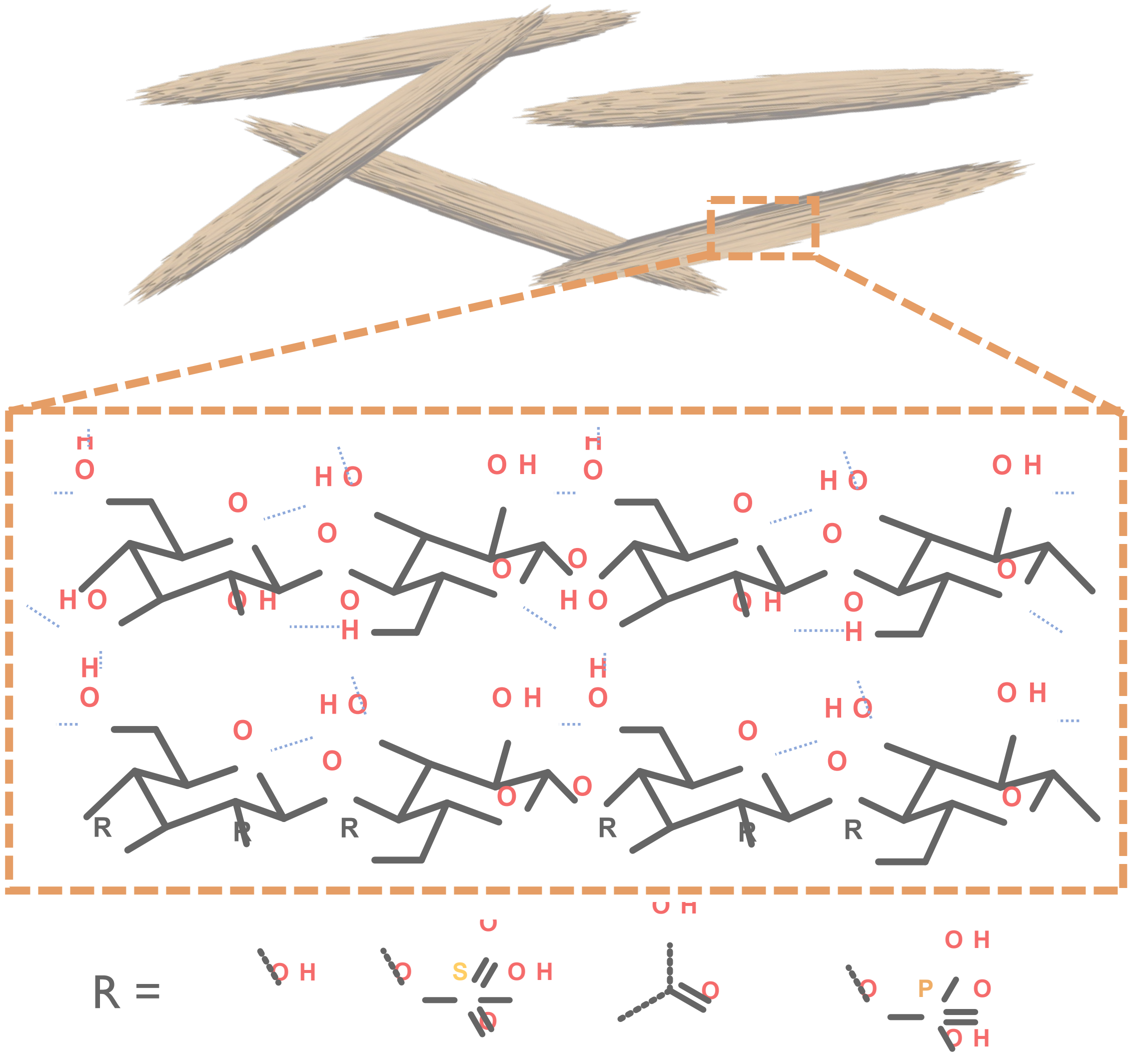
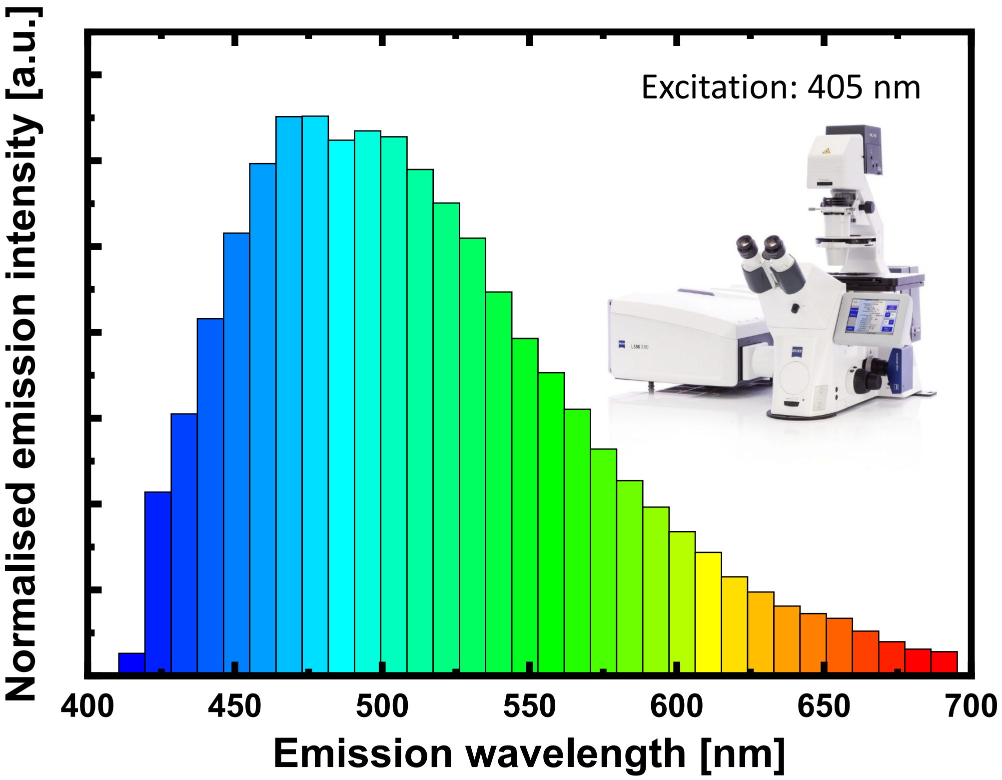
# Nanocellulose mechanisms of cluster-triggered emission

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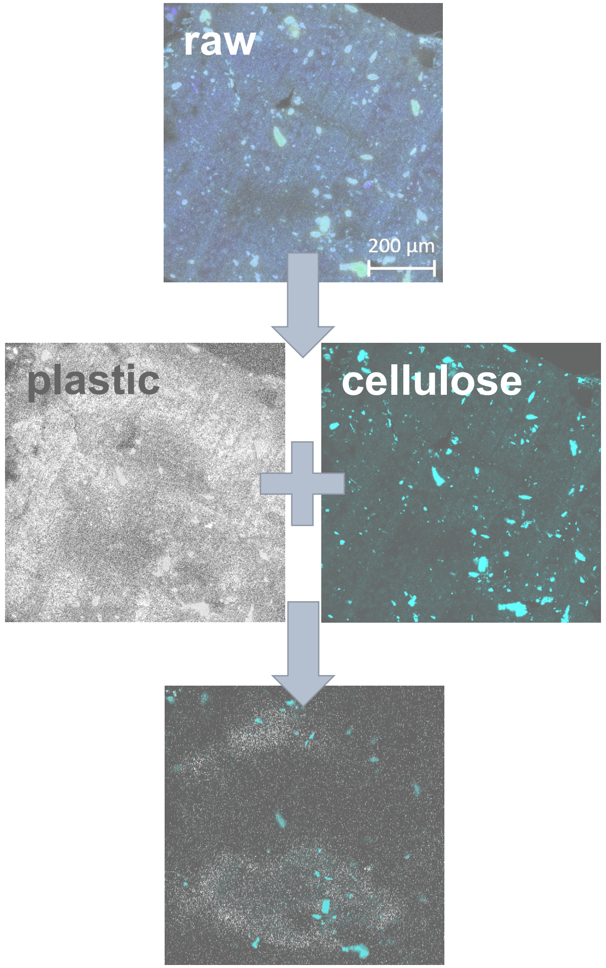
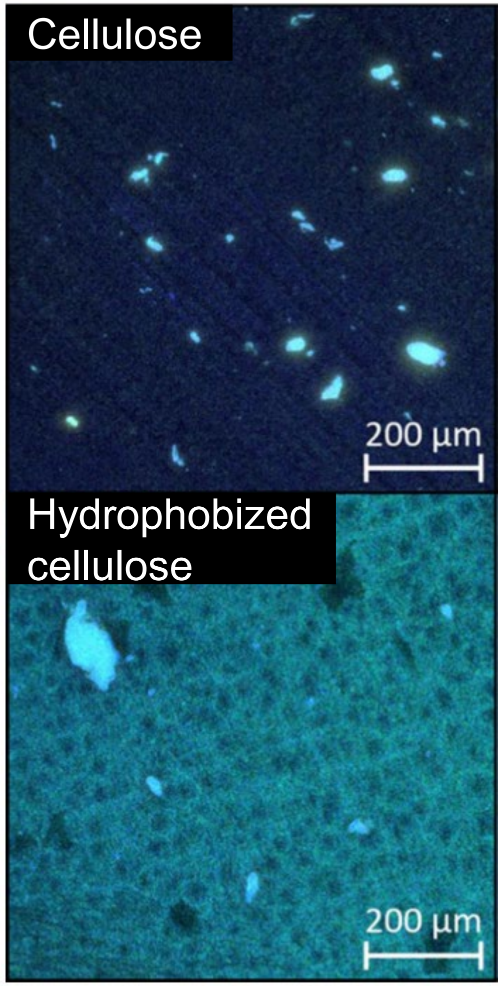
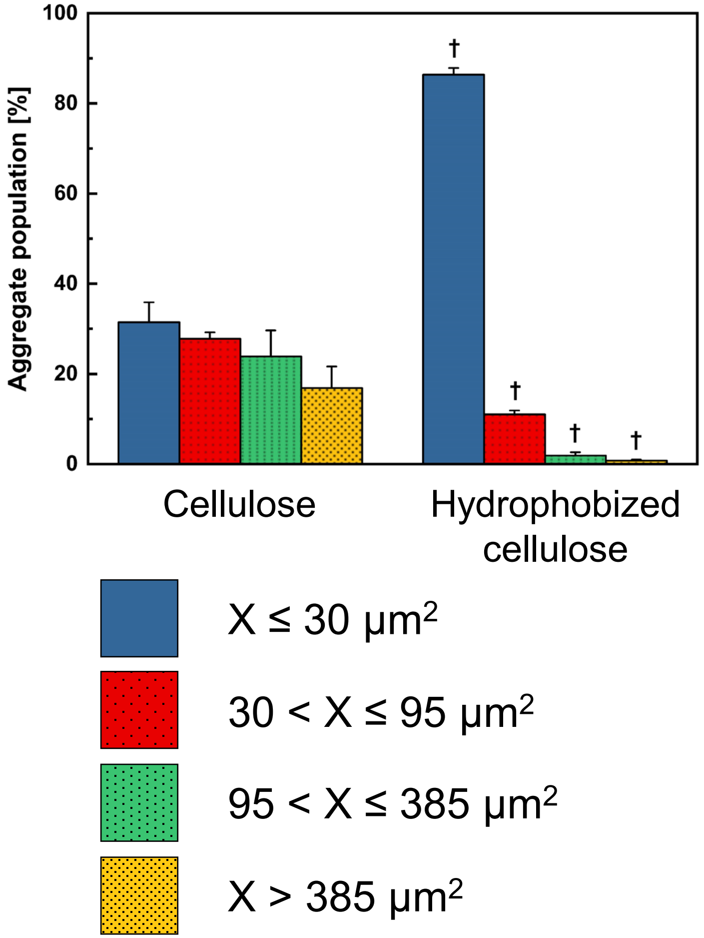
Johns et al. (**2019**) *Microsc. Microanal.* 25:682.

# Tracking nanocelluloses – composites

## Fluorescence imaging enables tracking of nanocellulose in solid materials




Johns et al. (**2019**) *Microsc. Microanal.* 25:682.
Palange et al. (**2019**) *Cellulose* 26:9645.

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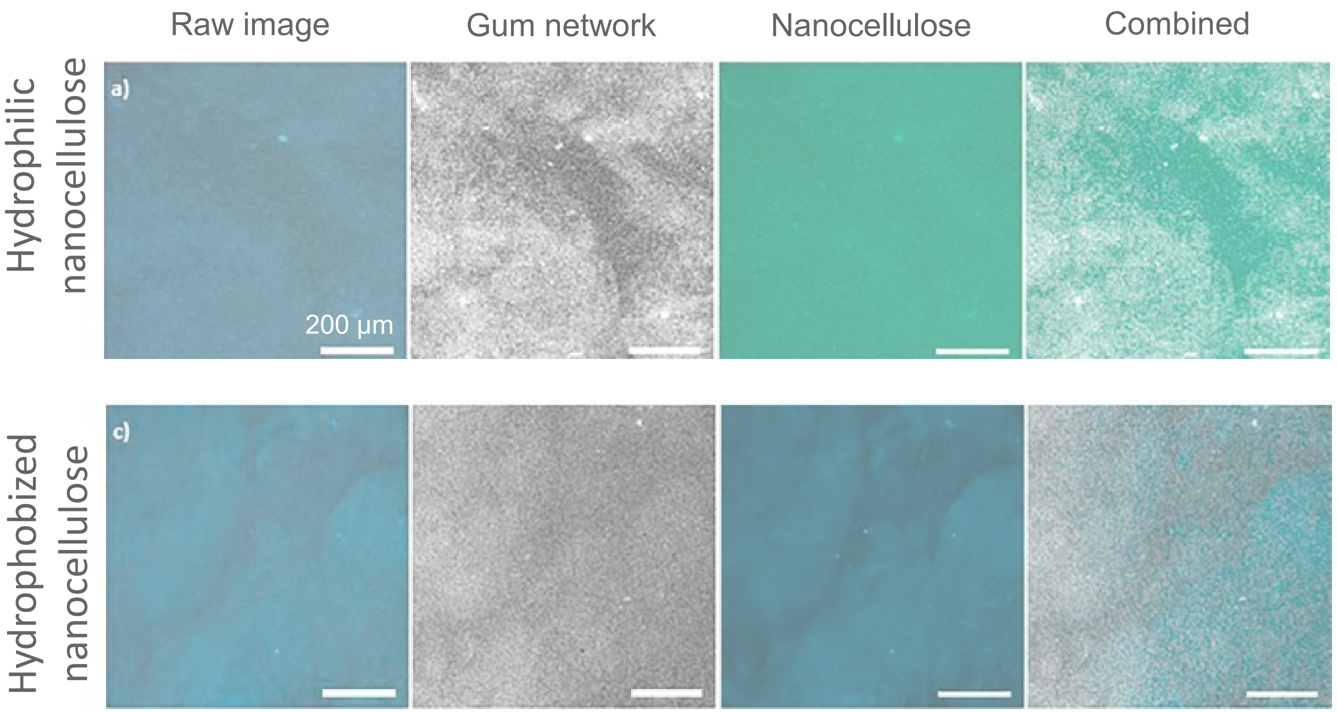
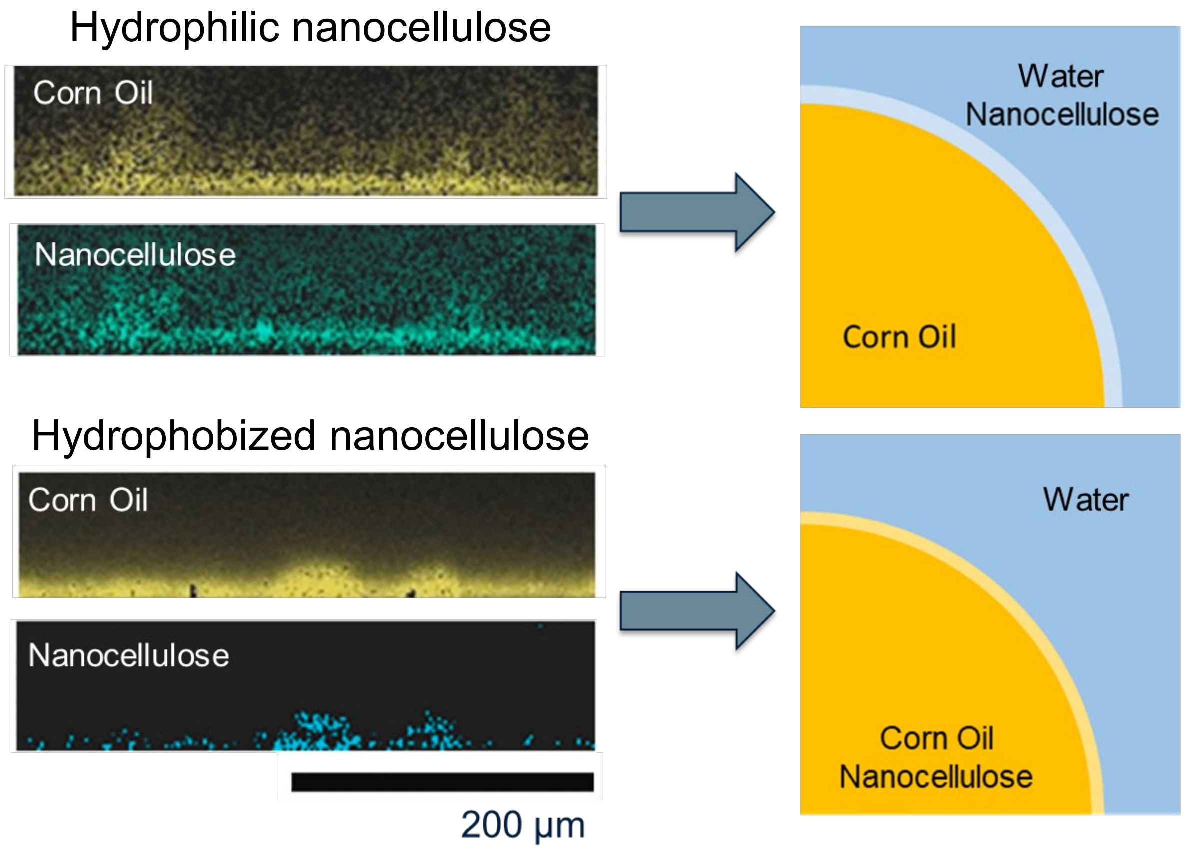
# Tracking nanocelluloses – gels and emulsions

## Fluorescence imaging enables tracking of nanocellulose in liquid systems

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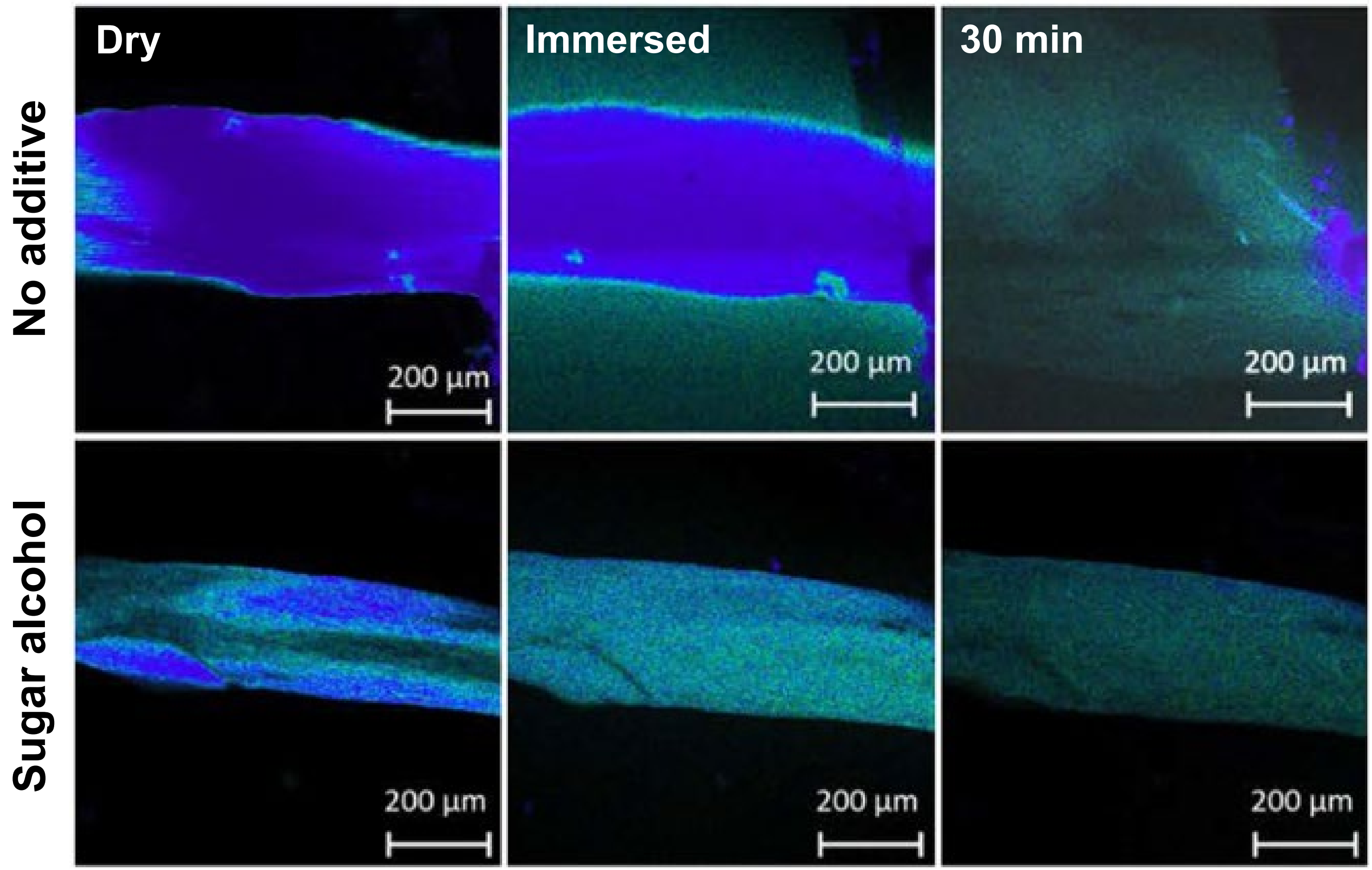
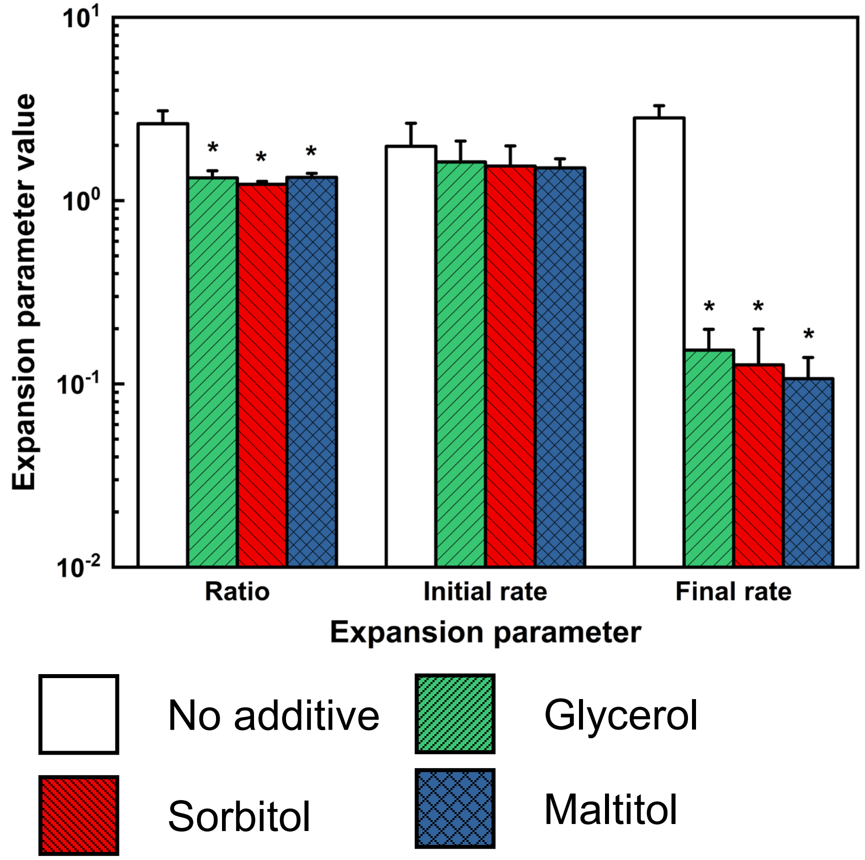
Nigmatullin et al. (**2020**) *Carbohydr. Polym.* 250:116953.

# Tracking nanocelluloses – dynamic analysis

**Fluorescence imaging enables tracking of material expansion in near real-time**




* $p < 0.05$

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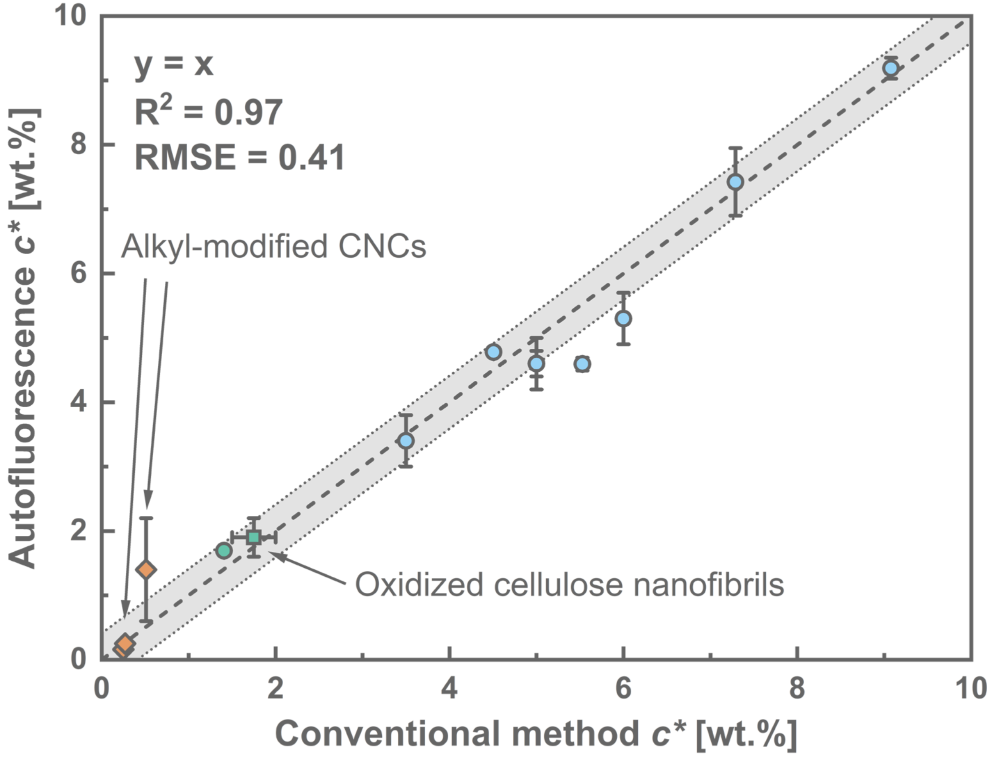
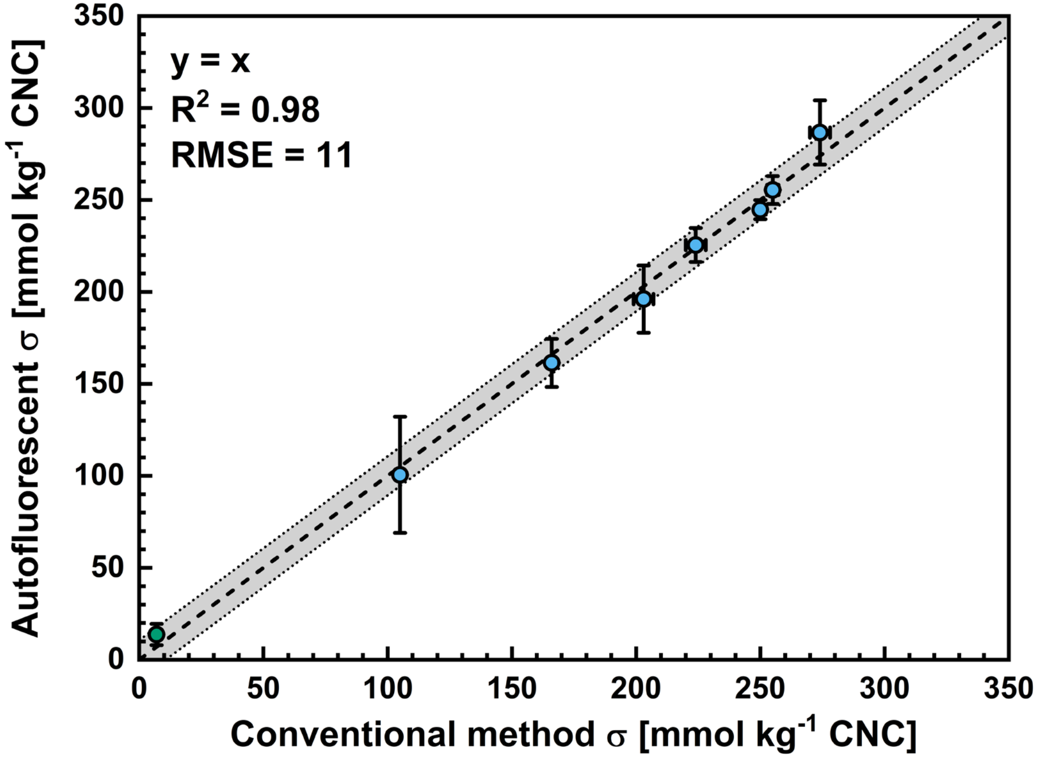
Johns et al. (**2021**) *Cellulose* 28:7829.

# Characterization of nanocellulose properties

## Critical concentration accurately determined from autofluorescence spectrum alone




## Surface charge content accurately determined from autofluorescence spectrum alone




Hydrophobic gelation  Gelation  Liquid crystalline phase formation

RMSE: Root mean square error

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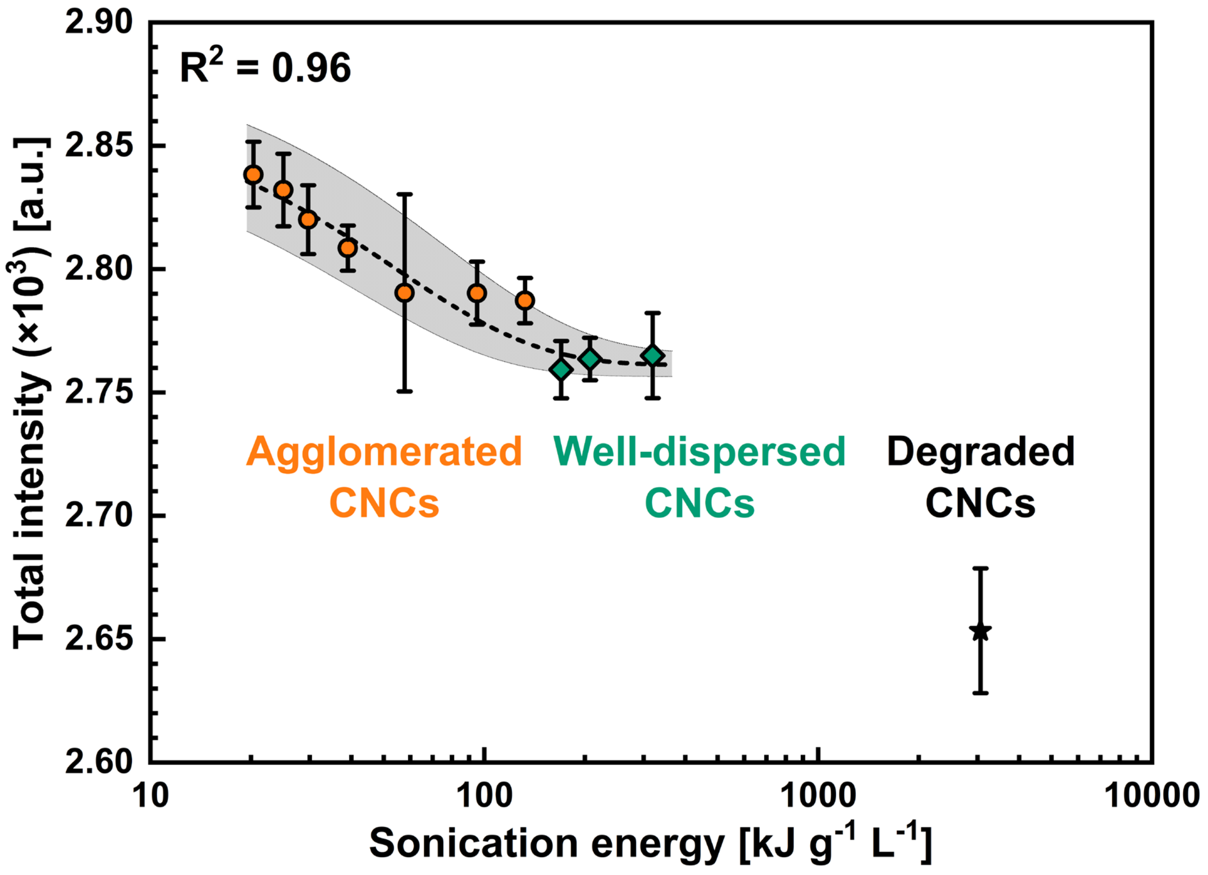
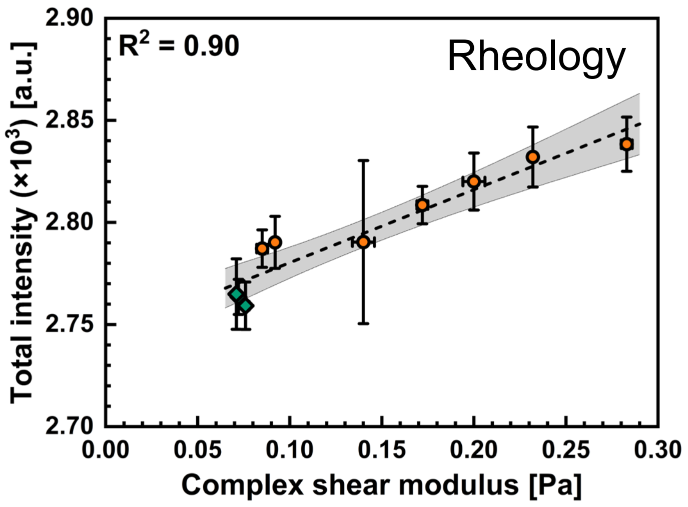
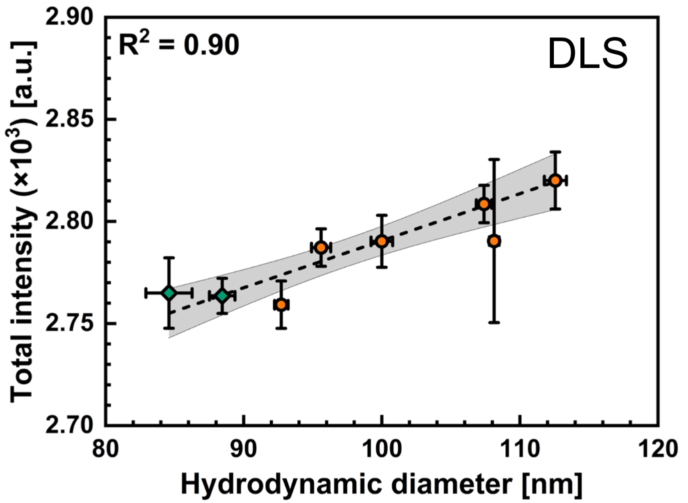
○ Johns et al. (**2022**) *Nanoscale* 14:16883.
□ Johns et al. (**2020**) *Analyst* 145:4836. ◇ Nigmatullin et al. (**2020**) *Biomacromolecules* 21:1812.

# Dispersion of dried cellulose nanocrystals

**Fluorescence imaging enables tracking of nanocellulose dispersion/agglomeration**

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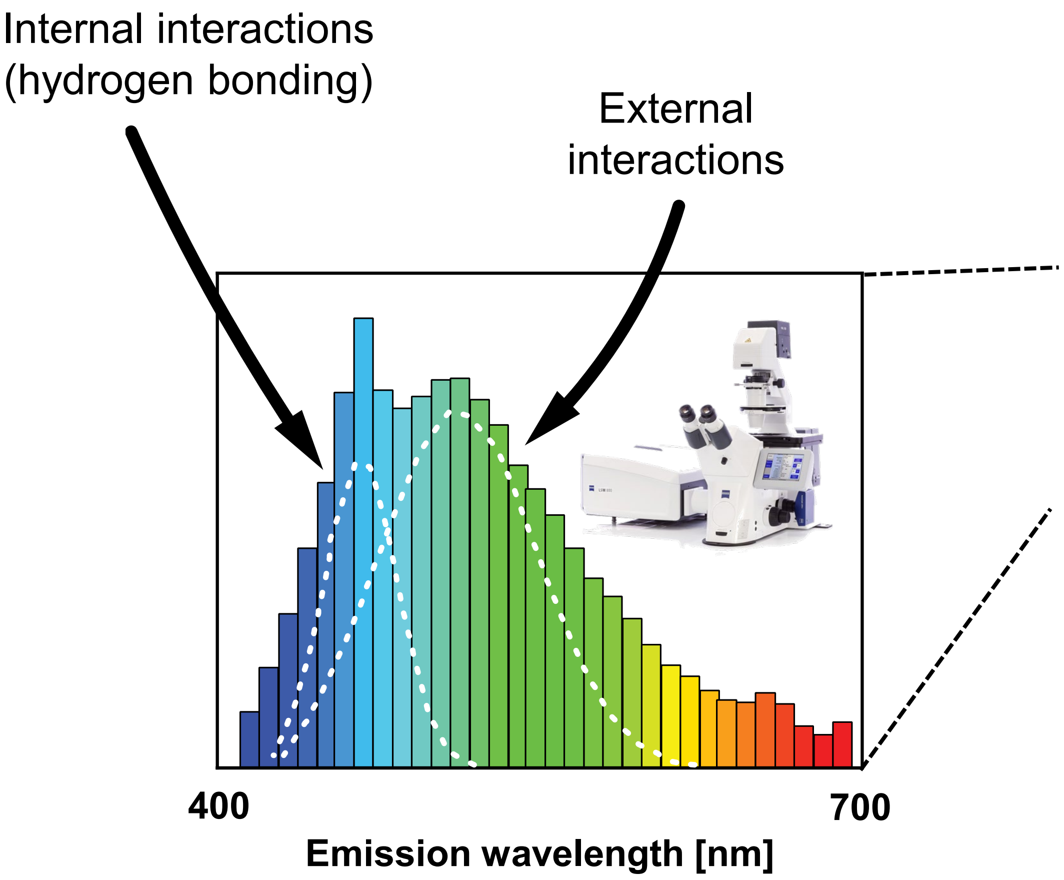
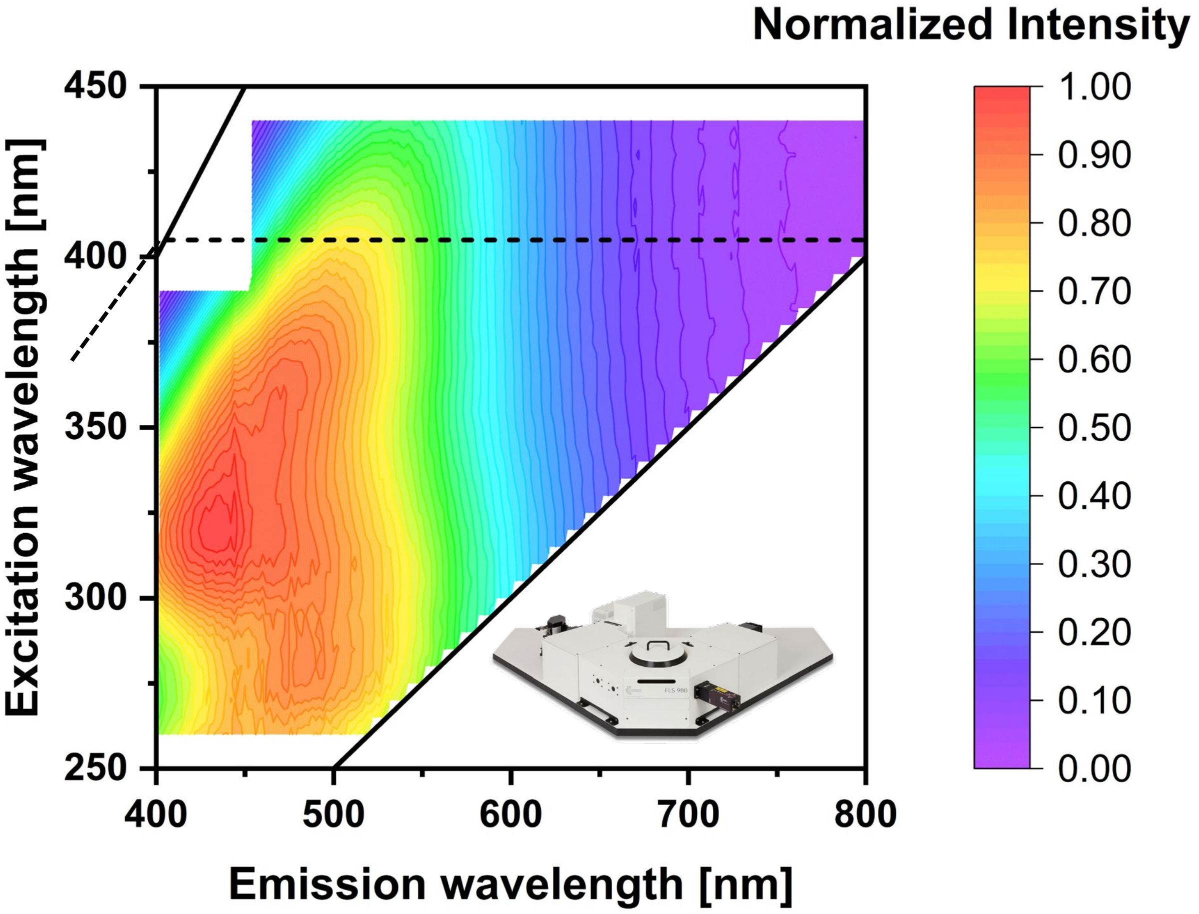
# Origins of nanocellulose fluorescent bands

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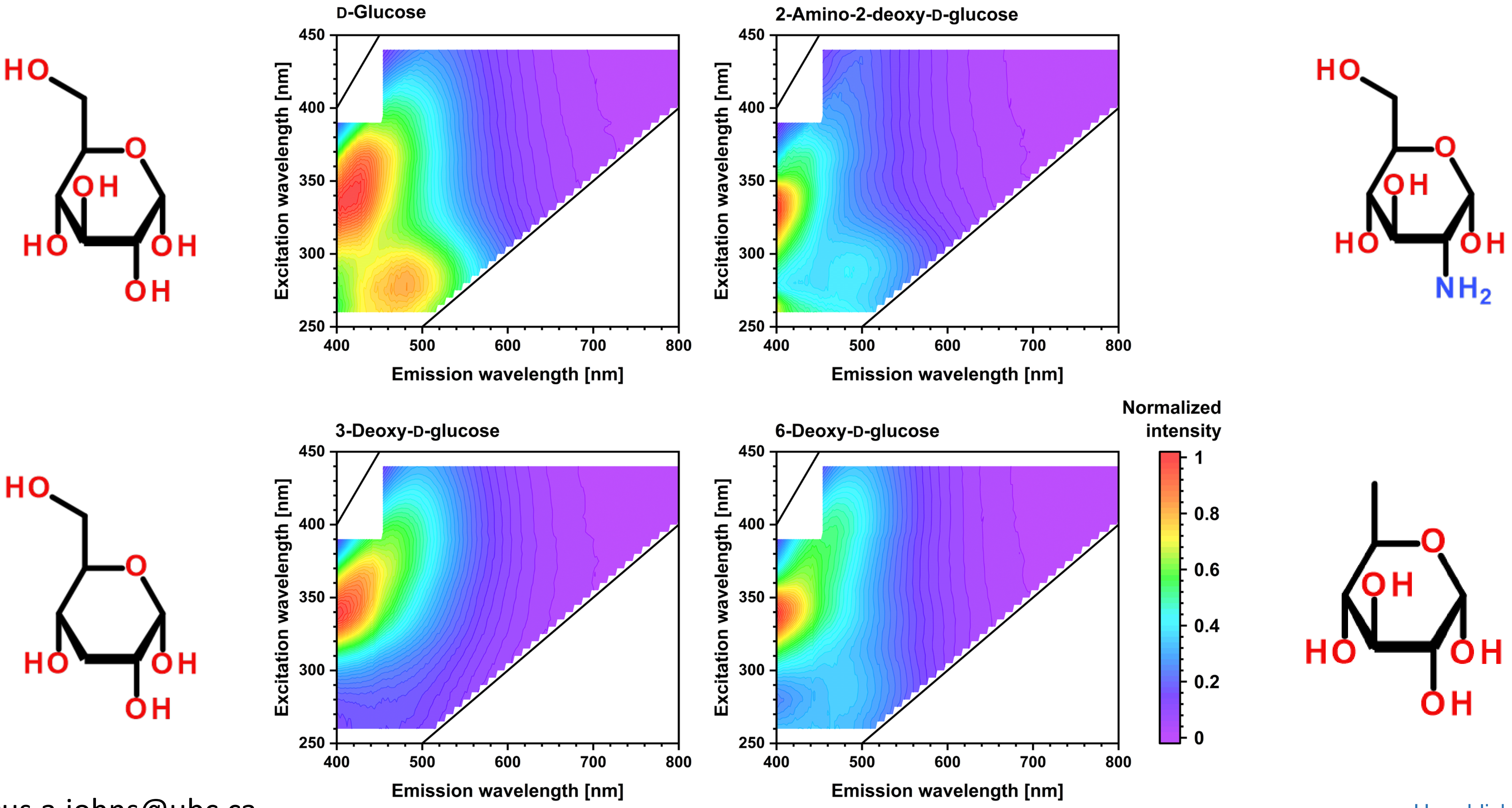
Johns et al. (**2022**) *Nanoscale* 14:16883.

# Origins of nanocellulose fluorescent bands

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# Conclusions

**Fluorescence arising from intermolecular interactions enables tracking of cellulose nanomaterials and determination of their key properties**

| Positives | Negatives |
|---|---|
| Minimal sample preparation required | Bulk measurement |
| Can distinguish different materials from one another | Weak emission intensity limits detection at low concentrations |
| Can determine multiple properties simultaneously | Conventional fluorophores, e.g. lignin, will dominate fluorescence spectra if present |
| Applicable in a variety of situations | |
| Rapid technique | |
| Highly sensitive to surface modification | |
| In-line analysis technically feasible | |

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# Acknowledgements


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Dr Hongying Zu


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