Templated CNC Bouligands

American University

- NW Washington, DC
- Private, Methodist affiliation
- 7200 UG, 3800 GR, 1400 JD
- 12:1 student – faculty ratio
- 90% internships, 70% study abroad
- Known for Political Science & International Service
- Growing science programs
  - ACS Programs in Chemistry & Biochemistry
  - Tailored MS Programs
    - Applied Chemistry
    - Clinical Biochemistry
    - Chemistry & Society

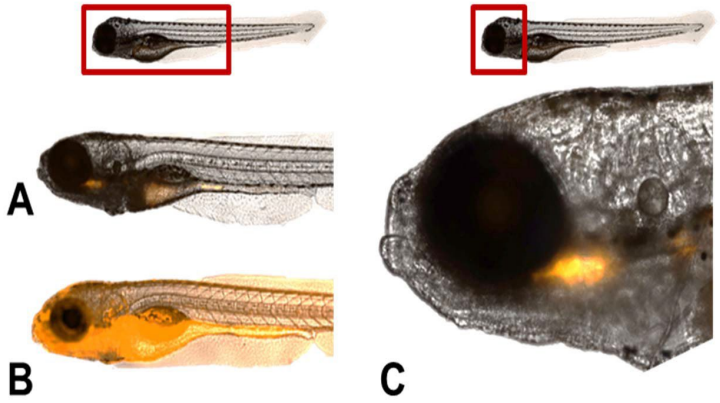
American University Research

Natural Product Flame Retardants

Cellulose – Polymer Nanocomposites

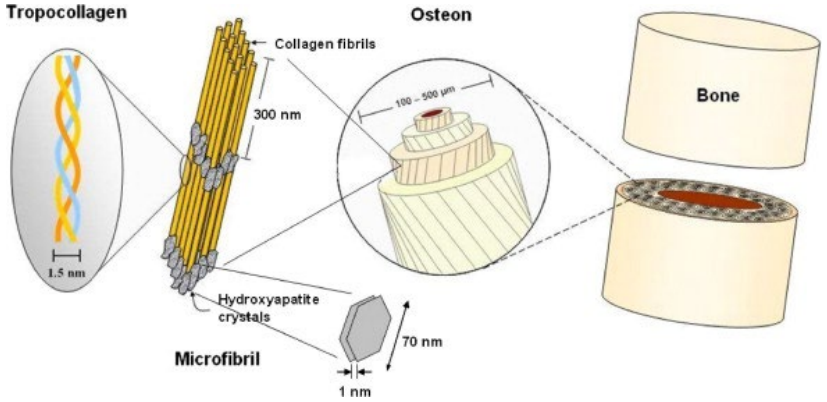
Natural Product Solvent Properties

Environmental Health & Safety of Cellulose Nanomaterials

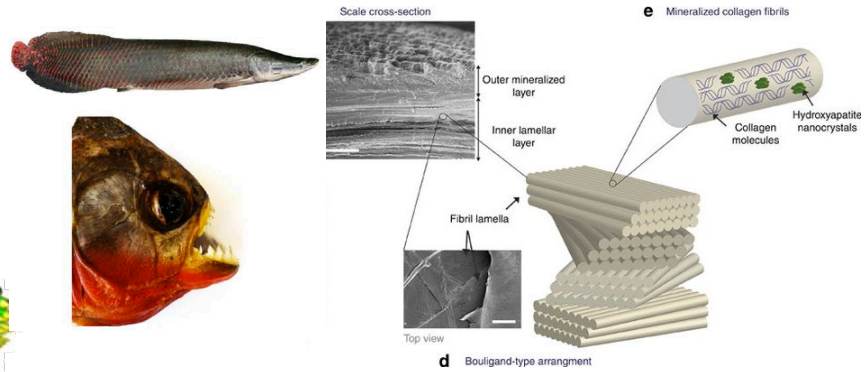


Structural Hierarchy in Nature's Composites

Bone



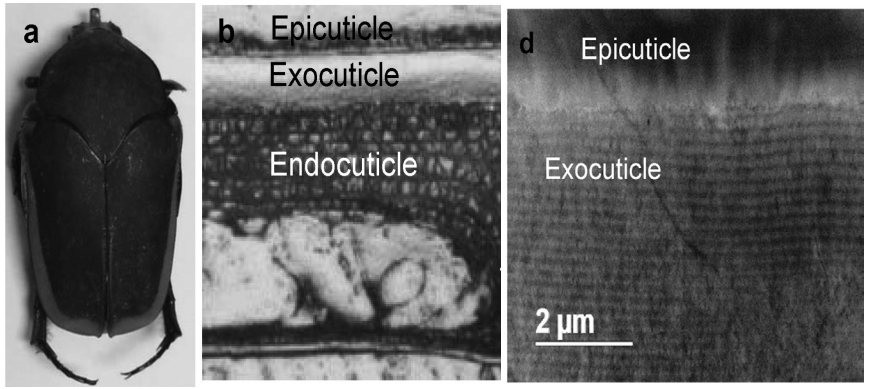
Arapima Fish Scales



Zimmermann, EA., et al. Nature communications (2013) 4.

Bouligand Structures

Beetle Exoskeleton

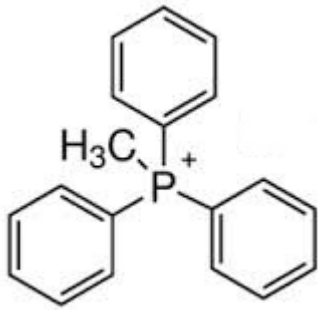


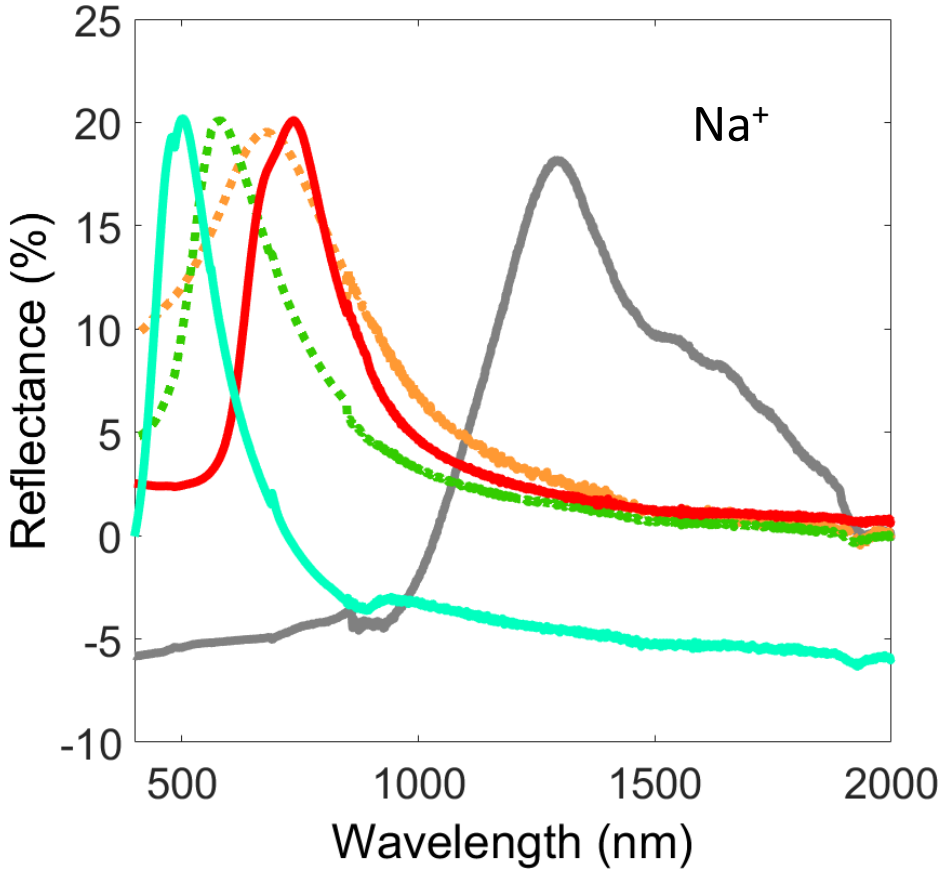
Materials Today: Proceedings 1S (2014) 161 – 171

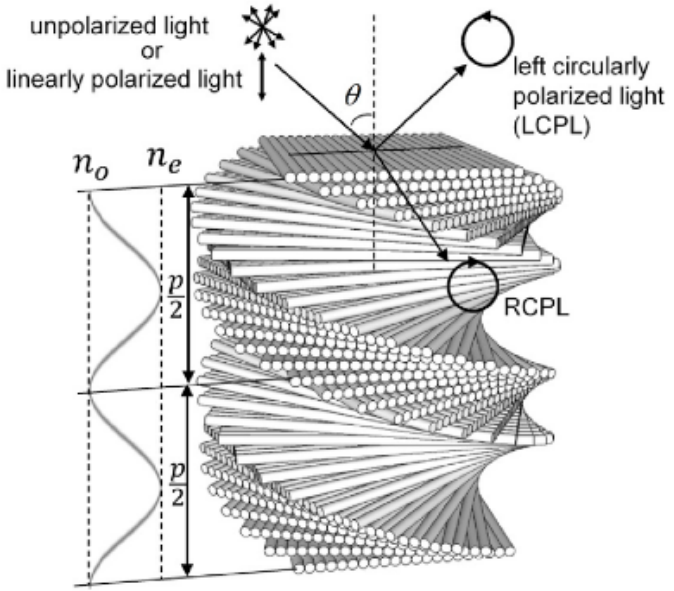
Mantis Shrimp Club

Guarín-Zapata, Nicolás, et al. Acta biomaterialia 23 (2015): 11-20.

Reflectance







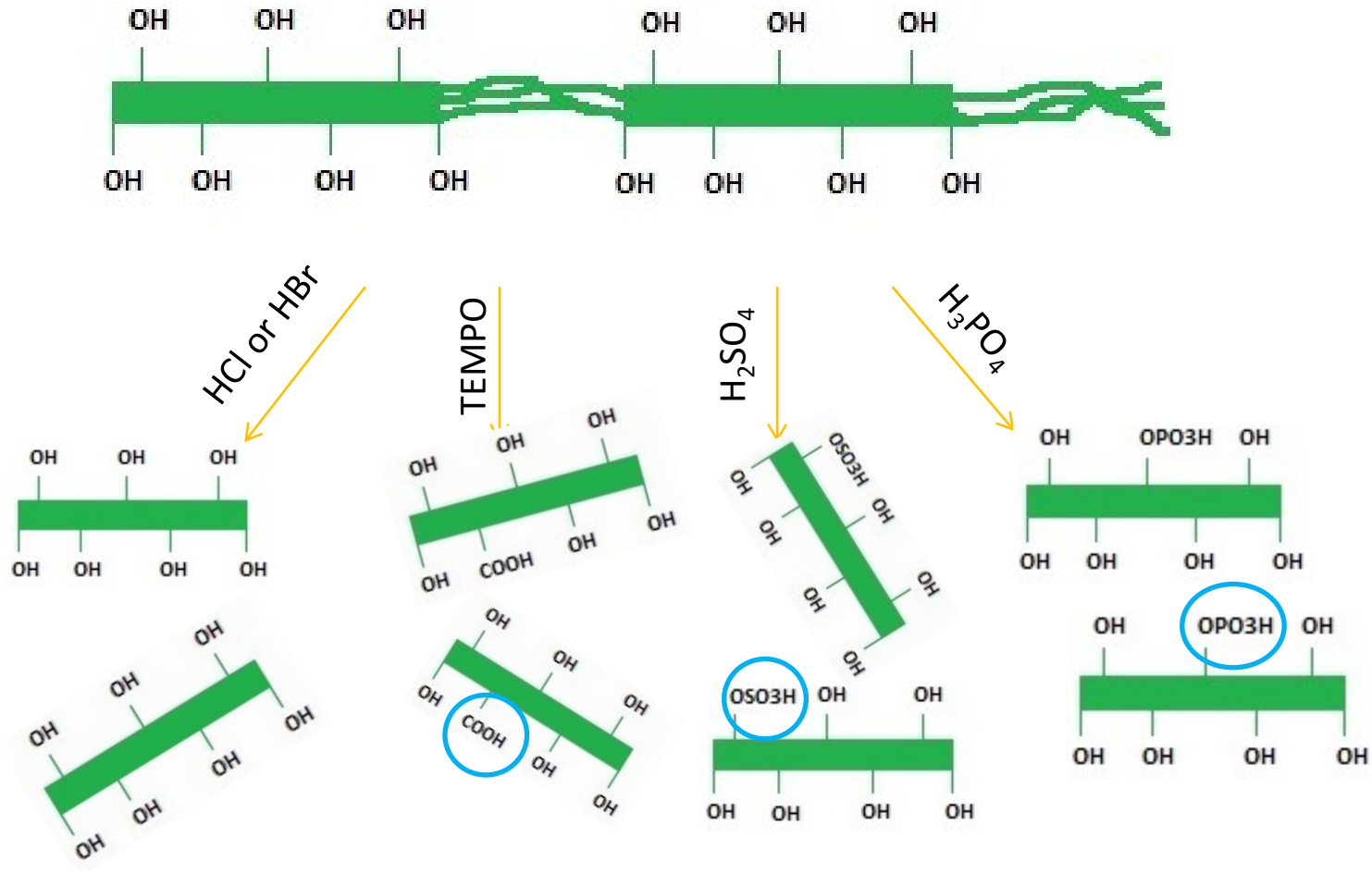
$$\lambda = \left(\frac{P}{2}\right) n_{CNC}$$

H. de. Vries. Acta Cryst. (1951). 4, 219

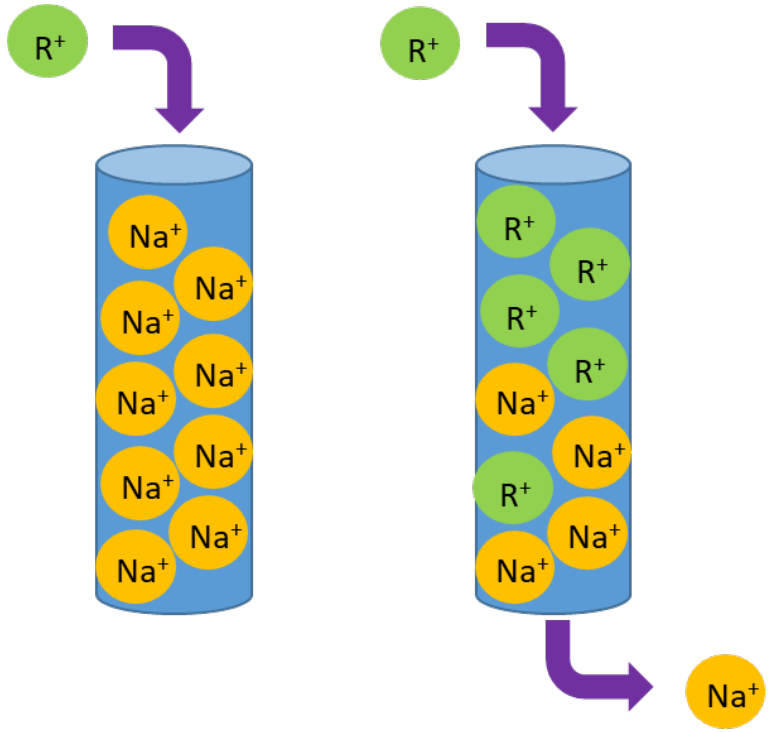
Material	Drying rate	λ_1 (nm)	$\Delta\lambda_1$ (nm)	λ_2 (nm)	$\Delta\lambda_2$ (nm)
Na-CNC	Slowest	517	98	-	-
Na-CNC	Slow	736	118	-	-
Na-CNC	Fast	1274	149	1570	270
P^+-CNC	Slow	590	175	-	-
P^+-CNC	Fast	655	279	1097	452

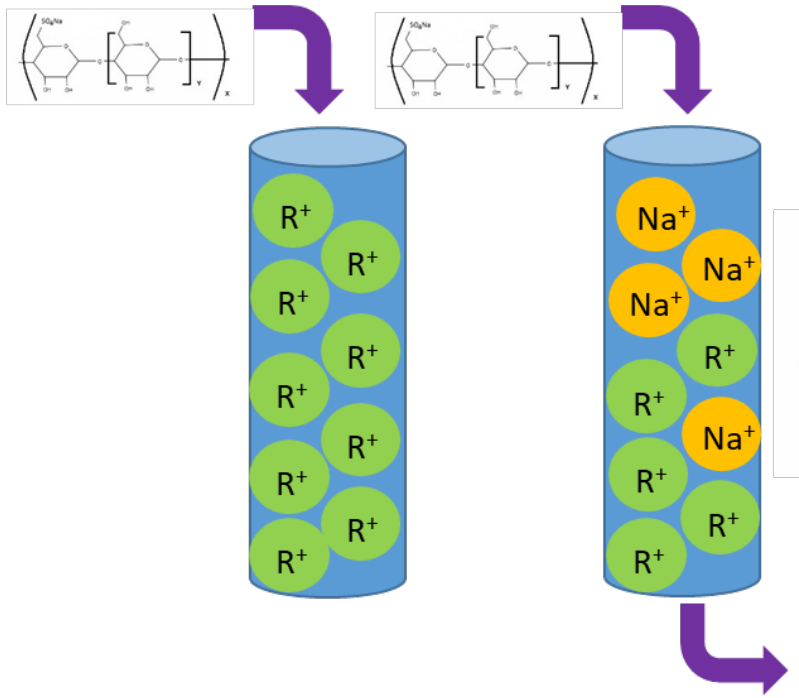
Lowered rate of drying and Phosphonium functionalization leads to blue shifting

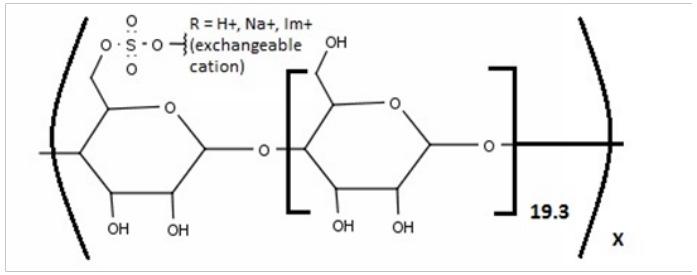
Preparation of Cellulose Nanocrystals



Modification Process

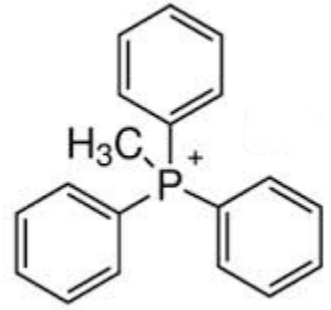




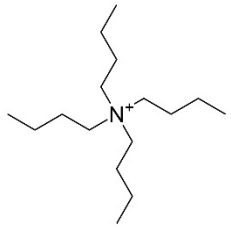


Tailored Surface Energies

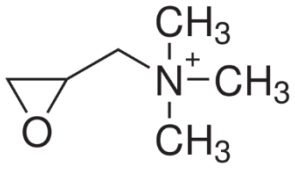
CNC-SO4
CNC-PO4
CNF-COOH
CNC-COOH



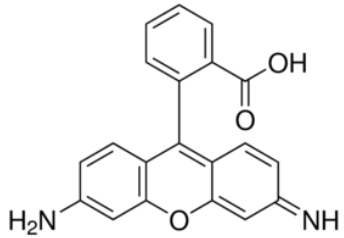
Epoxy
PS
ABS
PLA/silk



PCL
PLA
PP?

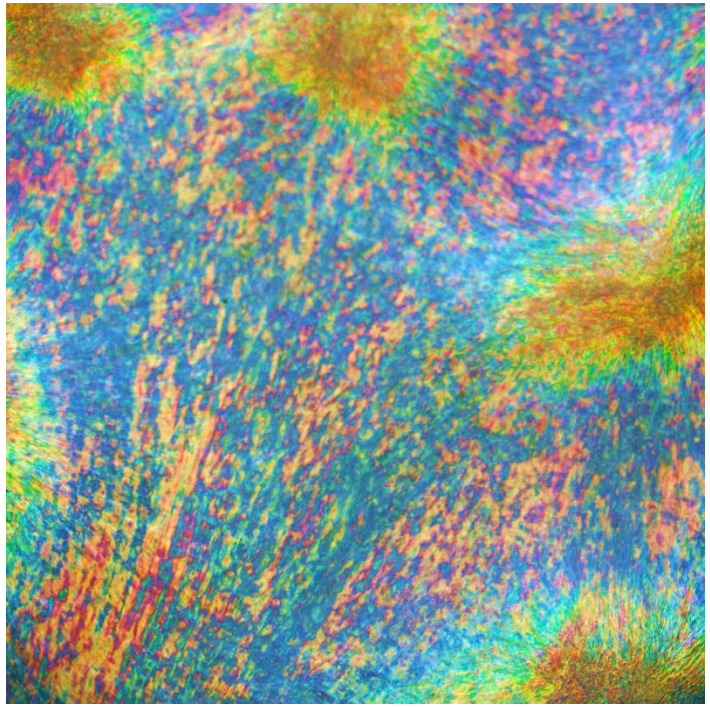


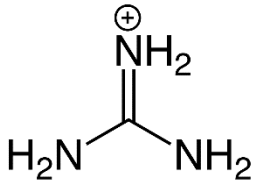
Epoxy
Polyurethane
Polyester
Polycarbonate

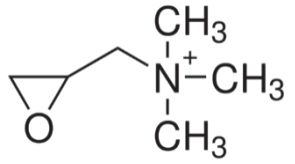


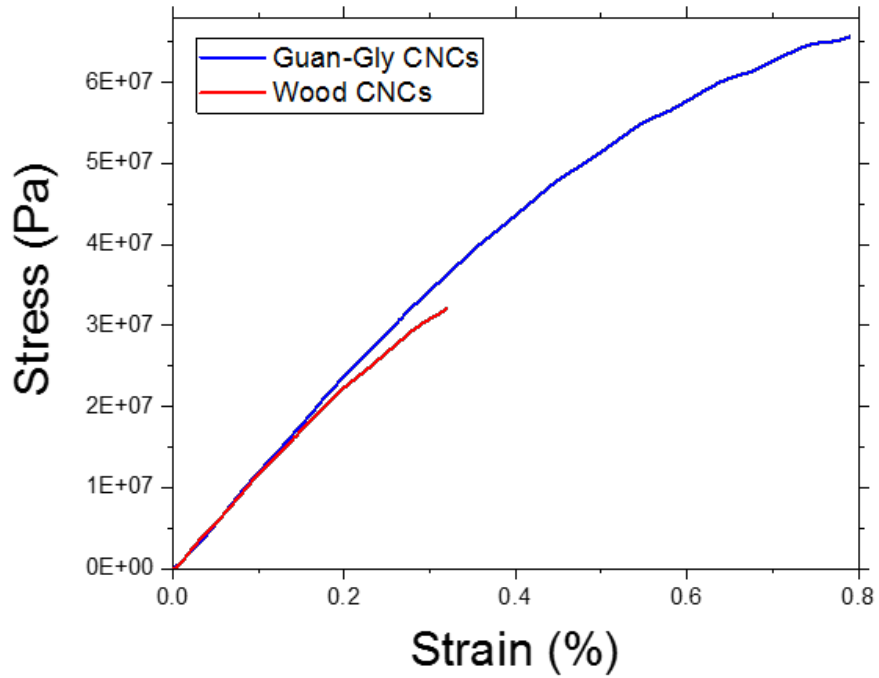
Imaging
Dispersion
Detection

Reactive Cations on CNCs films





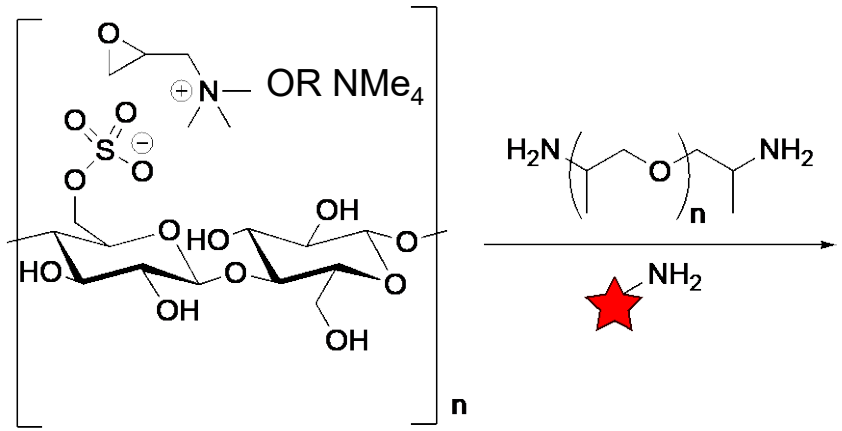


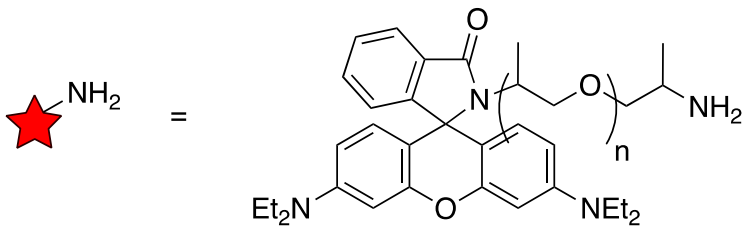


	Strength (MPa)	Strain to Failure	Modulus (GPa)	Toughness (MPa.m/m)
Guan(50)-Gly(50)	60.35 ± 9.6	0.72 ± 0.11	11.86 ± 0.66	0.216
Wood CNCs	32.85 ± 5	0.36 ± 0.10	9.11 ± 0.52	0.059

Collaborators: Bharath Natarajan, Richard Sheridan

Film self-assembly





- Drying in humidity chamber
- Thin films possessing Bouligand structure
- Fluorophore randomly distributed throughout structure

ADA Science & Research Institute

Samples Studied

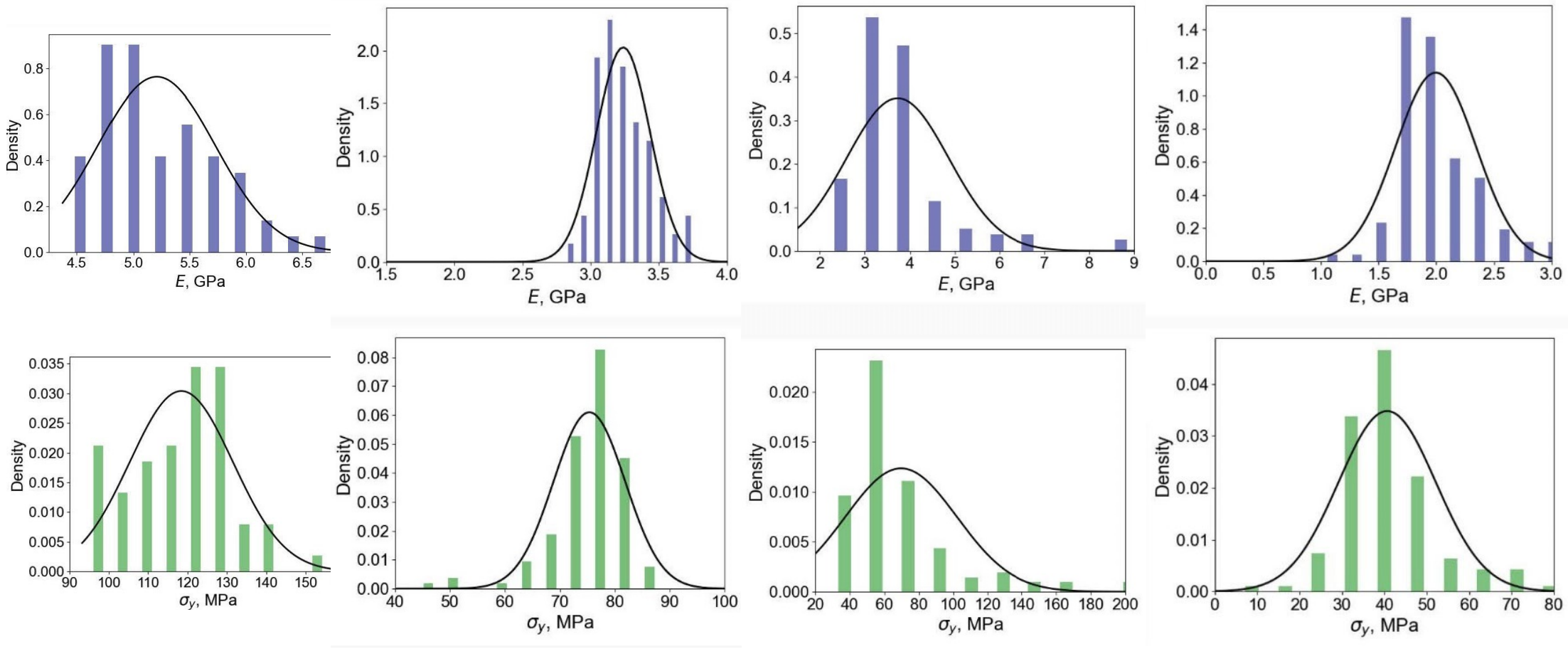
Sample	Mass ratio (CNC:JA)	Mole ratio (NH:Gly)
Gly-CNC + D230	9.4 : 1	5.2 : 1
Gly-CNC + D400	9.4 : 1	2.7 : 1
Gly-CNC + D2000	9.4 : 1	0.6 : 1
Gly-CNC + D400	5 : 1	5.1 : 1
Gly-CNC + D2000	1.1 : 1	5.2 : 1
TMA-CNC + D230	9.4 : 1	---
TMA-CNC + D400	9.4 : 1	---
TMA-CNC + D2000	9.4 : 1	---

Code	Name	AHEW or EEW
D230	Jeffamine D230	60
D400	Jeffamine D400	115
D2000	Jeffamine D2000	514
Gly	Glycidyltrimethylammonium	2950
TMA	Tetramethylammonium	0

Nanoindentation – Nonreactive Cations

Young's modulus

Yield strength

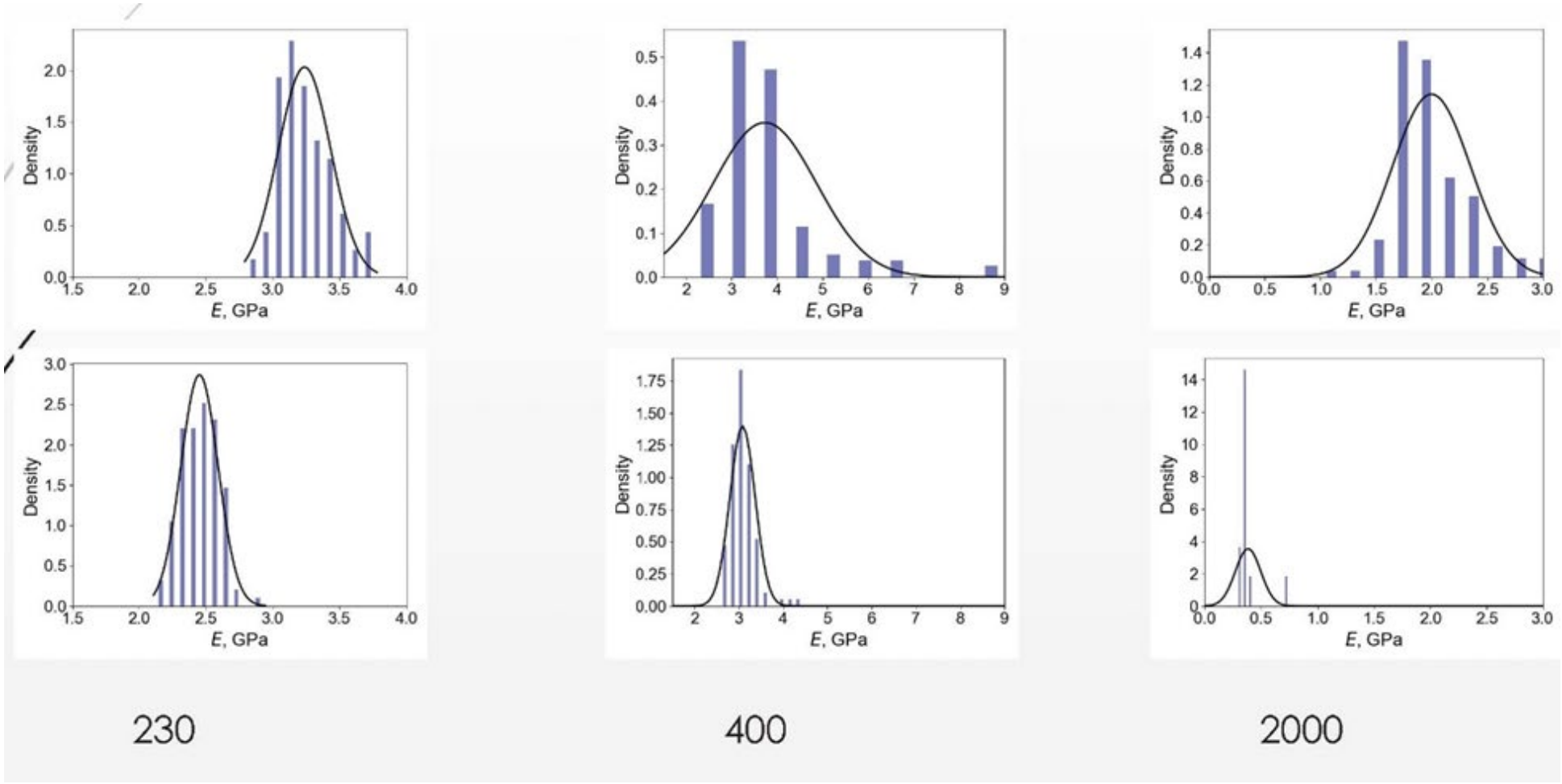


$GlyMe_3N^+CNC$ Me_4N-D230 Me_4N-D400 Me_4N-D2000

Nanoindentation – Effects of Reactive Cations

Me_4N^+
10% amine

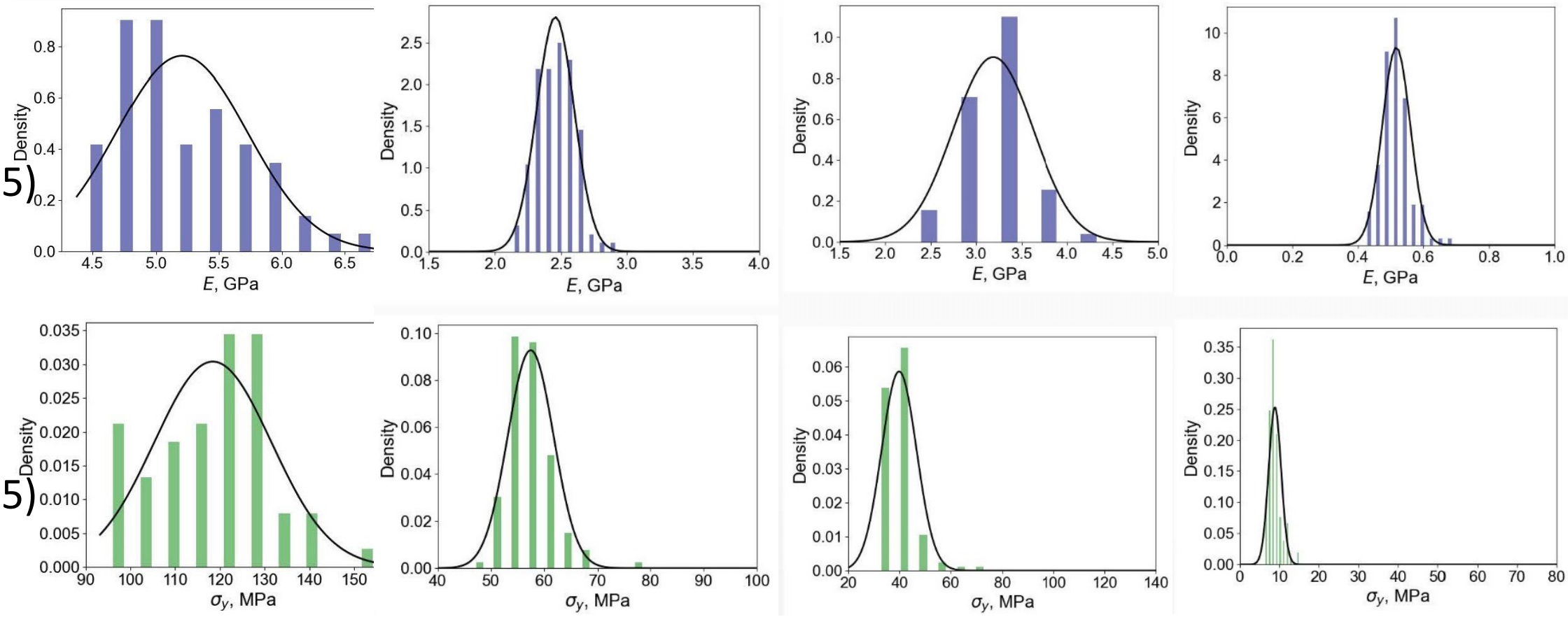
$GlyMe_3N^+$
10% amine



Nanoindentation – Effects of Diamine Length

Young's modulus (NH:Gly = 5)

Yield strength (NH:Gly = 5)



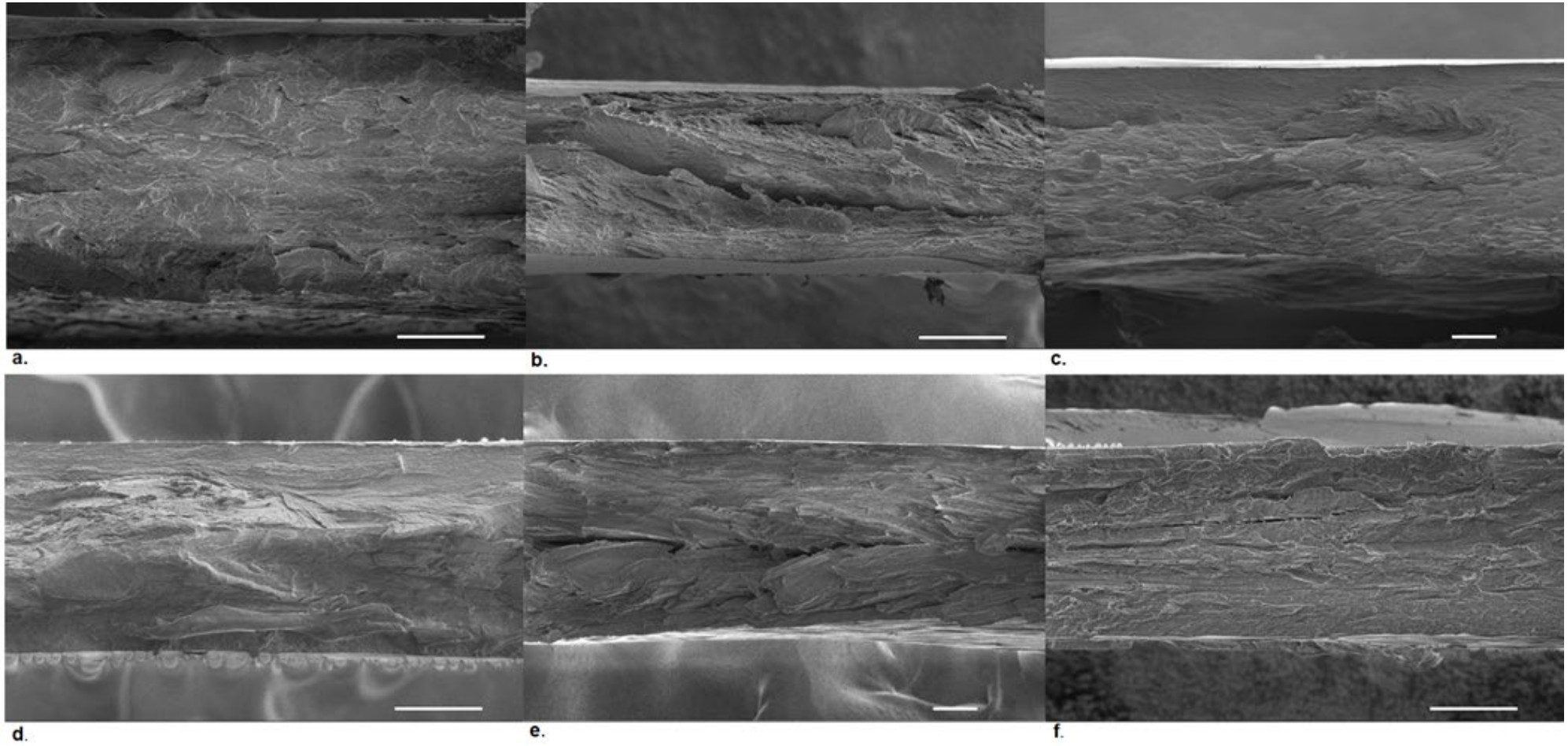
$GlyMe_3N^+CNC$ D230 D400 D2000

FESEM – Film compaction

Most compact, correlating with highest stiffness

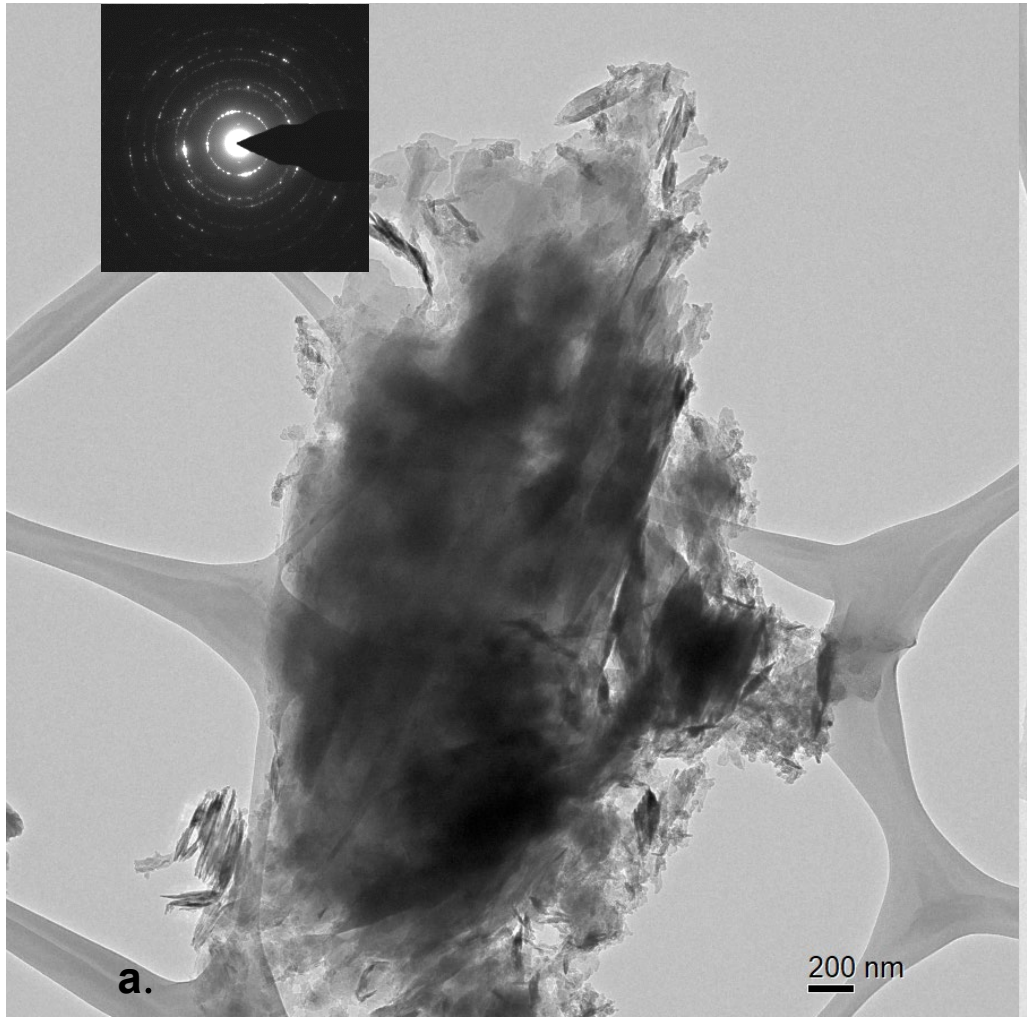
$GlyMe_3N^+$
10% amine

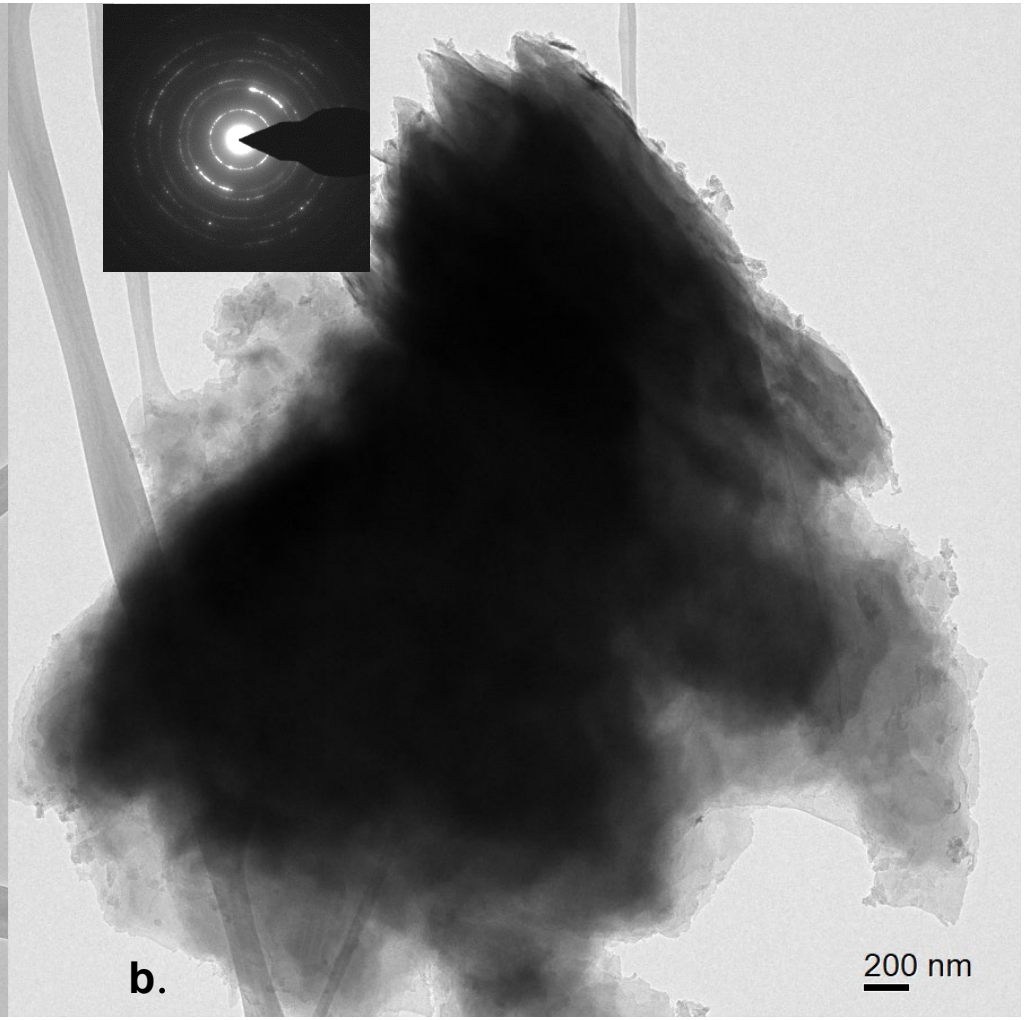
Me_4N^+
10% amine



D230 D400 D2000

TEM – Fragment Morphology





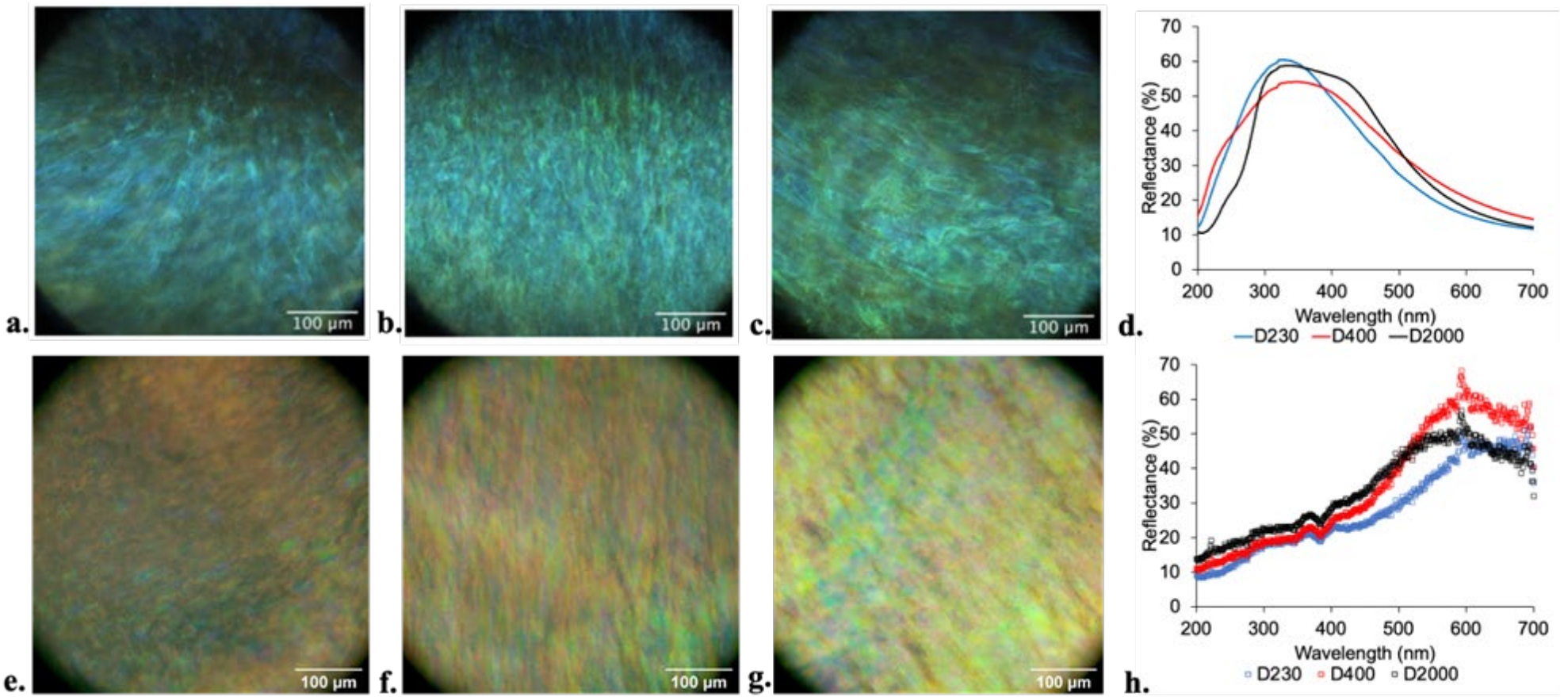
$GlyMe_3N^+$ 10% D400

Me_4N^+ 10% D400

Effects of Cation on Bouligand Pitch

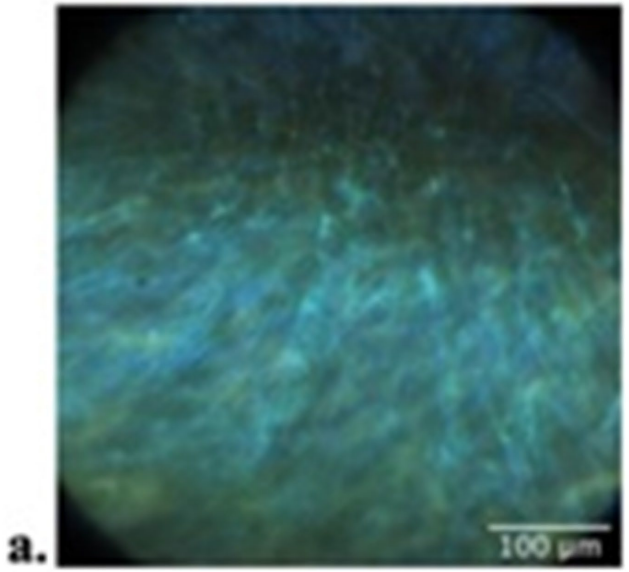
$GlyMe_3N^+$
10% amine

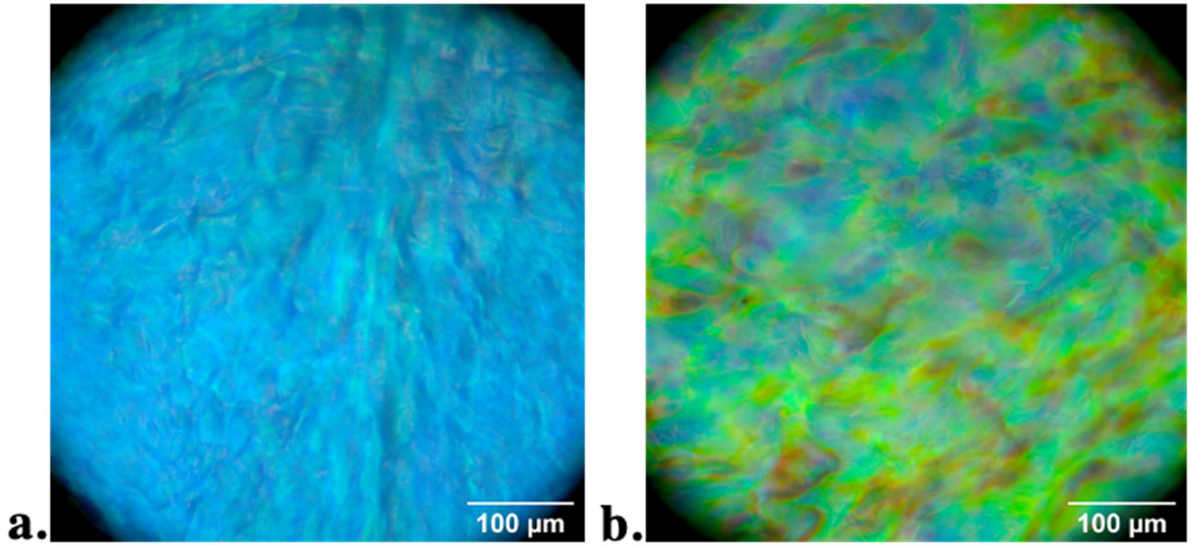
Me_4N^+
10% amine

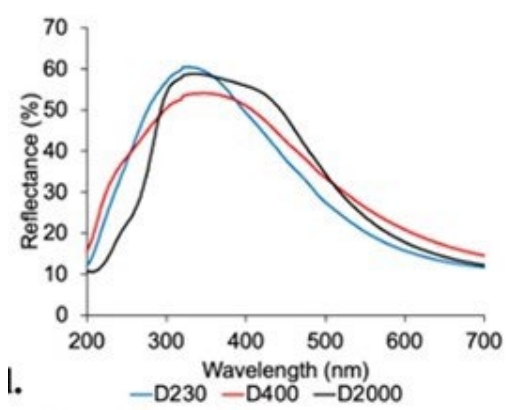


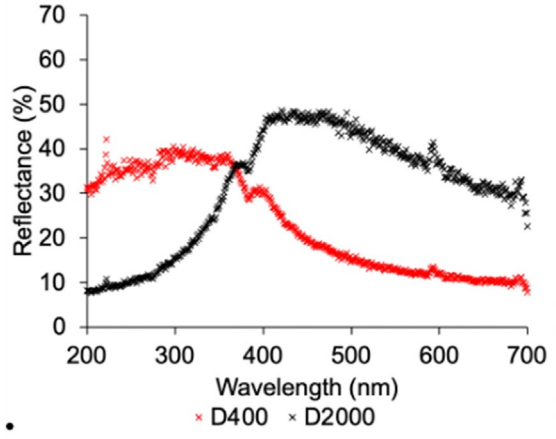
Non-reactive has similar pitch to Na-CNC, with blue shifts as diamine becomes more hydrophobic
Reactive has large blue shift with broader pitch as diamine length increases

Effects of Diamine on Bouligand Pitch





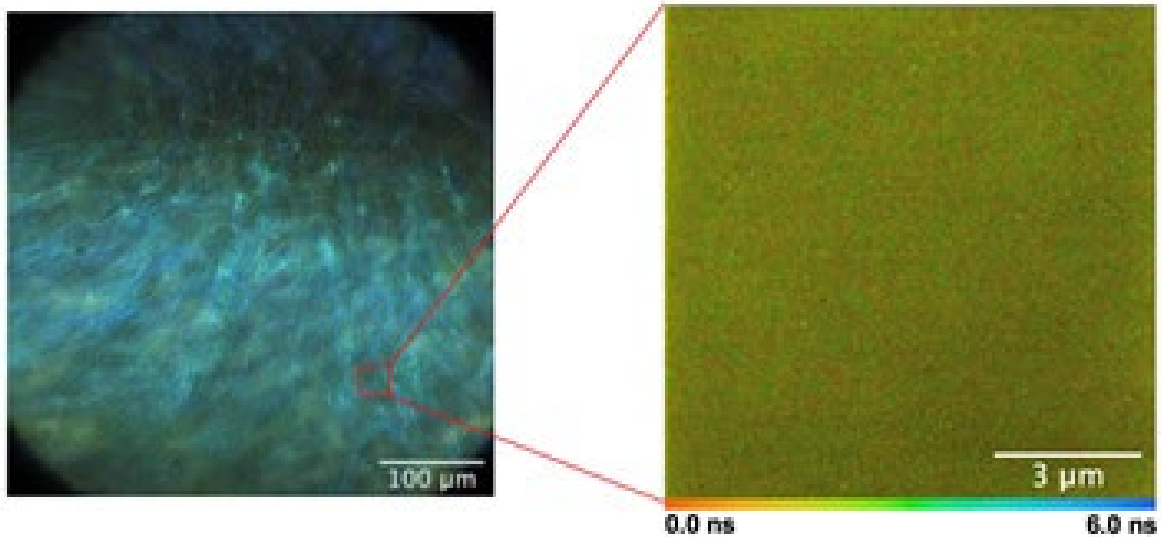




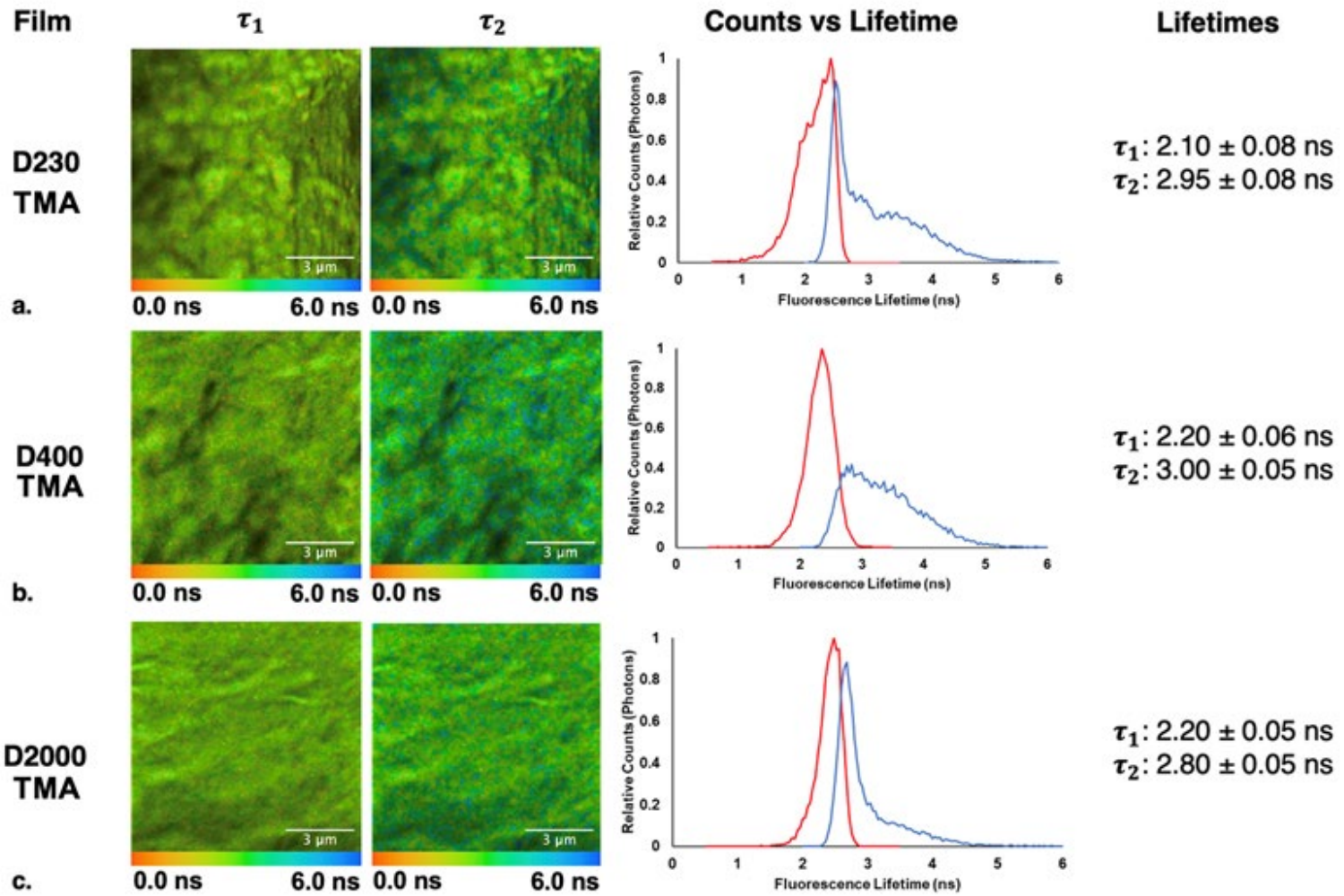
Red shift upon greater diamine content suggests exclusion within Bouligand

Fluorescence Lifetime Imaging (FLIM)

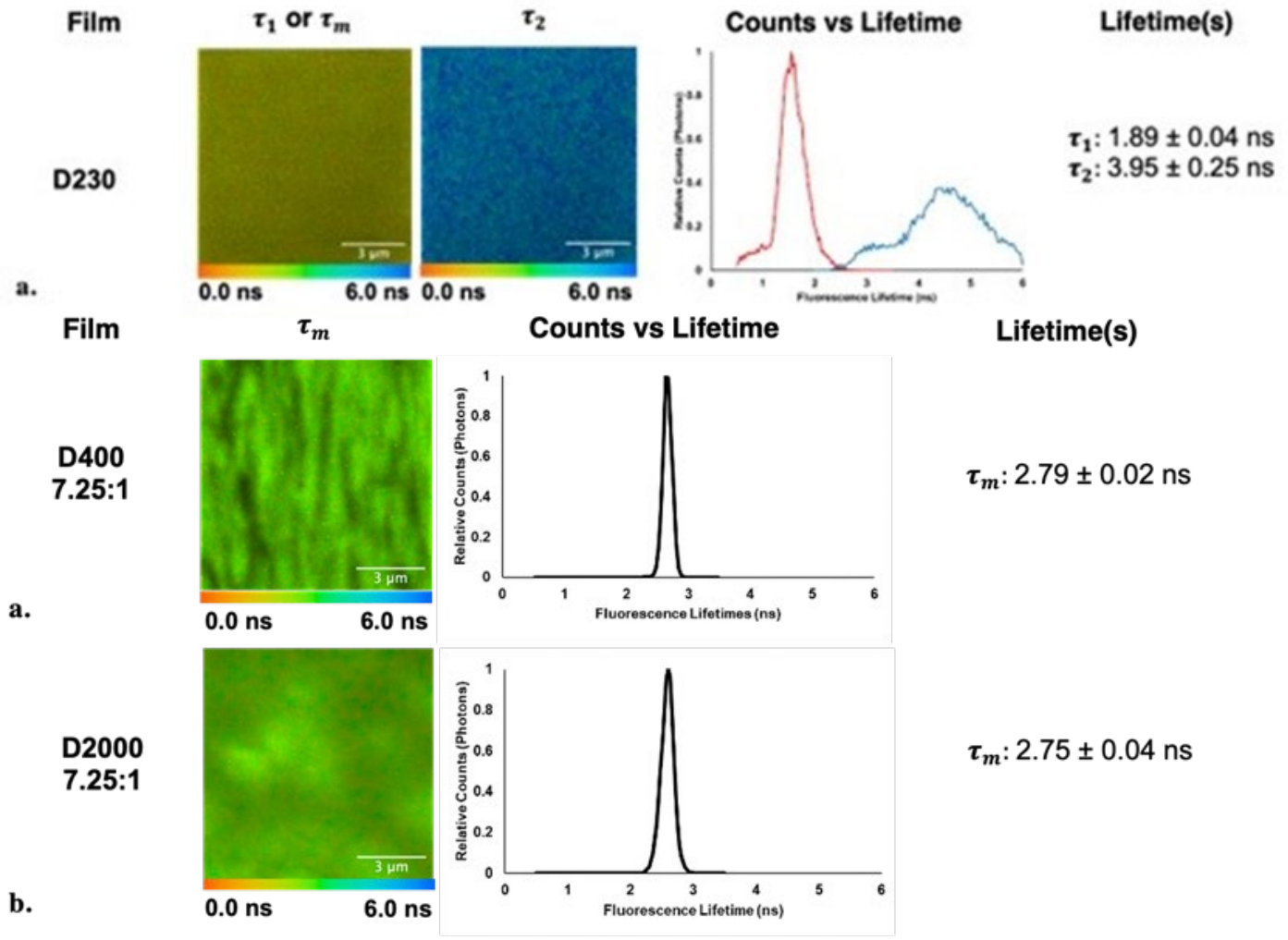
- Lifetime probes local environment of fluorophore
  - Free moving fluorophores have more chances for collisions and other non-radiative energy transfer
  - Confined/constrained fluorophores have longer lifetimes
- Multiple lifetimes mean heterogenous environments
- Smaller region examined



Nonreactive systems



Reactive Systems



Conclusions

- Non-reactive Systems
  - Micro/meso Homogeneity, Nano heterogeneity
  - E: D400 > D230 > D2000
  - σ_y: D230 > D400 > D2000

- Reactive Systems
  - Better homogeneity, significant loss in stiffness & strength
  - E: D400 > D230 > D2000
  - σ_y: D230 ≥ D400 > D2000
  - Tighter packing of Bouligand & composite
  - Longer diamines on edges or outer surface of Bouligand

Acknowledgments

- Jeremiah W. Woodcock
- Quinn T. Easter
- Shawn H. Chen
- Amanda J. Souna
- Sindhu Seethamraju
- Jan Obrzut
- Stephan J. Stranick
- Ange-Therese Akono
- Vladimir Oleshko
- Christopher L. Soles
- Jeffrey W. Gilman

Thank You!