Welcome

to today's episode:

Unveiling the Nanoscale:

PiFM for Chemical, Structural, and Surface Charactrization

Padraic O'Reilly
Application Scientist
Molecular Vista, Inc.

OCT 16, 2025
11 AM Pacific Time

MOLECULAR VISTA

COVALENT METROLOGY

COVALENT METROLOGY

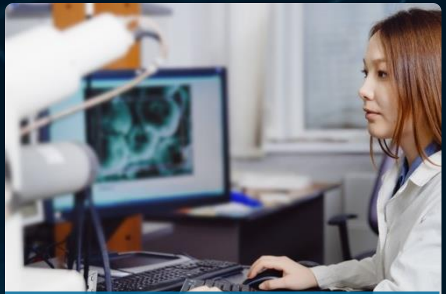
Modern, digitally-empowered analytical services platform delivering quality data and expert analysis to accelerate advanced materials and device innovation.

Comprehensive Solutions Stack

- *50+ Cutting-edge instruments in-house, 150+ Techniques*
- *Analytical Services*
- *Advanced Modeling*
- *Method Development*
- *Custom Consulting Solutions*

High-touch, High-Quality Services

- *Nexus Membership Program*
- *Enterprise Metrology Solutions*
- *Instant, Secure Access to Data and Reports*
- *Expanding Toolkit in Custom Digital Platform*



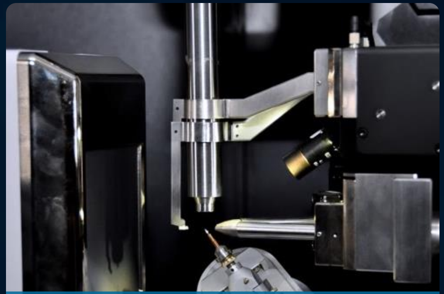
Flexible Business Models

- *LiveView^{TM} (real-time collaboration)*
- *Co-op and Tool-share Opportunities*
- *Training and Certification on Instrumentation*
- *Laboratory Audits*

Rigaku
Anton Paar
ThermoFisher SCIENTIFIC
Asylum Research
KEYENCE
J.A. Woollam
TA Instruments
PVA TePla
TELEDYNE CETAC TECHNOLOGIES Everywhereyoulook
HORIBA Scientific
Digital Surf

Rich Network of Partnerships

- *Partner to World's Leading Instrument Manufacturers and Labs*
- *Expanding access to Advanced Instruments and Analysis Tools*
- *Lab Connections and Applications Learning*



Who We Are, Who We Serve

- *80+ People, 21 PhDs*
- *Comprehensive, Modern Analytical Capabilities*
- *Headquarter Lab in Sunnyvale, CA*
- *800+ Clients, 15-30 new clients / week*

Covalent's Analytical Services & Technical Groups

COVALENT METROLOGY

Enterprise Metrology Solutions: Failure Analysis & EM

Electron Microscopy

- S/TEM
  with EDS; EELS; Electron Diffraction; SAED
- FIB-SEM & HR-SEM
  with EDS; EBSD; 3D Tomography
- Lamella Preparation
  incl. specialized lift-outs

Failure Analysis

- DPA / Mechanical X-section
- Dye & Pry Test
- EBIC / OBIC failure analysis
- Hot Spot Detection
- NIR / IR Imaging
- Emission Microscopy
- Root-Cause Failure Analysis

Materials, Chemicals, and Surfaces

Microscopy & Profilometry

- Chromatic Aberration
- Digital Optical Microscopy
- Laser Scanning Confocal Microscopy
- White Light Interferometry
- Scanning Acoustic Microscopy (SAM)

Analytical Chemistry

- Mass Spectroscopy:
  ICP-MS and LA-ICP-MS; GCMS
- ICP-OES / GDOES
- Raman
- NMR (solid / liquid + 1,2,3 nuclei)
- XPS, UPS, ISS
- SIMS, TOF-SIMS

X-ray Characterization

- X-Ray Diffraction (XRD)
- X-Ray Reflectometry (XRR)
- Micro-computed X-ray Tomography (Micro-CT)
- 2D / 2.5D / 3D X-ray Inspection & X-ray Radiography
- ED-XRF / WD-XRF

Mechanical Testing

- AFM & Advanced AFM Modes (EFM, KPFM, MFM, PFM, PiFM)
- Nano-indent / Nano-scratch
- Rheometry / Viscosity
- DMA / TMA (bend/stretch/compression)
- Tensile testing

Misc. Material Properties

- Thermal Analysis: DSC, TGA
- Surface Zeta Potential
- Porometry / Pycnometry
- Gas Adsorption / Chemisorption
- Foam Density / Skeletal Density / Tap Density
- Particle Analysis: DLS / ELS / size distribution / zeta potential

Optical Characterization

- Fourier Transformed Infrared Spectroscopy (FTIR and ATR-FTIR)
- **Spectral Ellipsometry & Advanced Optical Modeling**
- UV-Vis-NIR Spectroscopy

Introducing today's speaker

Padraic O'Reilly

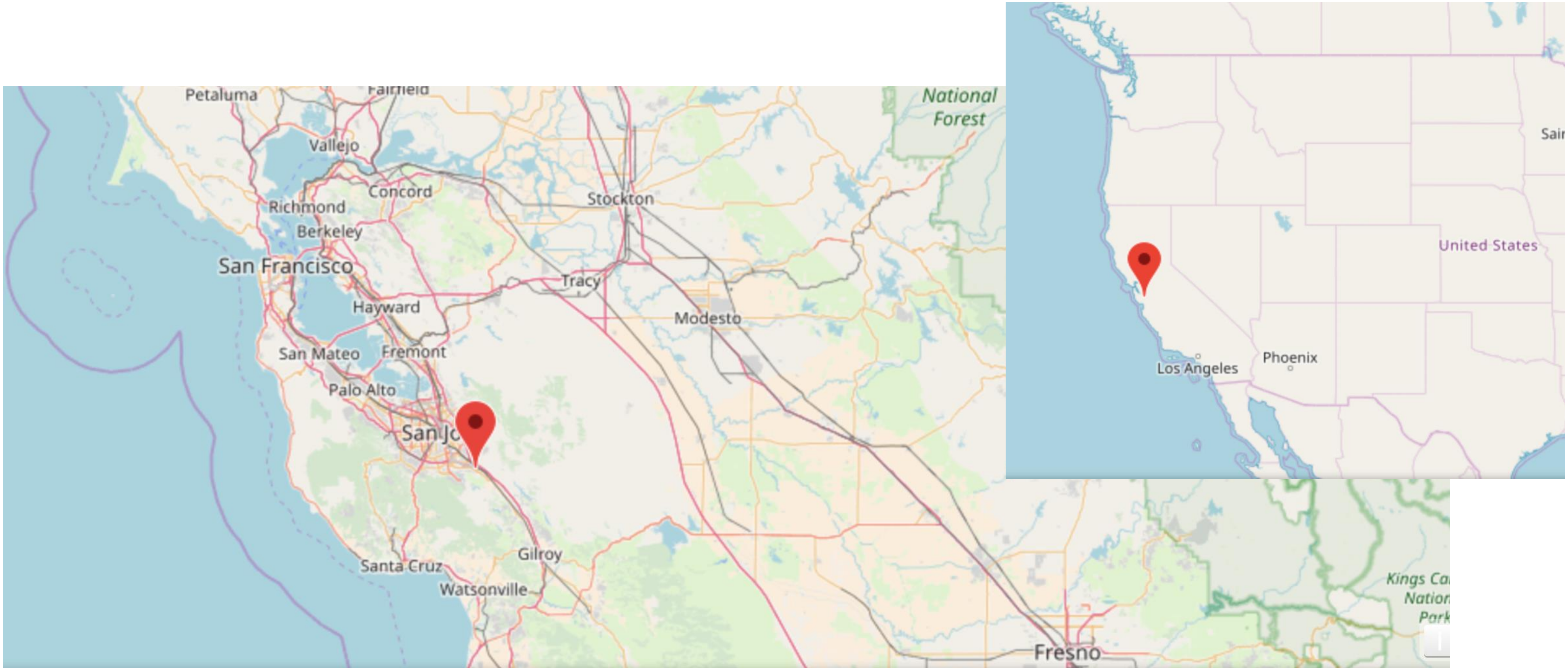
Applications Scientist

- Joined MVI in 2017 as an Applications Engineer, later promoted to Applications Scientist
- Collaborates with customers to design experiments using advanced AFM techniques
- Expertise in EFM, KPFM, and MVI's proprietary Photo-induced Force Microscopy (PiFM)
- Over thousands of hours of hands-on PiFM experience with diverse specimens
- Extensive work in visible and IR PiFM applications, including semiconductor defect and contaminant analysis

Agenda

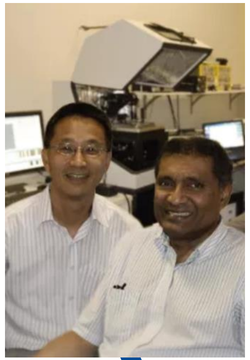
- Introduction to Molecular Vista and PiFM
- General examples of PiFM Results – If you can do AFM on the sample, you can do PiFM!
- Comparison with Other Techniques
- PiFM on Monolayers
- Summary

Molecular Vista Inc. (MVI)



MVI Over the Years

Founded by Dr Sung Park and Dr Kumar Wickramasinghe



VistaScope

Vista One

KLARF compatible

Vista 75

Vista 150/200

Vista 300

2011 2013 2016 2021 2023 2024

Functionality	
Imaging modes	nc-AFM, PiFM, KPFM, cAFM, nano DMA, FvD (force vs distance) mapping, Raman*, s-SNOM*
Spectroscopy modes	PiF-IR, FvD, Raman*
PiF Laser options	QCL (770 – 1840, 1995 – 2395 cm^{-1}), OPO/DFG (590 – 2050, 2250 – 4400, 5000 – 7000 cm^{-1}).
Depth Probed	20 nm in surface mode & greater than 100 nm in bulk mode.

* = Not available for 150, 200 or 300

What Is PiFM?

Commonly Used Analytical Techniques

	Raman	FTIR	TOF-SIMS	XPS	TXRF	SEM/EDS	TEM	Auger
Species Detected	M.I.	M.I.	M.I.	M.I.	E.I.	E.I.	E.I.	E.I.
Chemical Mapping	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Lateral Resolution	> 0.5 µm	> 10 µm	100 nm	Sub 5 µm	~ 10 mm	1 nm* 0.5mm EDS	0.2 nm* 1 ~ 20 nm EDS	8 nm
Depth Probed	> 500 nm	1 µm	1 nm	10 nm	10 nm	1 µm	~ 100 nm	10 nm

* Imaging M.I. Molecular information E.I. Elemental information

Elemental information cannot identify nanoscale organic defects and ultrathin residues, which are becoming more commonplace. Existing tools for molecular information do not have spatial resolution to analyze sub-100 nm particles.

FTIR – How to Make it Better

FTIR - Fourier Transform Infrared Spectroscopy

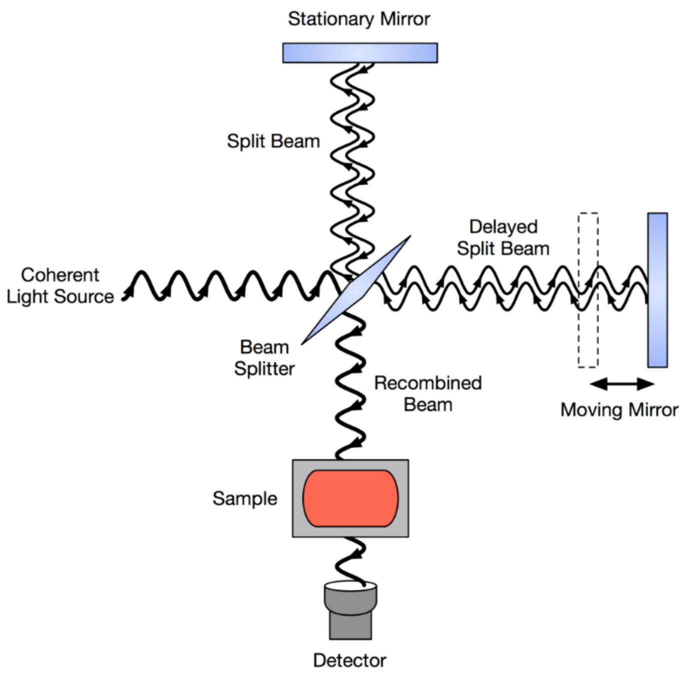


Image credit: Wikipedia

https://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy#/media/File:FTIR_Interferometer.png

Detailed absorption spectrum

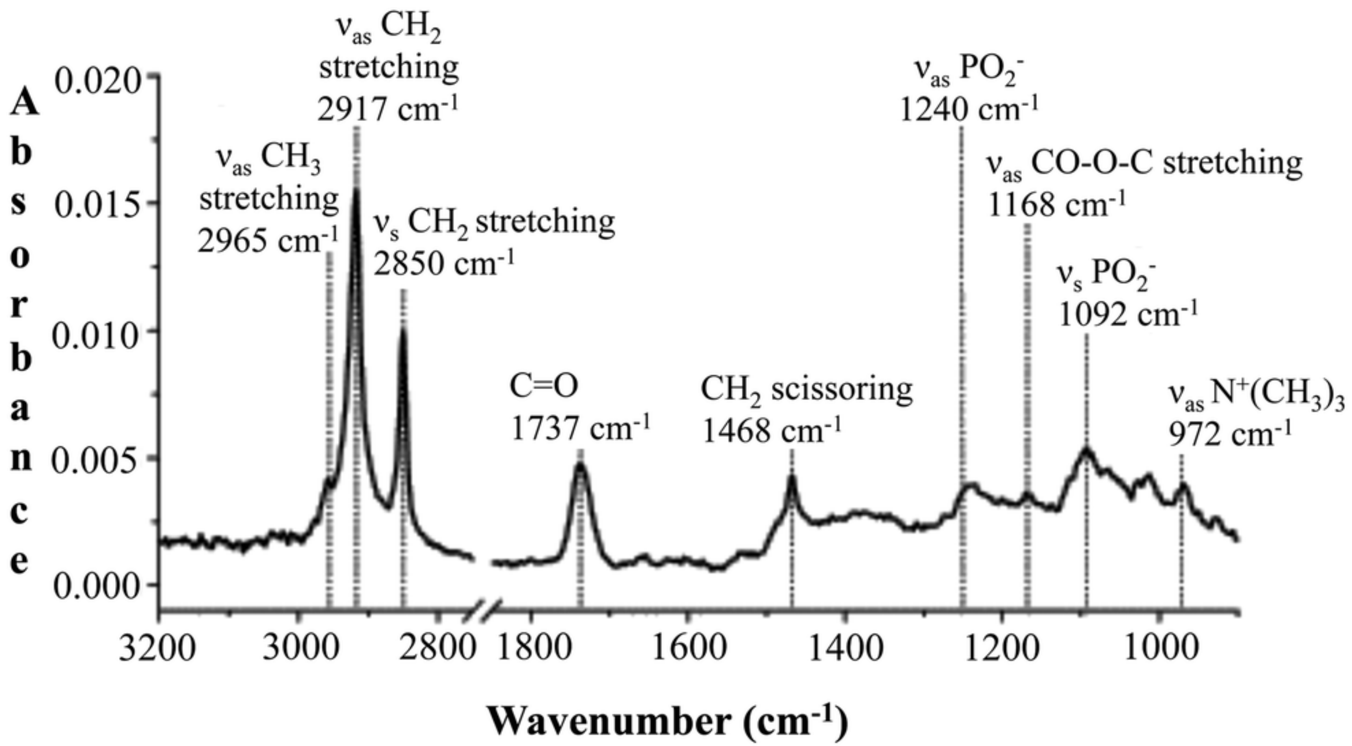
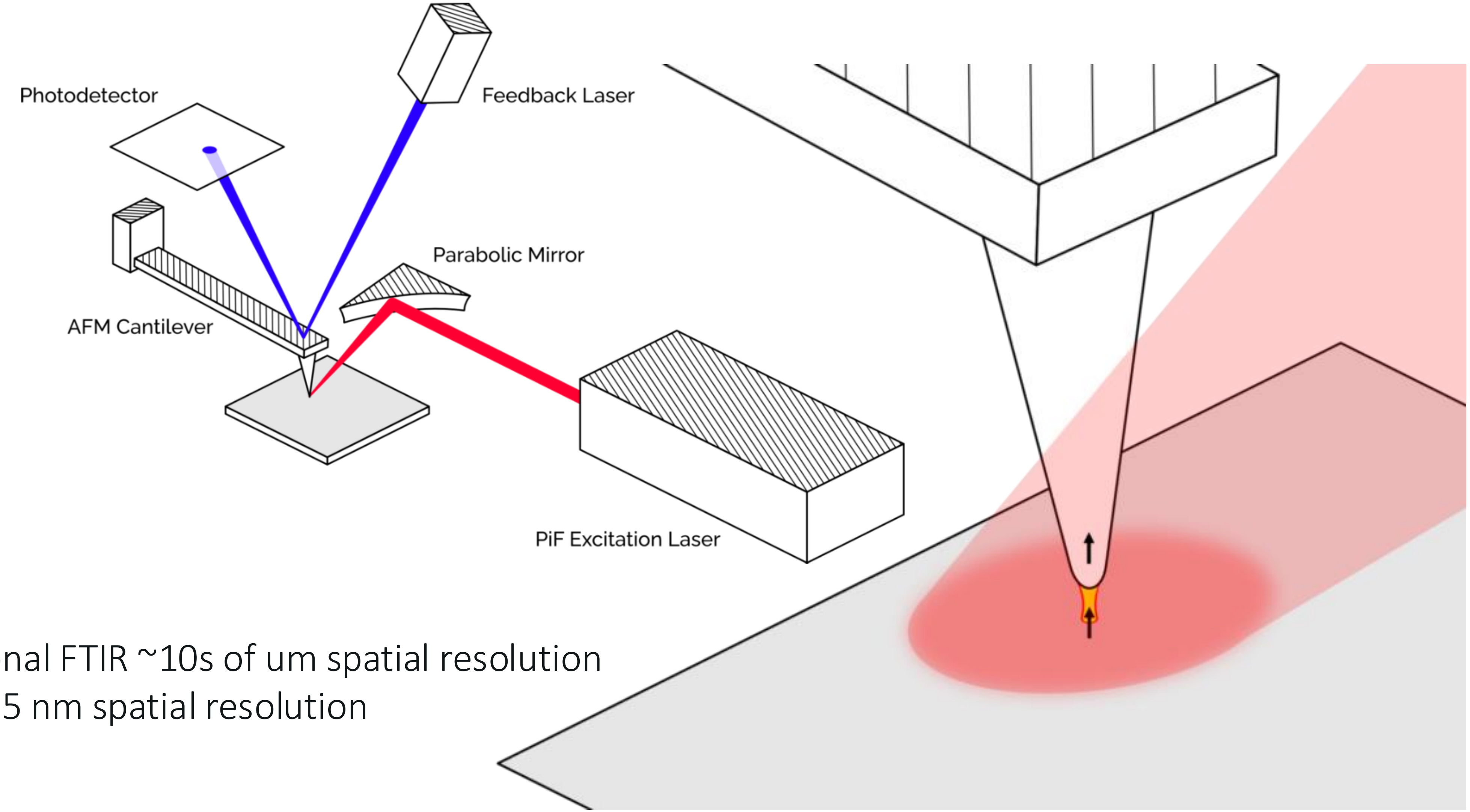


Image credit: Mudunkotuwa et al., Analyst 139, 870-881 (2014).

- Advantage – Detailed spectra for analysis and identification of molecular materials
- Disadvantage – Spatial mapping resolution limited by optical diffraction limit (~ 1 μm)

Breaking the Diffraction Limit – Using Photo-induced Force

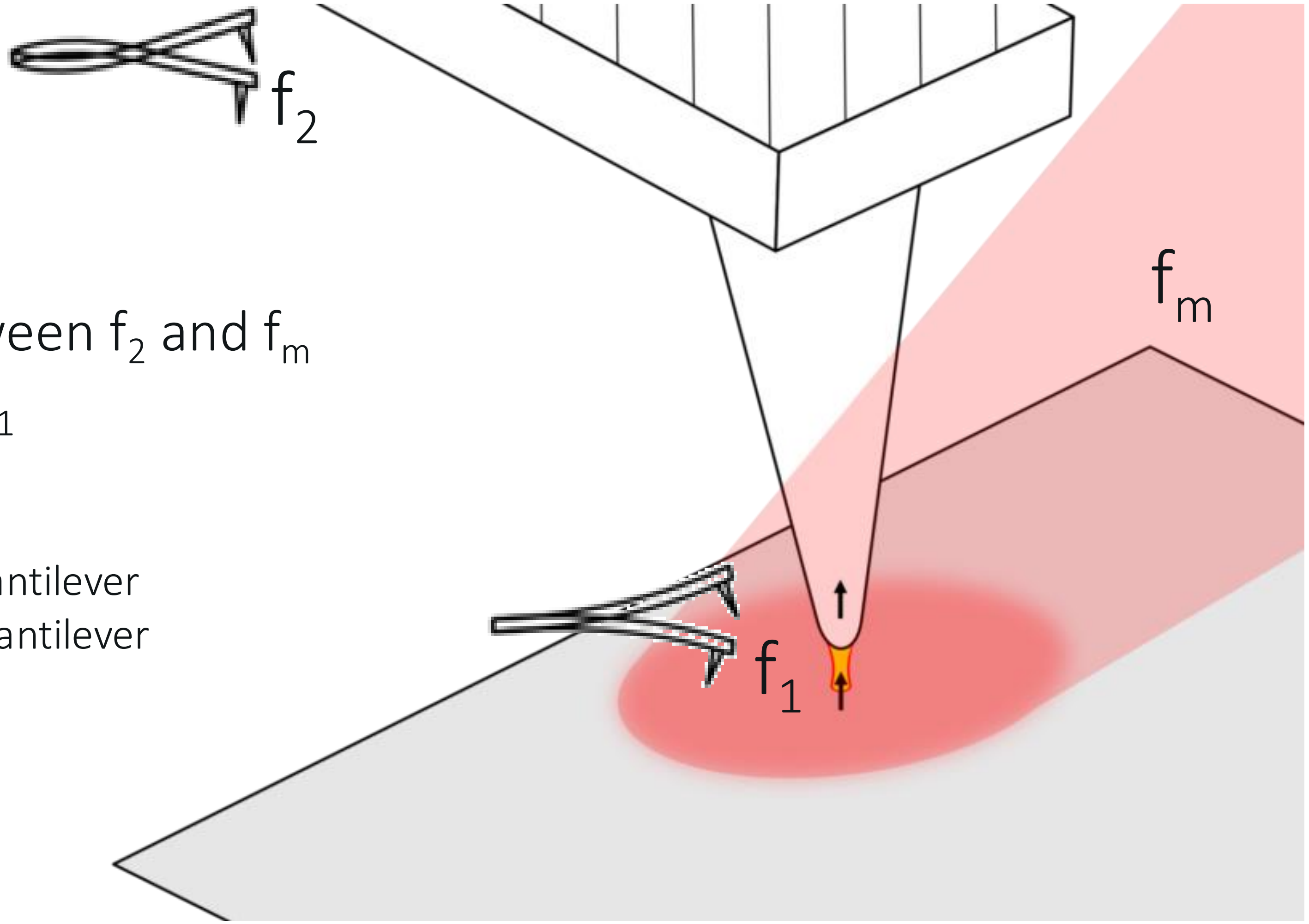


Traditional FTIR ~10s of um spatial resolution
PiFM < 5 nm spatial resolution

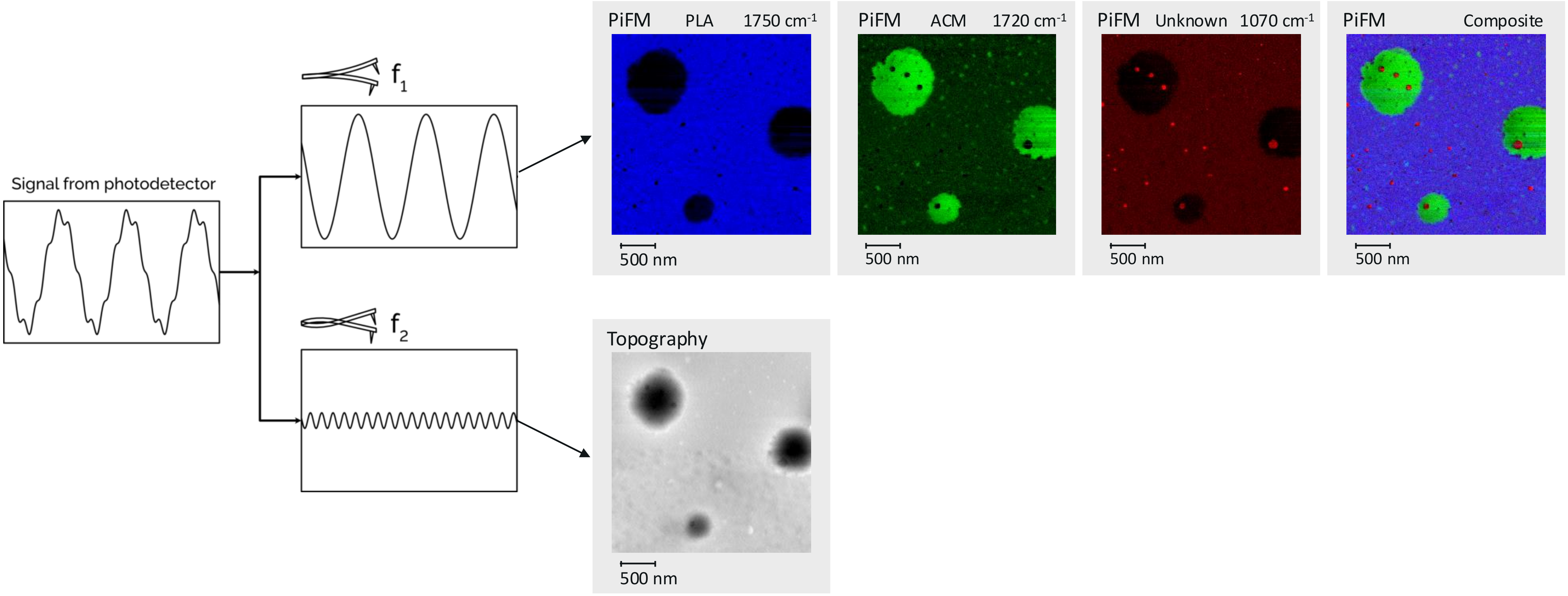
Breaking the Diffraction Limit – Using Photo-induced Force

- $f_m = f_2 - f_1$
- Frequency mixing between f_2 and f_m produces sideband at f_1

f_1 = 1st mechanical resonance of cantilever
f_2 = 2nd mechanical resonance of cantilever
f_m = laser modulation frequency



Breaking the Diffraction Limit – Using Photo-induced Force



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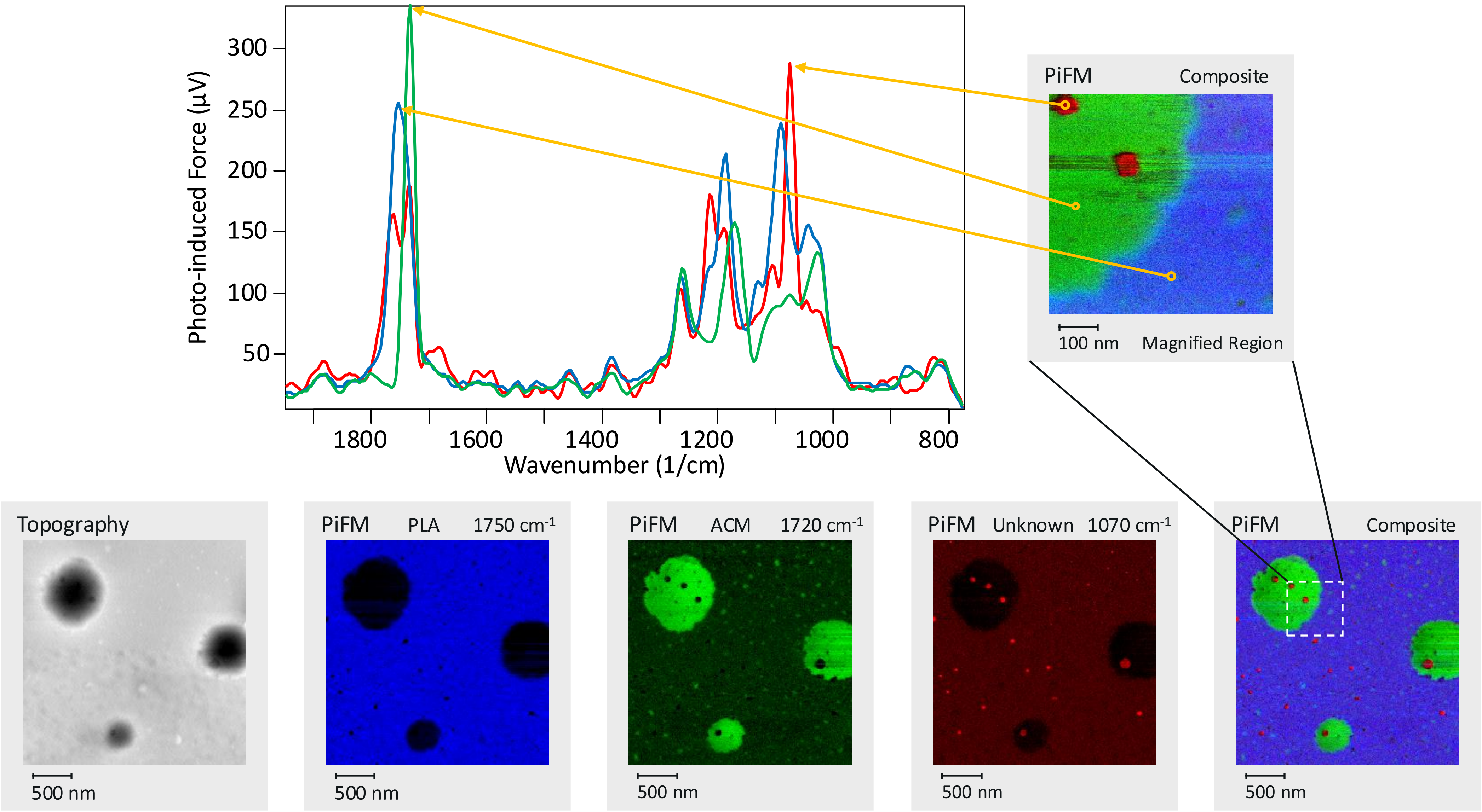
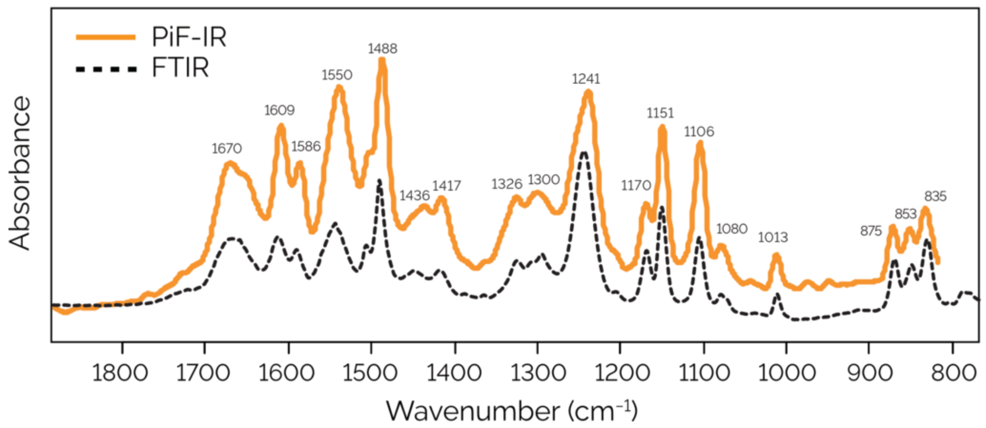
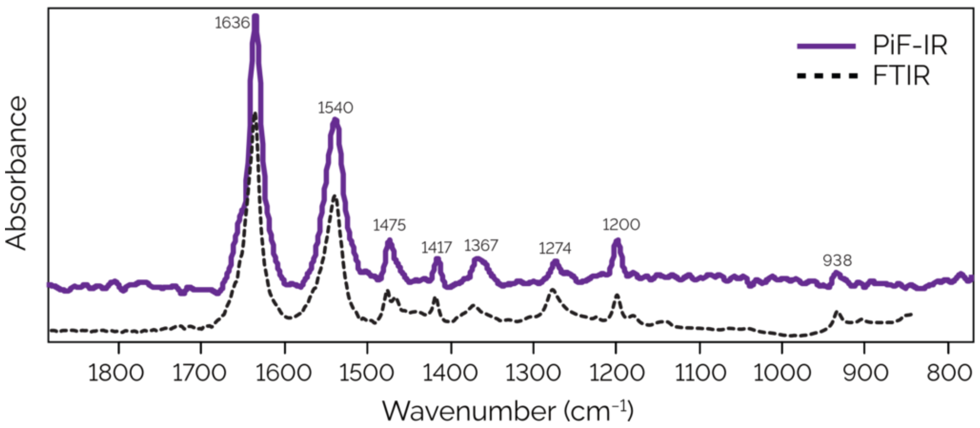


Agreement Between Nanoscale PiF-IR and Bulk FTIR Spectra

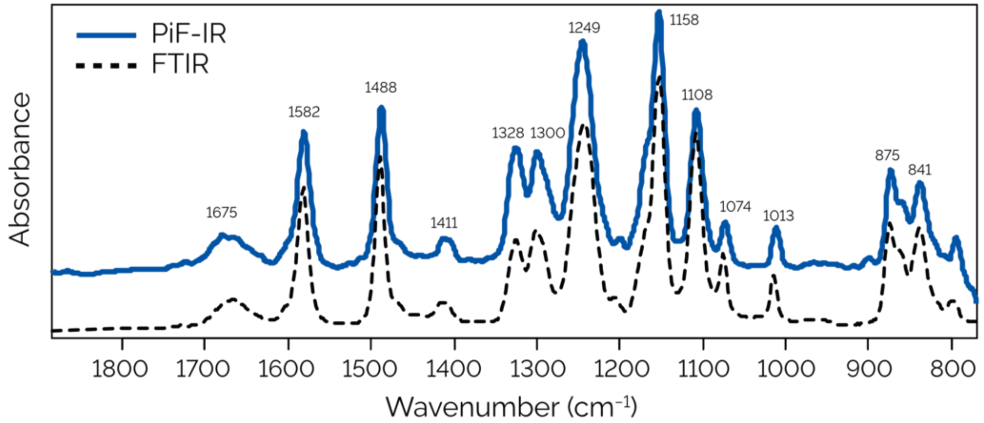
PiF-IR and FTIR of Polyimide



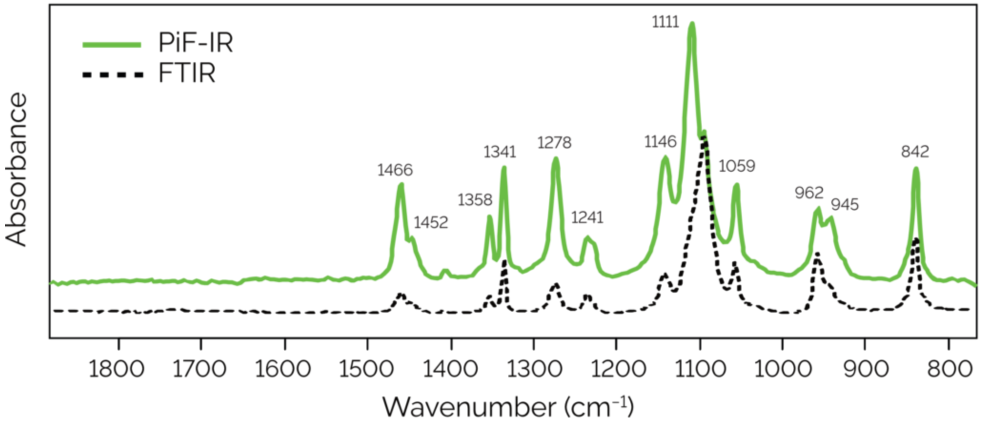
PiF-IR and FTIR of Nylon



PiF-IR and FTIR of PES (Polyethersulfone)



PiF-IR and FTIR of PEO Polyethylene Oxide



Excellent agreement on homogeneous samples.

Complements other Nanoscale Analytical Techniques

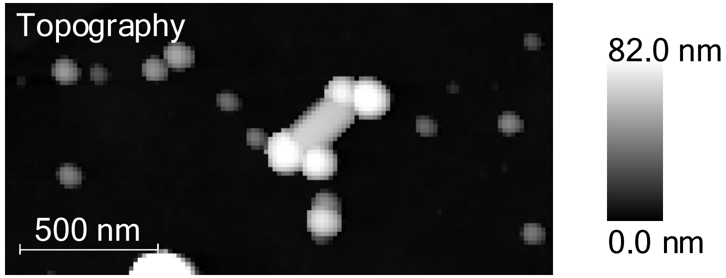
	IR PiFM	Raman	FTIR	TOF-SIMS	XPS	TXRF	SEM/EDS	TEM	Auger
Species Detected	M.I.	M.I.	M.I.	M.I.	M.I.	E.I.	E.I.	E.I.	E.I.
Chemical Mapping	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Lateral Resolution	sub 5 nm	> 0.5 µm	> 10 µm	100 nm	Sub 5 µm	~ 10 mm	1 nm* 0.5mm EDS	0.2 nm* 1 ~ 20 nm EDS	8 nm
Depth Probed	20 nm & bulk	> 500 nm	1 µm	1 nm	10 nm	10 nm	1 µm	~ 100 nm	10 nm

* Imaging M.I. Molecular information E.I. Elemental information

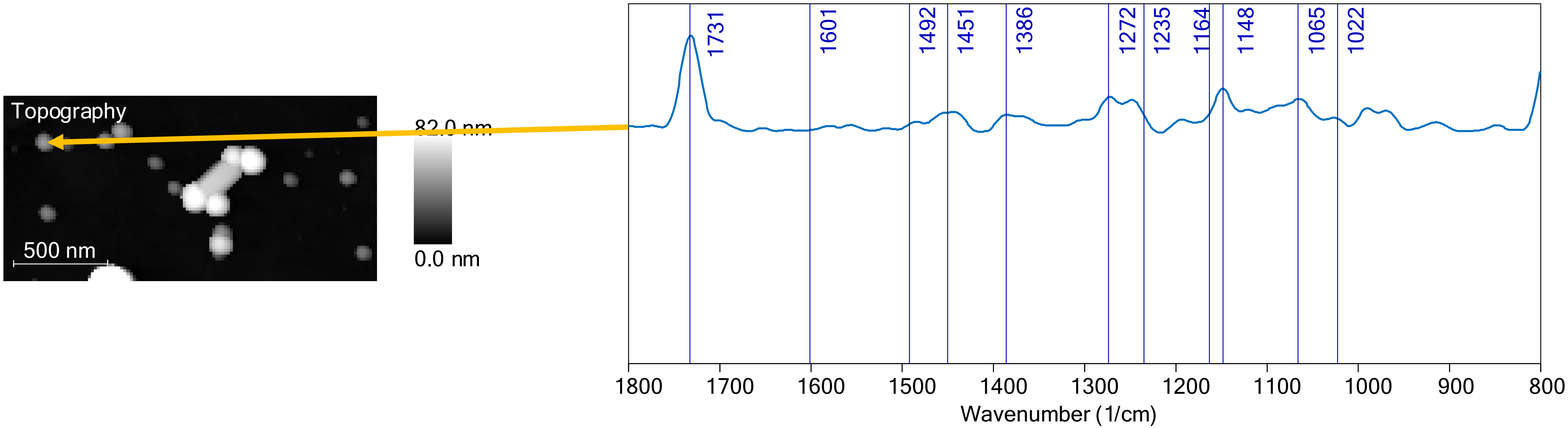
IR PiFM brings molecular analysis to the realm of true nanoscale, providing both IR absorption spectra and chemical mapping with ~ 5 nm spatial resolution and monolayer sensitivity.

General PiFM Results

Organic Contaminants (and PiFM workflow)



Organic Contaminants (and PiFM workflow)



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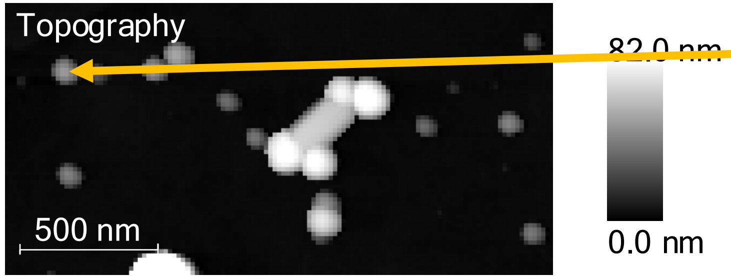

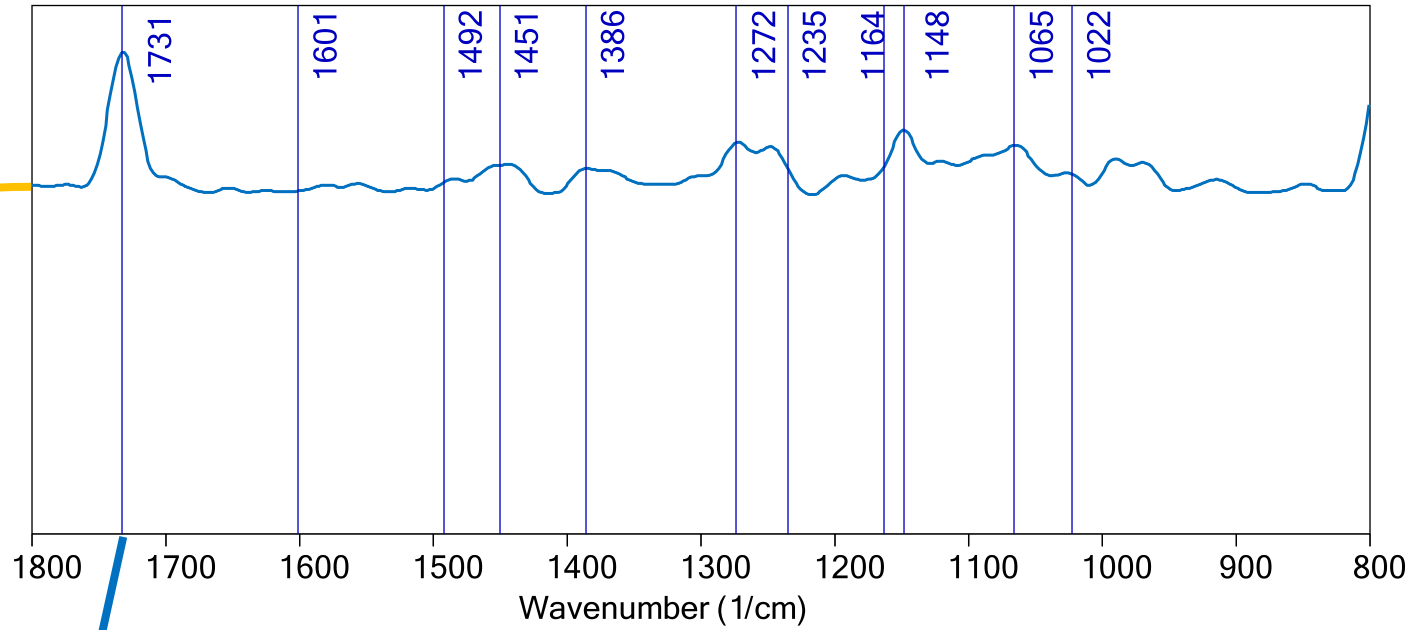

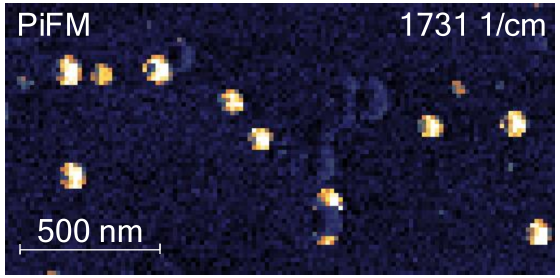

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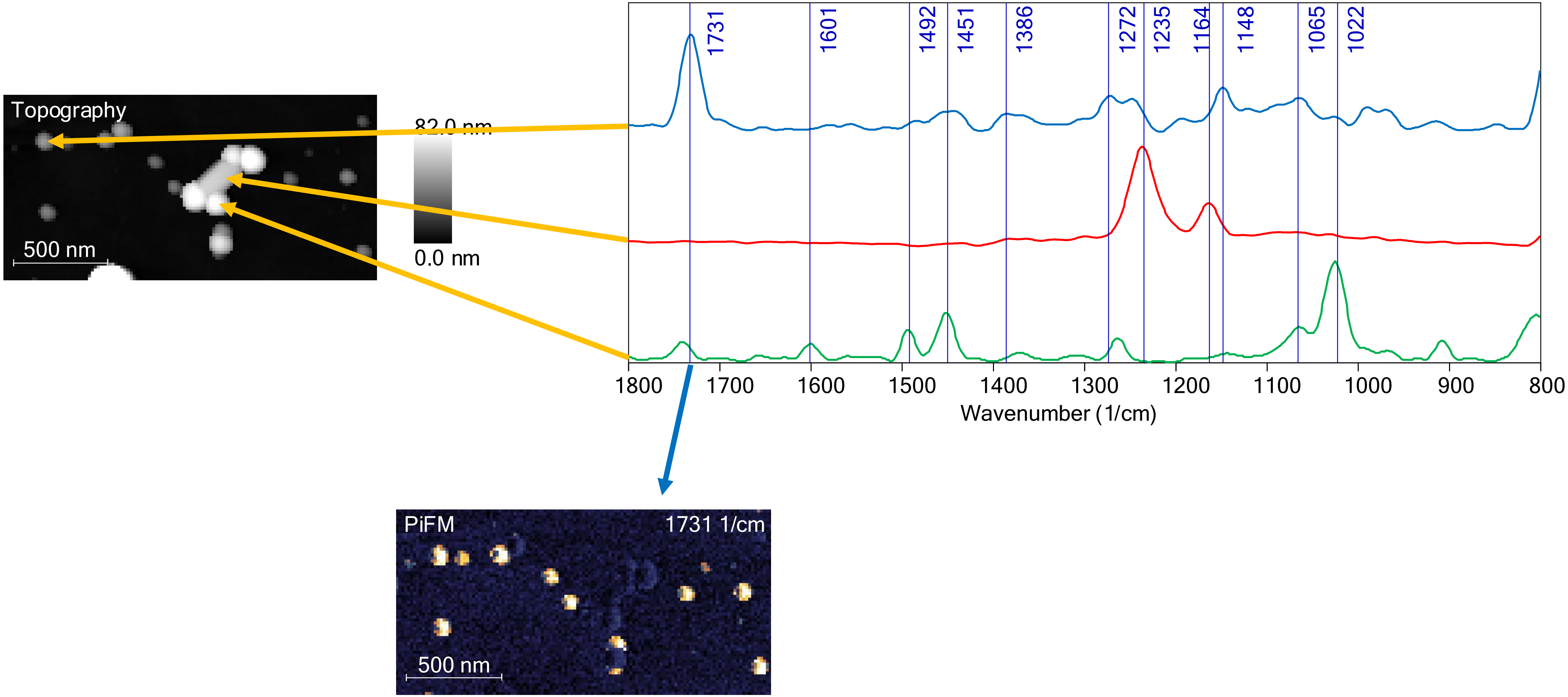
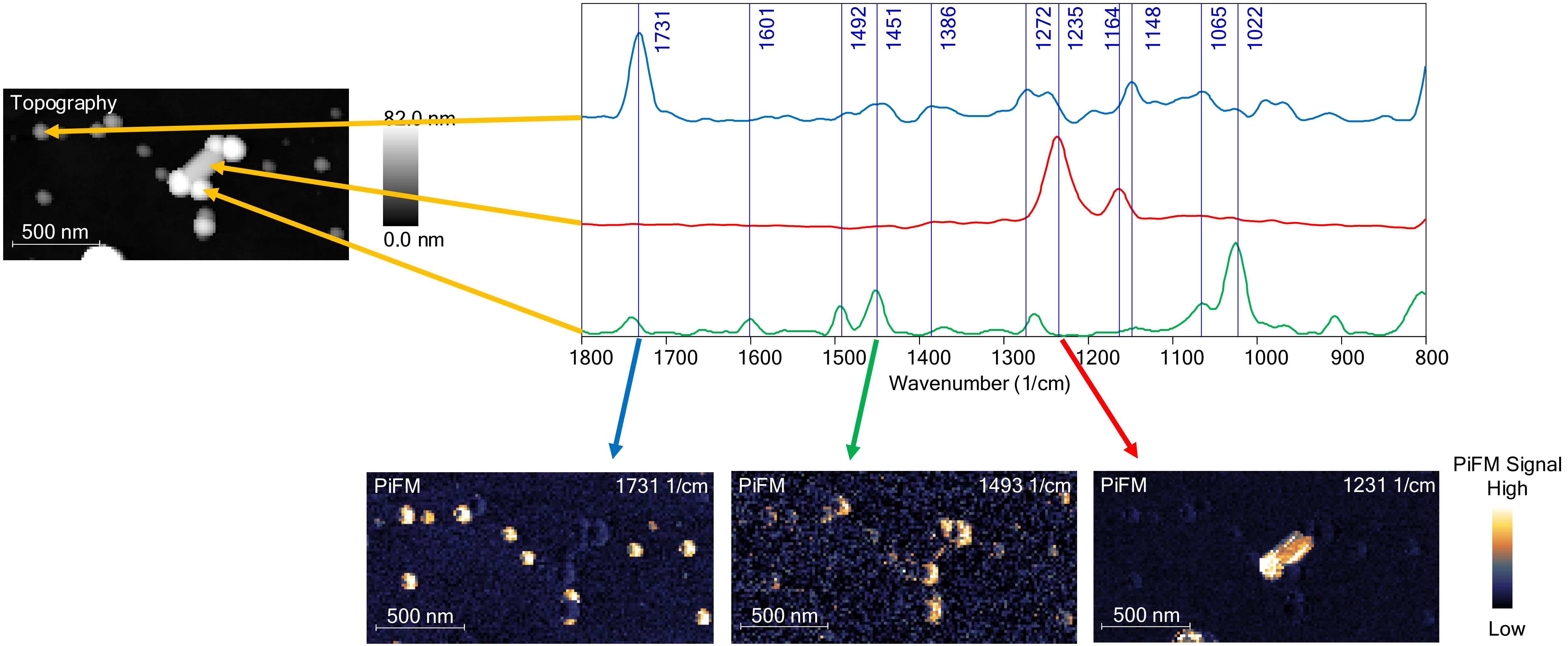
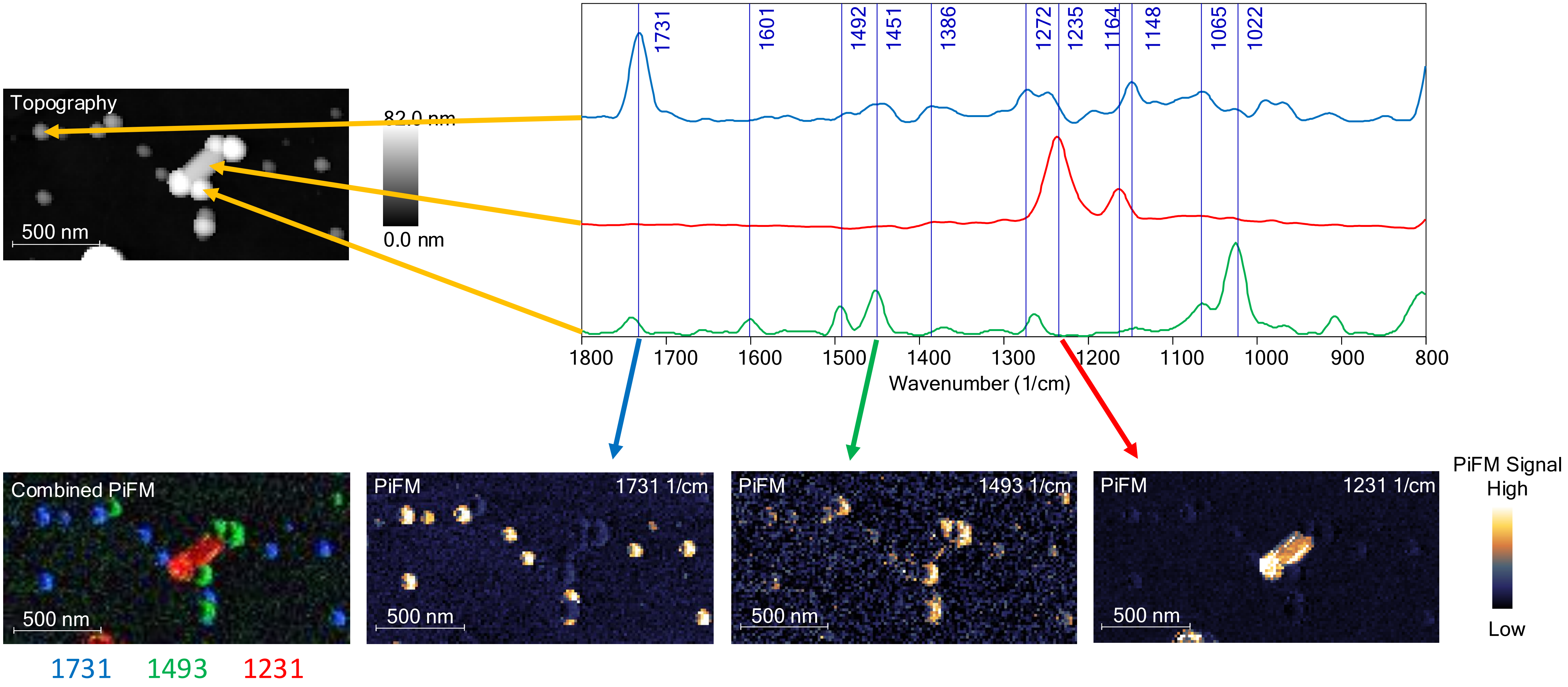


Applications Lab

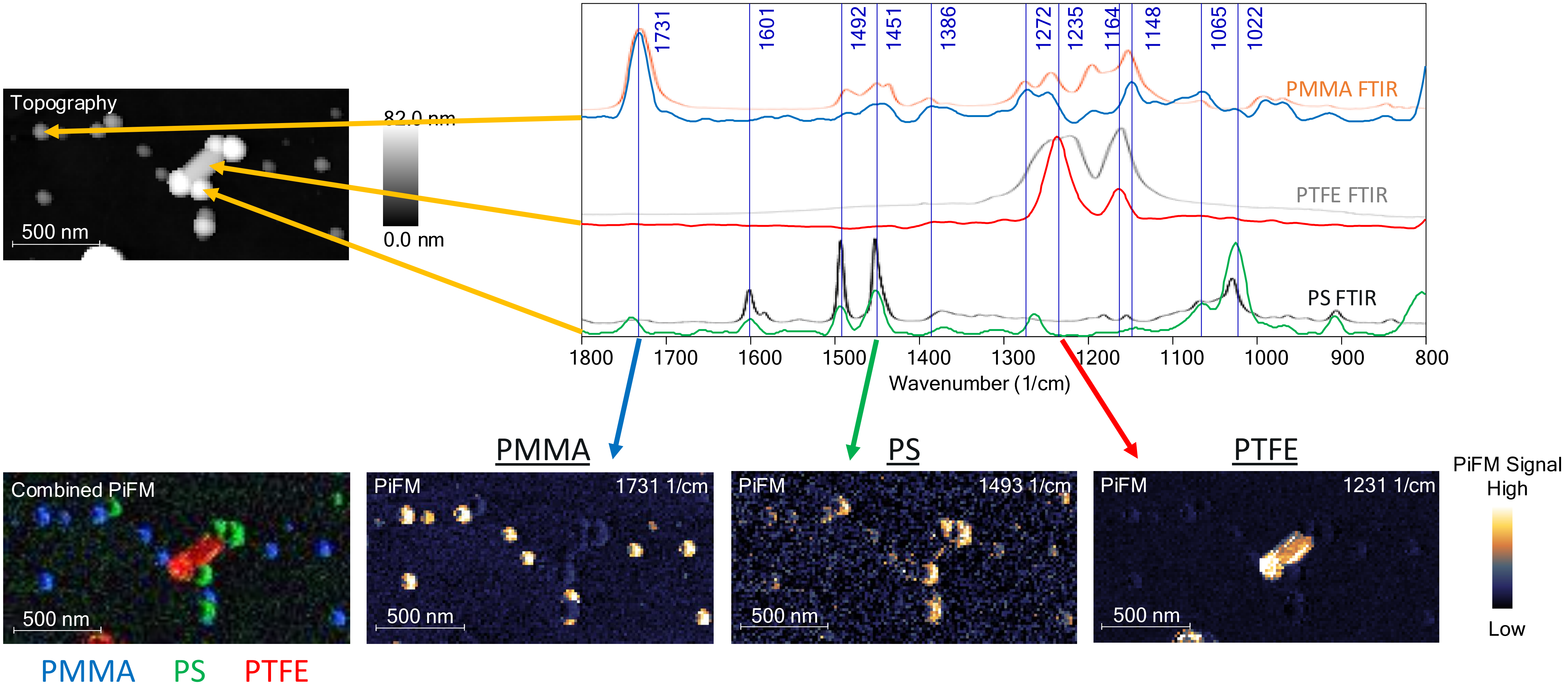
Organic Contaminants (and PiFM workflow)



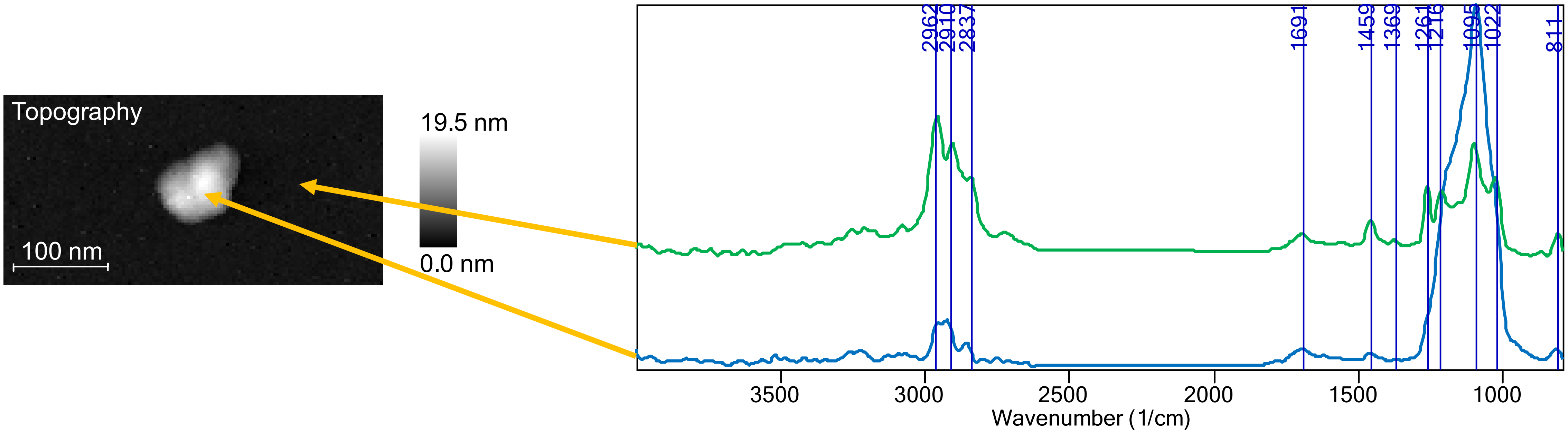
Organic Contaminants (and PiFM workflow)



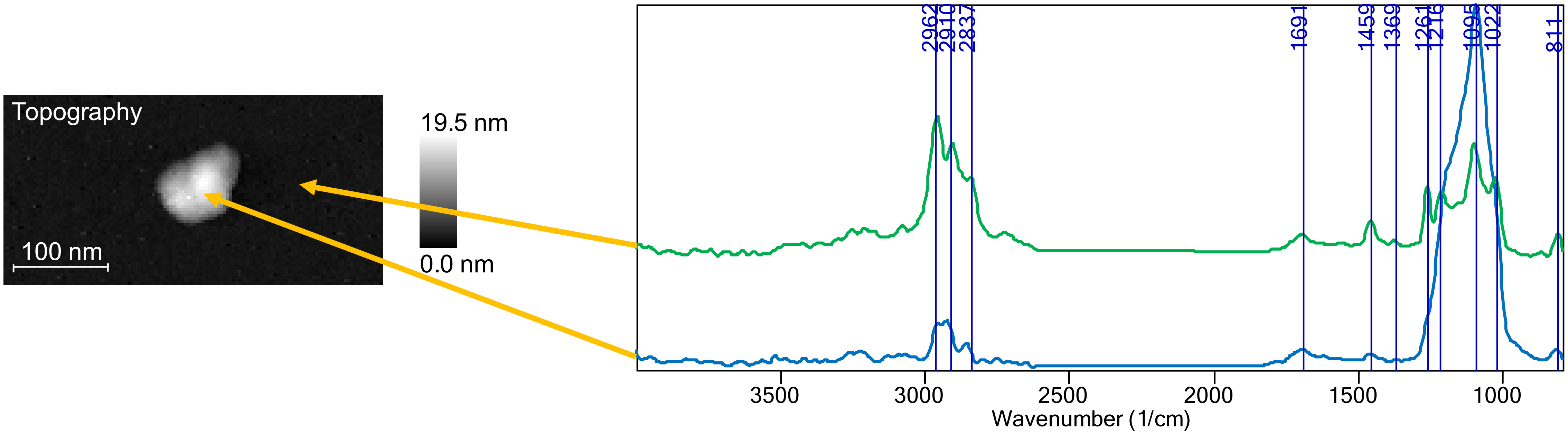
Organic Contaminants (and PiFM workflow)

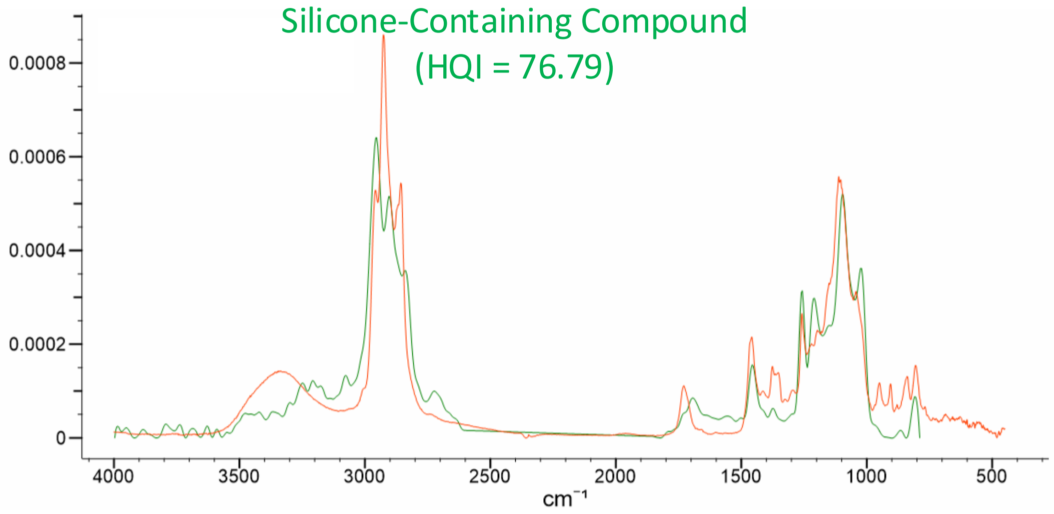


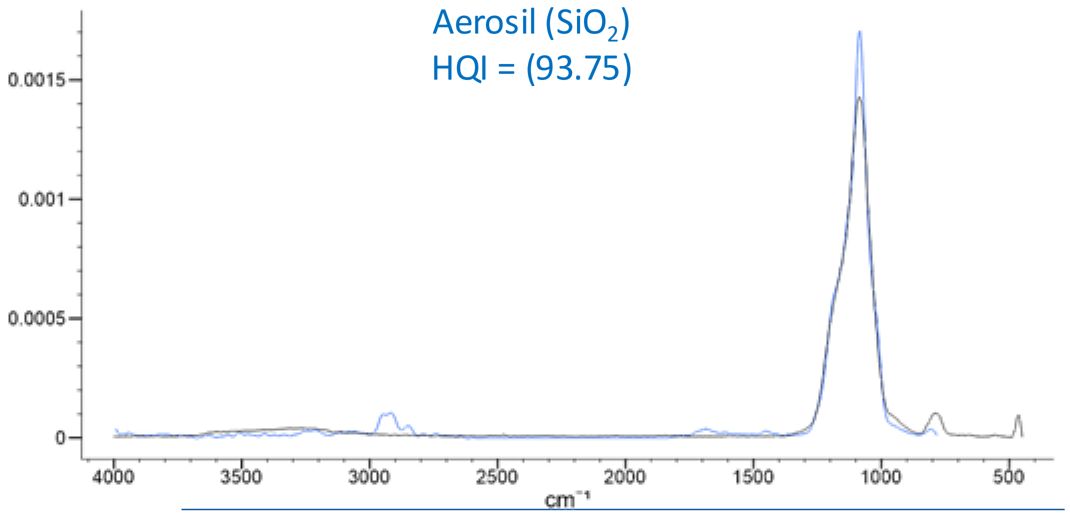
Inorganic Contaminant on Si



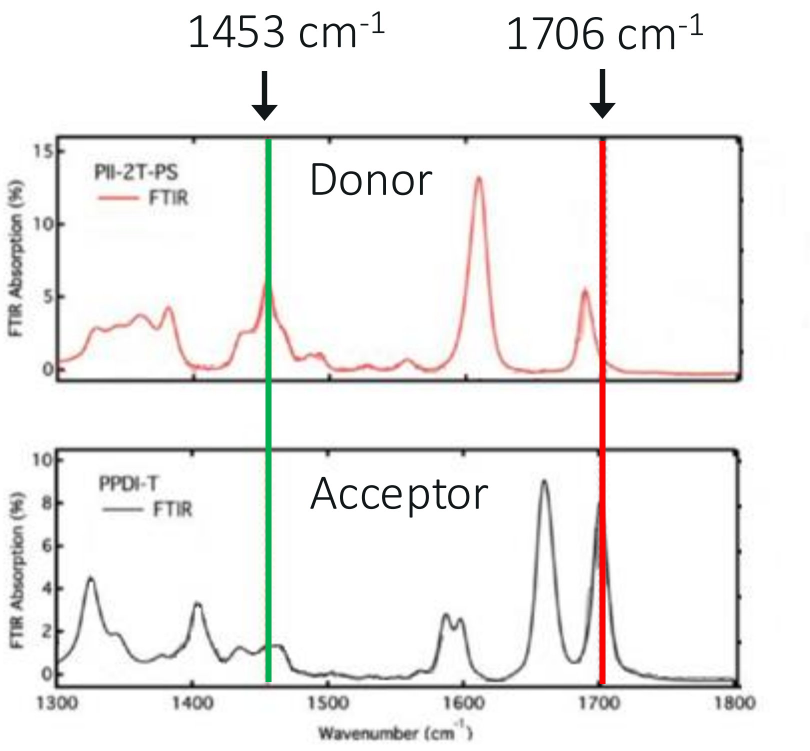
Inorganic Contaminants on Si (silica sample)





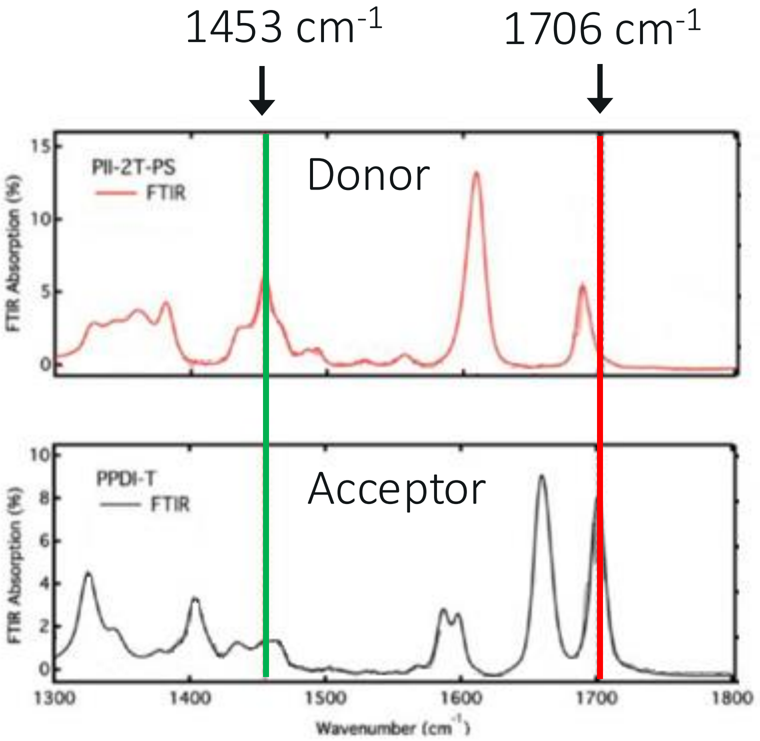


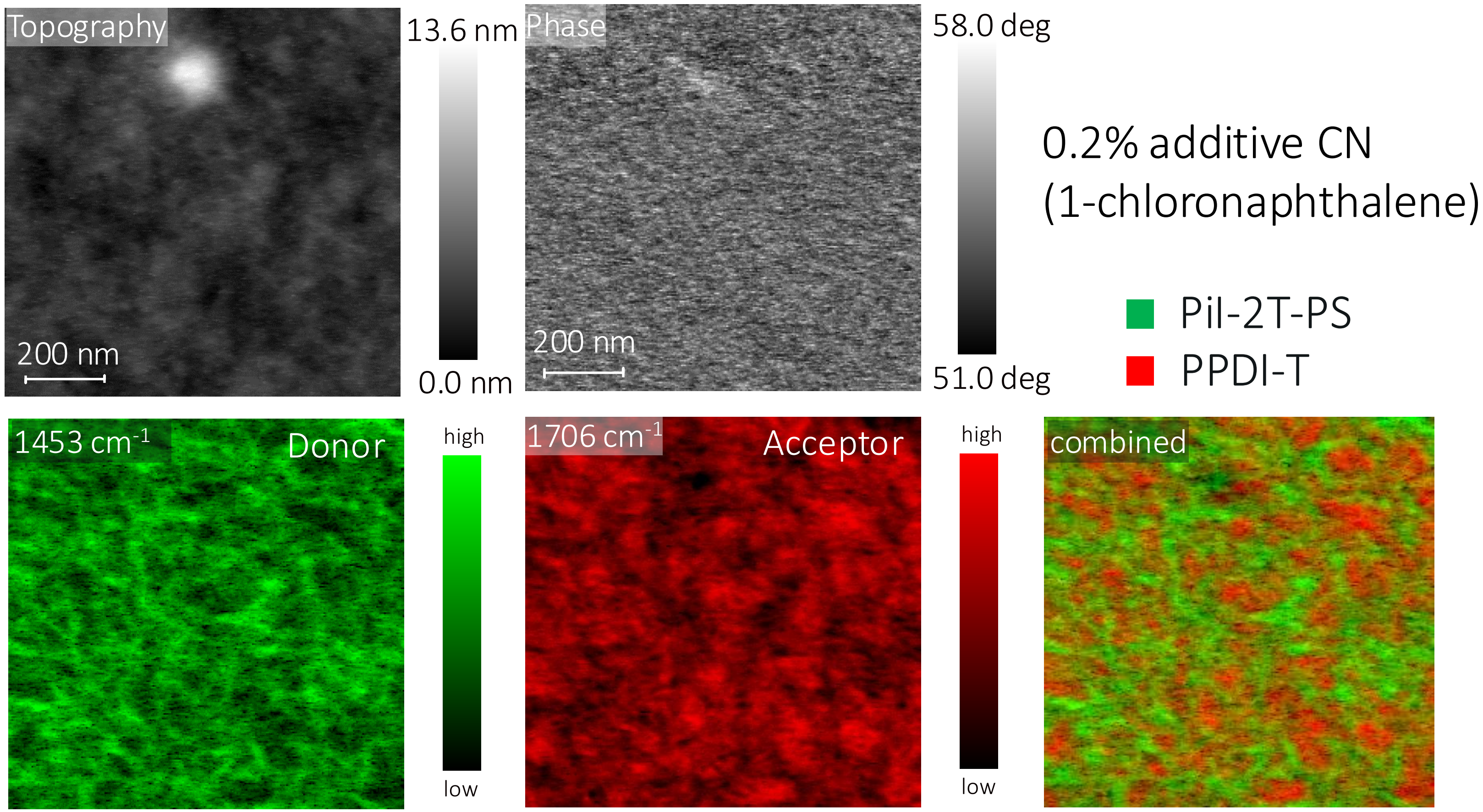
Domain Imaging of Polymer-Polymer Blend Solar Cell



"Nanoscale Domain Imaging of All-Polymer Organic Solar Cells by Photo-Induced Force Microscopy," Kevin L. Lu et al., ACS Nano, ***12***, 1473 (**2018**)

Domain Imaging of Polymer-Polymer Blend Solar Cell

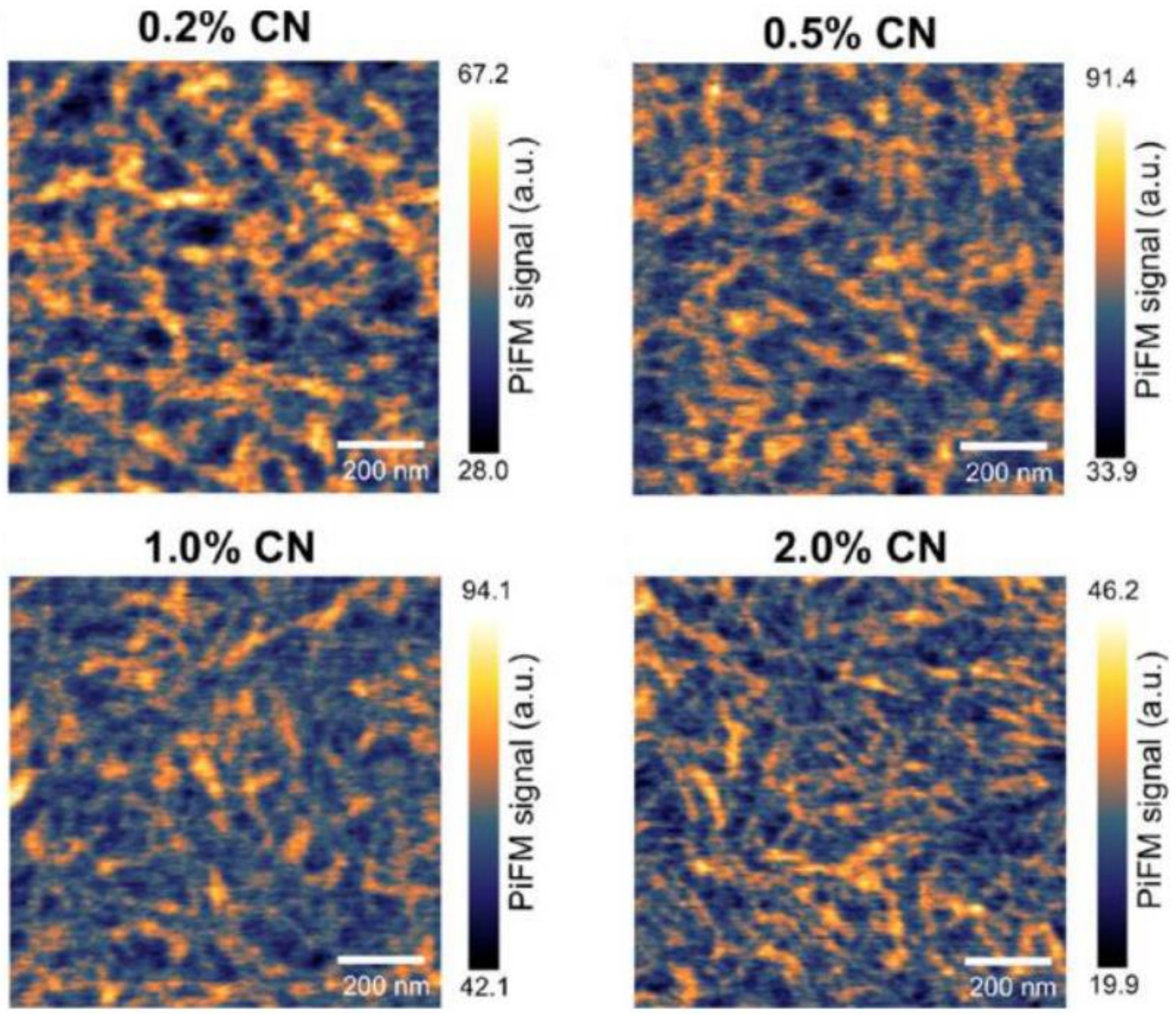




"Nanoscale Domain Imaging of All-Polymer Organic Solar Cells by Photo-Induced Force Microscopy," Kevin L. Gu et al., ACS Nano, ***12***, 1473 (**2018**)

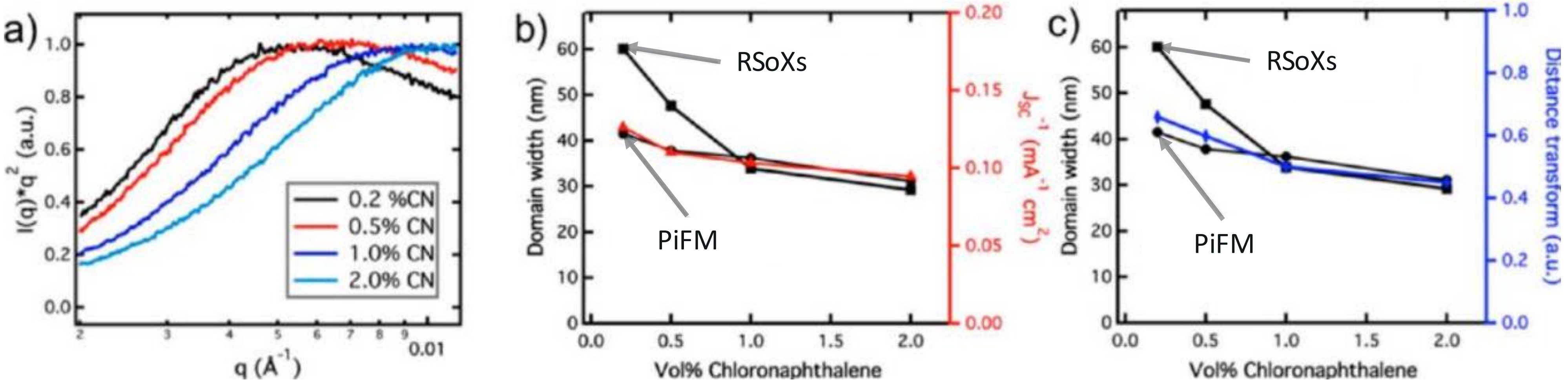
PiFM images clearly identify donor (PiI-2T-PS) and acceptor (PPDI-T) based on their known absorption bands: 1453 cm^{-1} and 1706 cm^{-1}.

Domain Imaging of Donor Component (at 1453 cm^{-1})



Average domain width for donor decreases with increasing concentration of CN.

Excellent Correlation with Cell Performance



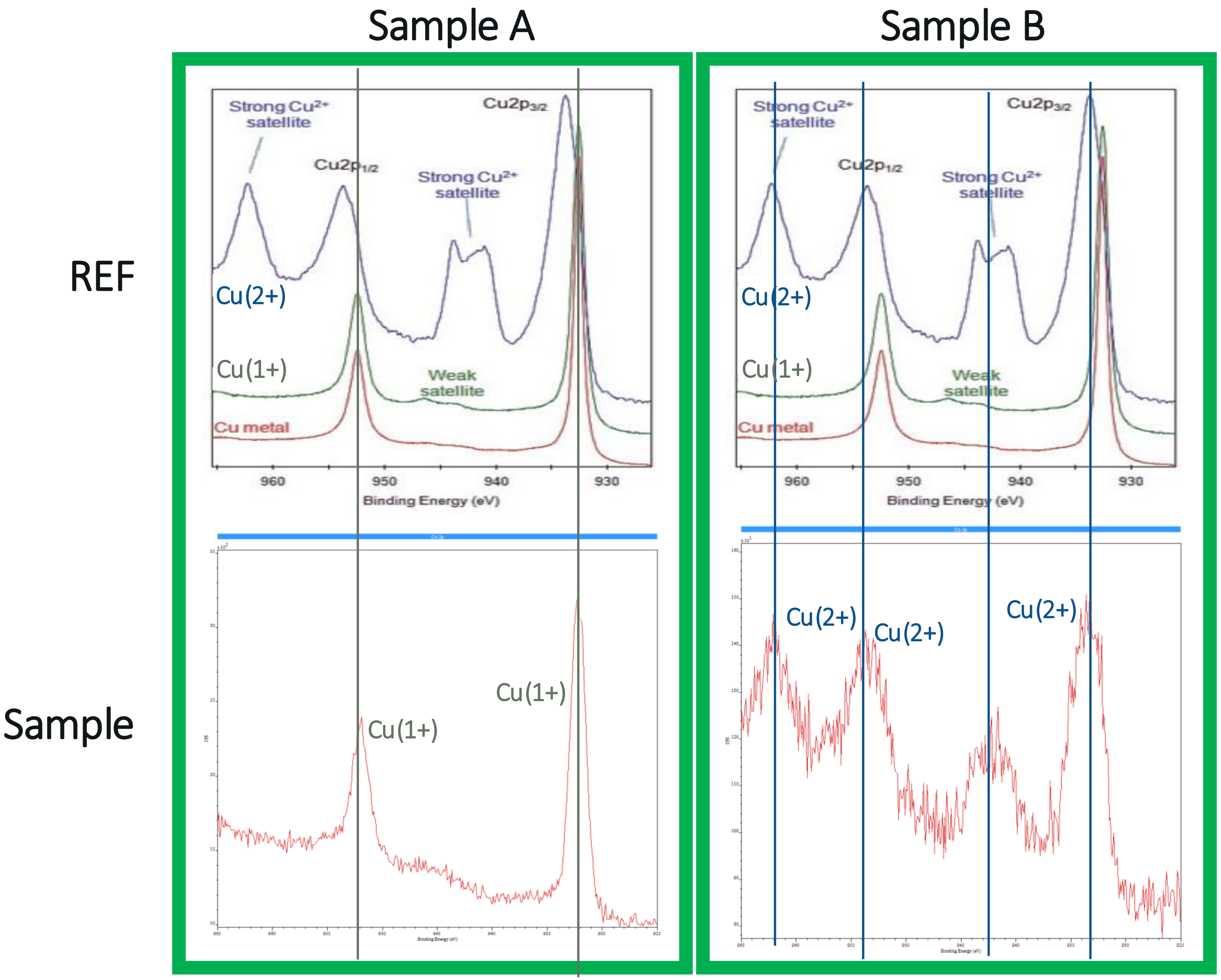
(a) 1D resonant soft X-ray scattering (RSoXS) curves for varying [CN]. The average domain spacing is represented by the peak in reciprocal space, where the center-to-center periodicity is given by 2π/q.

(b) Averaged domain widths as calculated from PiFM and RSoXS, compared to the inverse of the device short circuit current; the PiFM domain size tracks the inverse current very well, whereas RSoXS is skewed for large domains.

(c) Photoactive volume calculated from the distance transform plotted vs PiFM and RSoXS domain size.

Comparison and Compatibility with Other Techniques

Copper Oxide – XPS

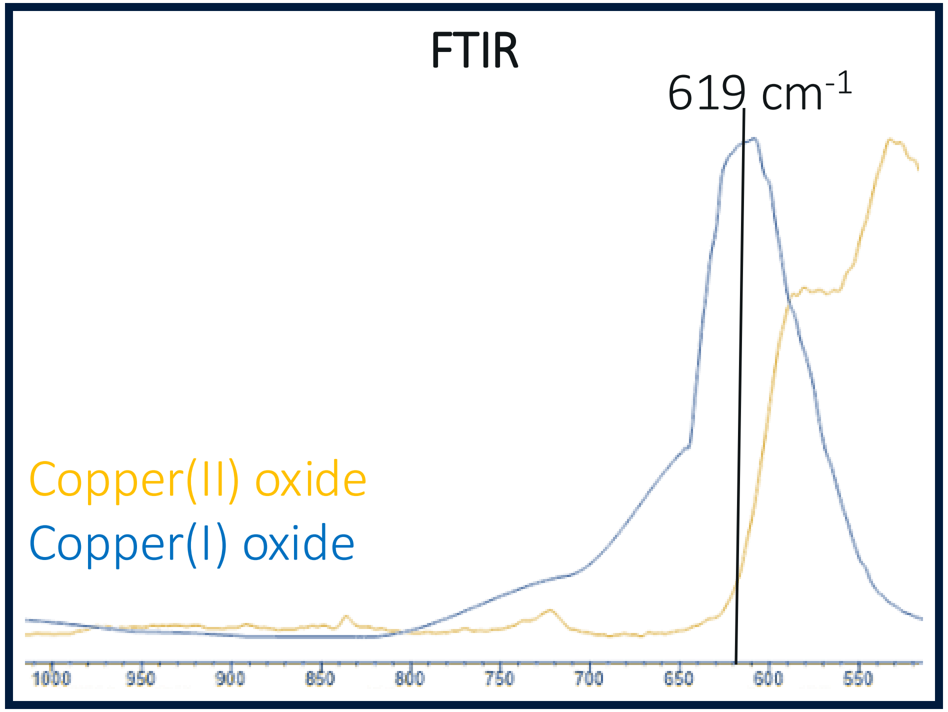


XPS Summary:

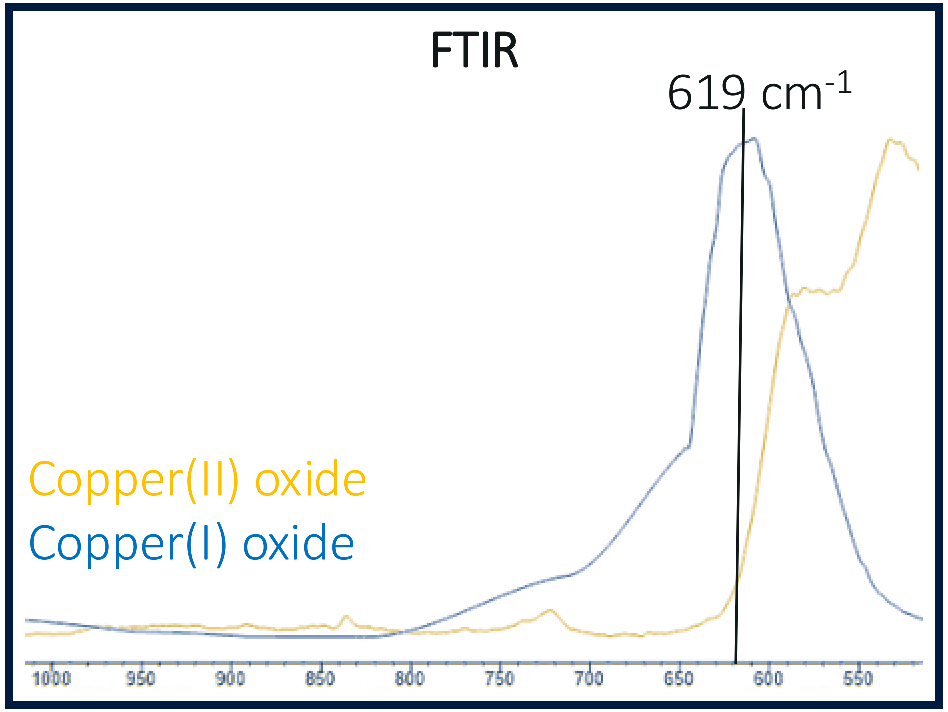
A. Copper(I) oxide

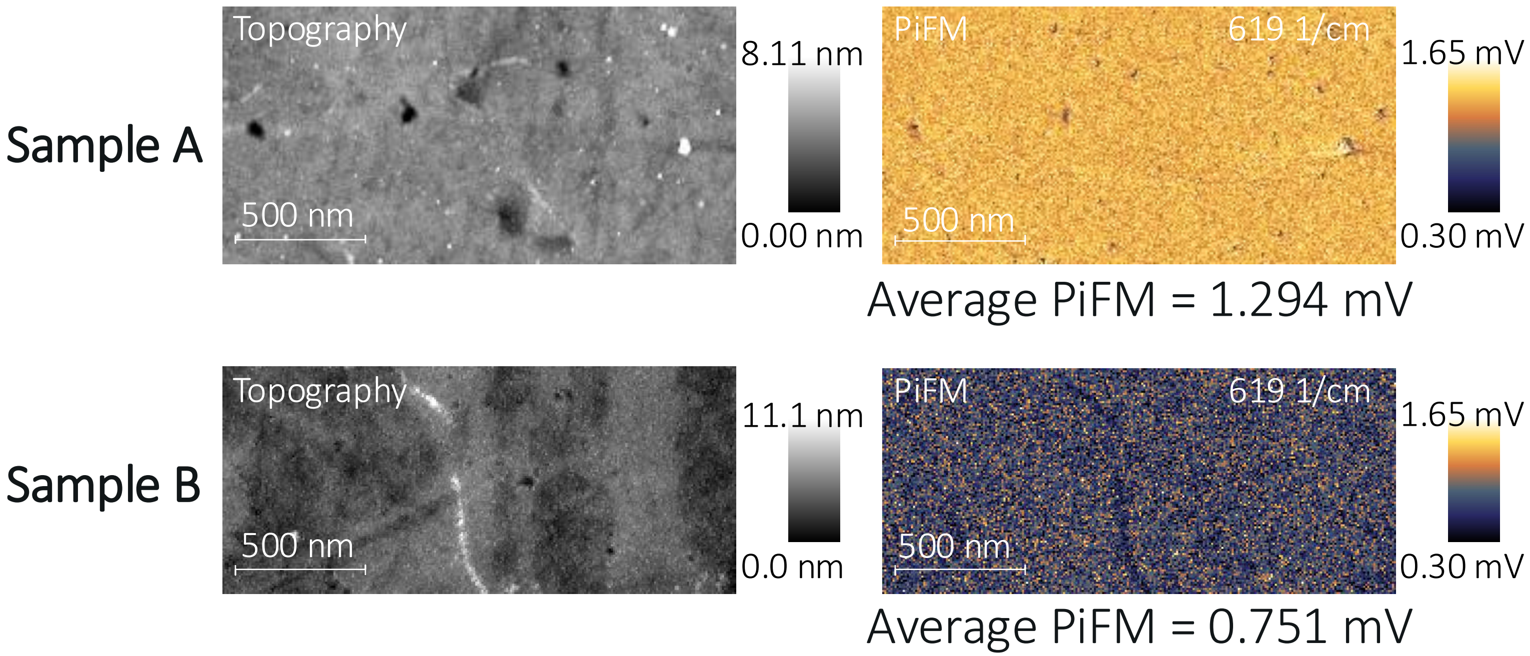
B. Copper(II) oxide

Copper Oxide – PiFM Compared to XPS



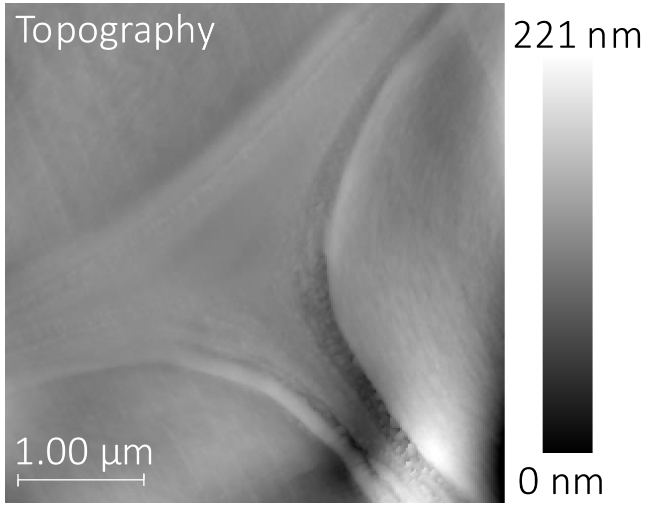
Copper Oxide – PiFM Compared to XPS

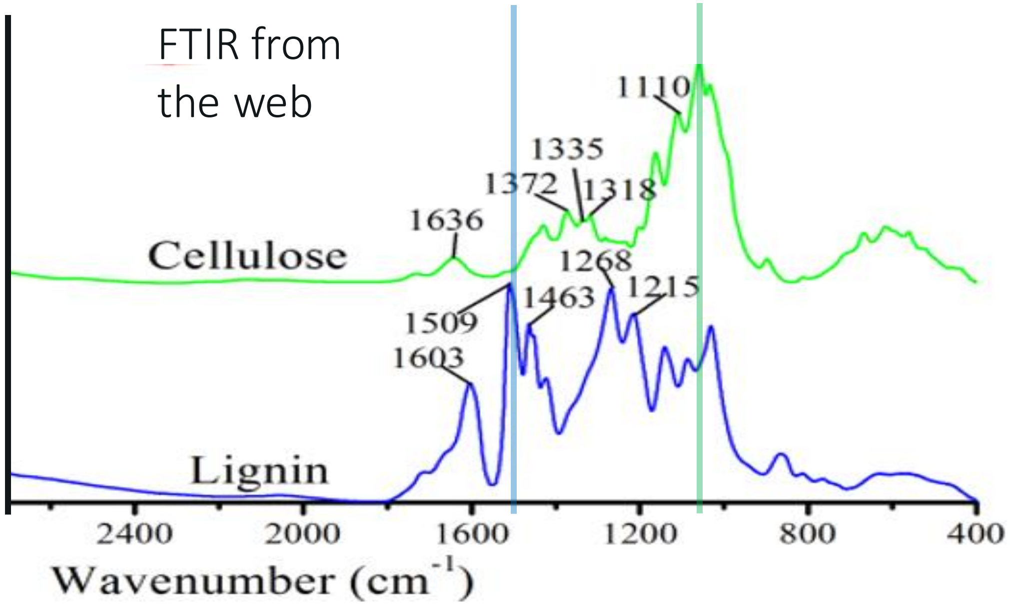




Results match XPS – Sample A shows much more copper(I) oxide, but PiFM will also show nanoscale variations

Wood Cell Wall – Spruce (4 µm x 4 µm)





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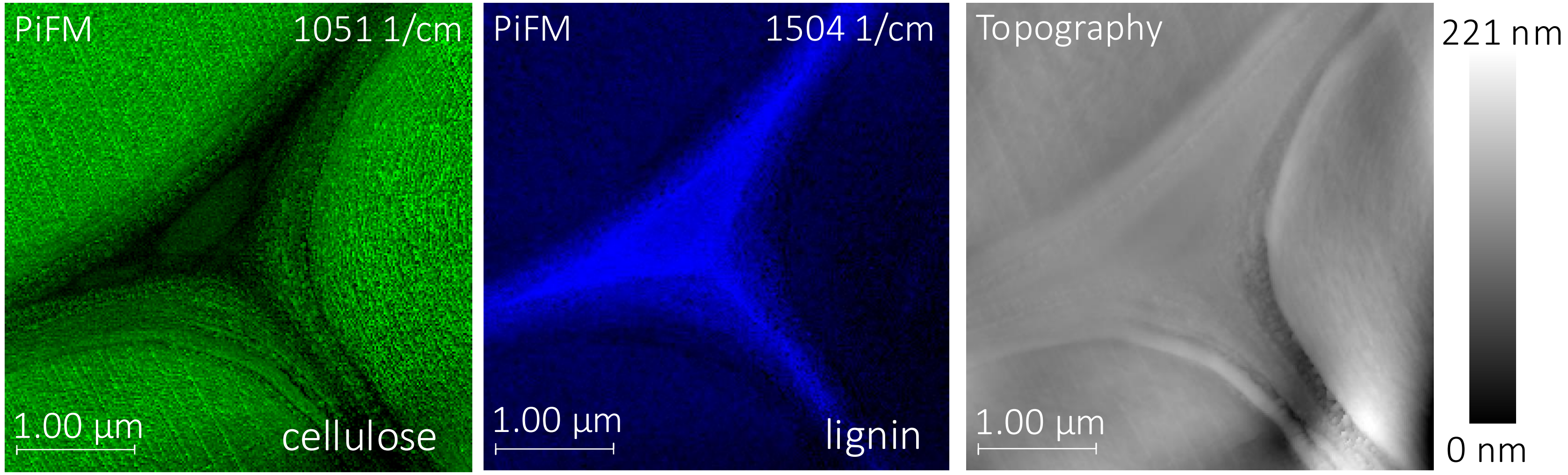
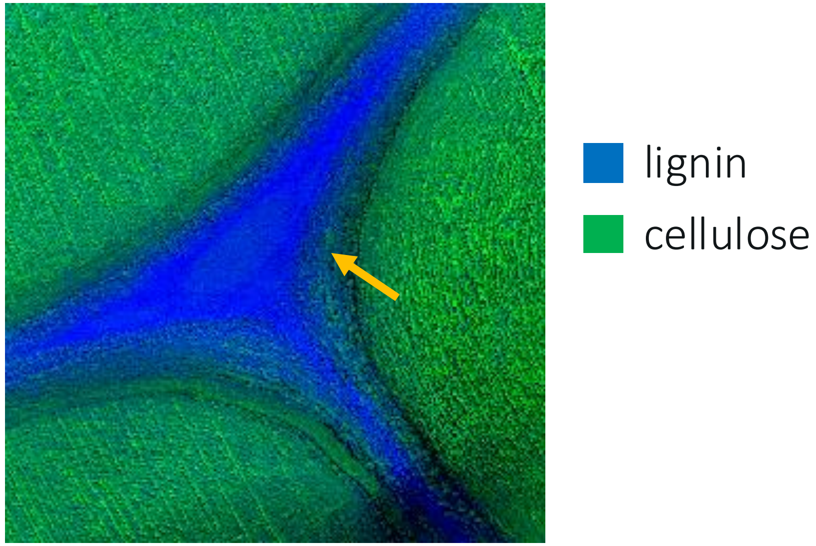
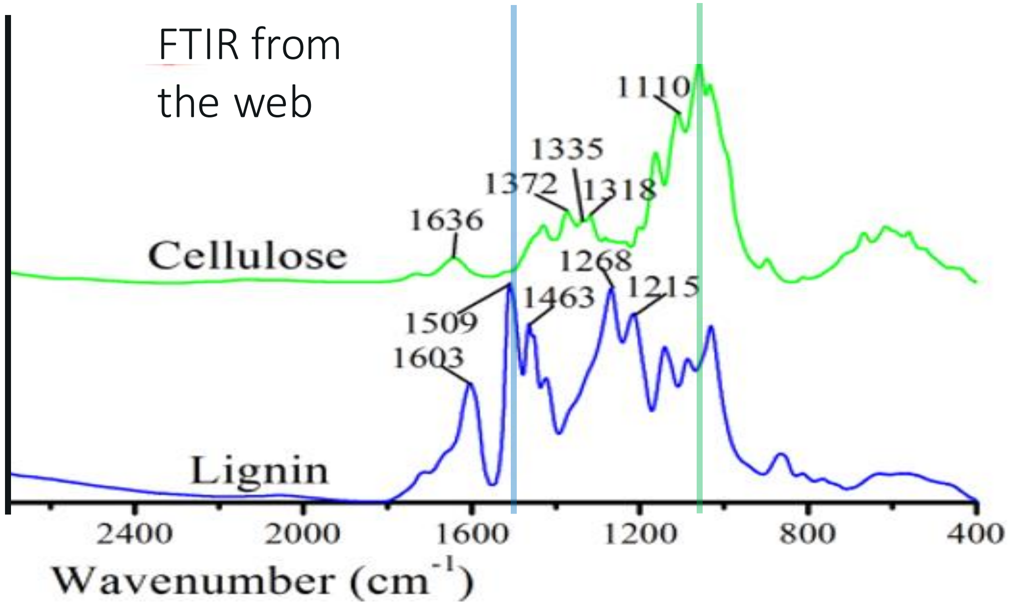
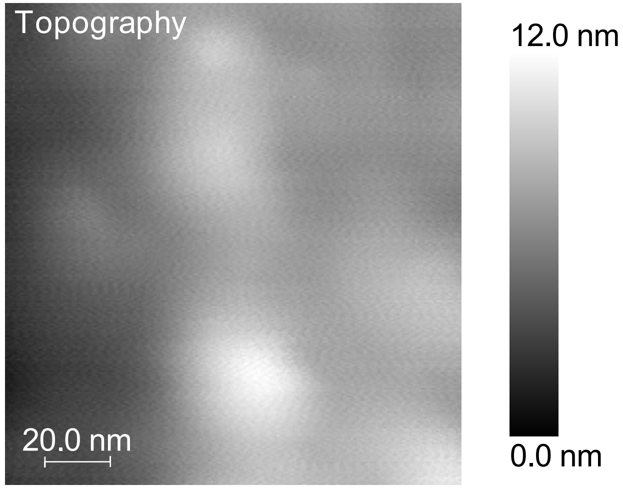
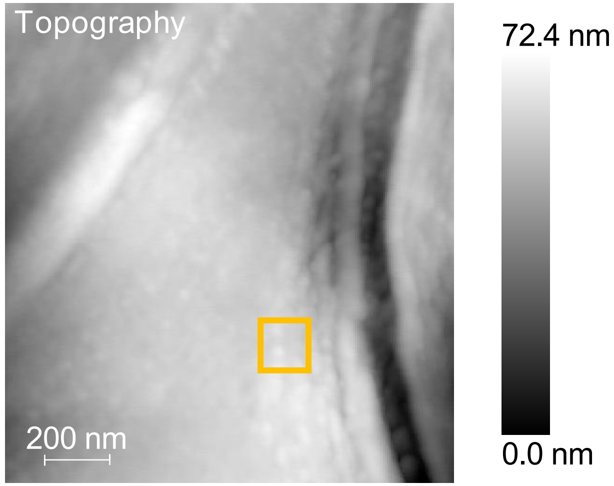






Spruce Spectra (High-Magnification)





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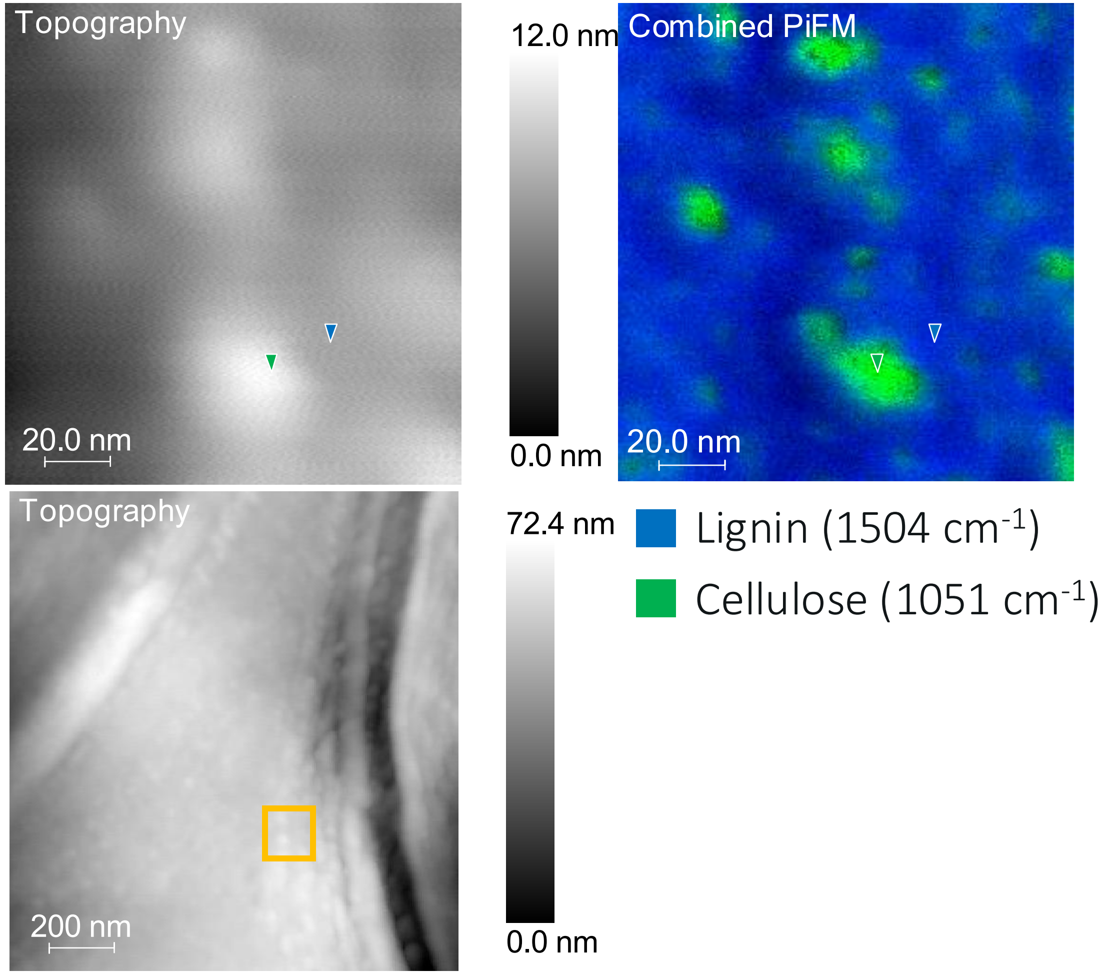
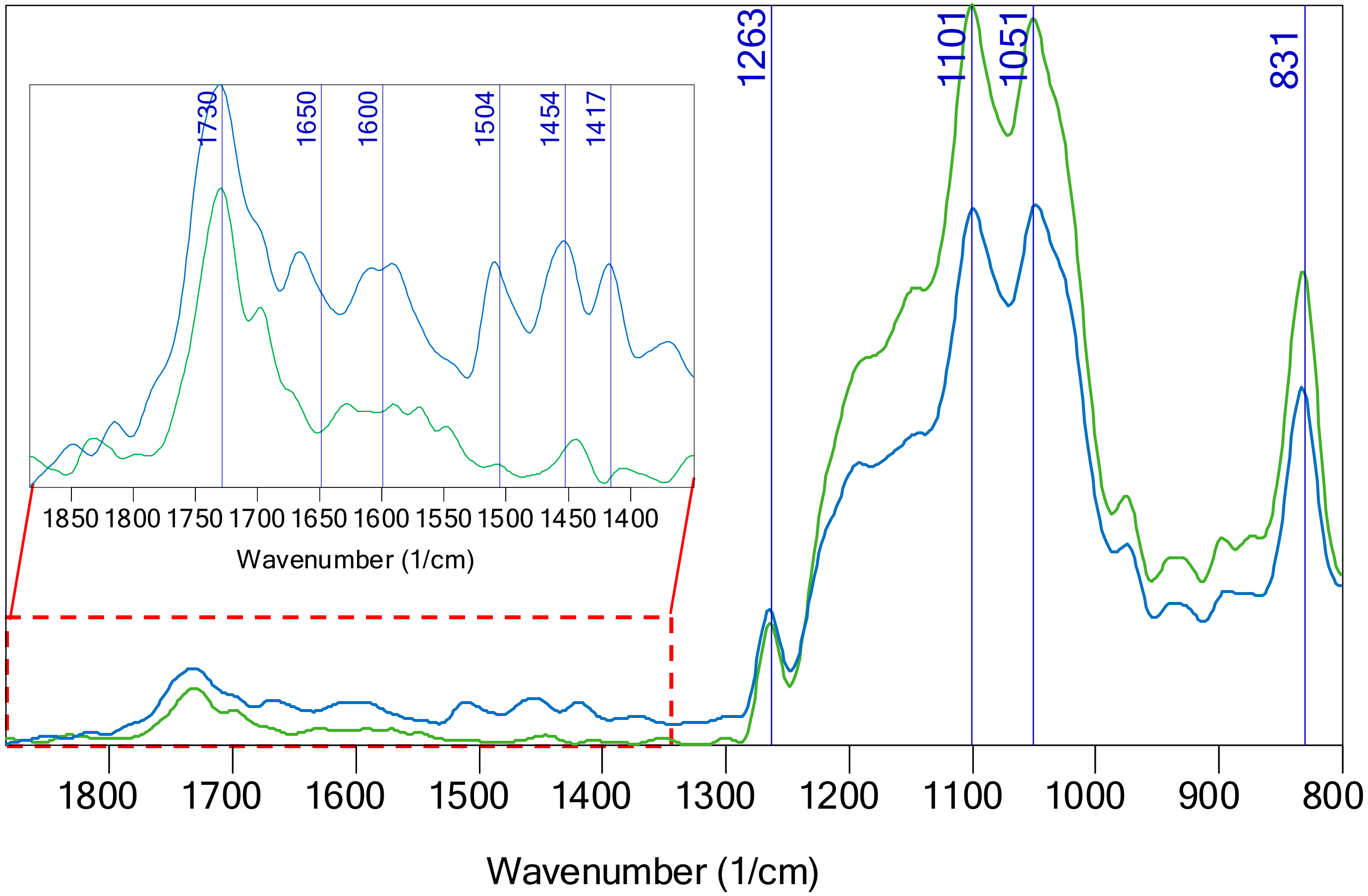
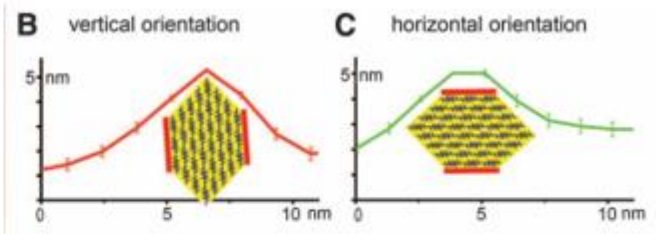


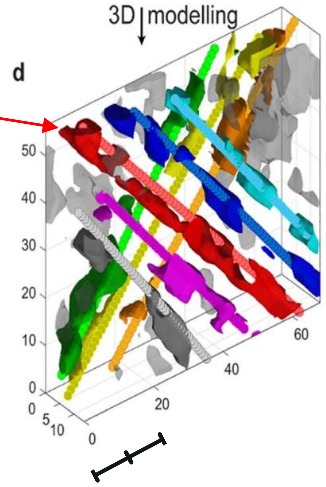


Individual Cellulose Elementary Fibrils – TEM tomography



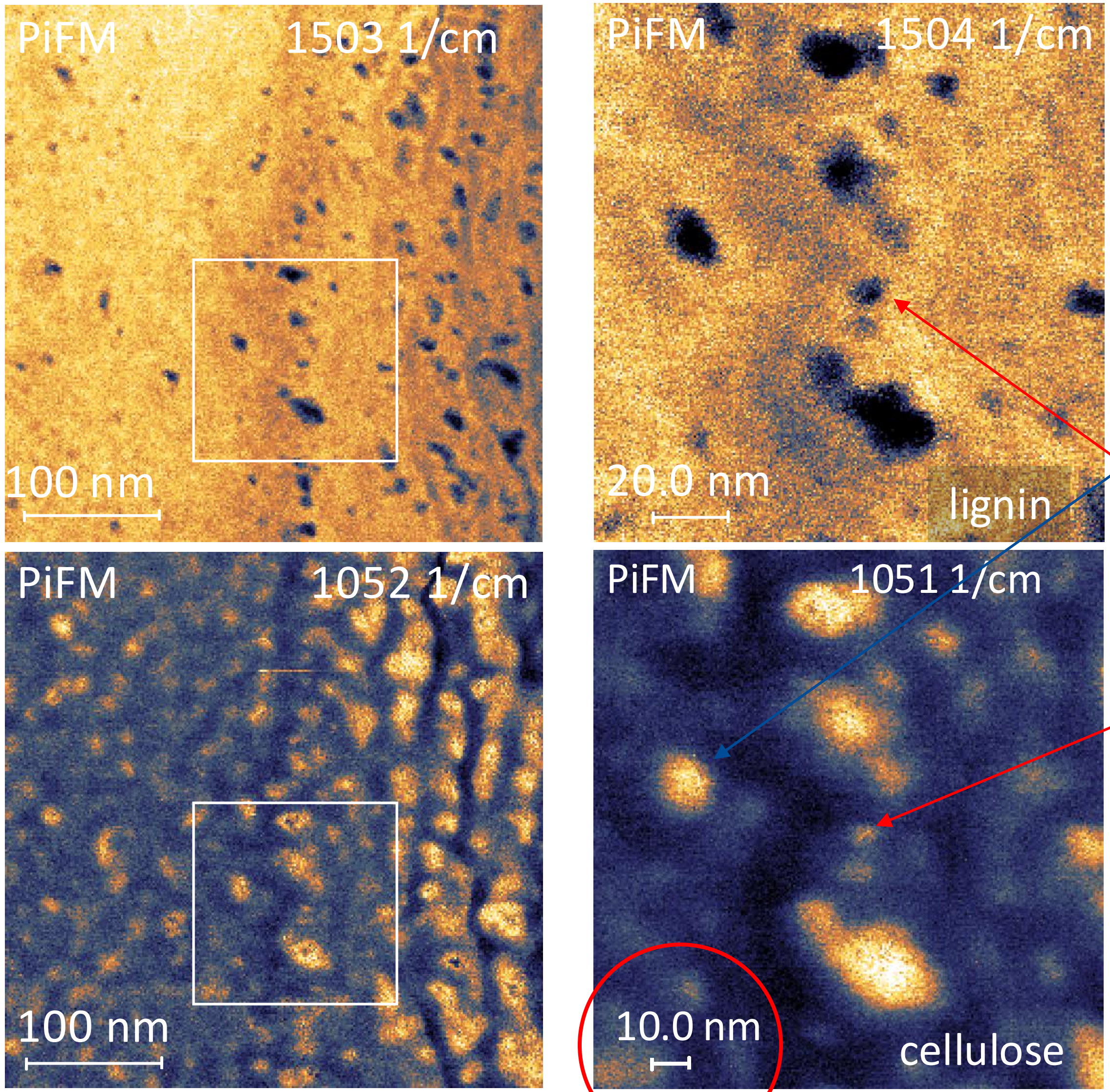
elementary fibril

elementary fibril

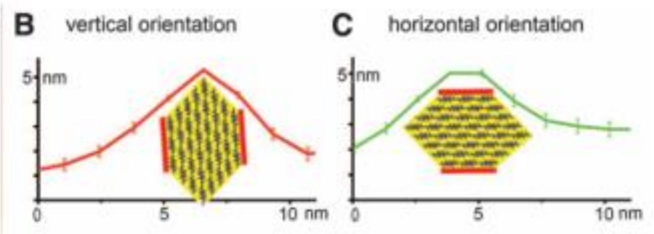


Applications Lab

Individual Cellulose Elementary Fibrils – TEM Tomography

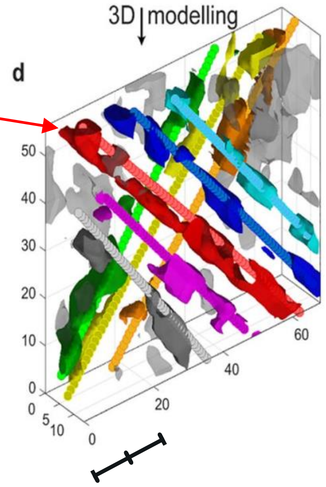


fibril bundles



cellulose elementary fibril

cellulose elementary fibril

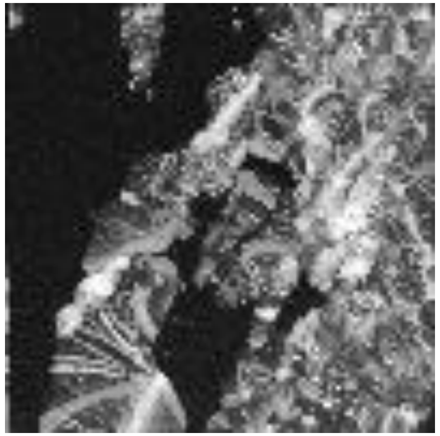


Applications Lab

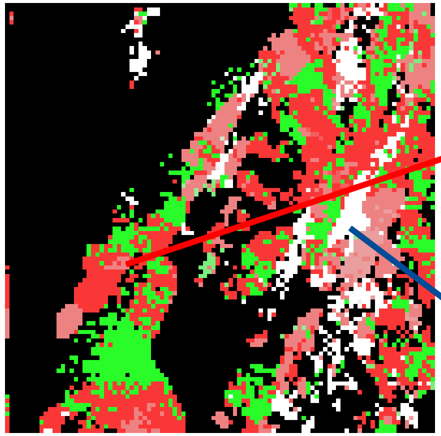
Ascorbic Acid Electron Microscopy – TEM

4D STEM of Recrystallized Ascorbic Acid

Scan area: 2.5 µm * 2.5 µm

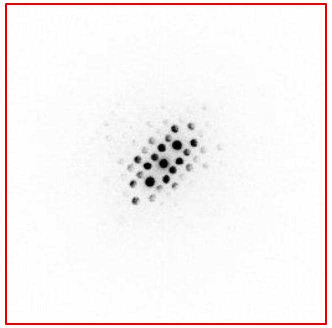


Virtual Dark-field Image

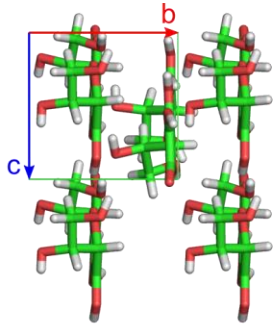


Orientation Map

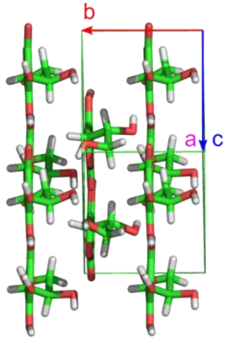
[100] or [101]
red and green areas



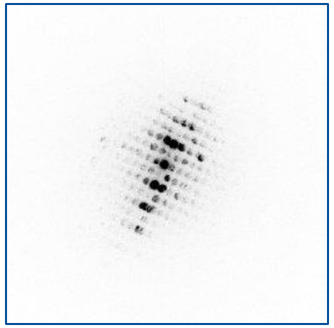
[100] :



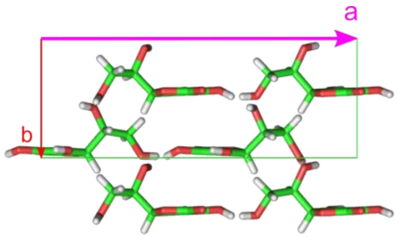
[101] :



[001] : white areas



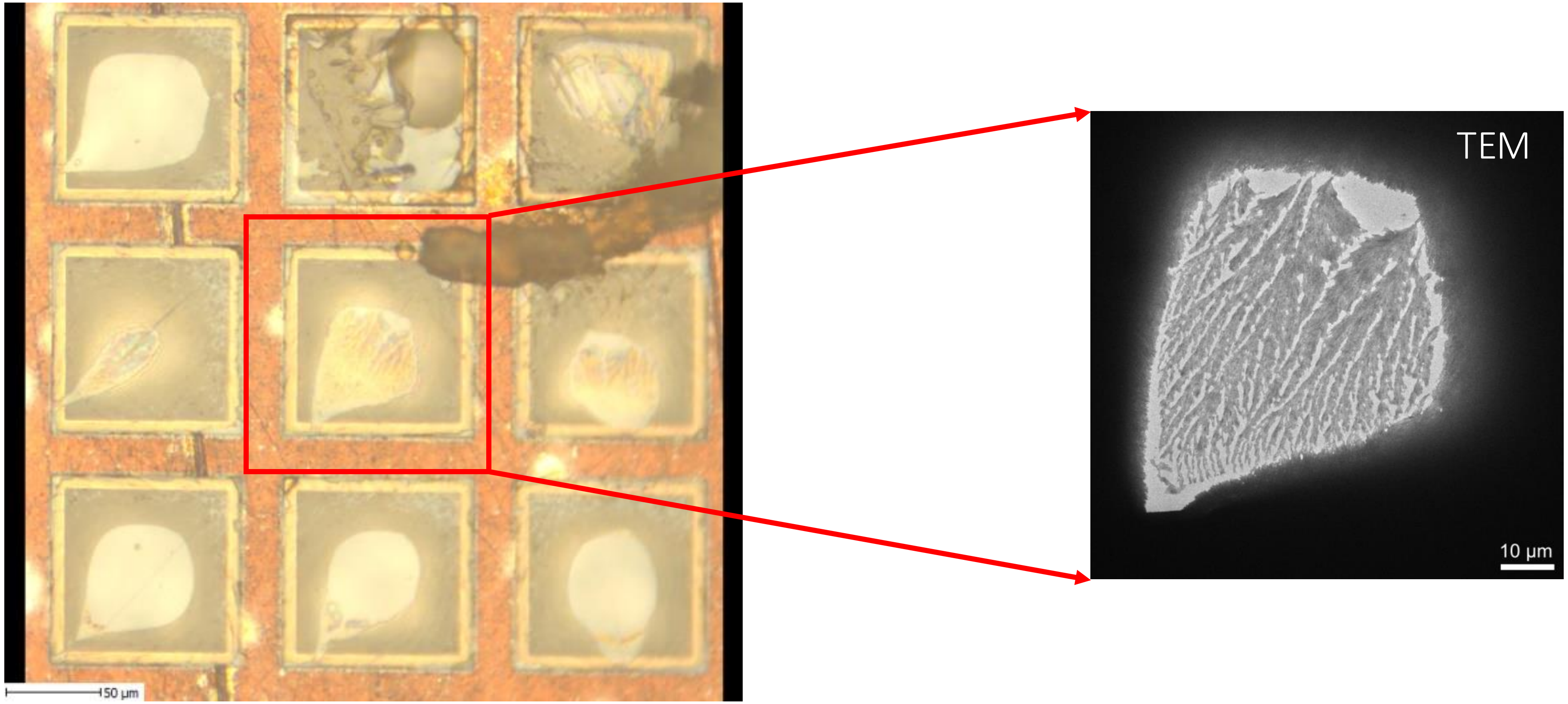
[001] :



Upon drying, ascorbic acid recrystallized on the grid presenting two predominant orientations. The orientation map below highlights these main crystal orientations, represented by green/red and white.

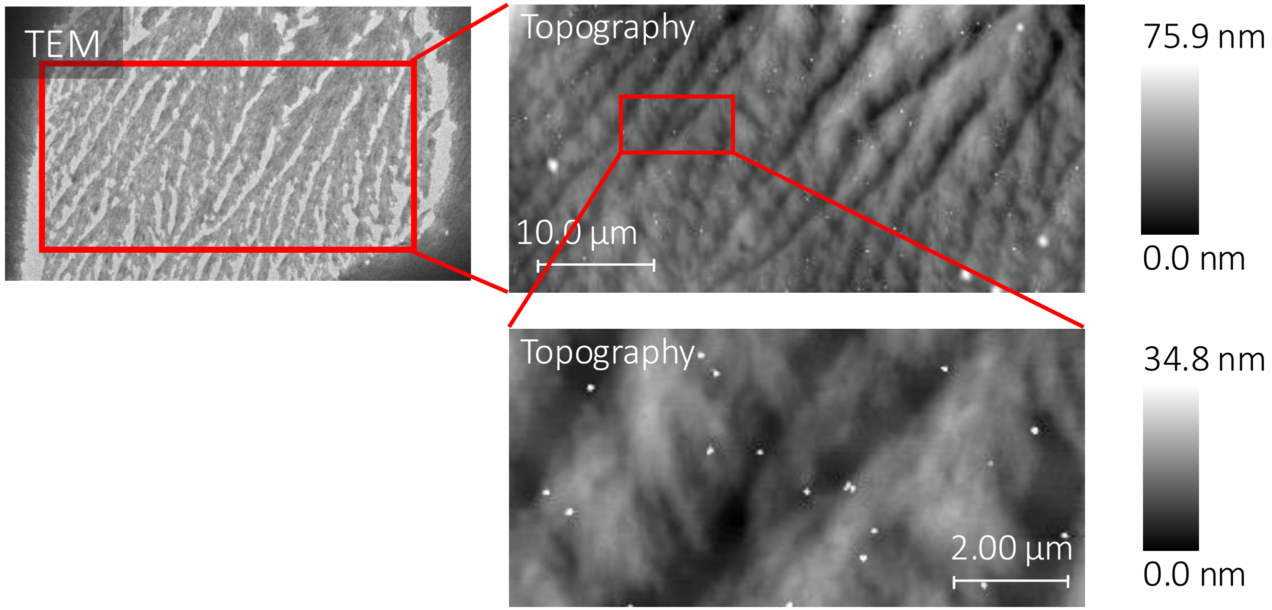
Sample Information

Most of the grid spaces area are usable, but most of the crystals were recrystallized only along the edge of the grid spaces. The highlighted area is a good example that contains more crystals (red box).

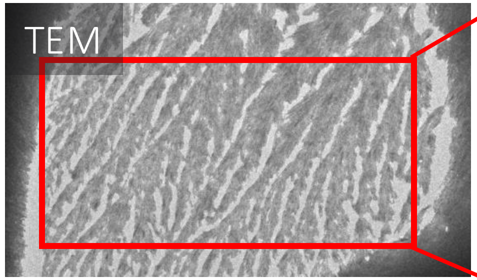


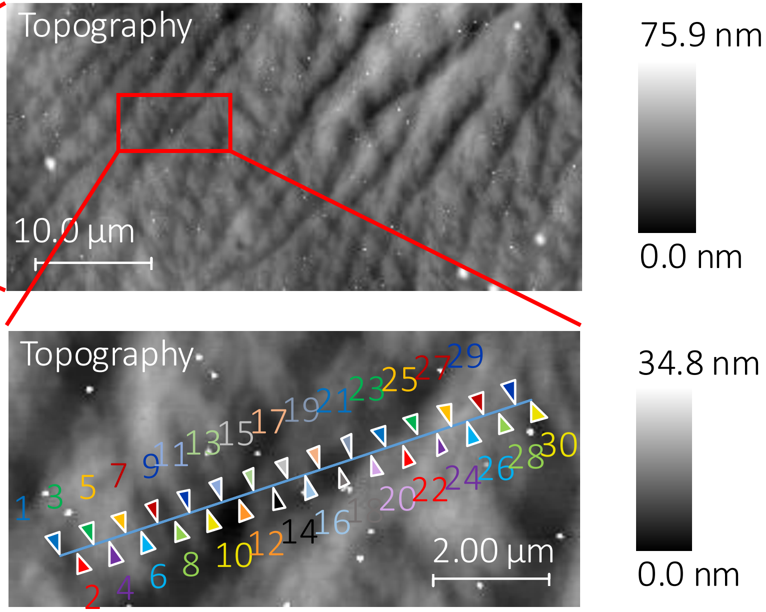
The optical image from Molecular Vista Microscope

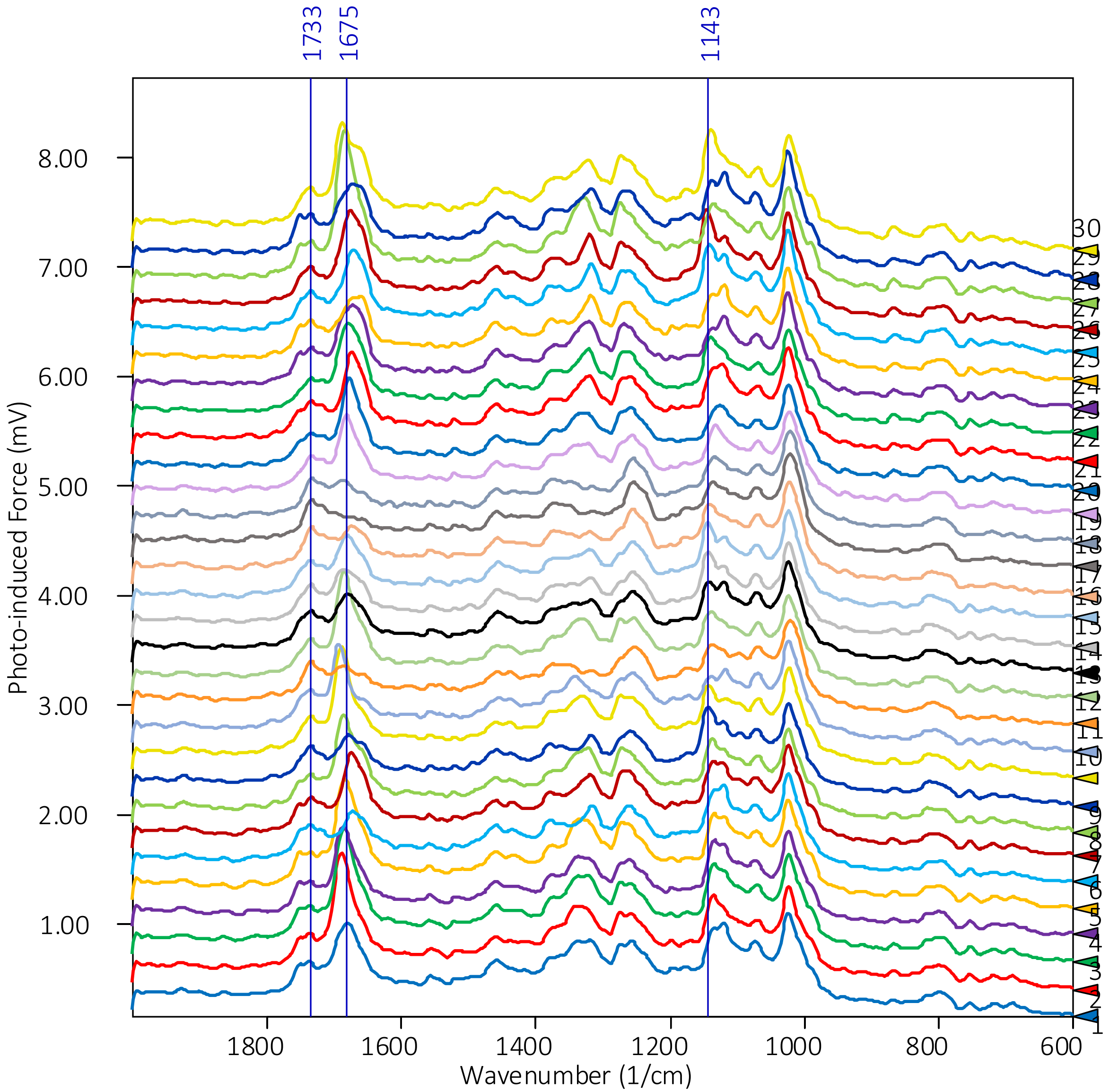
PiF-IR: 10 x 5 μm²



PiF-IR: 10 x 5 µm^2

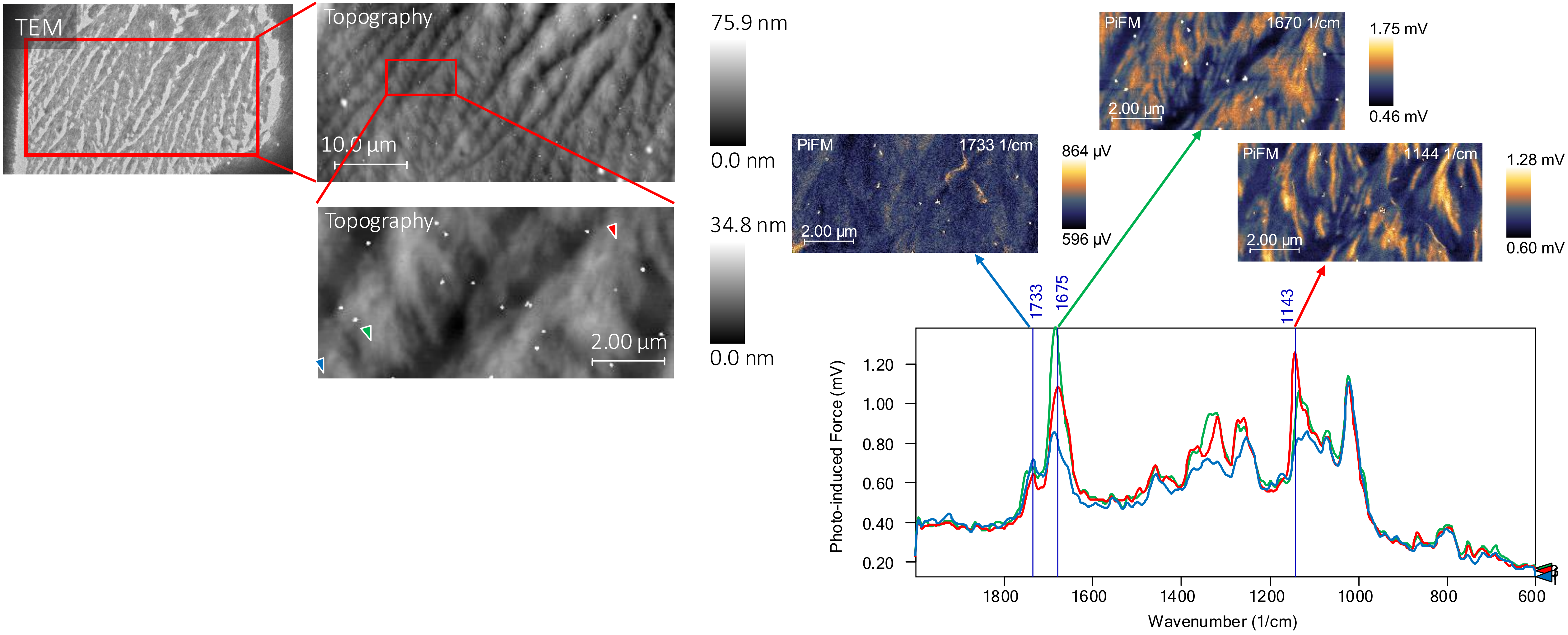




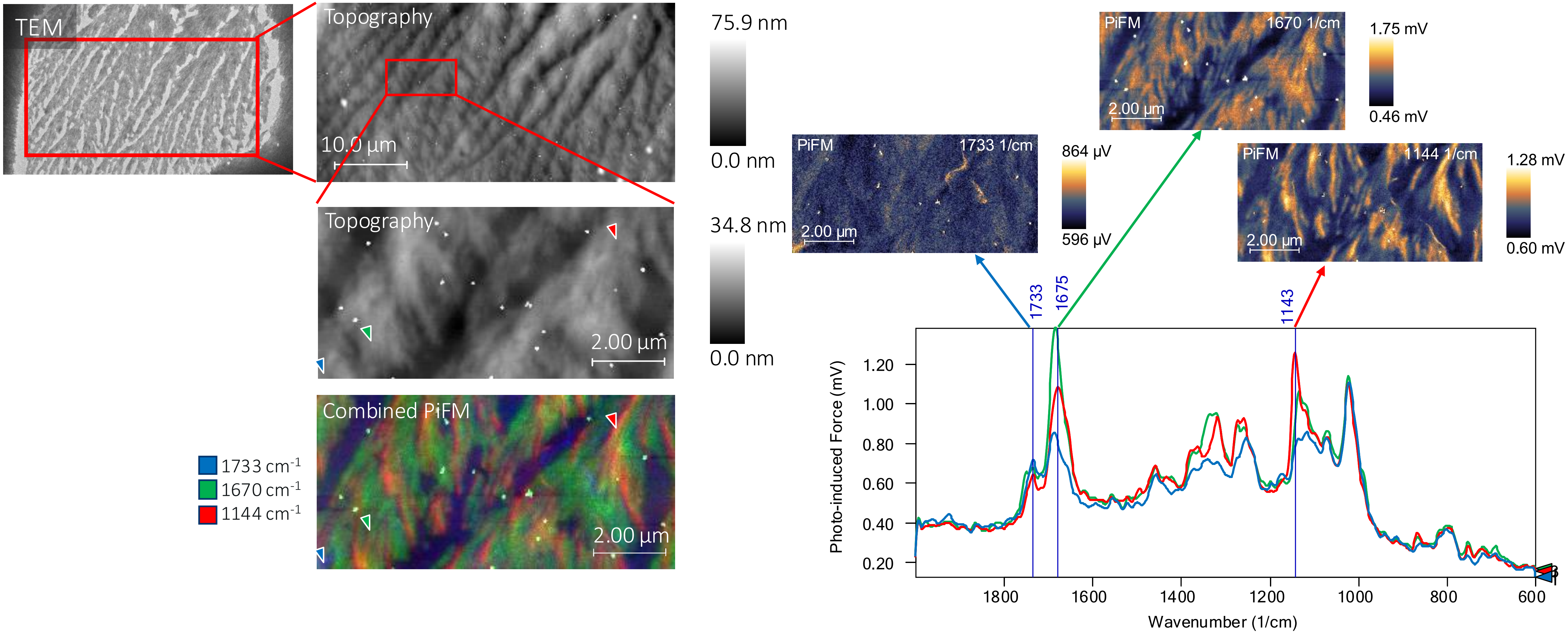


Applications Lab

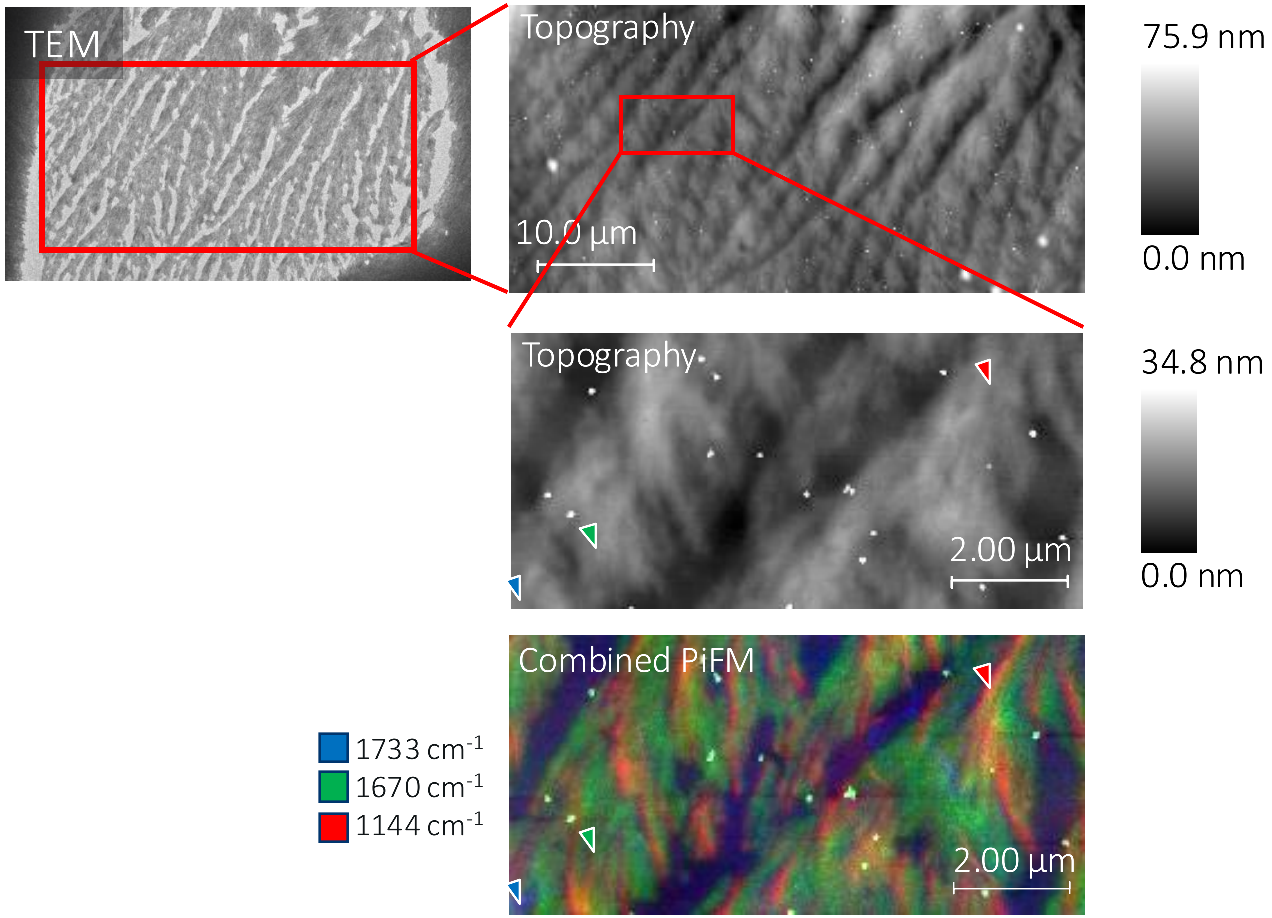
PiF-IR: 10 x 5 μm^2



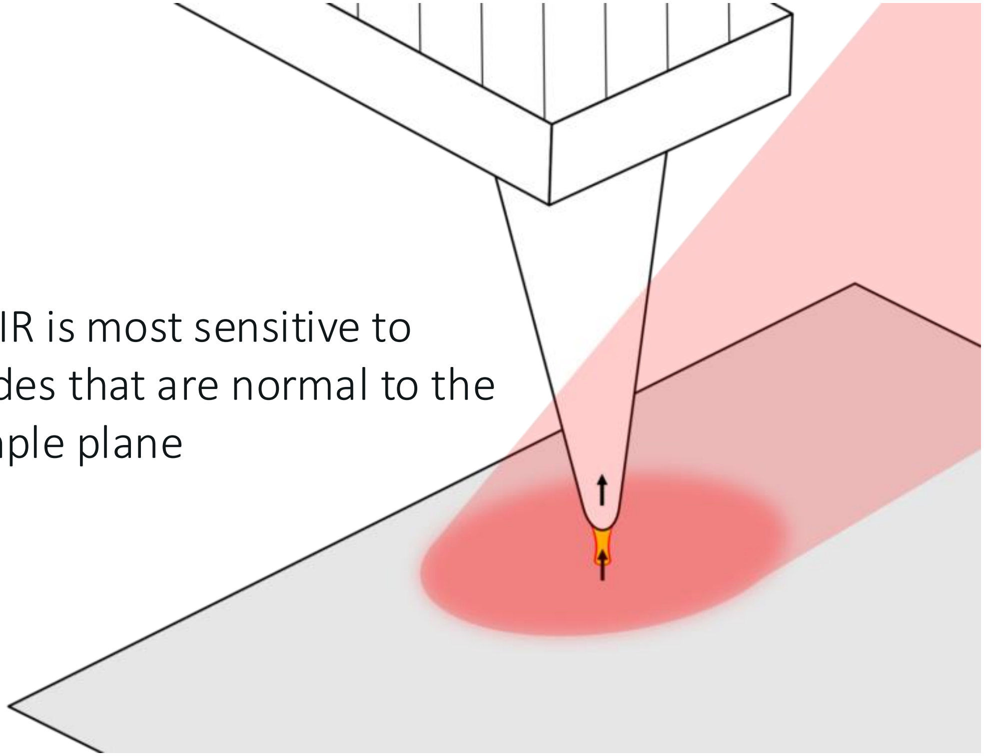
PiF-IR: 10 x 5 μm^2



PiF-IR: 10 x 5 μm^2



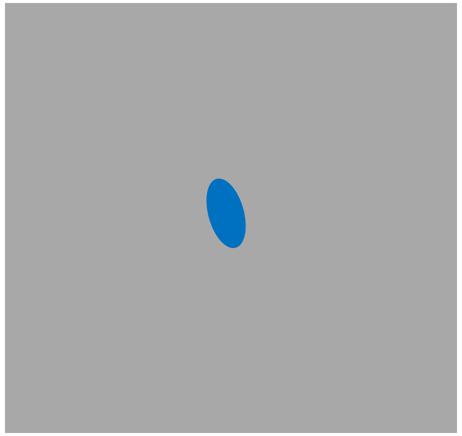
PiF-IR is most sensitive to modes that are normal to the sample plane



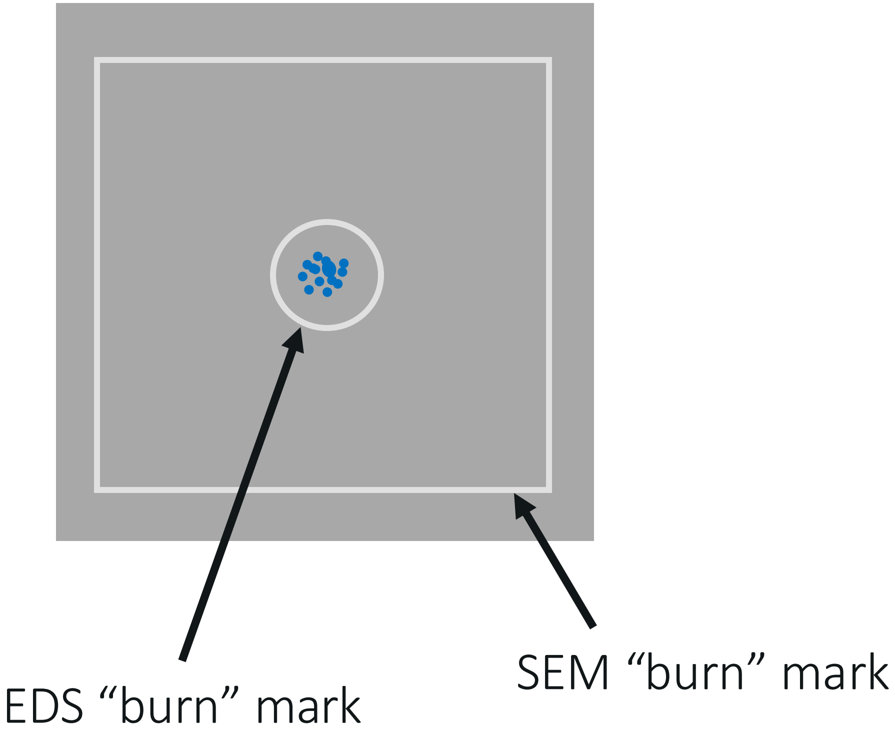
SEM-EDS – General Comments

- SEM commonly used as primary analytical tool for wafer defect analysis
- However, it can damage defects and contaminate them
- PiFM is non-destructive – run PiFM before SEM-EDS
    - KLARF compatible

SEM Image



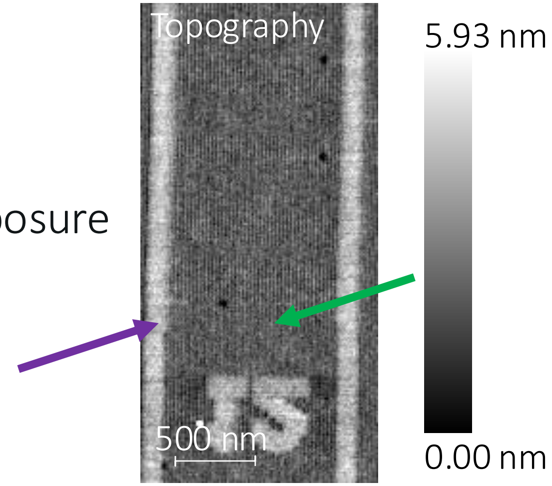
AFM after SEM-EDS



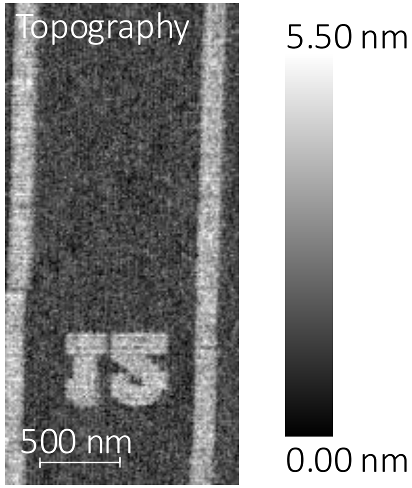
Applications Lab

EUV resist with 12 nm half-pitch

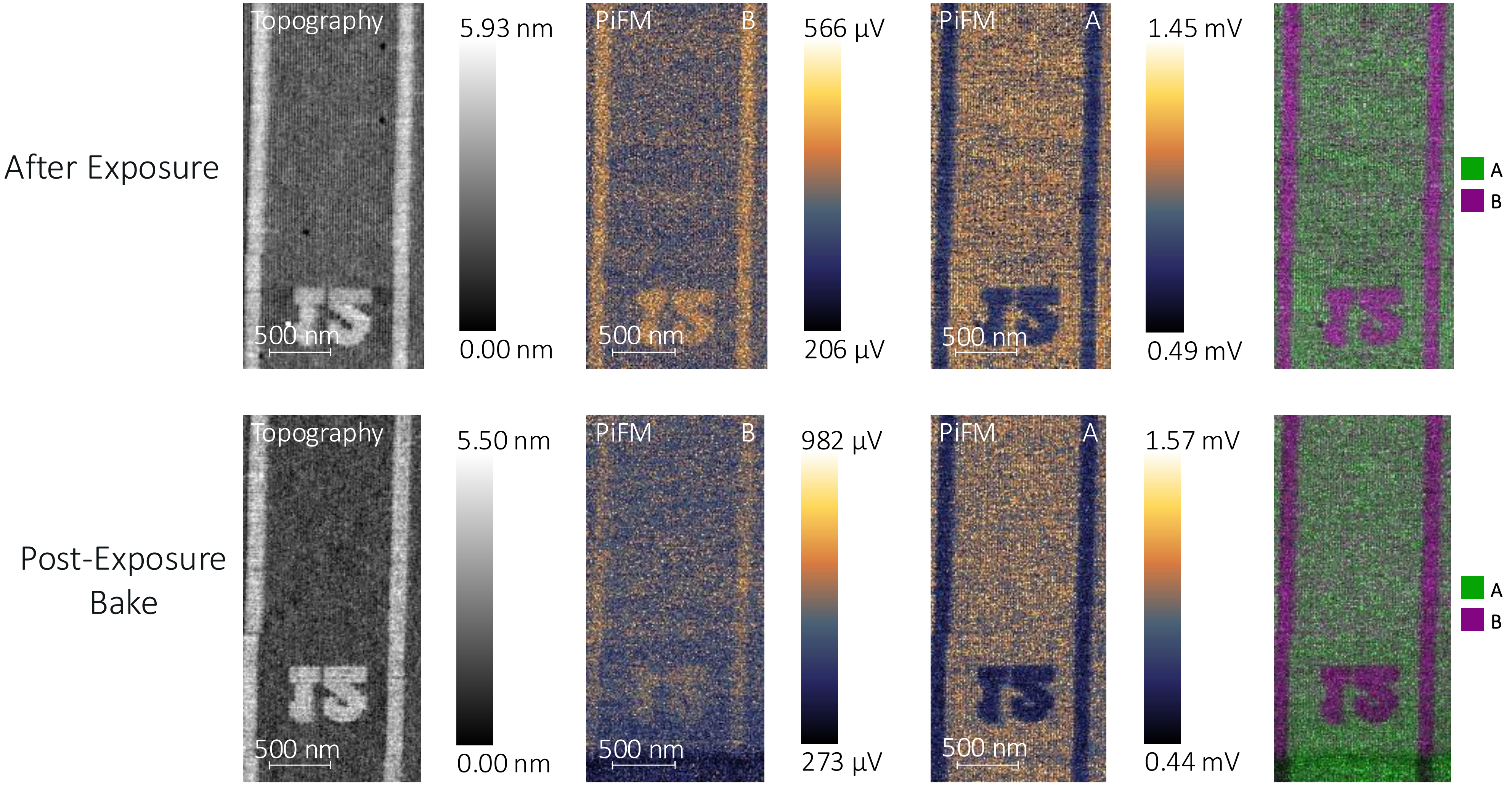
After Exposure



Post-Exposure Bake

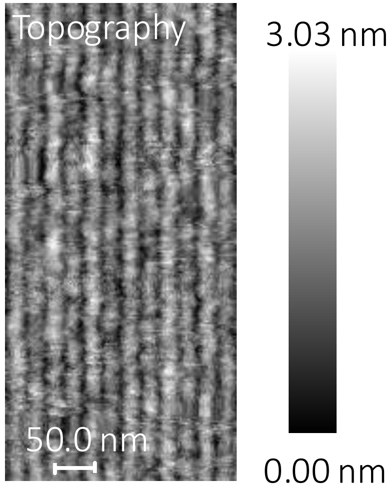


IR-PiFM – Initial Steps

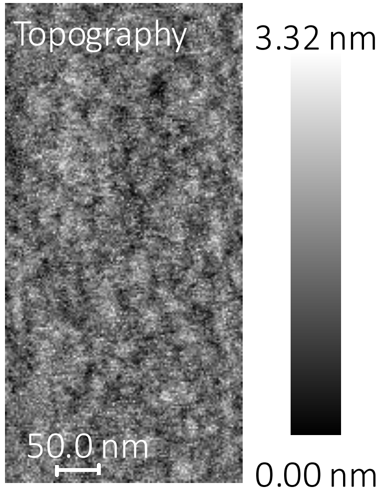


IR-PiFM – 12 nm Half-Pitch Lines

After Exposure

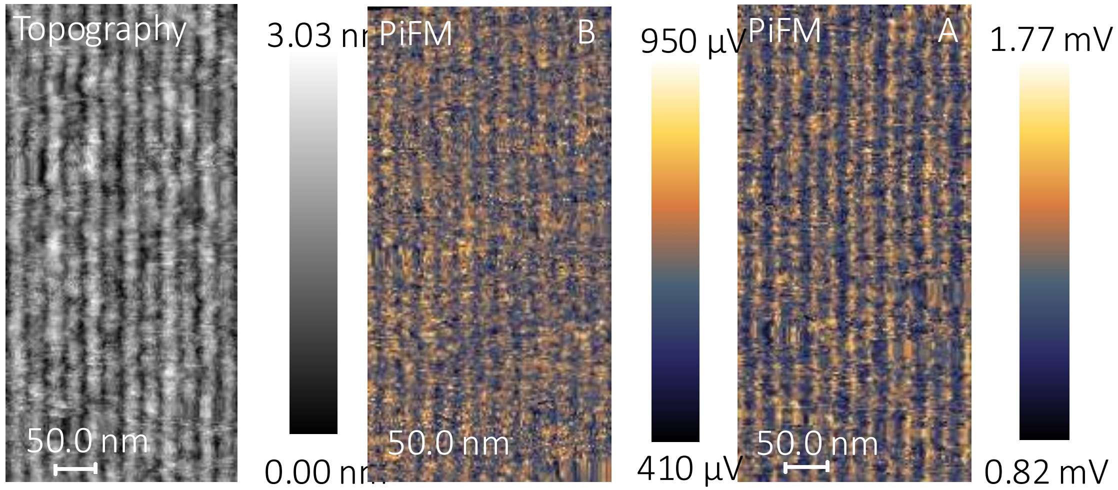


Post-Exposure Bake

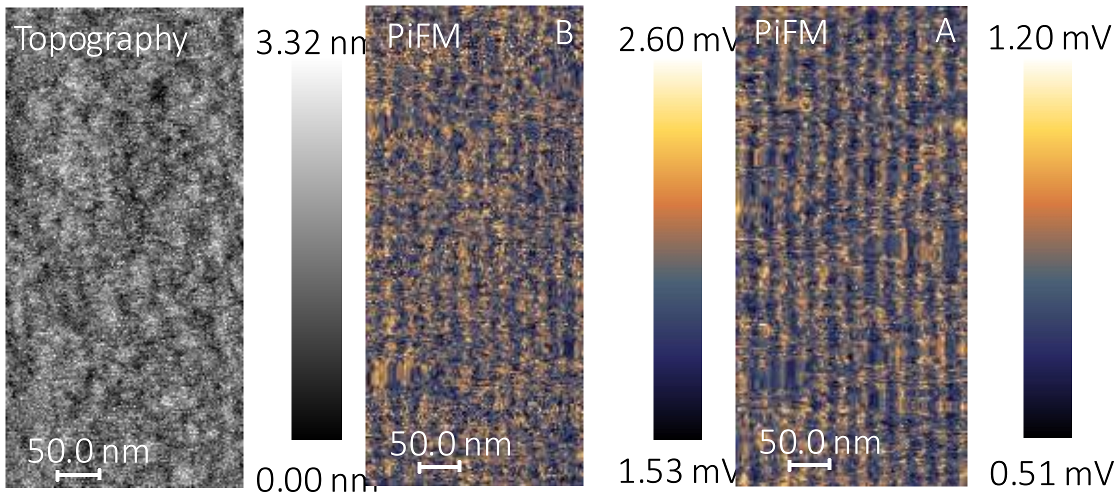


IR-PiFM – 12 nm Half-Pitch Lines

After Exposure

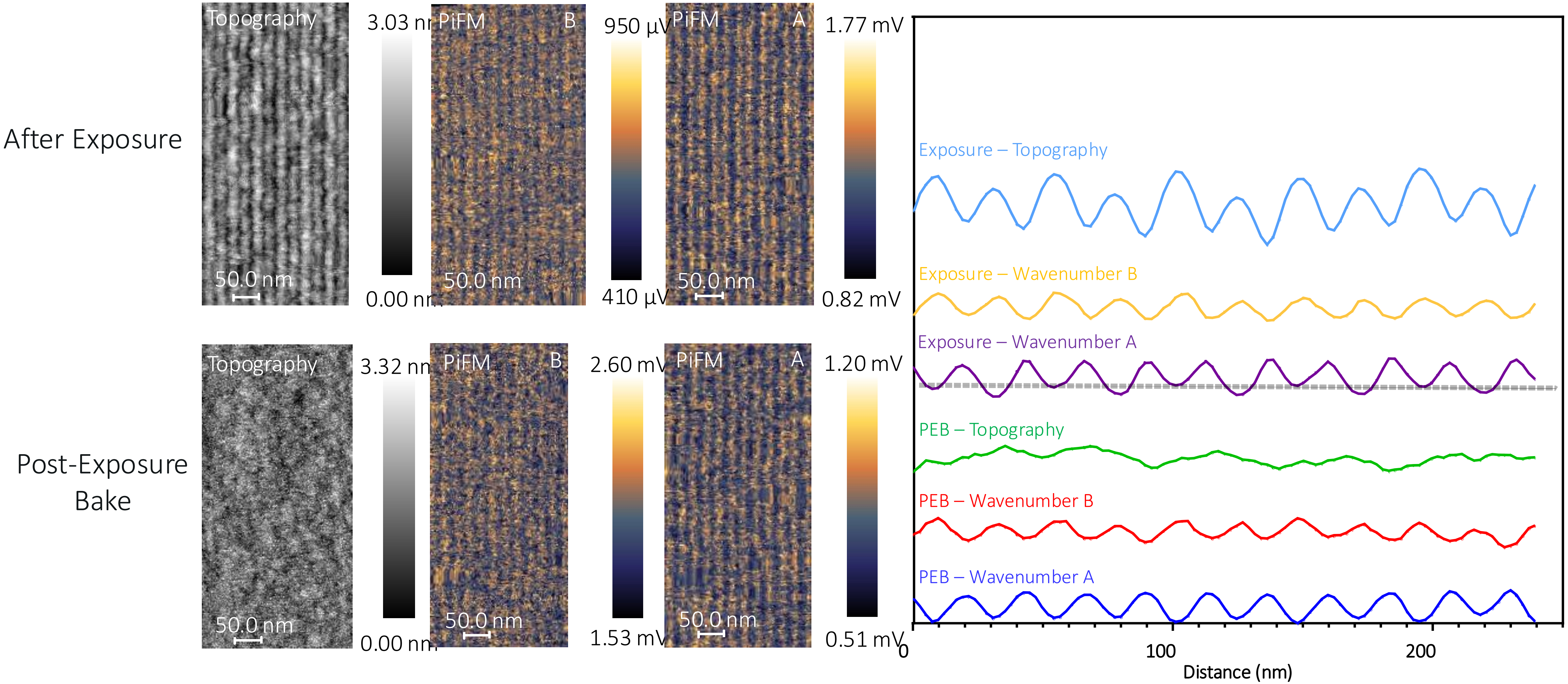


Post-Exposure Bake

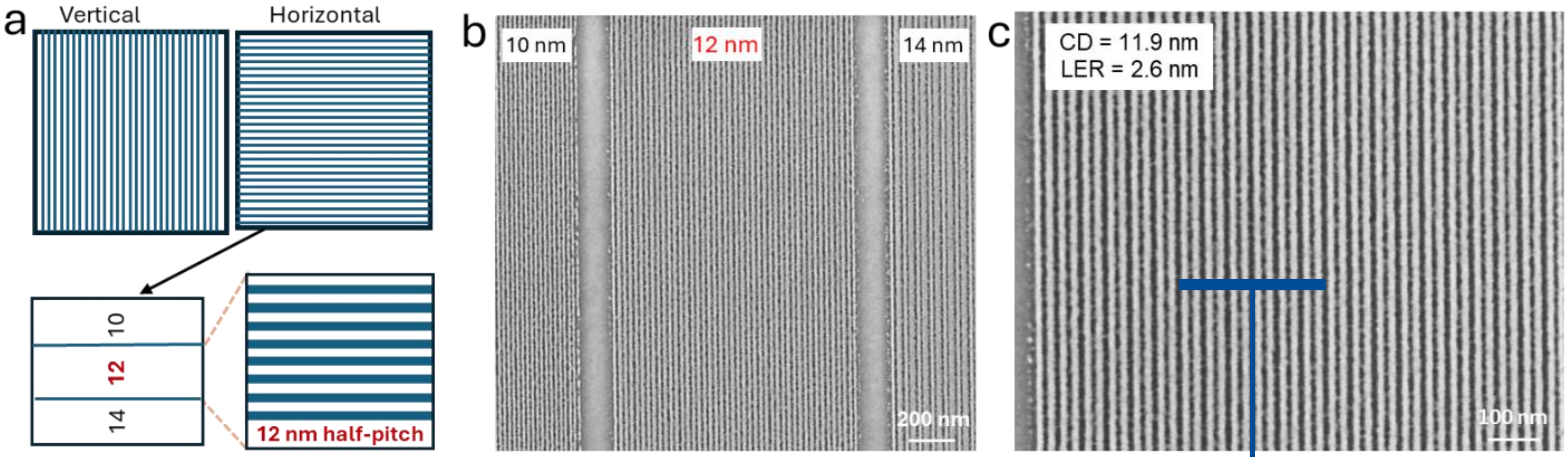


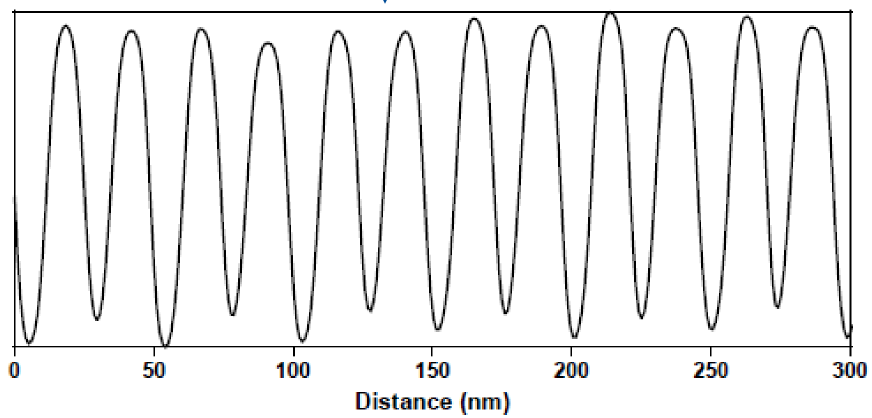
Applications Lab

IR-PiFM – 12 nm Half-Pitch Lines: Line Profile



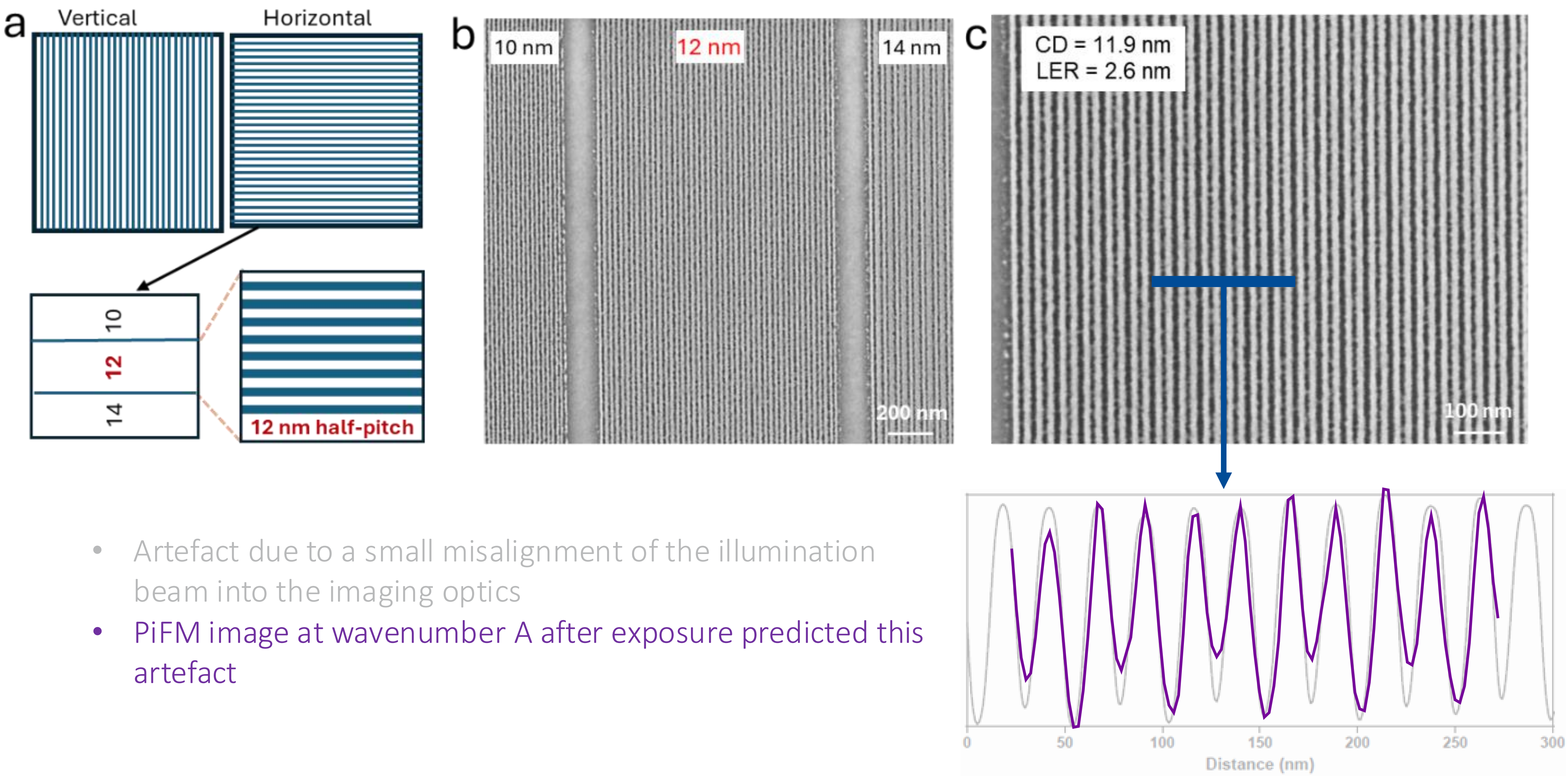
SEM – 12 nm Half-Pitch Lines





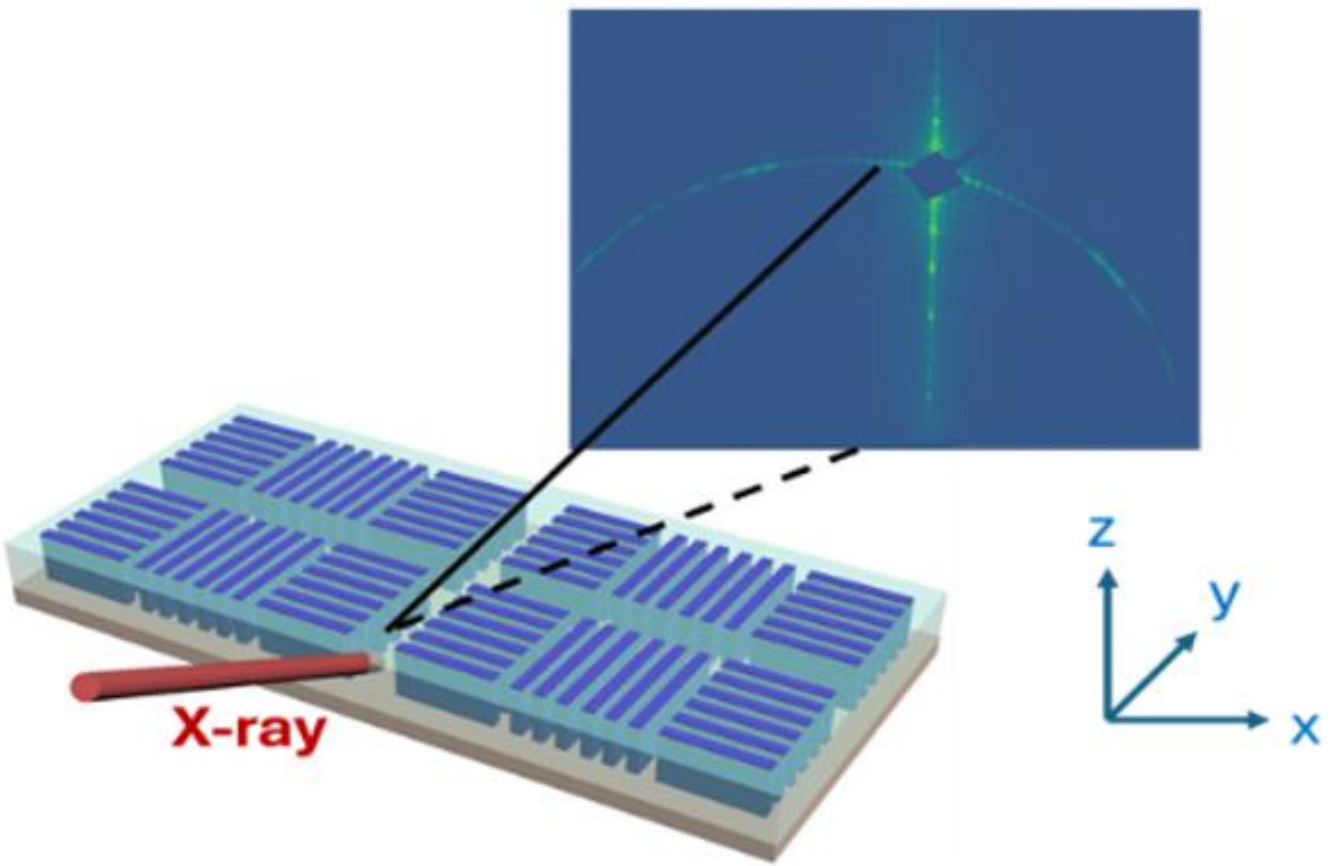
- Artefact due to a small misalignment of the illumination beam into the imaging optics

SEM – 12 nm Half-Pitch Lines

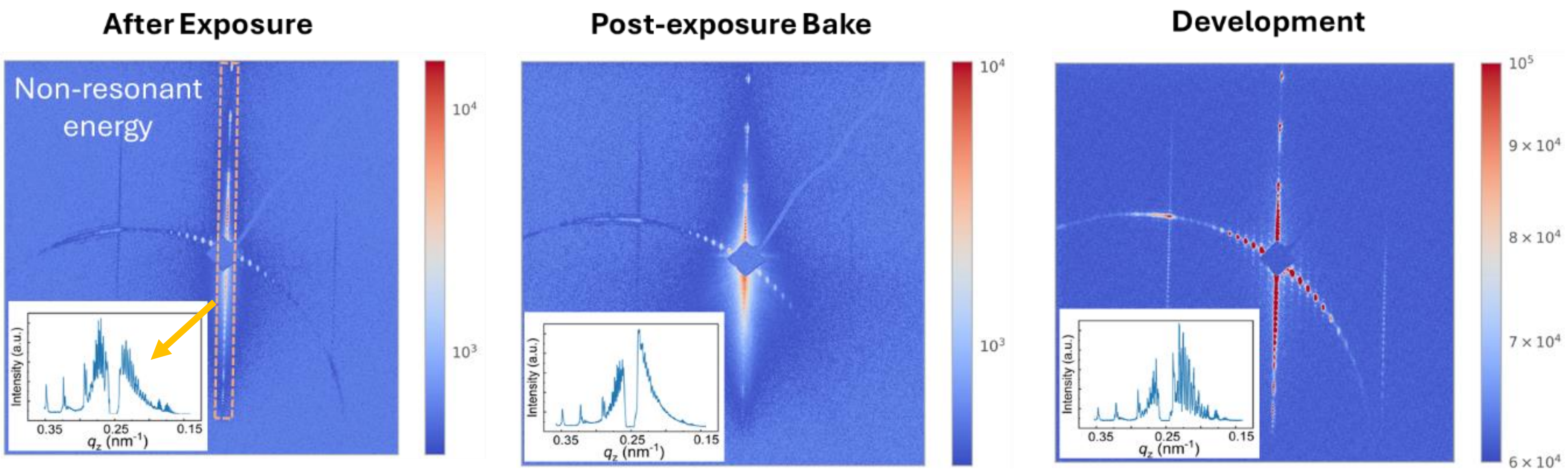


- Artefact due to a small misalignment of the illumination beam into the imaging optics
- PiFM image at wavenumber A after exposure predicted this artefact

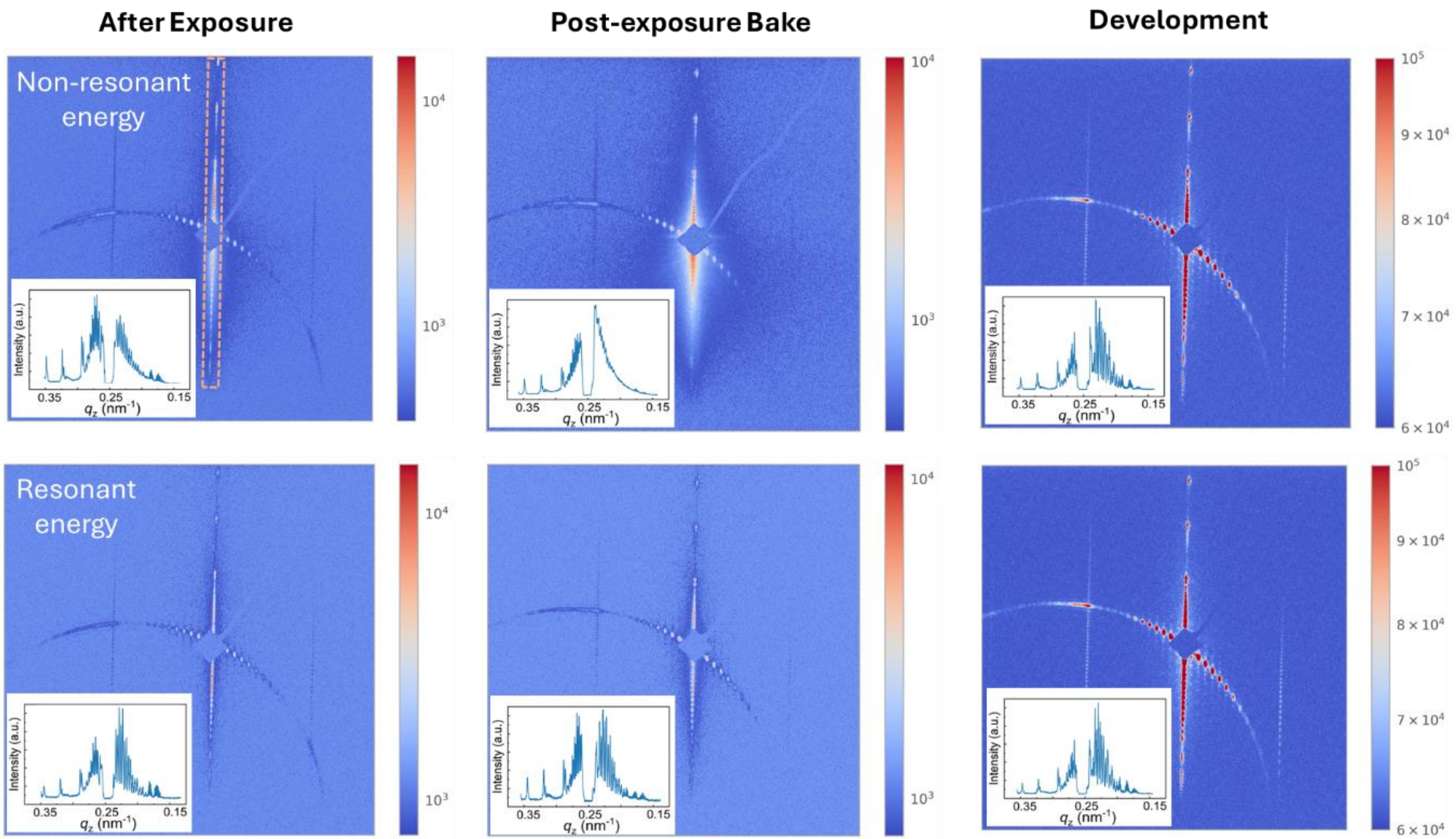
CD-RSoXS – 12 nm Half-Pitch Lines



CD-RSoXS – 12 nm Half-Pitch Lines

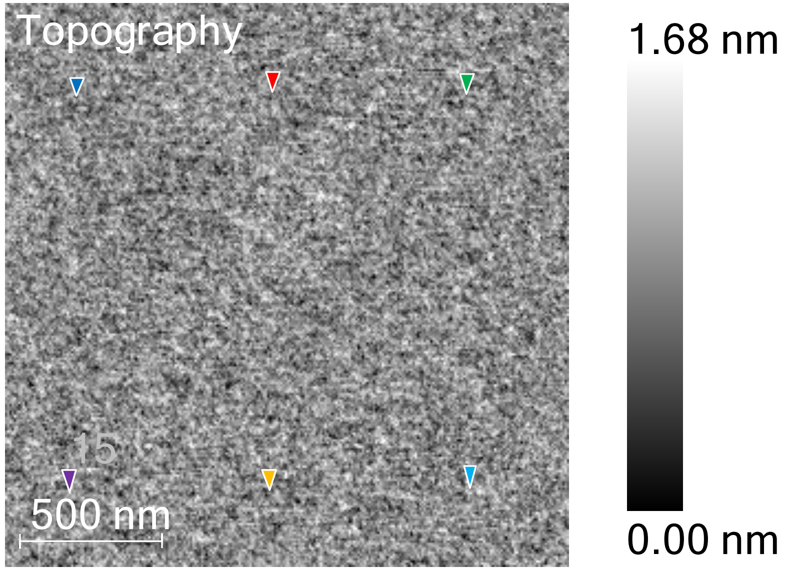


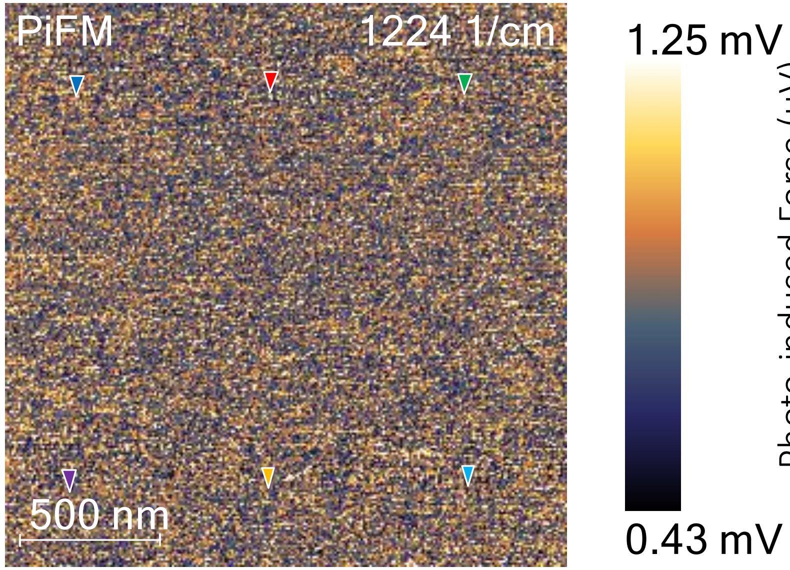
CD-RSoXS – 12 nm Half-Pitch Lines

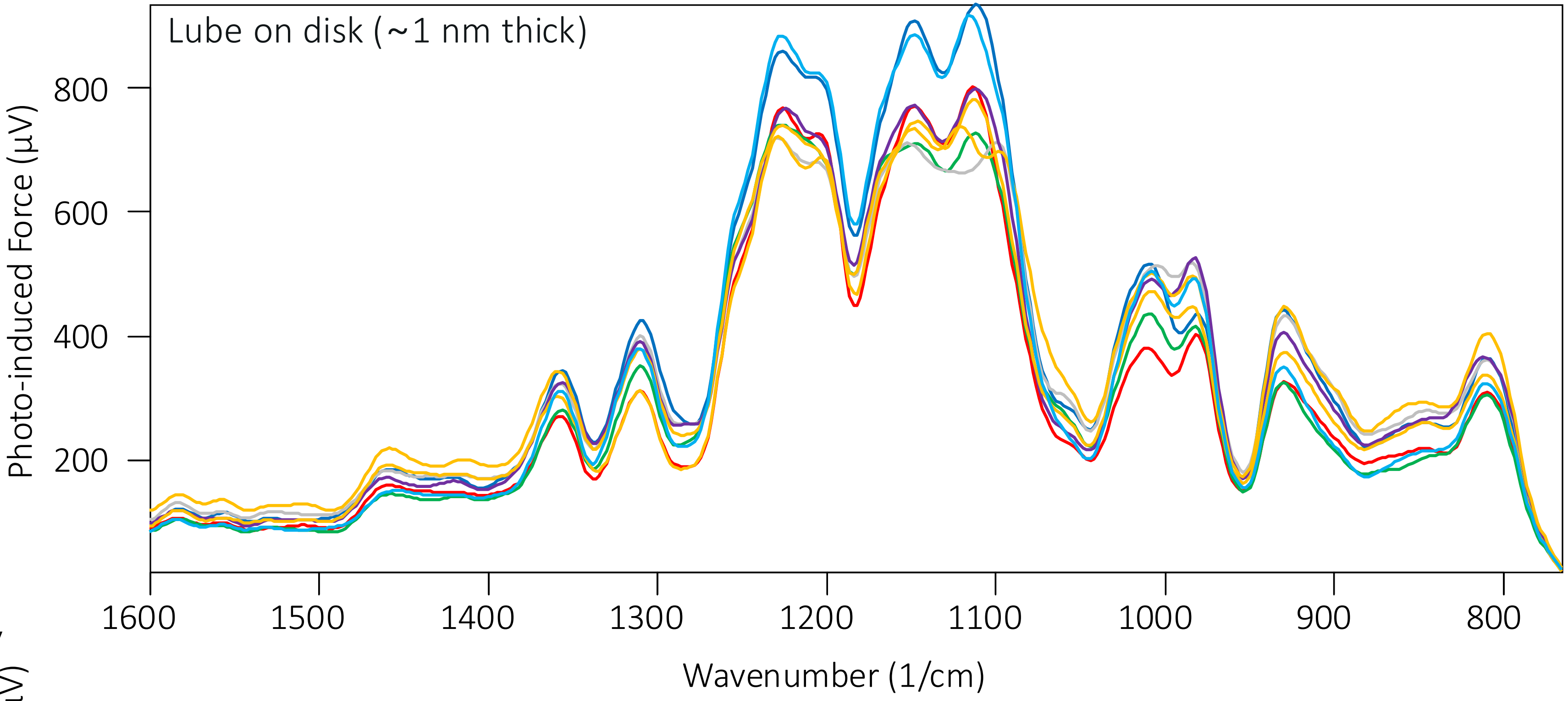


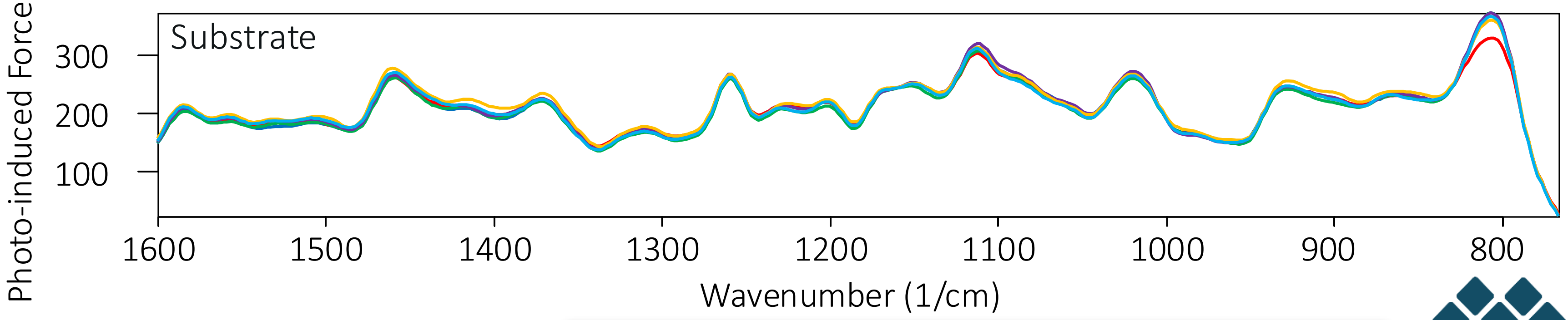
Monolayer Results for Anti-Stiction Compatibility

Lube on HDD



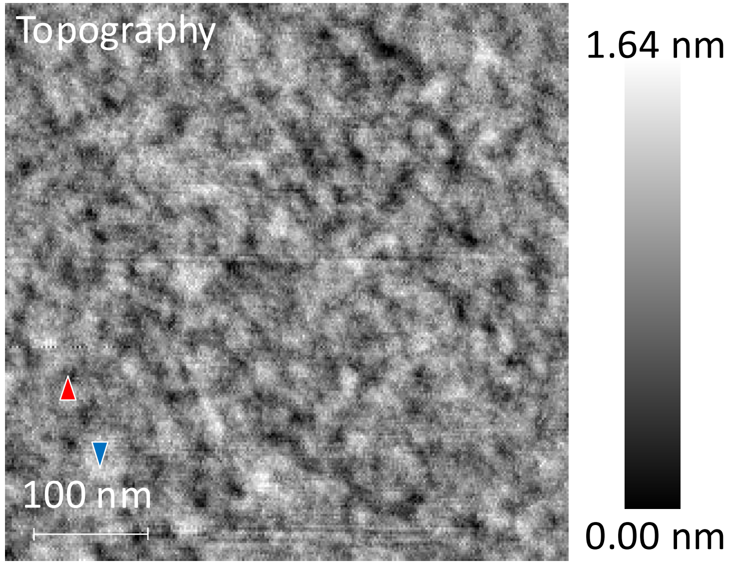


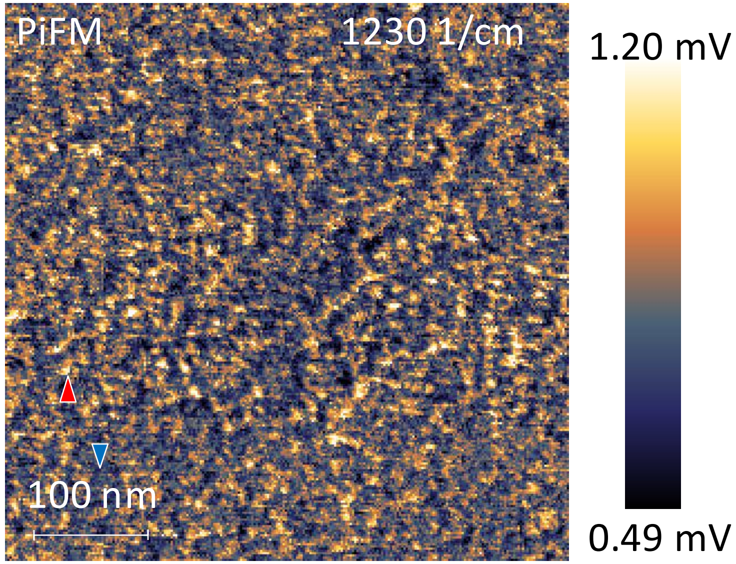


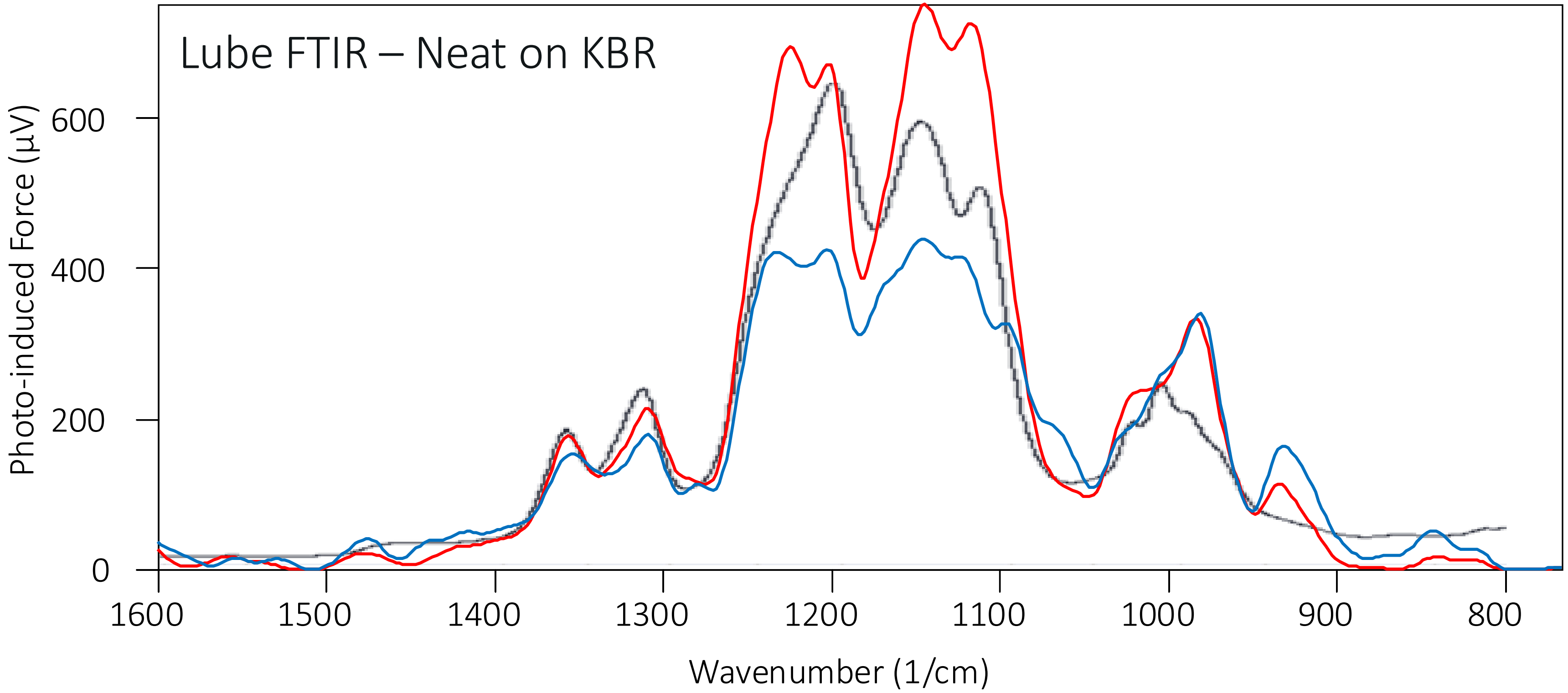


Applications Lab

Lube on HDD



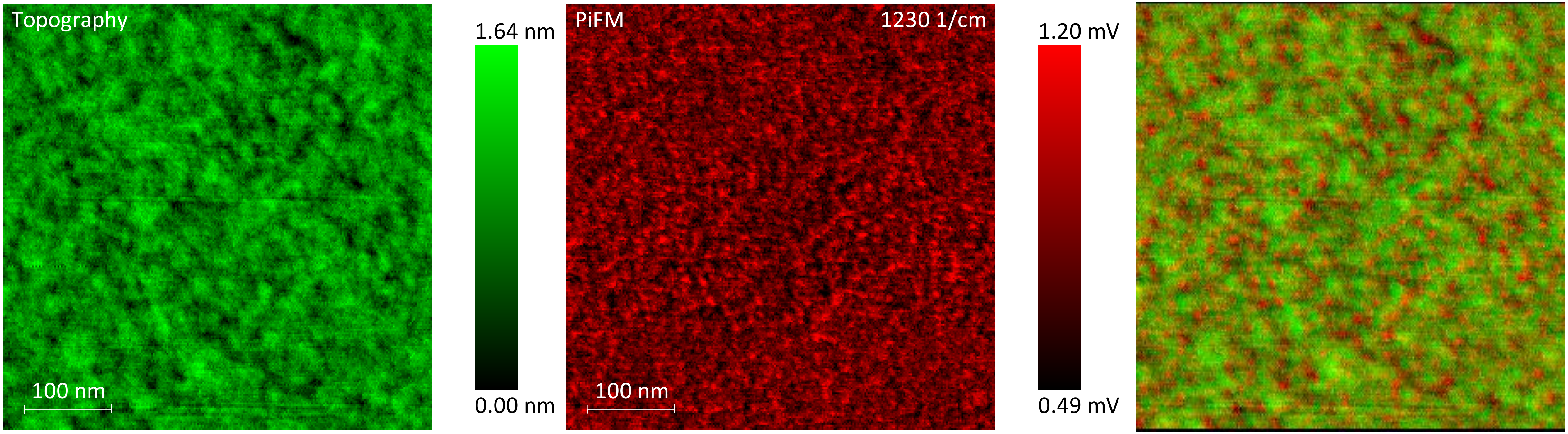




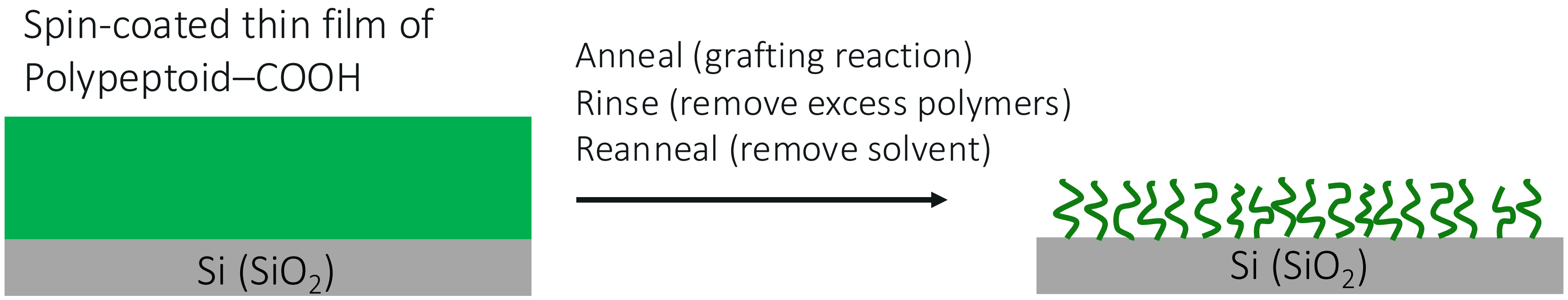
- Substrate spectrum subtracted
- Lube thickness variation detected by PiFM

Lube on HDD

Correlation between High Topography and PiF Signal



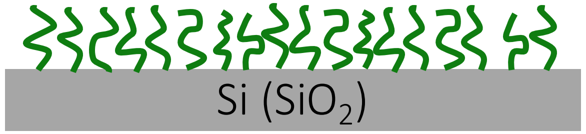
Polypeptoid Monolayer – Water Contact Angle



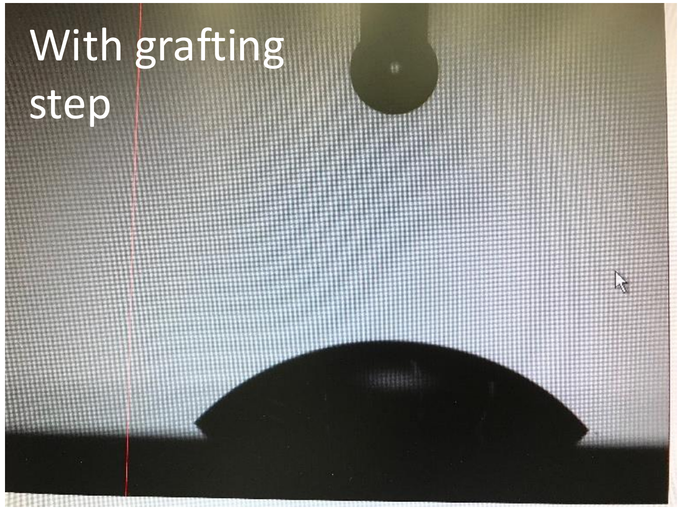
Polypeptoid Monolayer – Water Contact Angle

Spin-coated thin film of
Polypeptoid–COOH

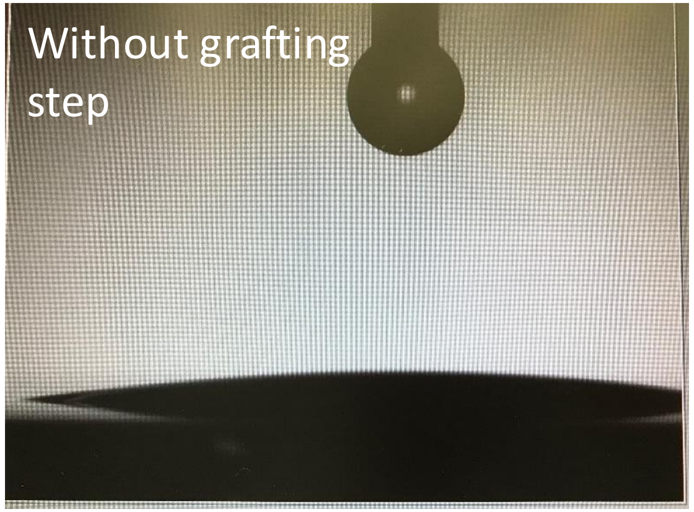
Anneal (grafting reaction)
Rinse (remove excess polymers)
Reanneal (remove solvent)



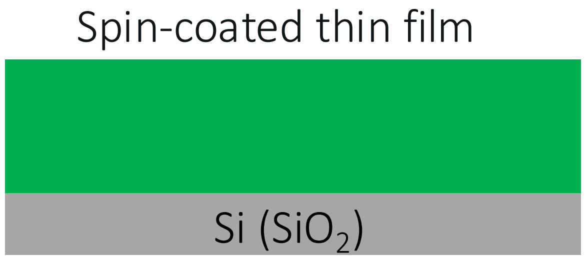
Spin coated thin film → anneal → rinse away excess brush → reanneal

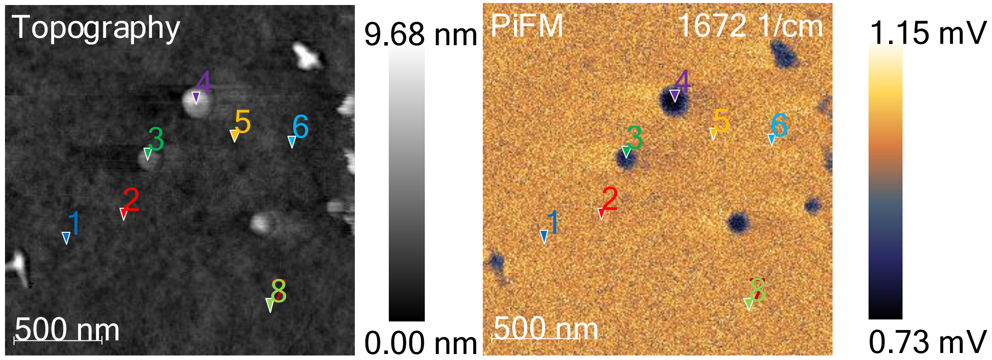


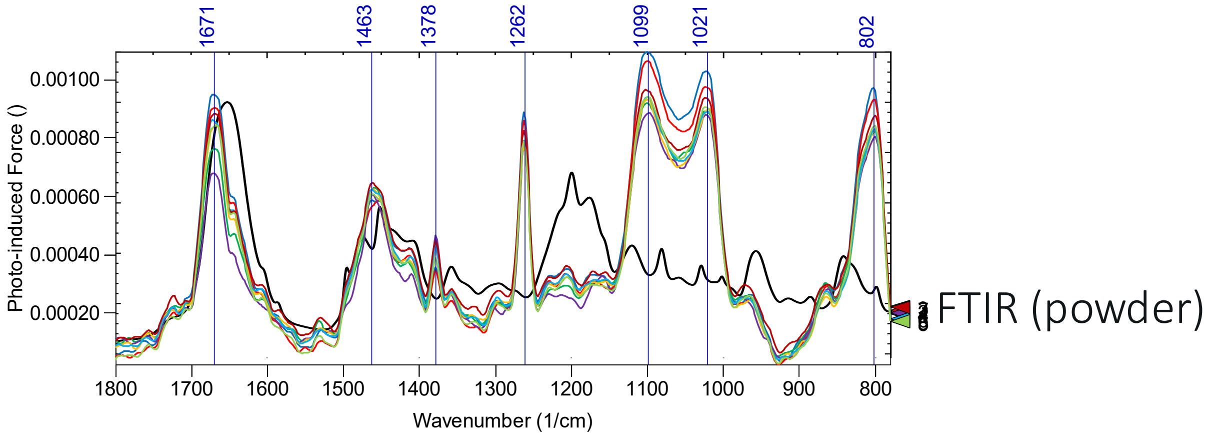
Spin coated thin film → no anneal → rinse away excess brush → reanneal



Polypeptoid Monolayer – PiFM



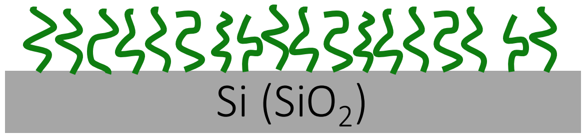


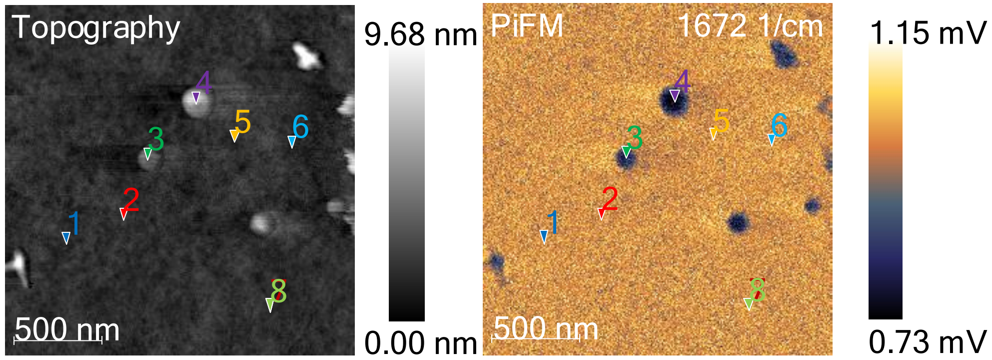


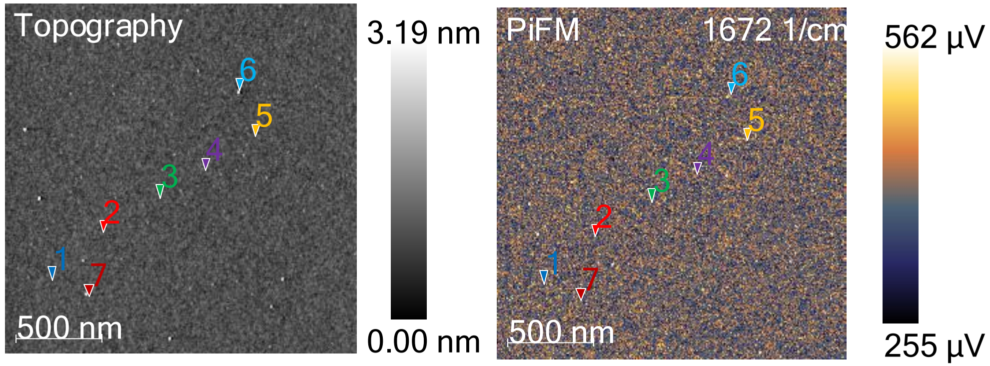
Polypeptoid Monolayer – PiFM

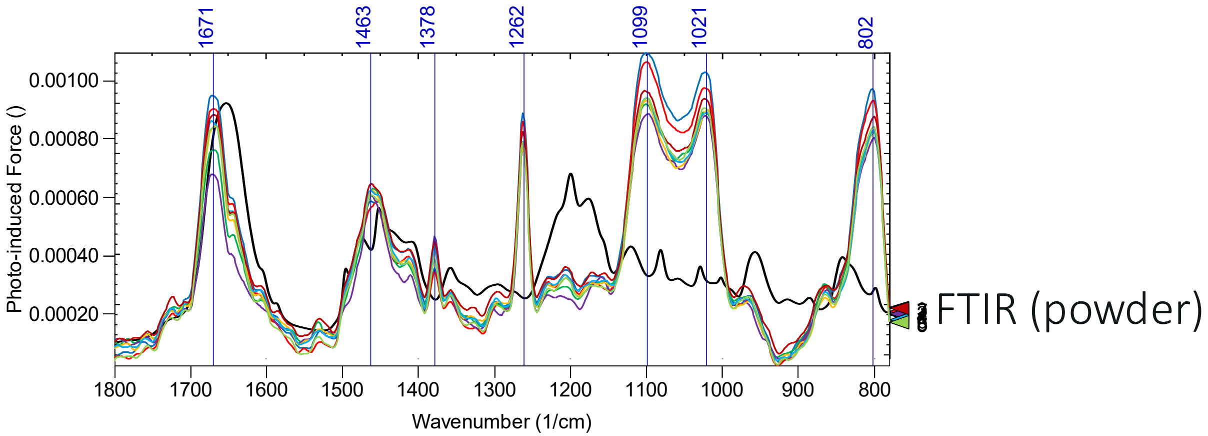
Spin-coated thin film

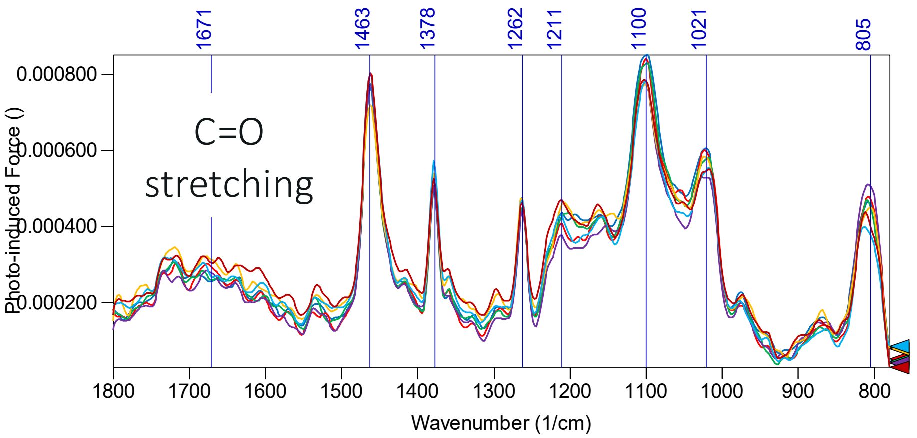
Anneal (grafting reaction)
Rinse (remove excess polymers)
Reanneal (remove solvent)









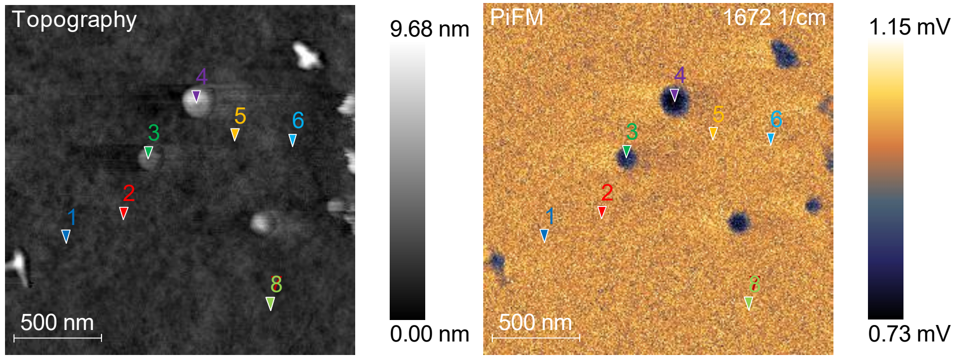


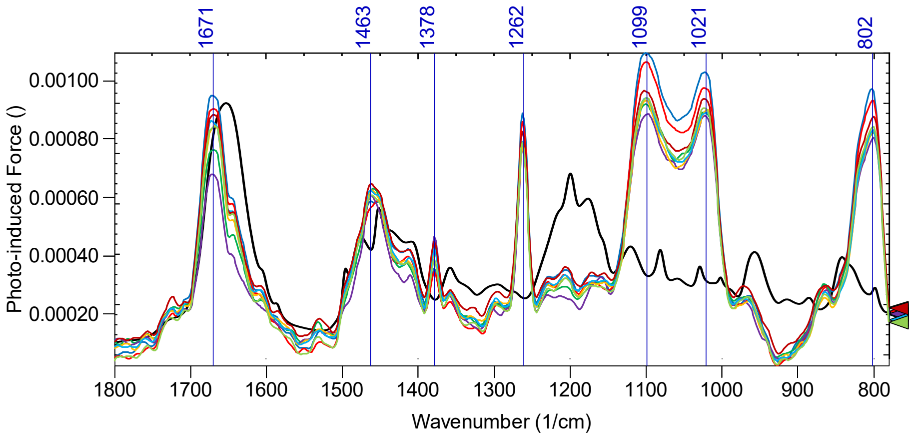
Polypeptoid Monolayer – PiFM

Spin-coated thin film

Anneal (grafting reaction)
Rinse (remove excess polymers)
Reanneal (remove solvent)

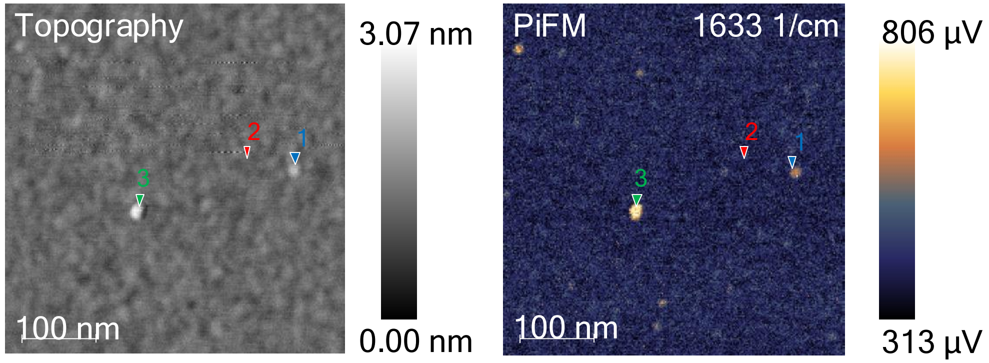
OR actually:

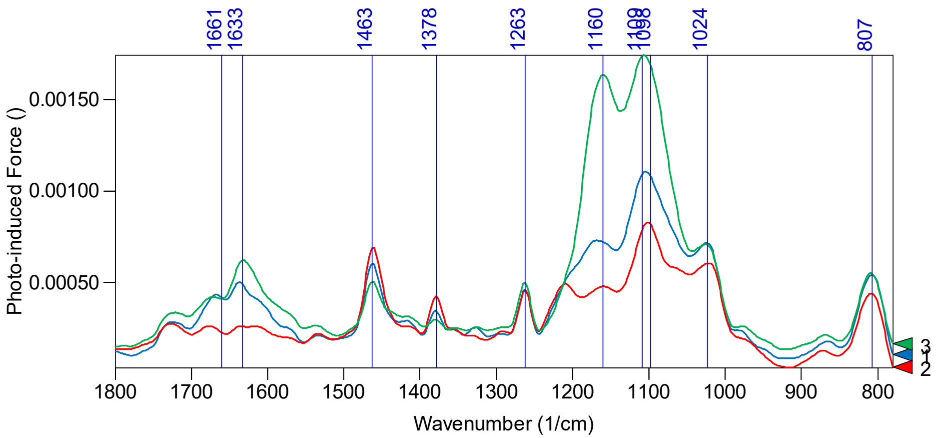




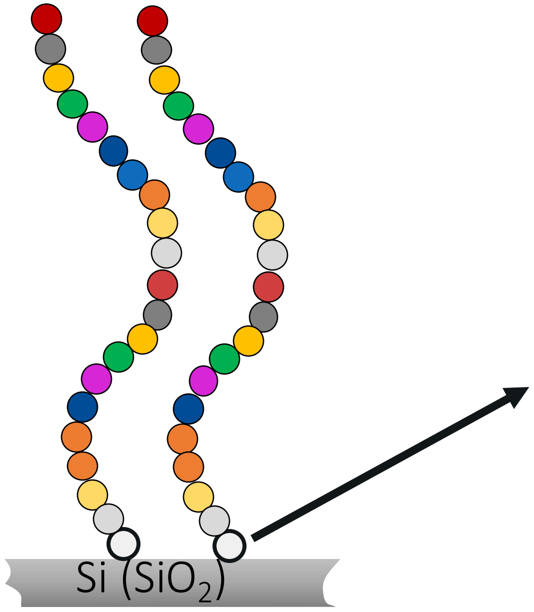
FTIR (powder)

Zoomed in:

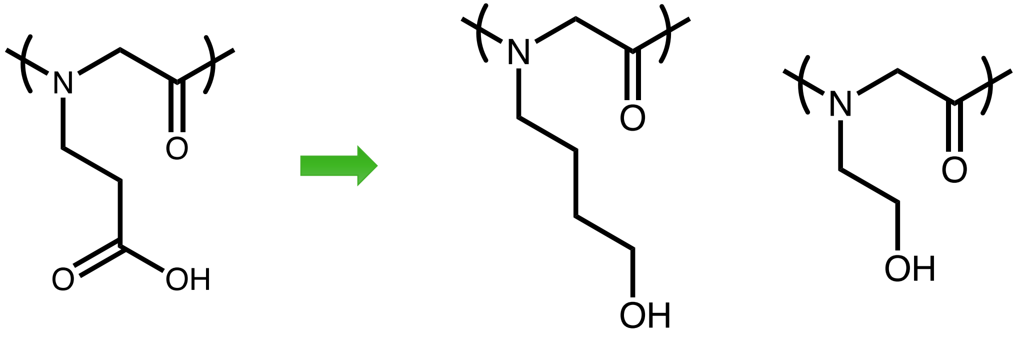




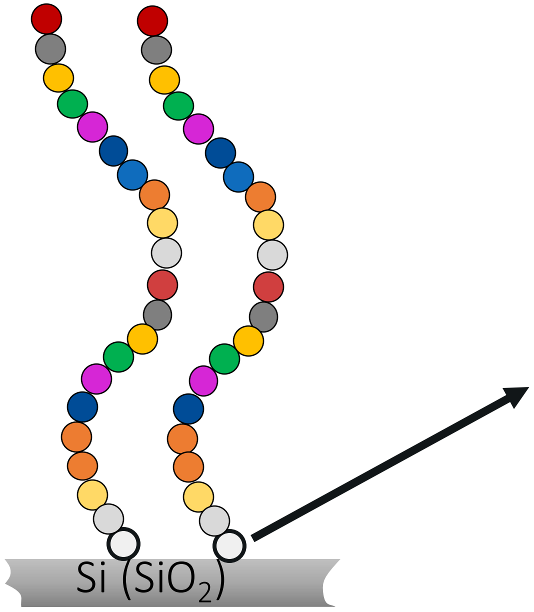
Polypeptoid Monolayer – Water Contact Angle and Ellipsometry



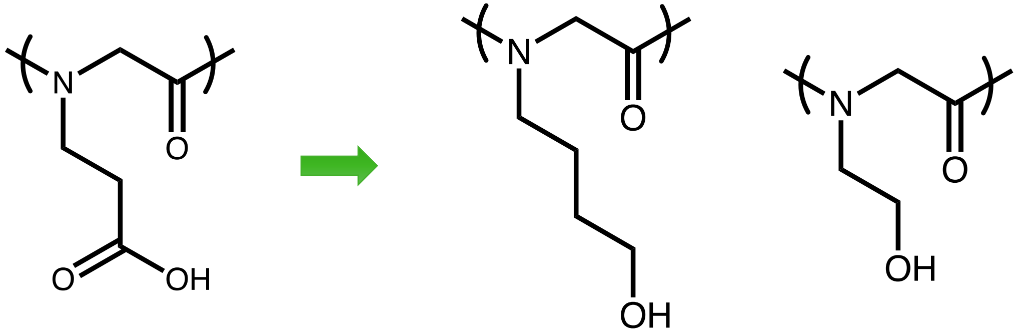
Switching from –COOH to –OH for melt grafting



Polypeptoid Monolayer – Water Contact Angle and Ellipsometry

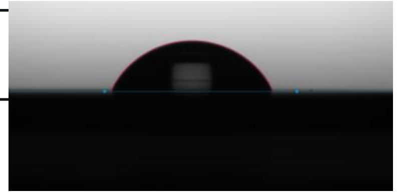


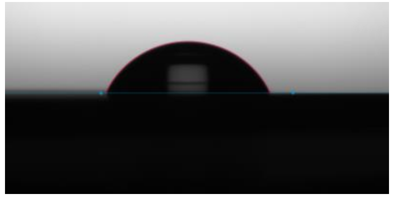
Switching from –COOH to –OH for melt grafting



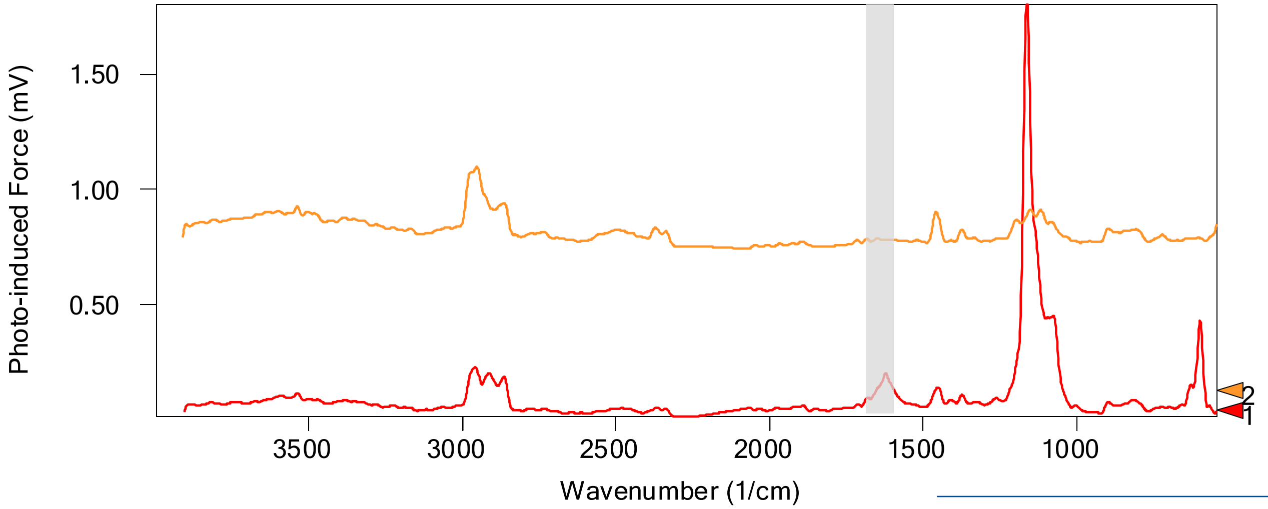
Water contact angle and ellipsometry of “monolayer brushes”:

Polymer	Water contact angle	Thickness
Polypeptoid–COOH, 2971.6 g/mol	55.3 ± 0.9°	1.15 nm
Polypeptoid–OH, 2943.5 g/mol	58.5 ± 1.8°	1.16 nm

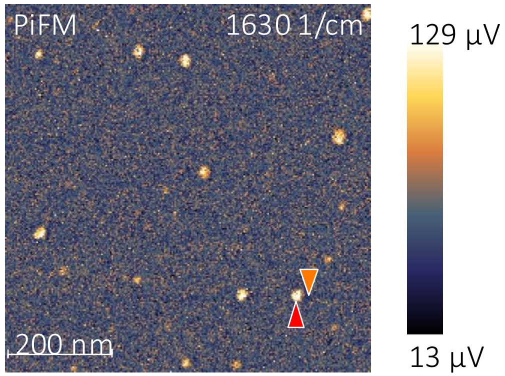




Polypeptoid Monolayer – PiFM

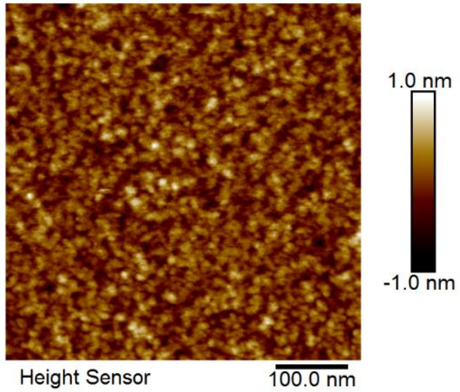


Polypeptoid–COOH

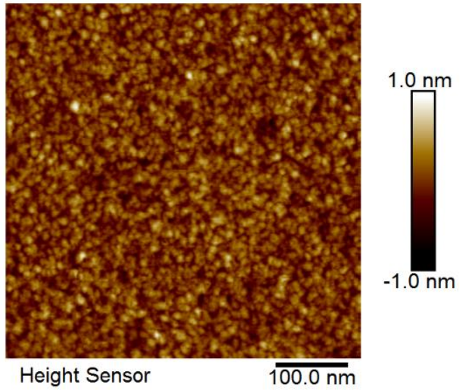


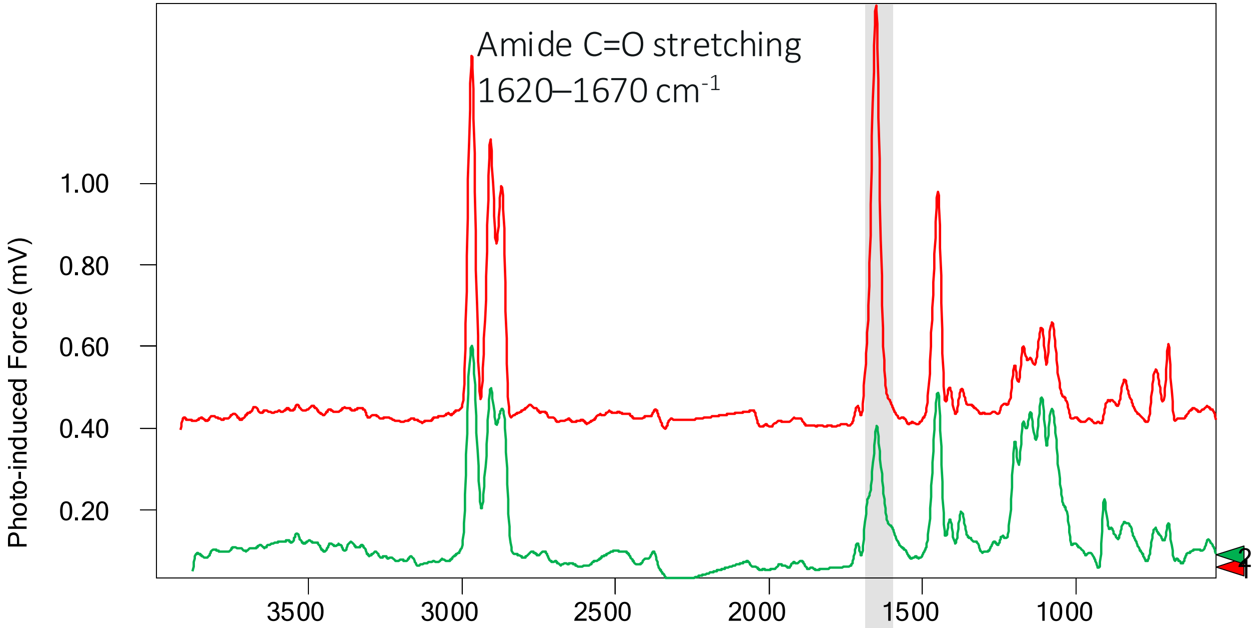
Polypeptoid Monolayer – PiFM

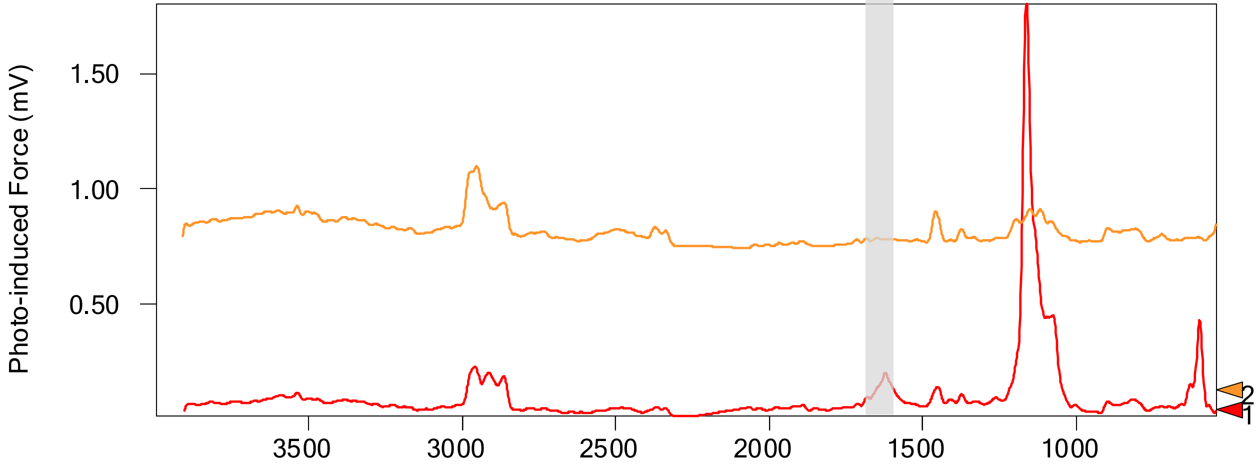
Si substrate with polypeptoid–OH brush monolayer



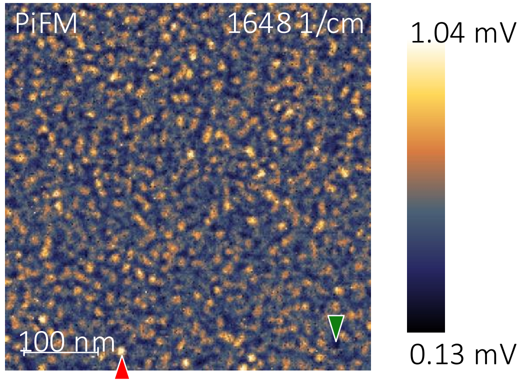
Bare Si substrate



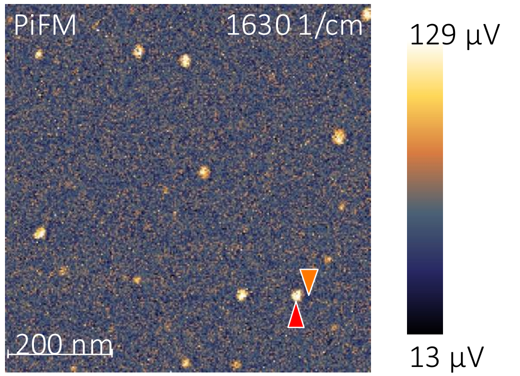




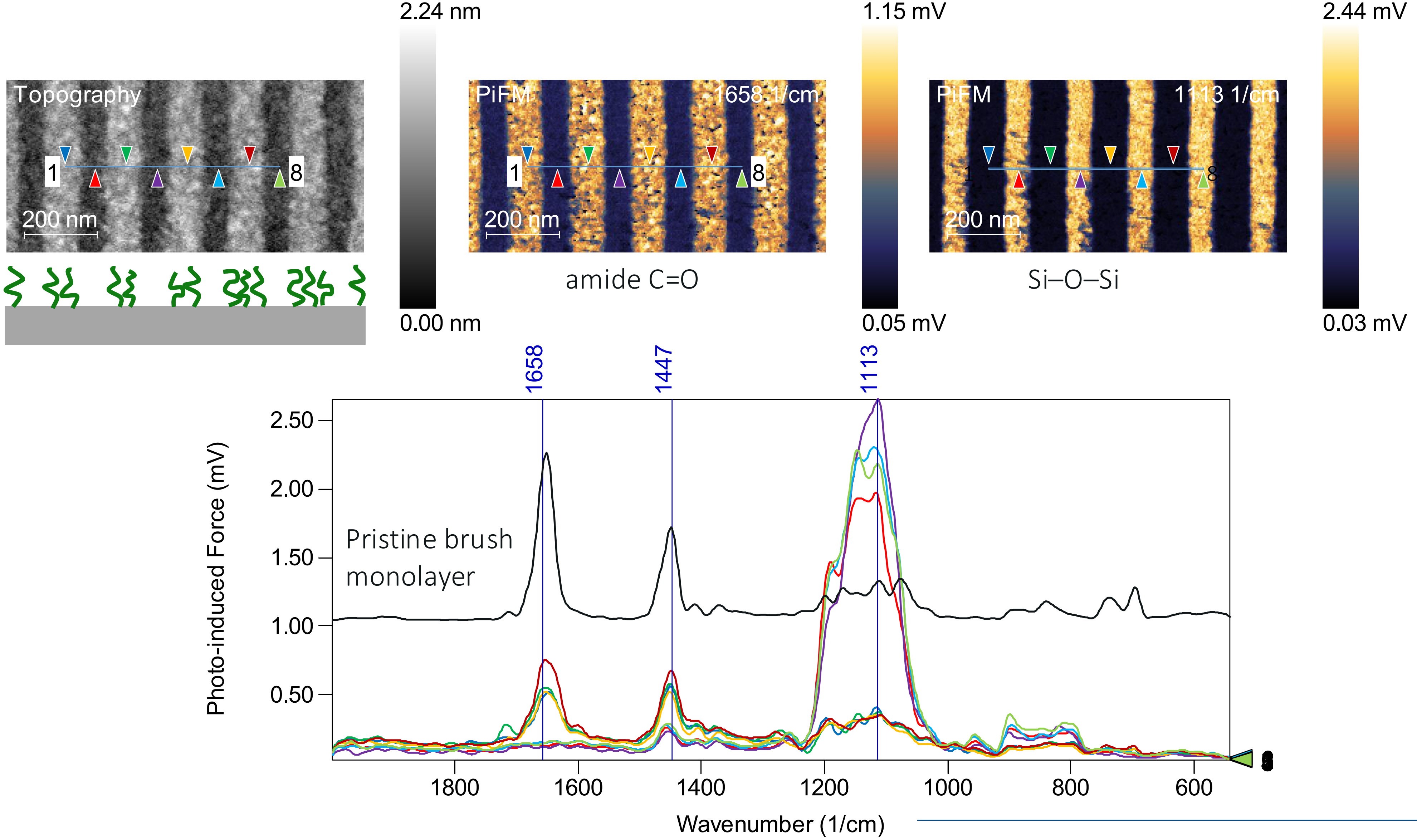
Polypeptoid–OH



Polypeptoid–COOH



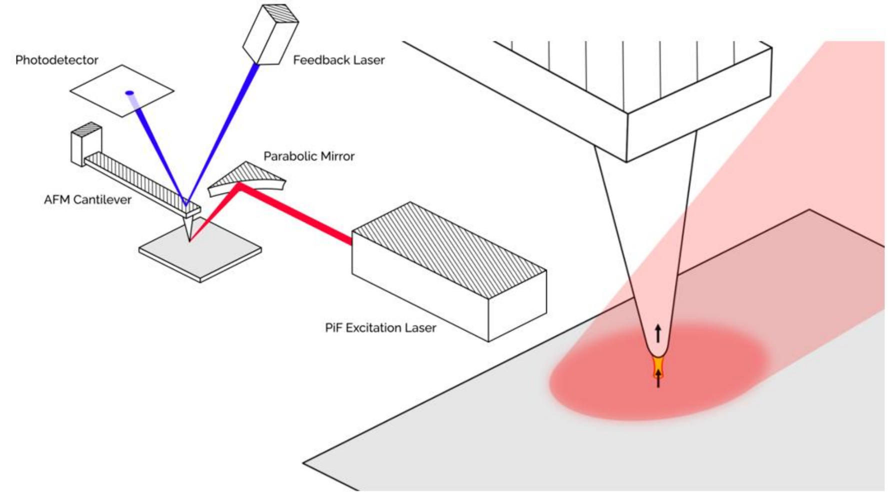
Polypeptoid Pattern – PiFM

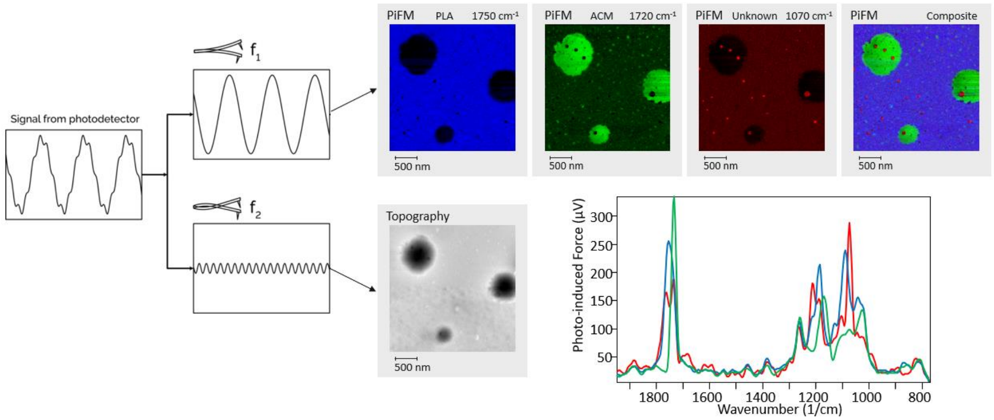


Applications Lab

Summary

Summary





- IR PiFM is introduced.
- AFM-based technique – If you can do AFM on it, you can do PiFM!
- Provides exceptional spatial resolution (< 5 nm), excellent surface sensitivity (monolayer)
- Chemically map and identify organic and inorganic compounds
- KLARF compatible
- Non-destructive, PiFM can (and should) be carried out prior to other metrology

Acknowledgements

- Organic contaminant – McGill University (Brian Nguyen)
- Polymer-polymer blend solar cell – Stanford (Kevin L. Gu)
- Copper oxide – UCSD (Andrew Kummel)
- Wood cell wall – Aalto University (Kavindra Kesari, Tapani Vuorinen
- Ascorbic acid – CERMAV (Yu Ogawa)
- EUV resist – LBNL (Qi Zhang, Ricardo Ruiz)
- Polypeptoid monolayer – LBNL (Beihang Yu, Ricardo Ruiz)

Concluding Remarks

Thank you for joining us today!

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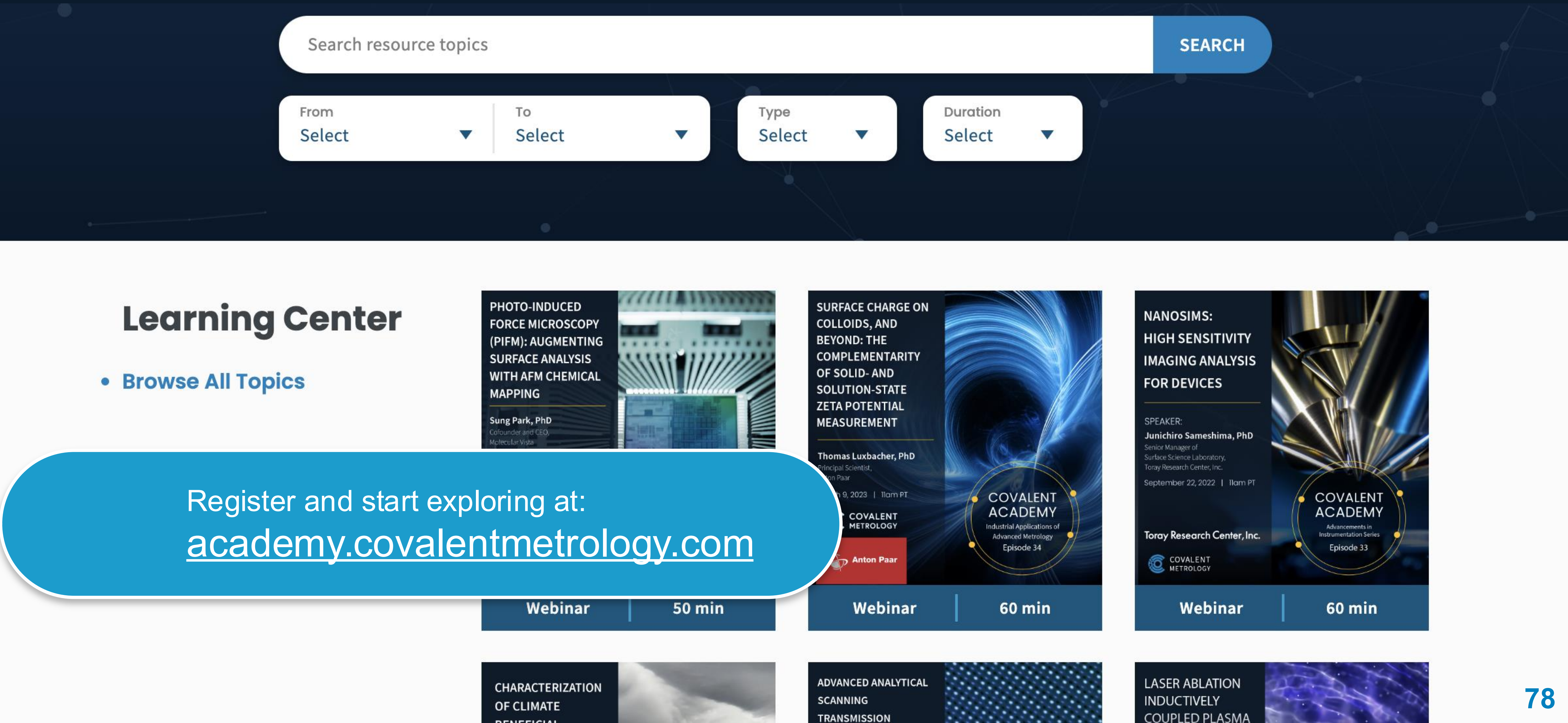

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Q & A Session

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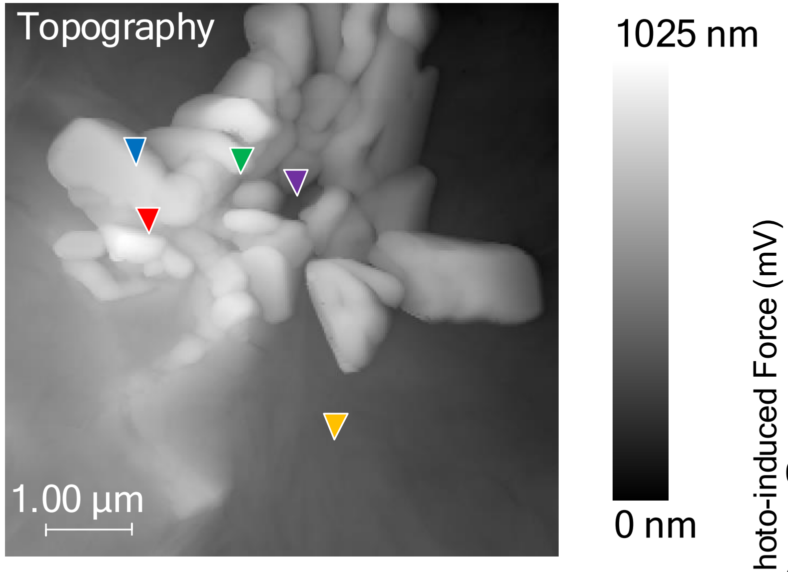
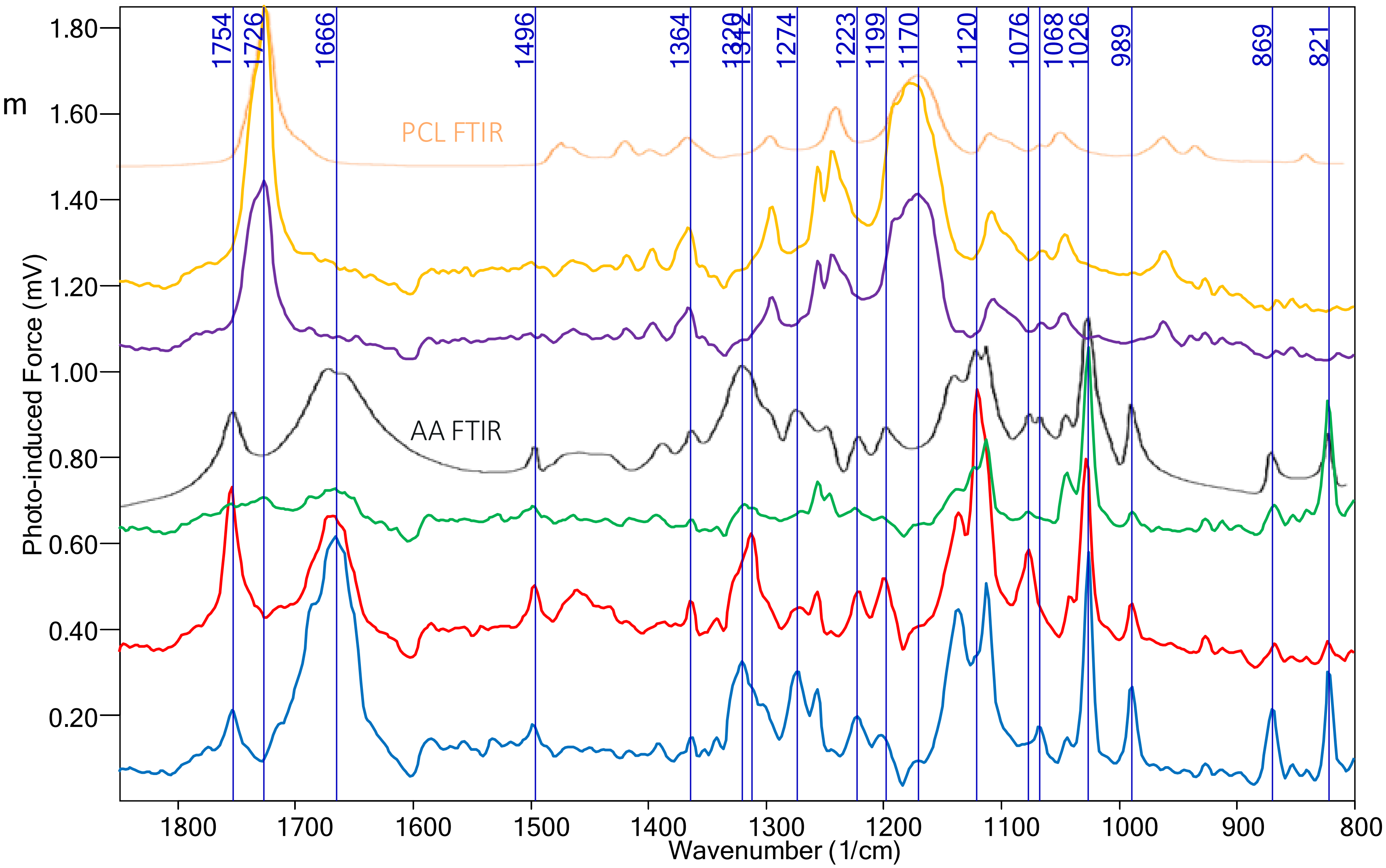
Thank you.

Extra Slides

Molecular Orientation – Poly(ε-Caprolactone)/Ascorbic Acid (PCL/5AA)

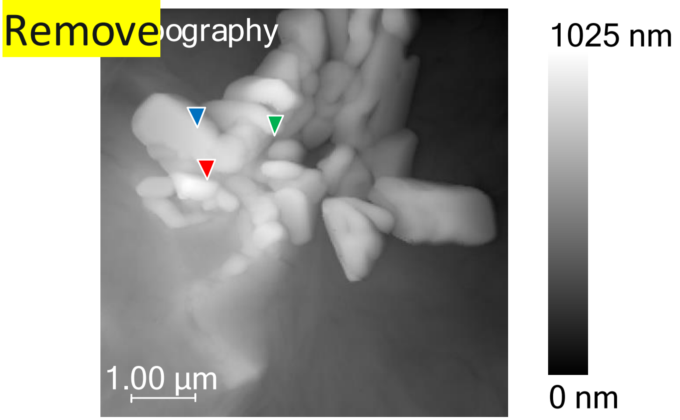
Remove



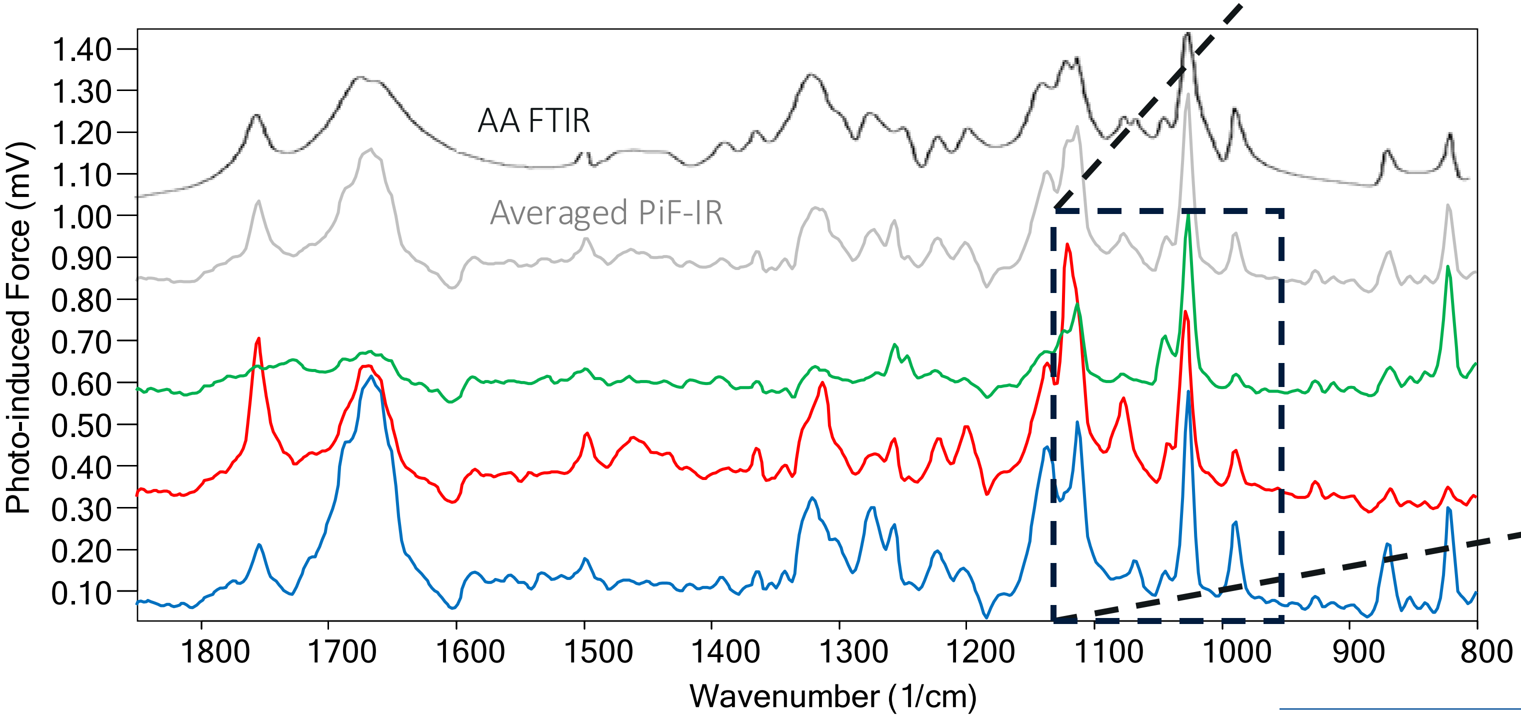


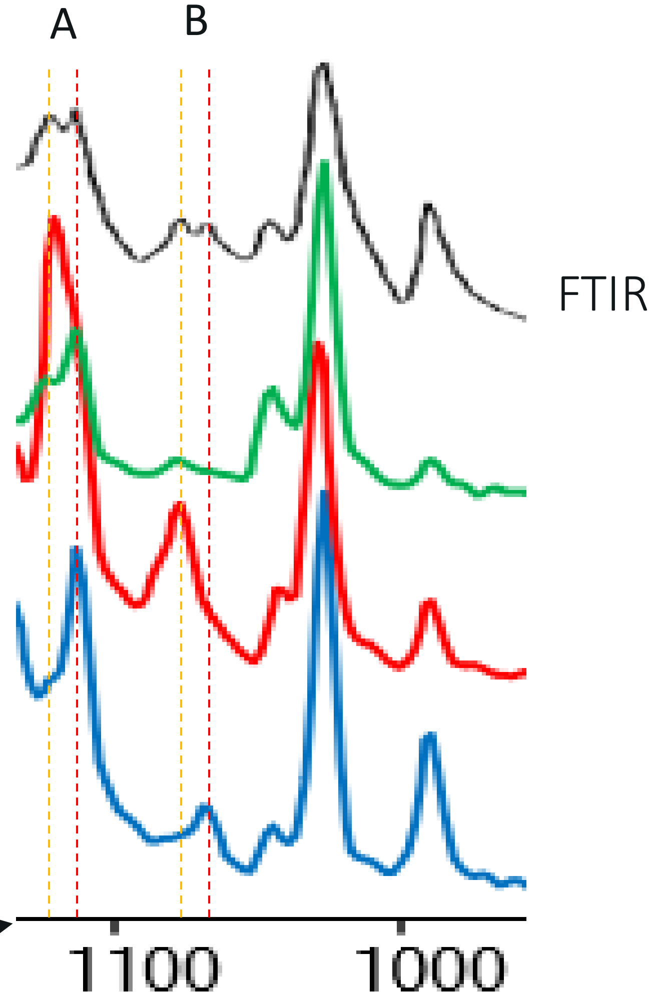
The two spectra (purple and gold) on homogeneous PCL match the PCL FTIR well. The three spectra acquired on the AA crystals show different peak strengths compared to the AA FTIR.

Molecular Orientation – Poly(ε-Caprolactone)/Ascorbic Acid (PCL/5AA)



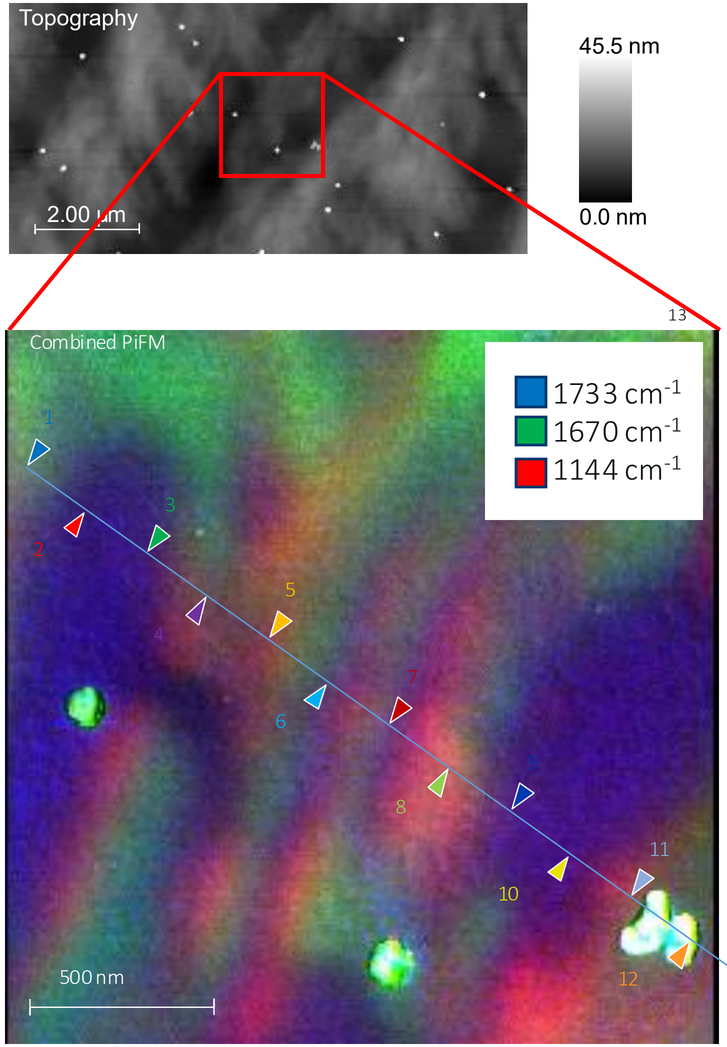
PiF-IR is most sensitive to modes that are normal to the sample plane. As such, PiF-IR spectra on different crystal orientations highlight different peaks compared to FTIR, which is an ensemble average of billions of PiF-IR spectra. Note that for the FTIR doublets A and B, the red and blue spectra each showcase different singlets.



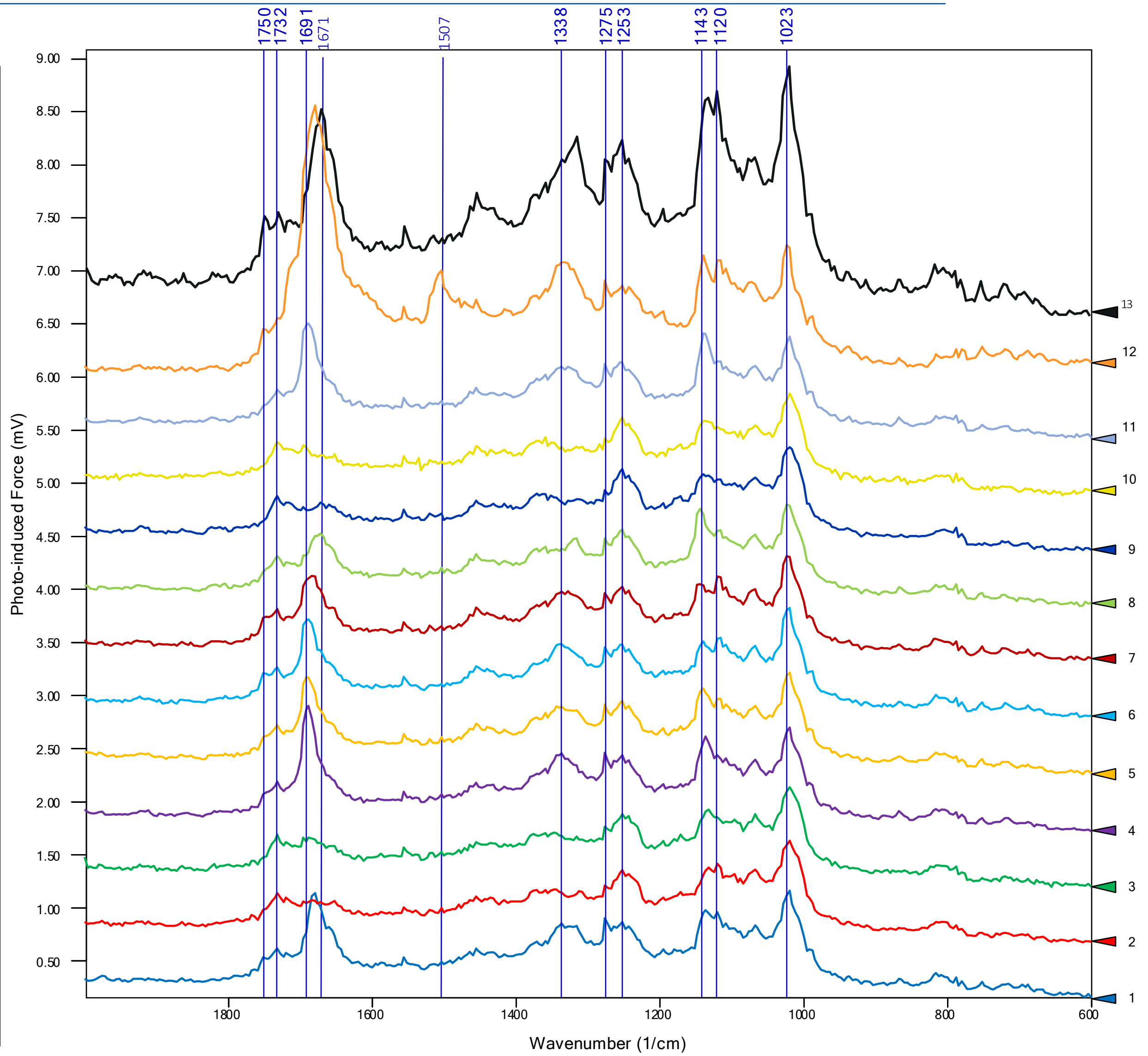


PiF-IR: 2 µm²

Simplify, or remove



Line spectra with 200 nm pitch were taken across the features. The No. 2, 3, 9, 10 spectra on the purple highlighted regions show a little bit stronger peak around 1732 cm^{-1} than the green highlighted regions. The green highlighted regions (No. 13 and 1) show stronger peak around 1671 cm^{-1}. The red highlighted regions (No. 4, 5, 8, 11) show the similar peaks to the green highlighted regions across the range, while the red regions show obvious increasing of IR signal around 1143 cm^{-1}. The No. 12 spectrum on the defect shows much stronger peaks across the range, especially around 1679 and 1507 cm^{-1}.



Nacre S/TEM, TEM-EELS, APT