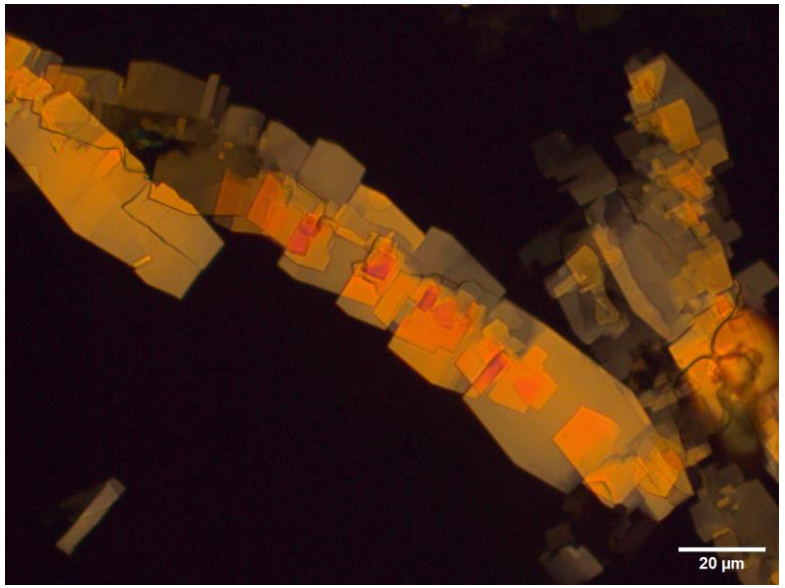
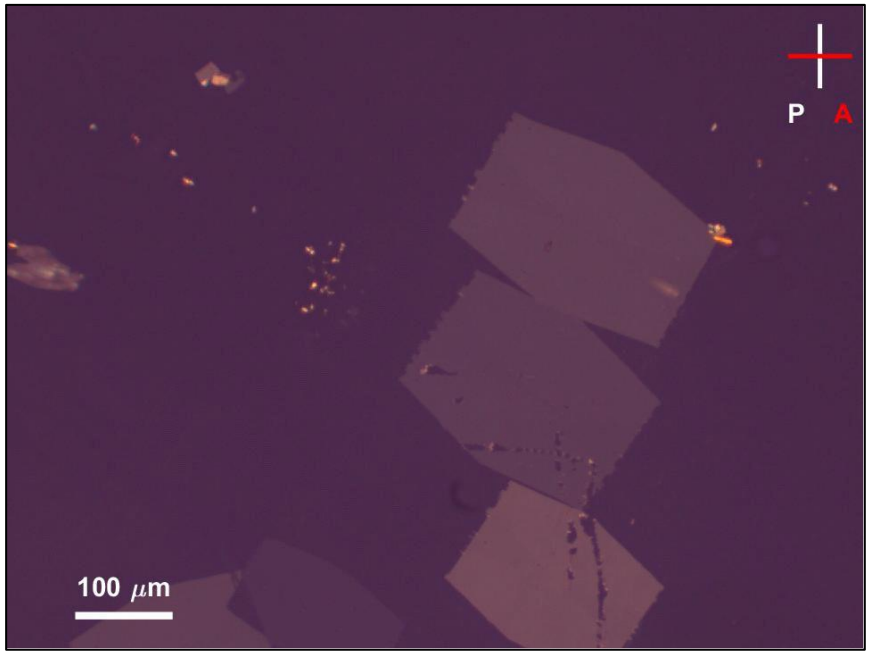
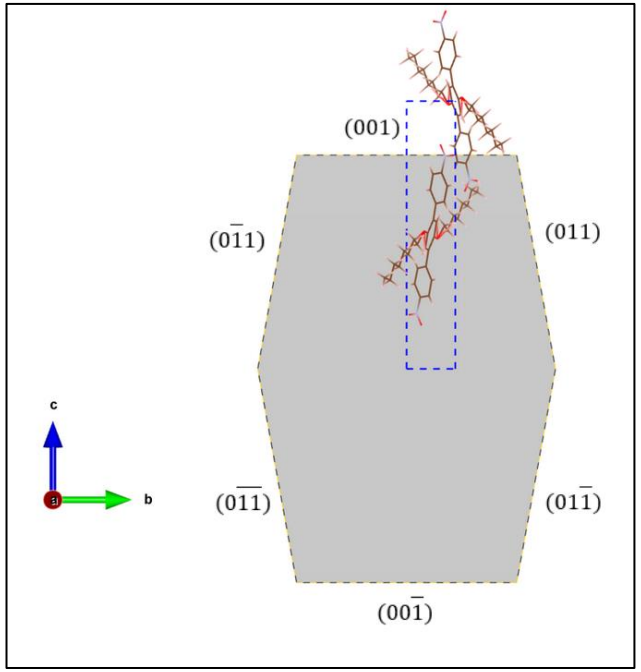
Growth and Characterization of Crystalline Organic Thin Films for Optoelectronic Applications







Samuel Fulbright

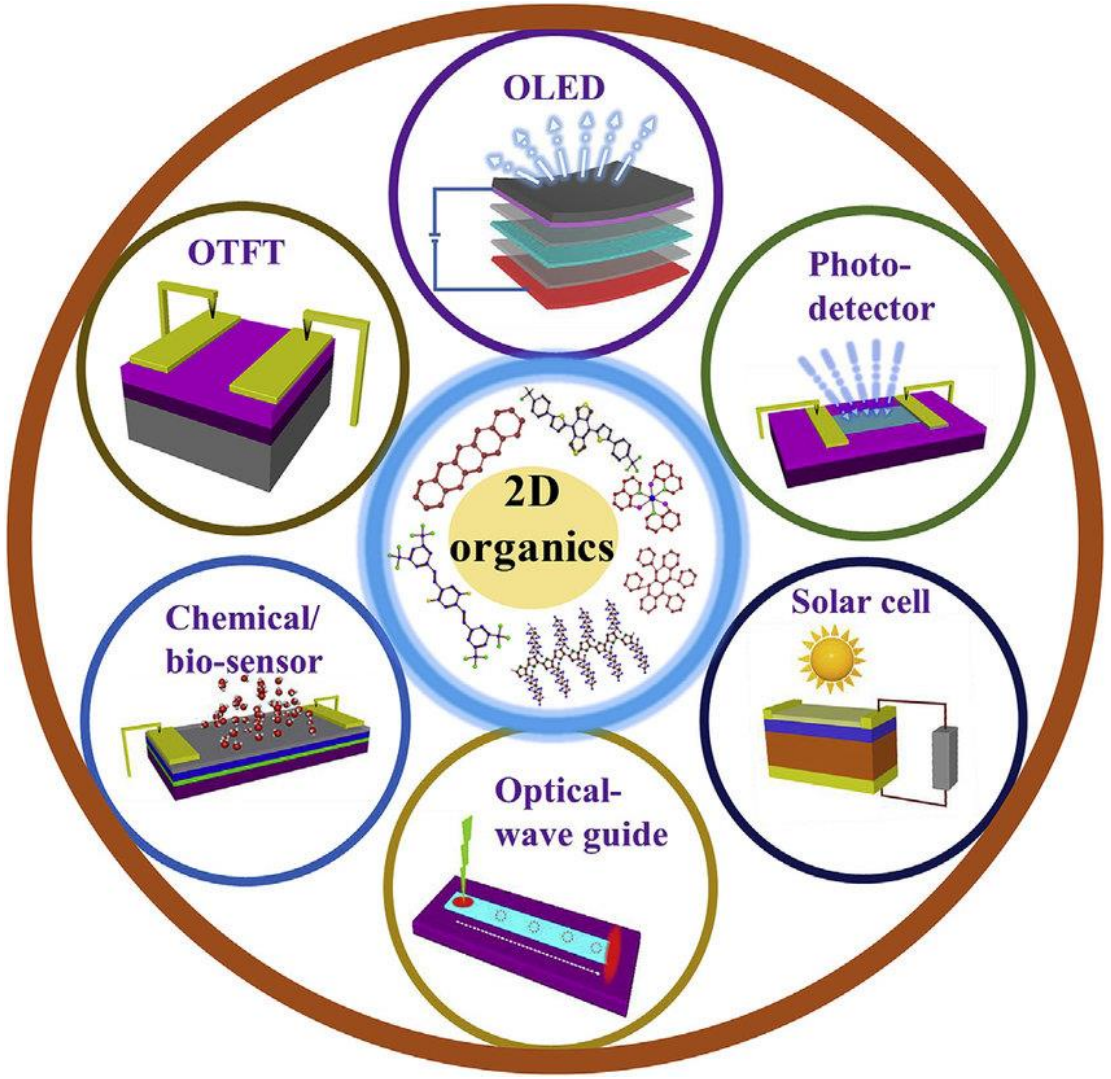
Mentors: Dr. Lloyd Bumm, Dr. Madalina Furis

Importance of Studying Organic Semiconductors

Applications in Electronics

Two Key Purposes

1. Easier processing methods
   - Deposition techniques are readily-available (Pen-writing, drop-cast, etc.)
2. Functionalization by chemical manipulation
   - Properties can be engineered into the molecule



https://www.researchgate.net/figure/Wide-scopes-of-2D-organic-semiconductors-for-emerging-nanotechnological-device_fig2_336480547

Jurchescu, O. D. (2006). *Molecular organic semiconductors for electronic devices*.

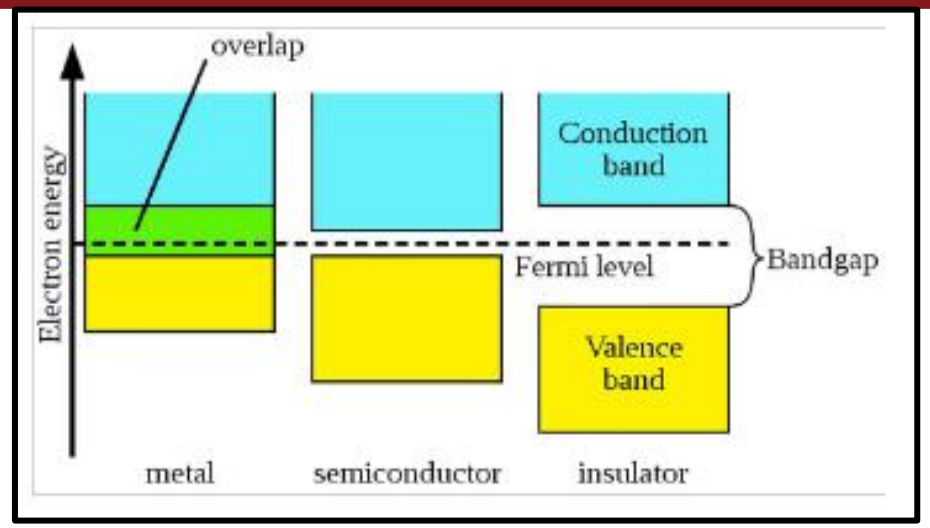
Organic Materials as a Substitute for Silicon

Advantages

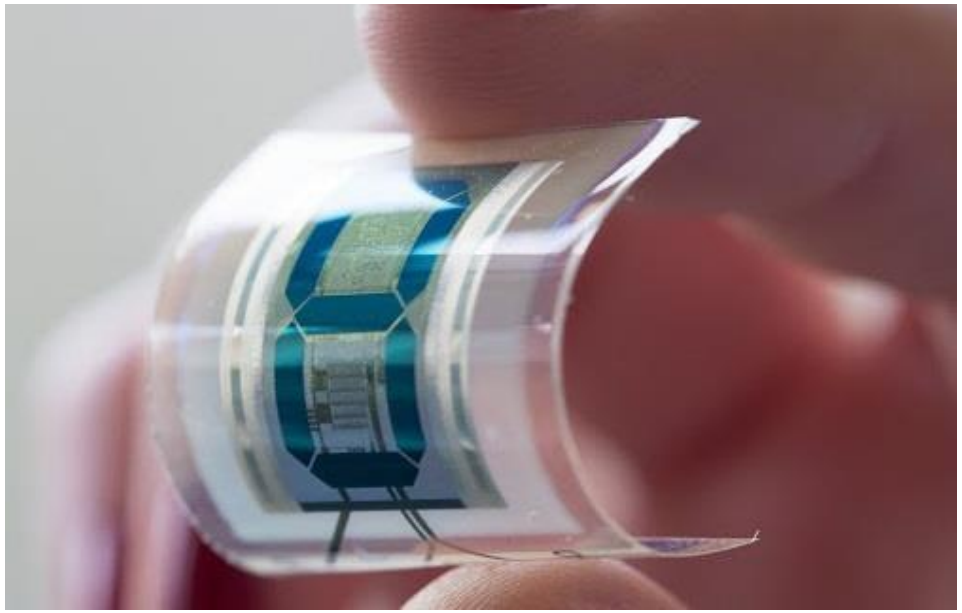
- Solution Processable
- Low Cost
- Biodegradable
- Flexible
- Lightweight
- Tunable

Disadvantages

- Lower Electron Mobility
- Disorder



Matthew Schwartz Statistical Mechanics, Spring 2019 Lecture 14: Semiconductors



https://www.eletimes.com/organic-semiconductors-for-flexible-electronic-devices

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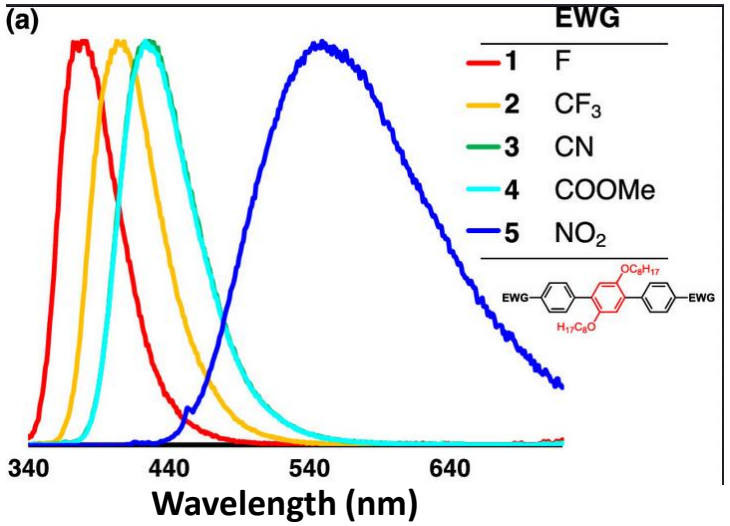
Molecular Materials

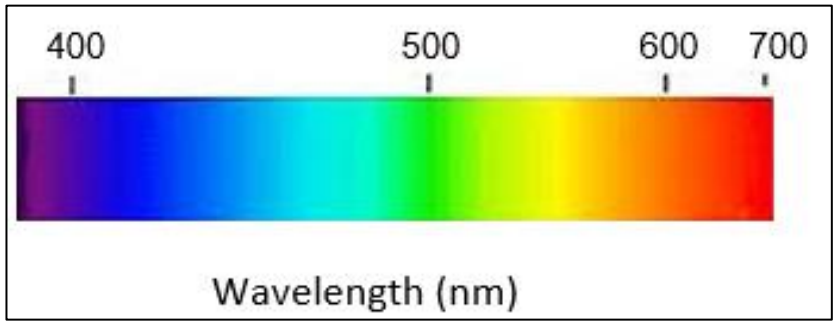
Alkoxy-Substituted Quadrupolar Fluorescent Dyes

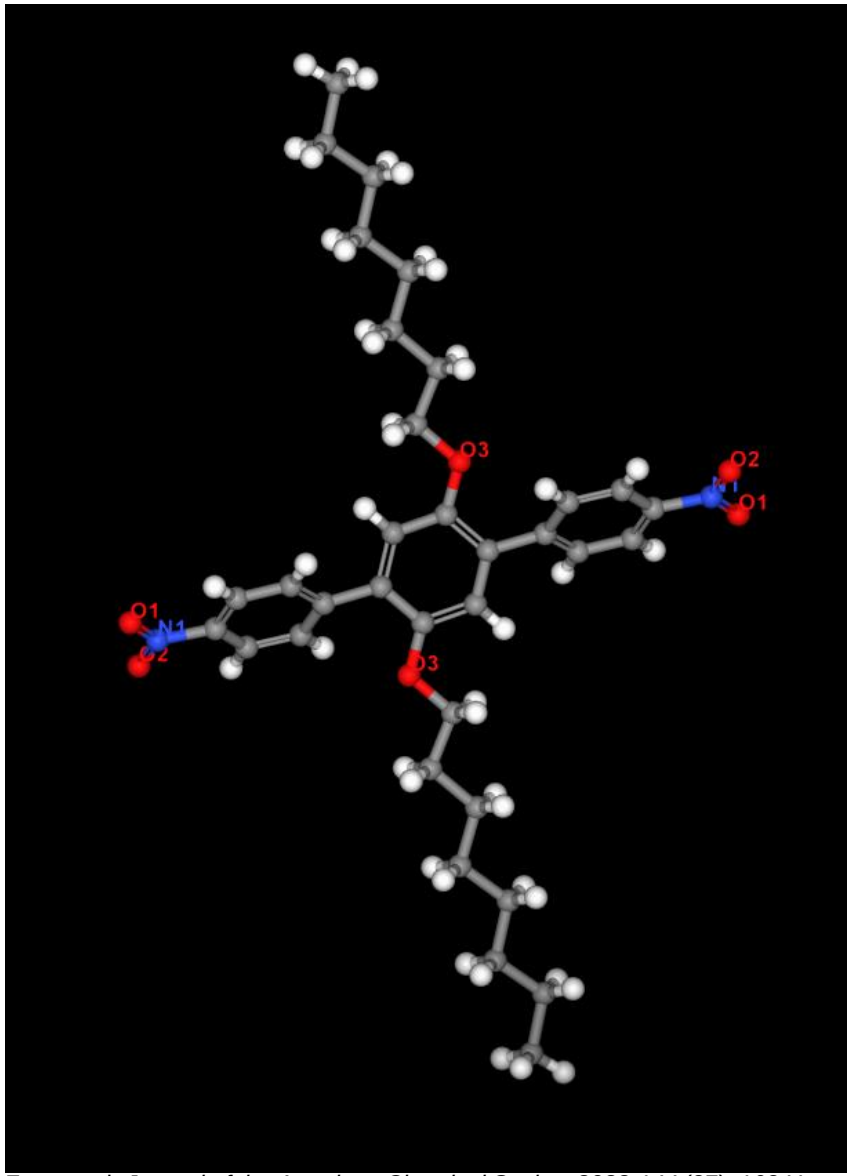
- Specific Absorption and Emission Spectra
- Modular structure

Alkoxy-Nitro Para-Terphenylene (ANPT)

PL Emission



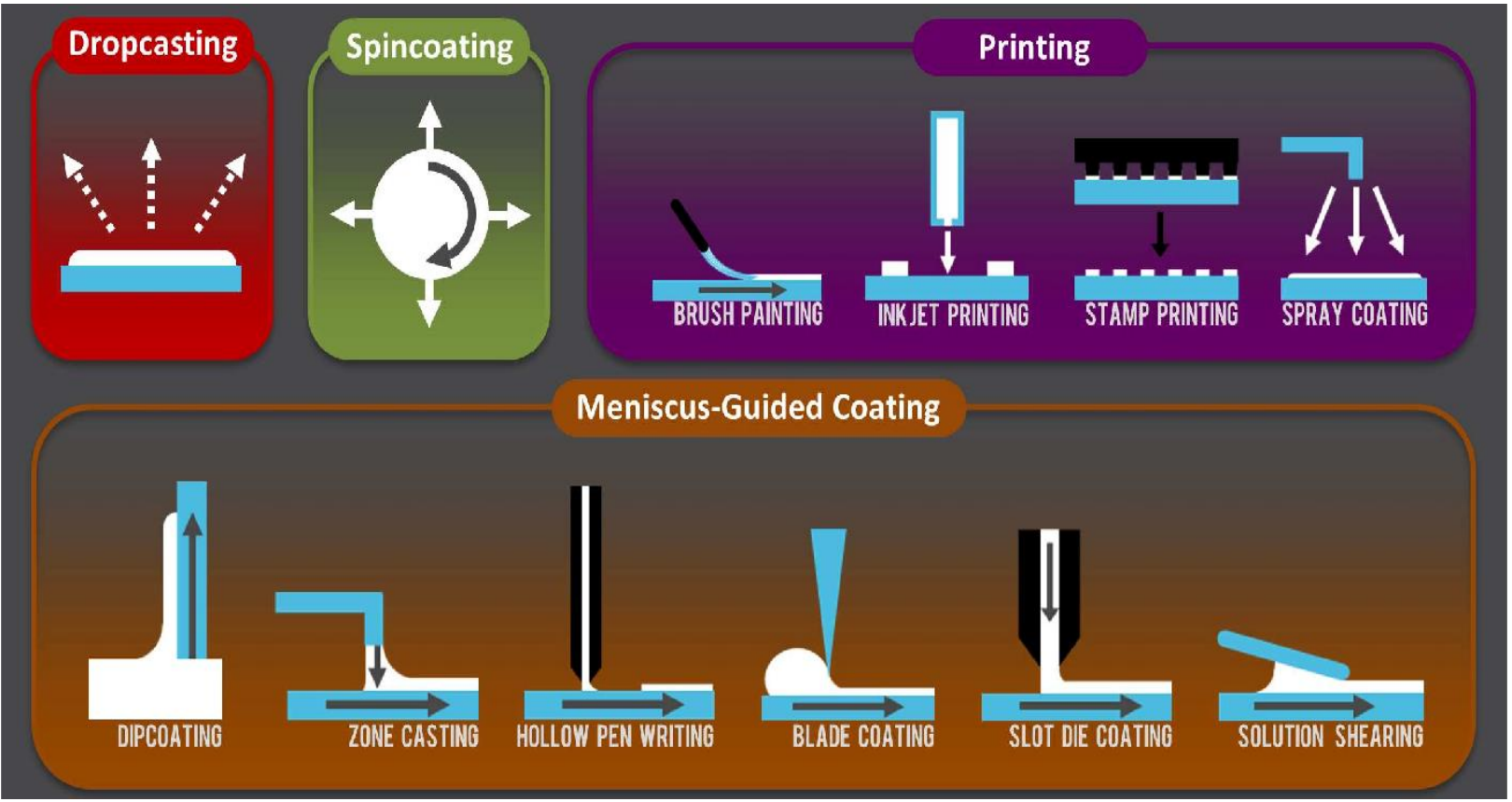




Feng et al. *Journal of the American Chemical Society* **2022** *144* (37), 16841-16854
DOI: 10.1021/jacs.2c04906

Feng et al. *Journal of the American Chemical Society* **2022** *144* (37), 16841-16854
DOI: 10.1021/jacs.2c04906

Film Printing: Pen-Writing and Drop-Cast



Diao, Y., Shaw, L., Bao, Z., & Mannsfeld, S.C. (2014). Morphology control strategies for solution-processed organic semiconductor thin films. Energy and Environmental Science, 7, 2145-2159.

1. Preparations
    1. Cleaning substrates and equipment
    2. Prepare solution
2. Deposition
    1. Pen-Writing
        1. Capillary is filled
        2. Lowered onto substrate until meniscus touches
        3. Substrate is moved via flat motorized stage
    2. Drop-Cast
        1. A drop is placed onto a substrate from a pipette

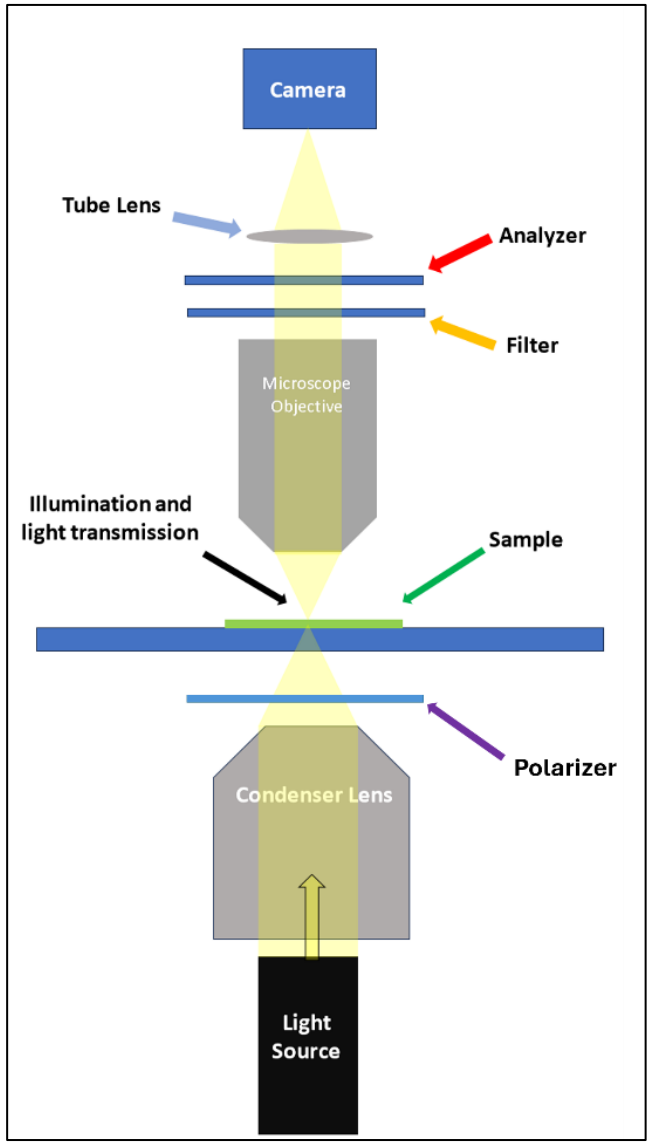
Polarized Light Microscopy

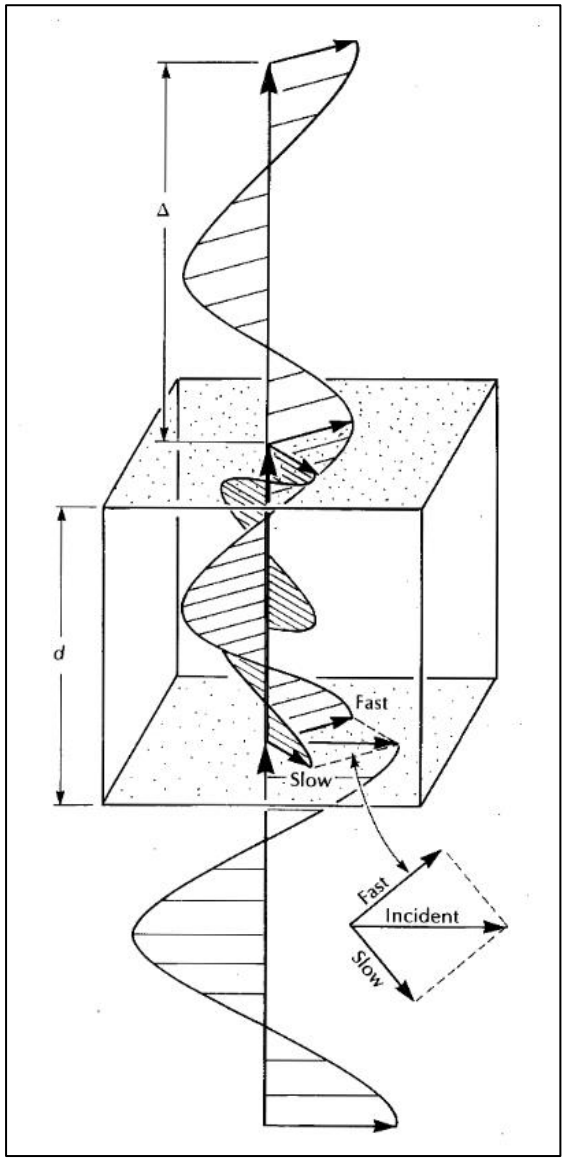
Birefringence:

- Light passing through an anisotropic material is split into two rays that oscillate at right angles to each other
  - Wave interference (angle of rotation)
  - Extinction angles along optic axes

Dichroism:

- (Analyzer removed) The fast and slow rays can be directly observed when they are parallel with the polarizer
- Fast/slow rays often appear as different colors and are at right angles to each other





Nesse, William D. (2004). *Introduction to optical mineralogy*. New York: Oxford University Press.
Perkins, Dexter. (2022). *Mineralogy*. (2nd edition). University of North Dakota.

Nesse, William D. (2004). Introduction to optical mineralogy. New York: Oxford University Press.

Atomic Force Microscopy

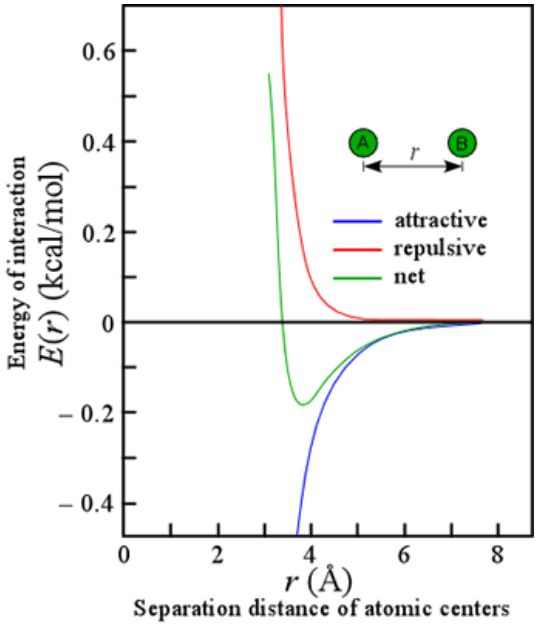
Basic Principle:

- Cantilever is oscillated near resonance frequency
- Tip-surface force interactions alter cantilever oscillation
- Laser reflecting off the surface of the cantilever detects alterations, corrects cantilever
- Corrections of cantilever compose the image

Force Interactions:

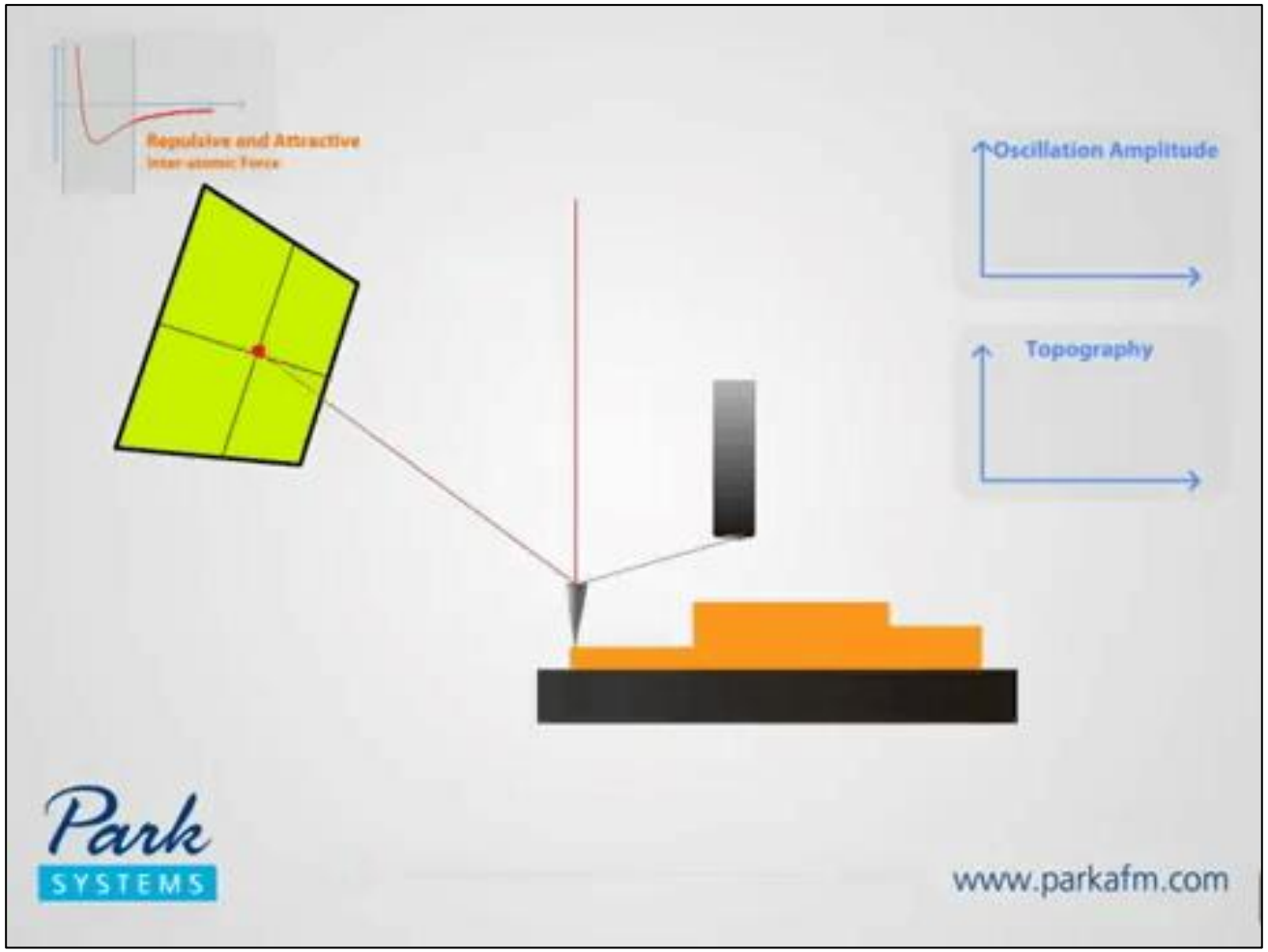
➢Short-range: Van der Waals (!!!)

➢Long-range: Electrostatic (!)



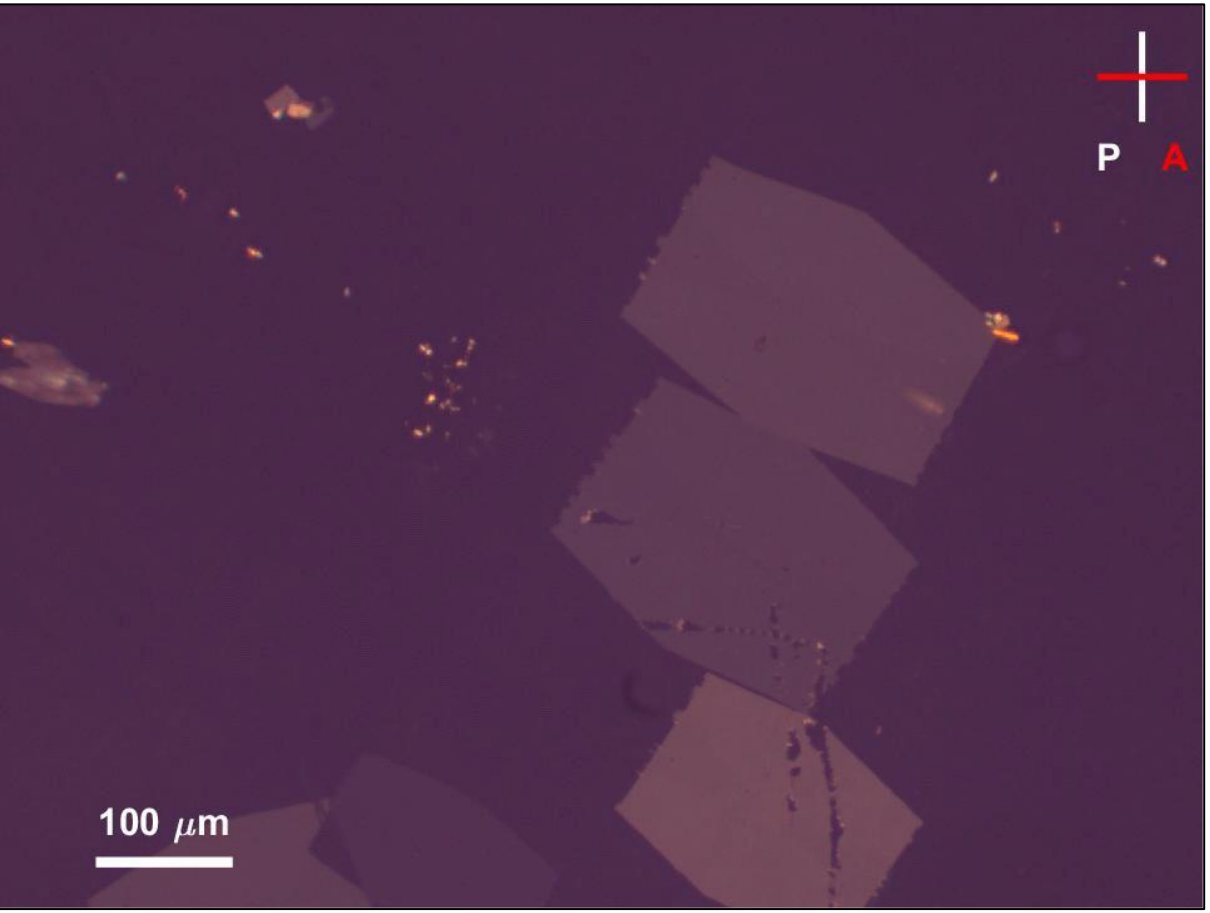
http://guweb2.gonzaga.edu/faculty/cronk/CHEM245pub/intermolecular_forces.html

1. Bonnell, D. A. (2000). *Scanning probe microscopy and spectroscopy: Theory, techniques, and applications*. New York : Wiley-VCH.
2. Oxford Instruments. (2024). *AFM principle - how does an atomic force microscope work?* https://afm.oxinst.com/outreach/how-does-an-afm-microscope-work

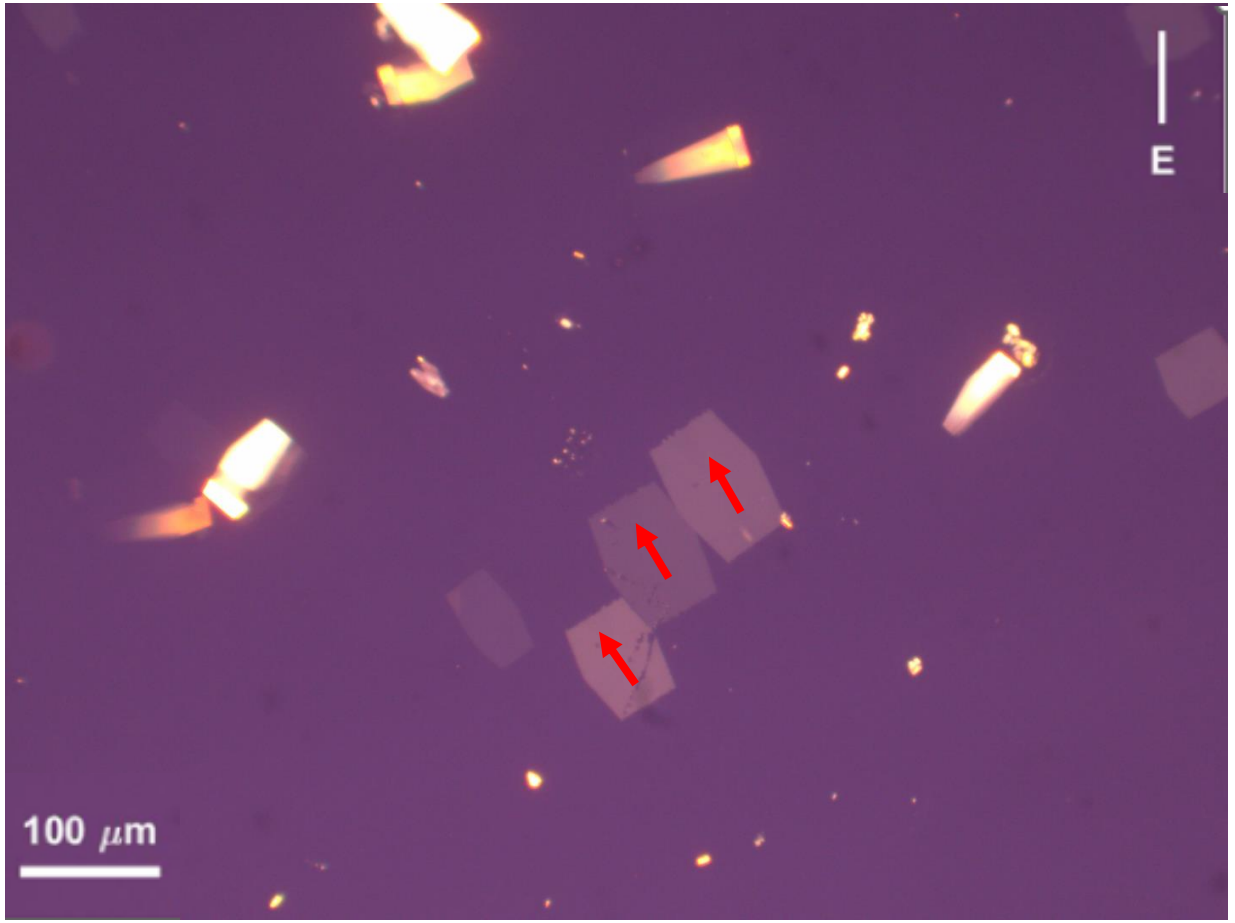


Crystal Structure and Molecular Orientation

Birefringence

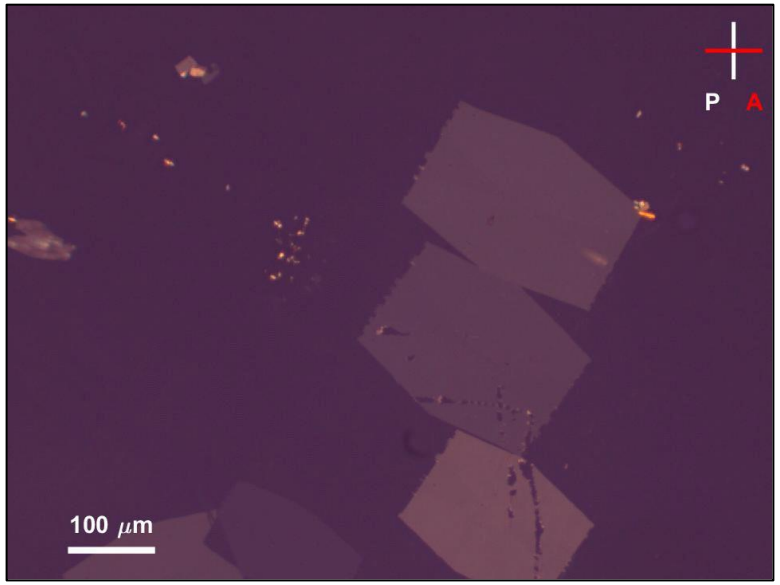


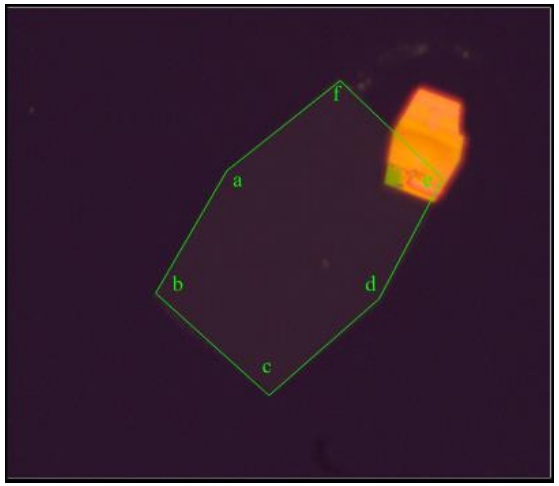
Dichroism



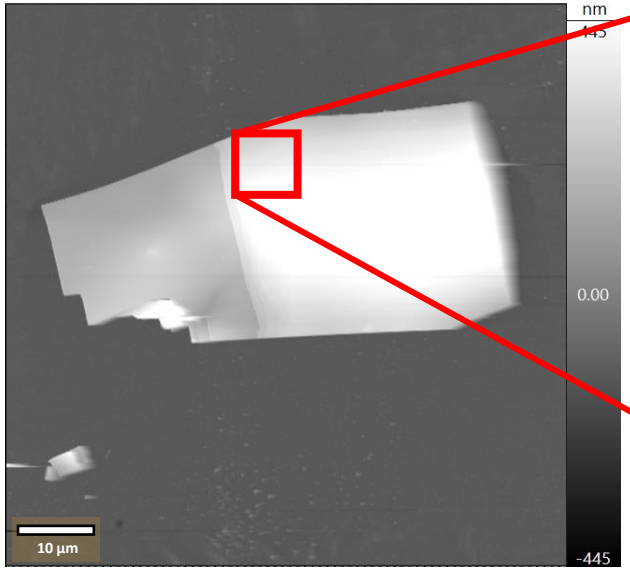
Crystal Structure and Molecular Orientation

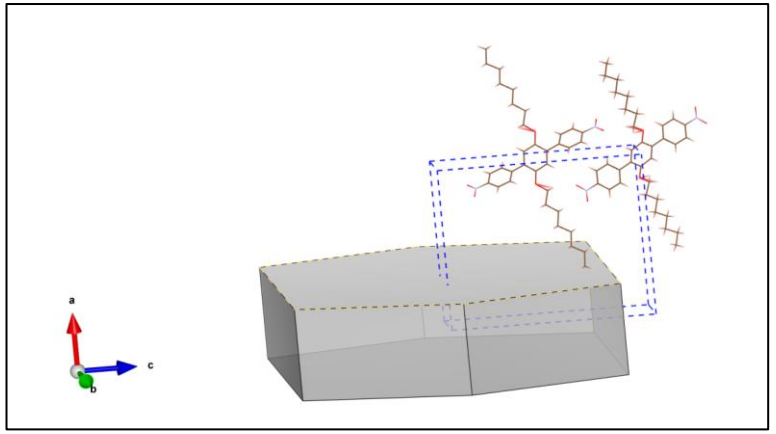
- Goal: Find the molecular orientation of ANPT in crystal structures
- Results: Success!

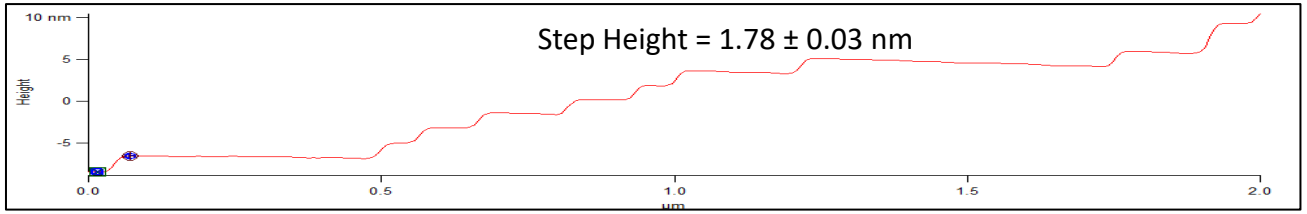


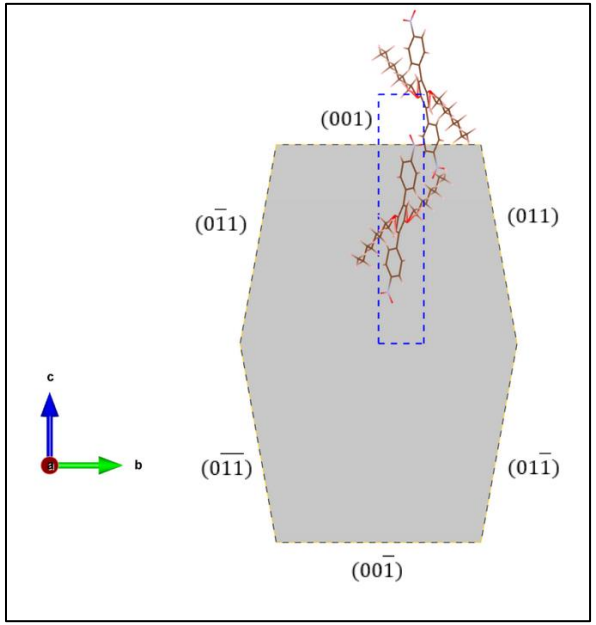


Angle	AVG Measurement (°)
a,d	160
b,c,e,f	100



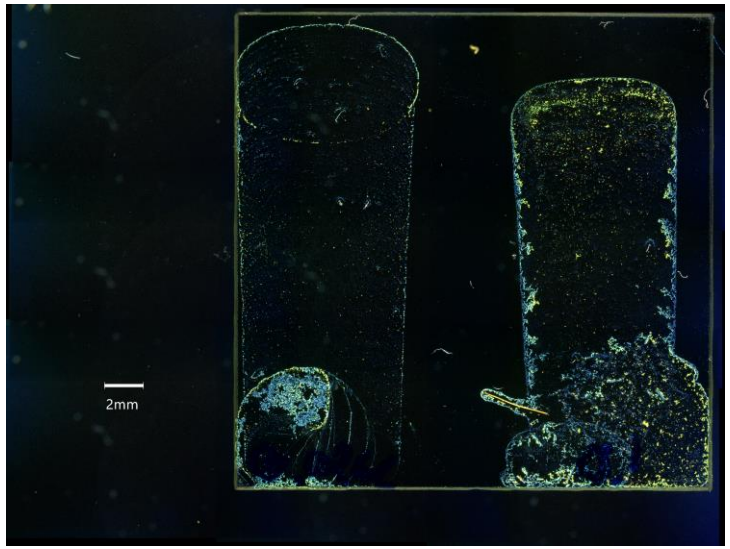




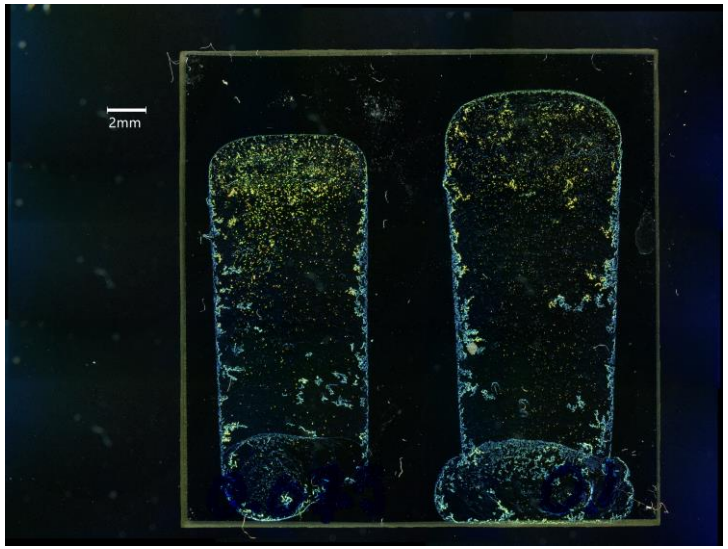


Pen-Writing: Concentration Dependence

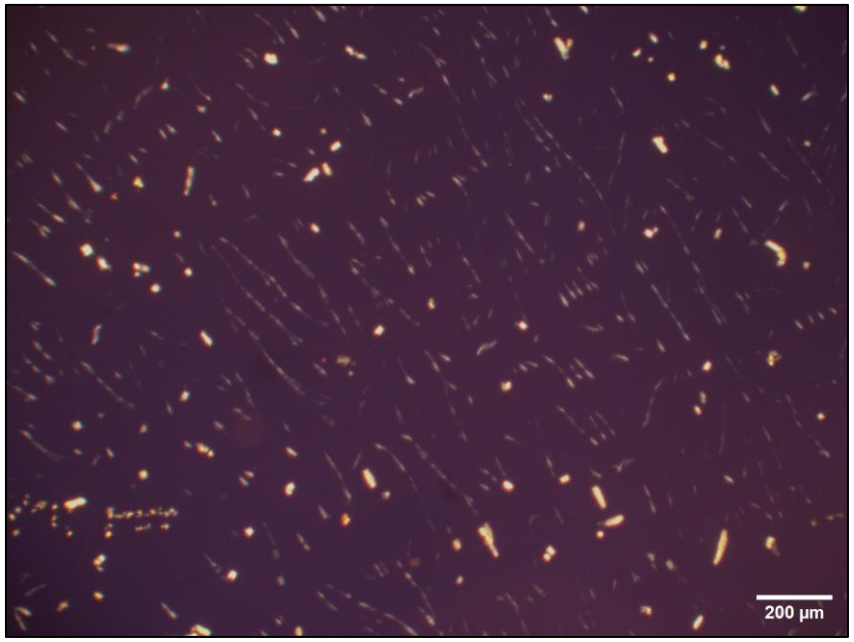
- Goal: Observe the effect concentration has on crystal growth
- Results: Effects observed; four crystal structures identified



0.0266% vs 0.1%

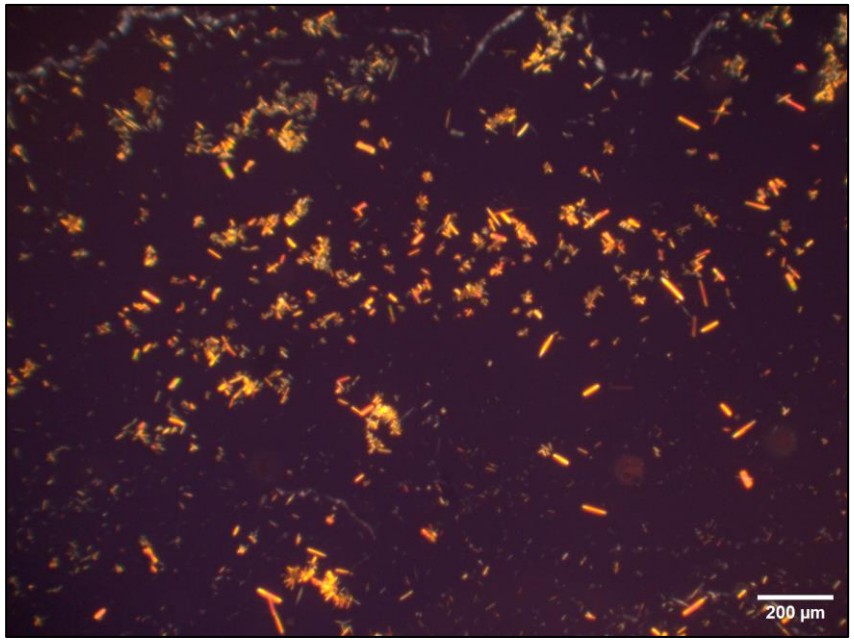


0.075% vs 0.1%



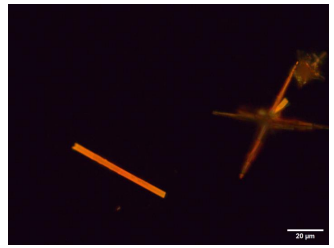
0.0266% Con

VS



0.1% Con.

(1)



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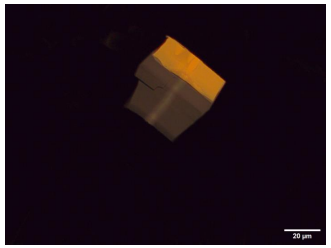

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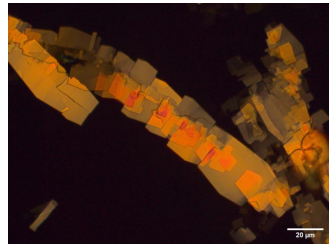

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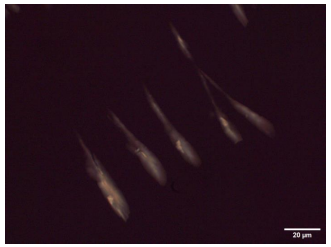
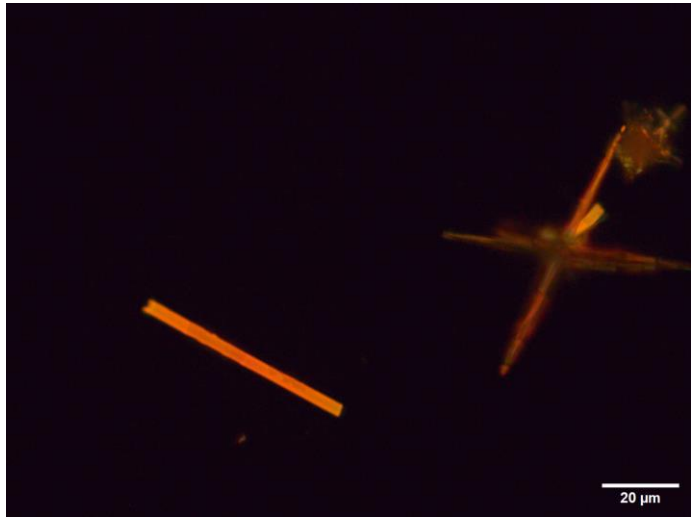
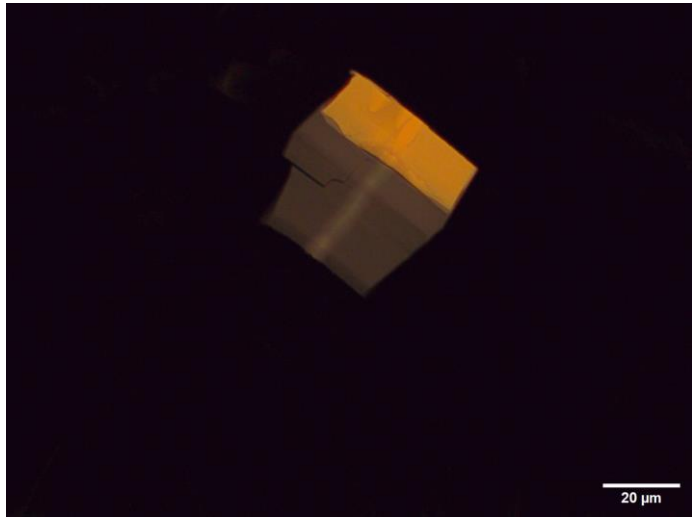


Crystal Structures Found in ANPT

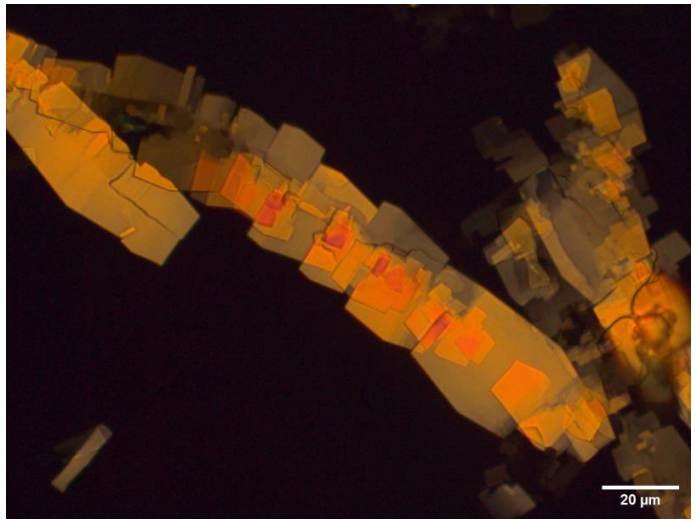
(1) Needles



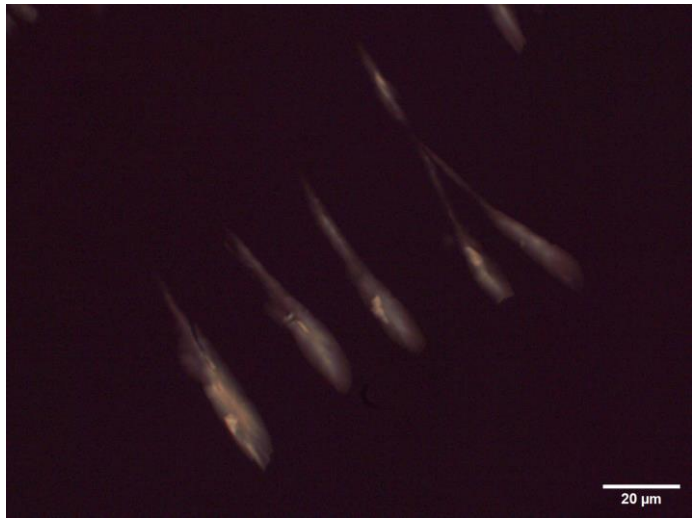
(2) Tabular Hexagons

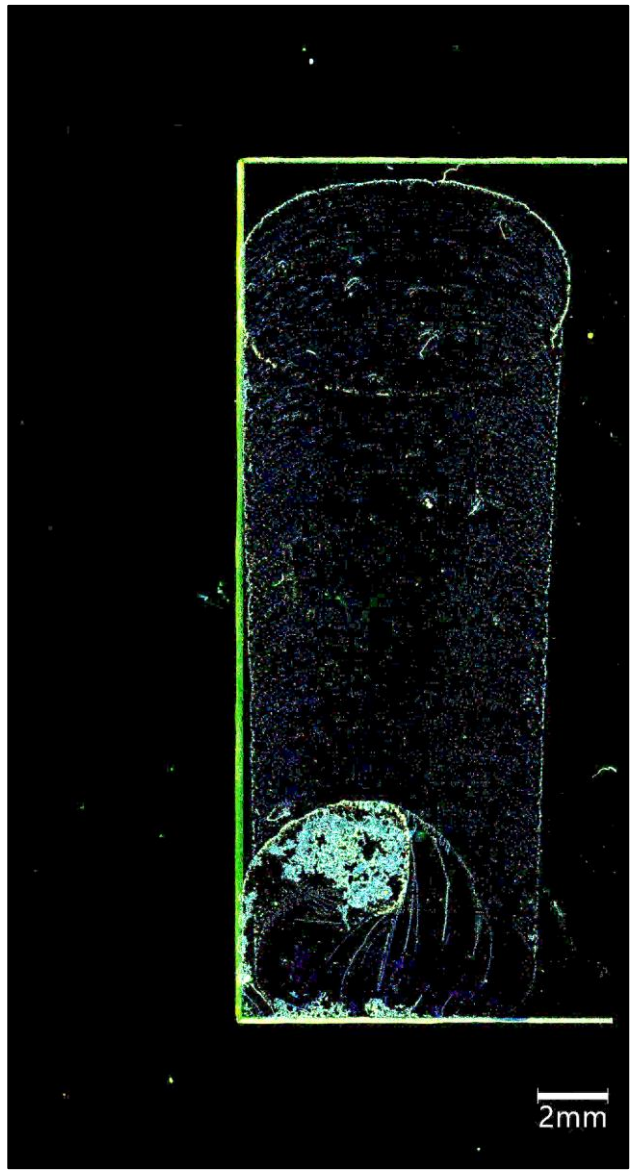


(3) Hexagonal Chains



(4) Feather-like

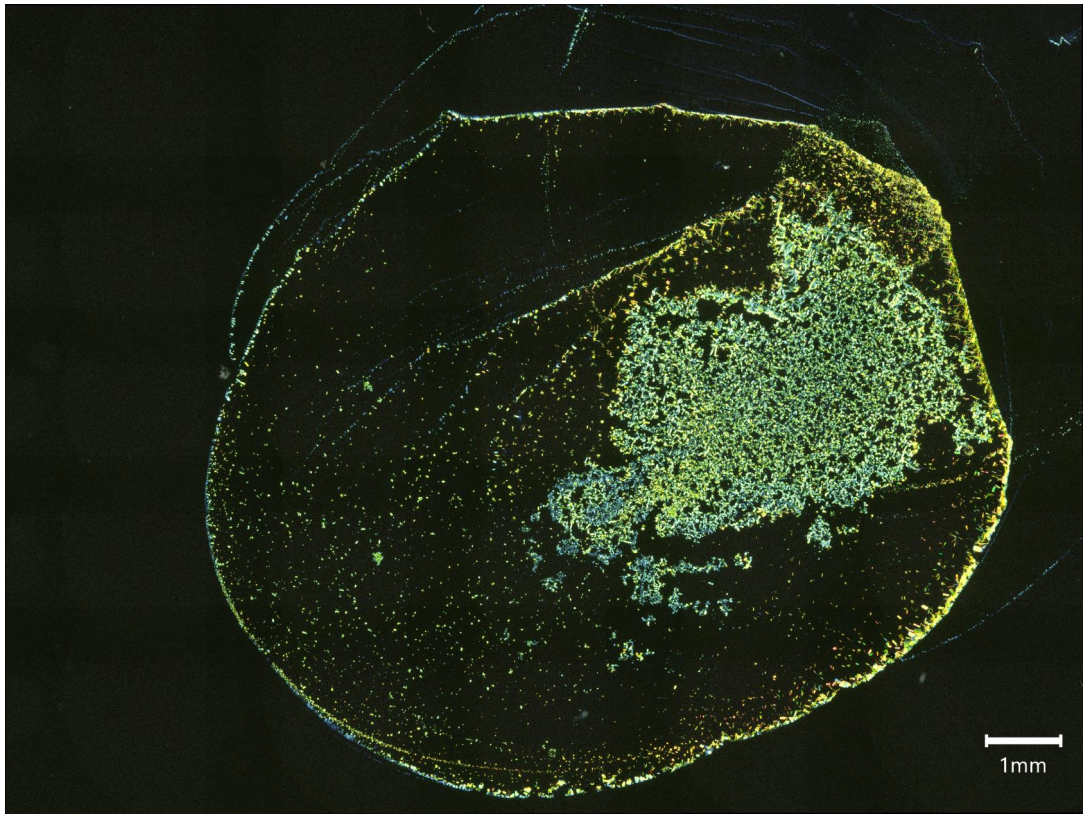




0.0266% Con

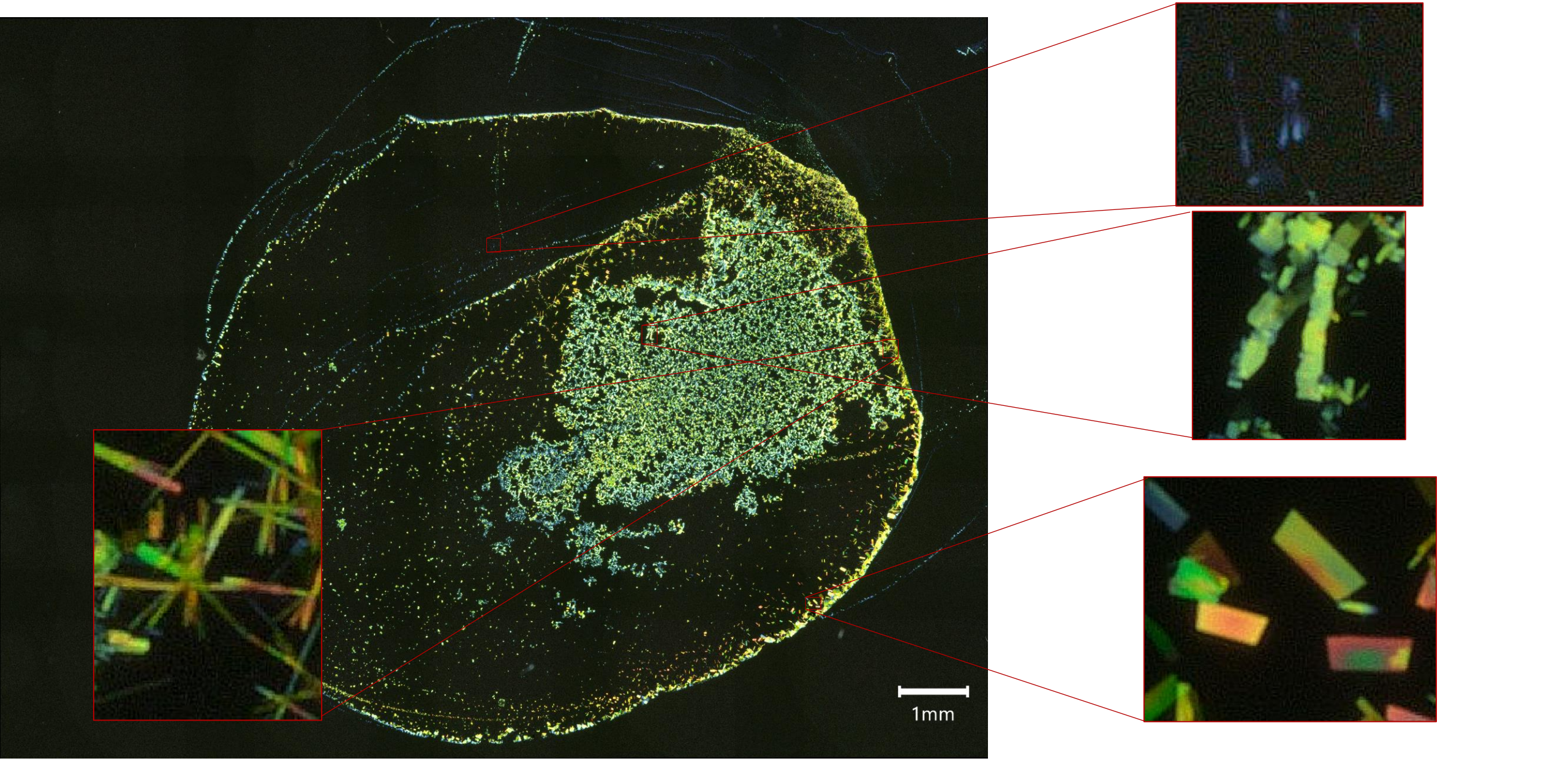
Formation of Crystal Structures

- Goal: Understand where different crystal structures form as the crystals grow in solution
- Results: Each type of crystal grows in specific spots



(5.5x Speed)

Locating Crystal Structures in Drop-Cast Sample



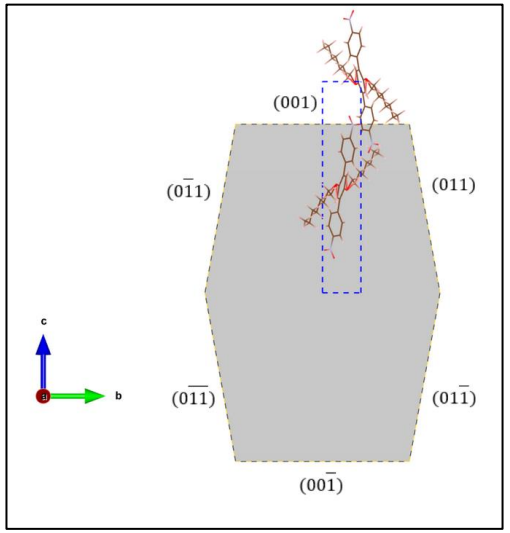
Summary and Future Directions

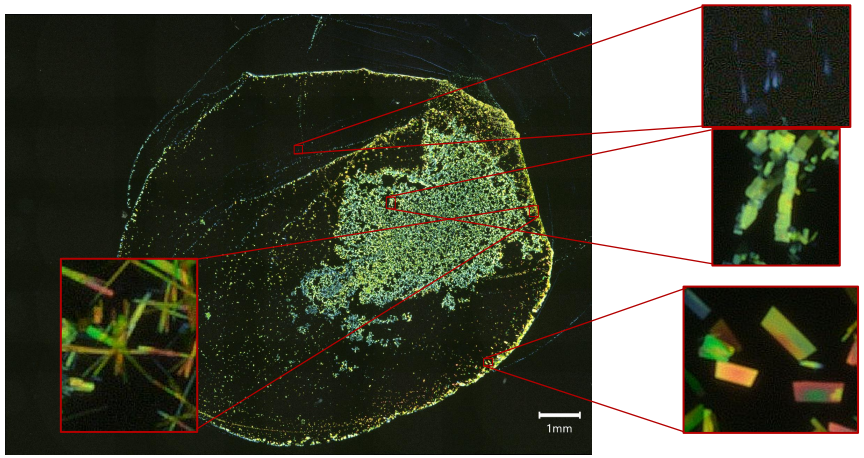
Summary

- Characterized the molecular orientation ANPT in its crystal formations
- Observed the effect that concentration has on crystal growth
- Characterized the different types of crystal growth based on how the solution dries

Future Directions

- Optical spectroscopy
- AFM optoelectronic measurements
- Exfoliation and patterning
  - PDMS (rubber) stamp





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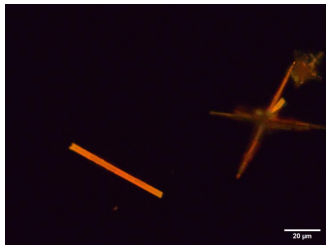

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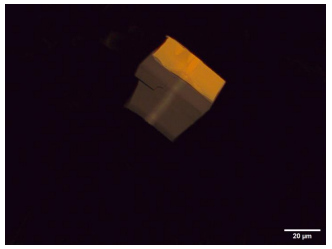

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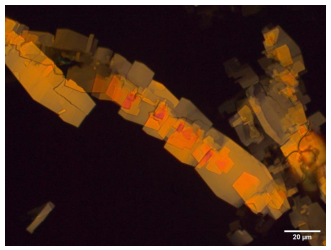

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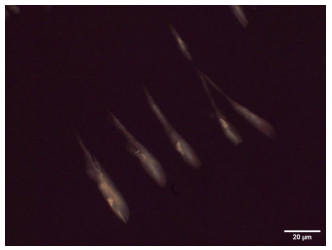

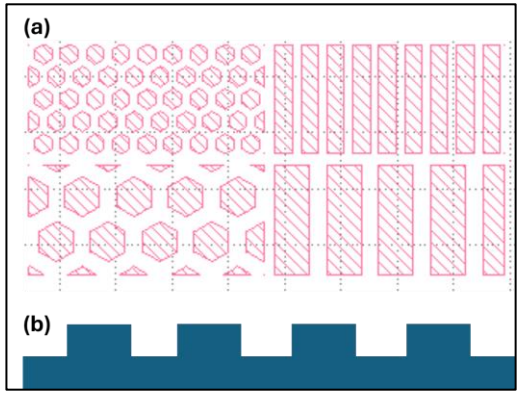

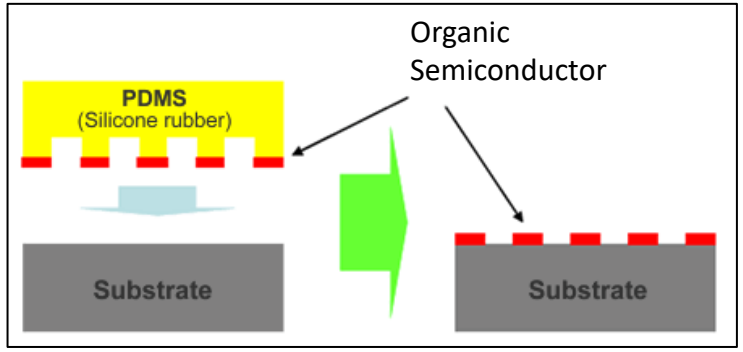

https://www.shinetsusilicone-global.com/news/2008/07.shtml

Acknowledgements

Bumm Group

- Dr. Lloyd Bumm
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  - AFM and Optical Microscopy
- Mikey Walkup

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- Dr. Feng
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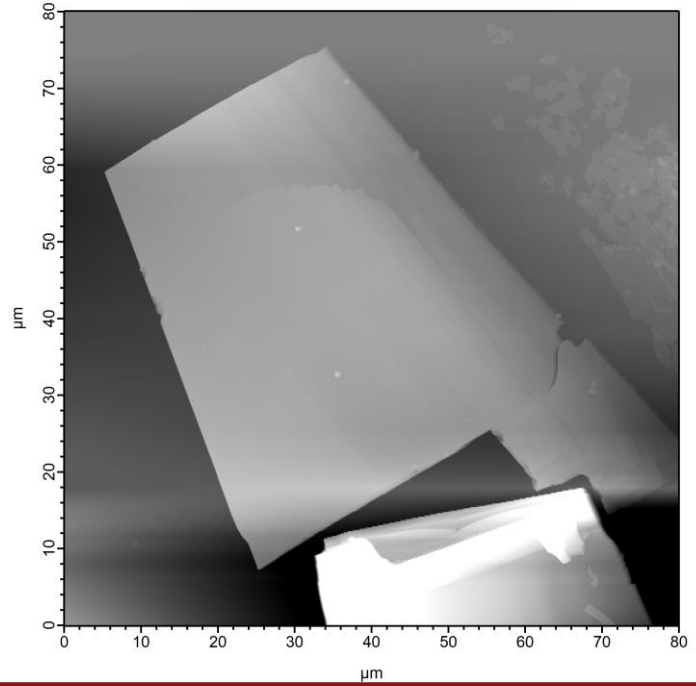
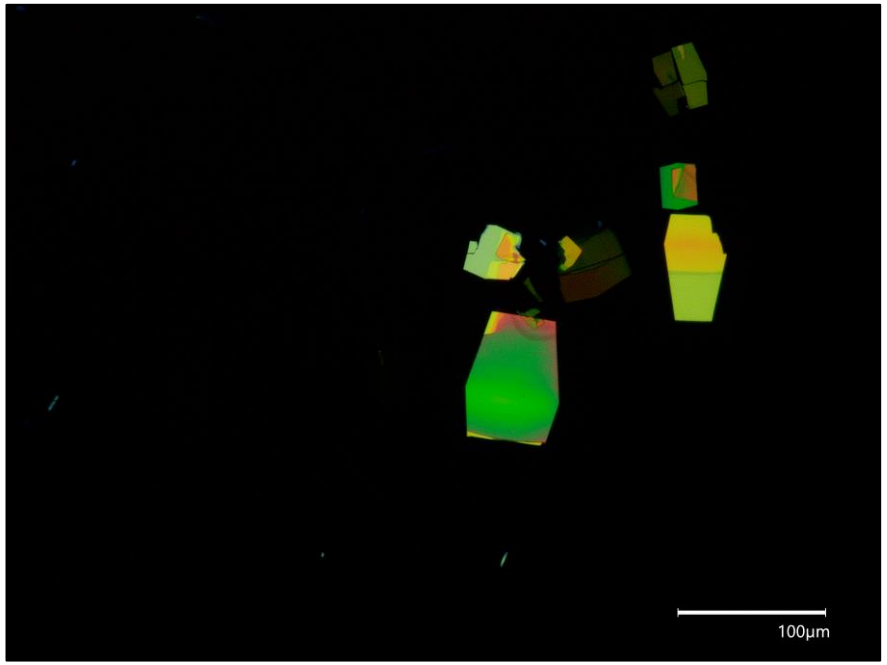
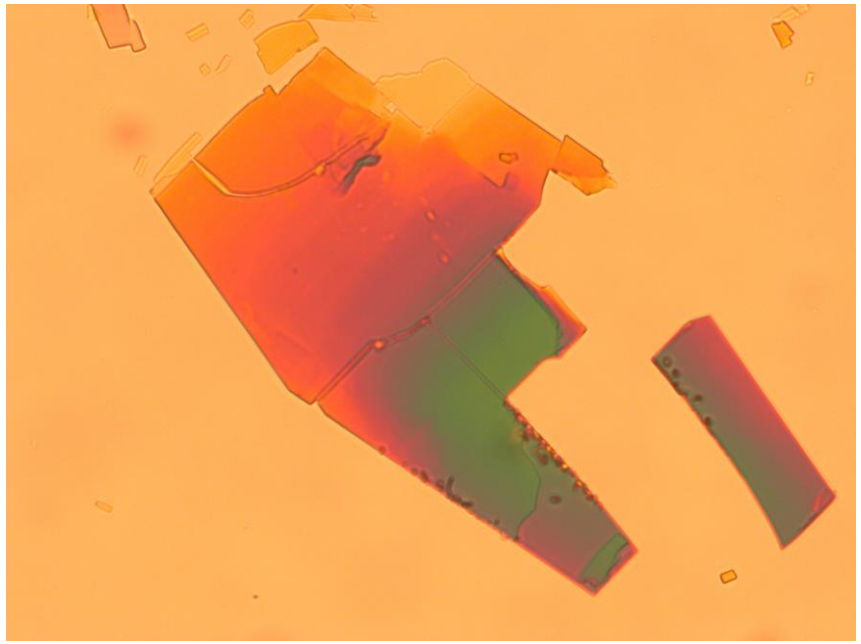
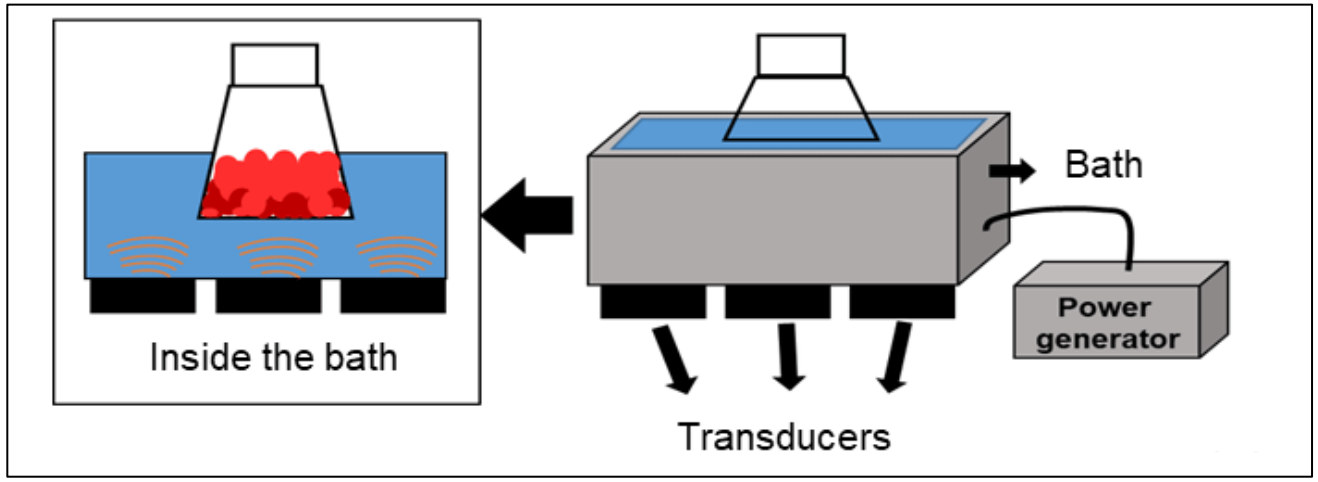
- Dr. Madalina Furis
- Hadi Afshari
- Hilbi Akbar
  - Film Printing







Film Printing: Pen-Writing and Drop-Cast



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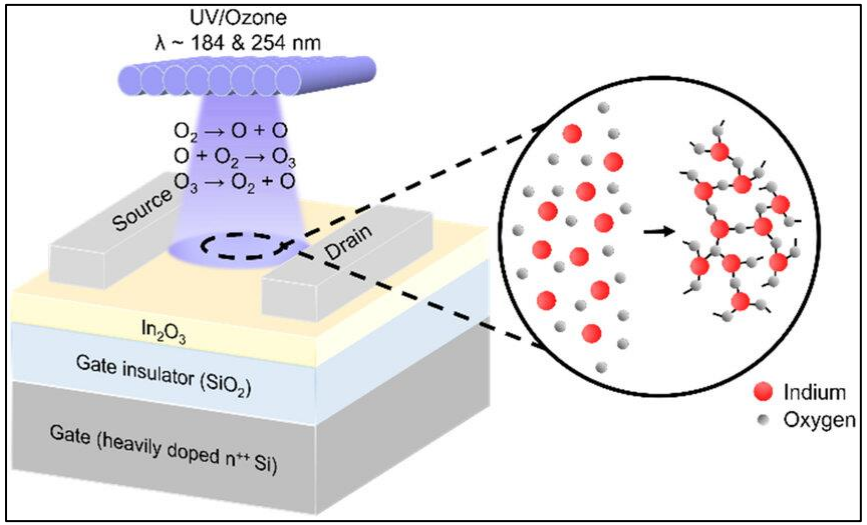
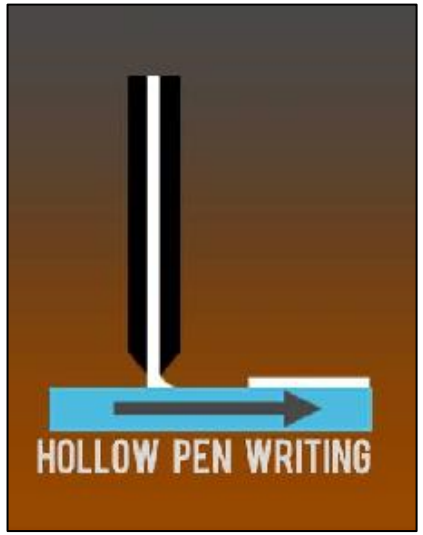


https://www.researchgate.net/figure/Schematic-diagram-of-UV-ozone-exposure-mechanism-and-device-manufacturing-process-of-In-2_fig1_360265814



https://www.semanticscholar.org/paper/Morphology-control-strategies-for-organic-thin-Diao-Shaw/c6865d1ff0faee8e3f85a0ee38defb5946b51a54

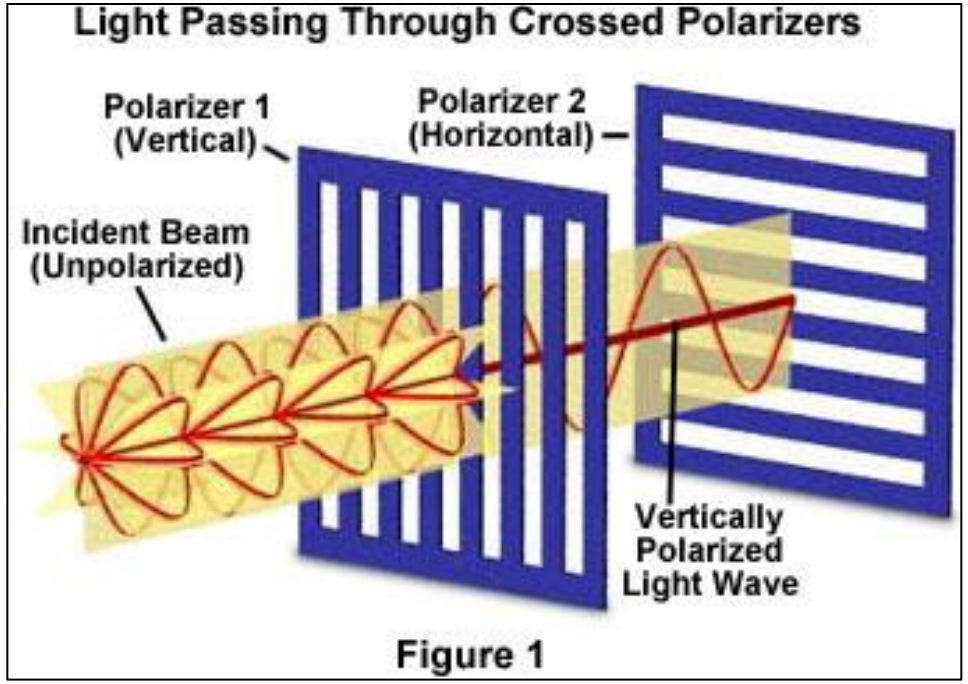
1. Preparations
    1. Cleaning substrates and equipment
        1. Sonicate materials with various solvents
        2. Put into UV ozone cleaner
    2. Prepare solution
        1. Ratio of solvent/solute (0.1% means 1 mg of solute per 1 mL of solvent)
        2. Sonicate solution
2. Deposition
    1. Pen-Writing
        1. Capillary is filled
        2. Lowered onto substrate until meniscus touches
        3. Substrate is moved via flat motorized stage
    2. Drop-Cast
        1. A drop is placed onto a substrate from a pipette

Polarized Light Microscopy

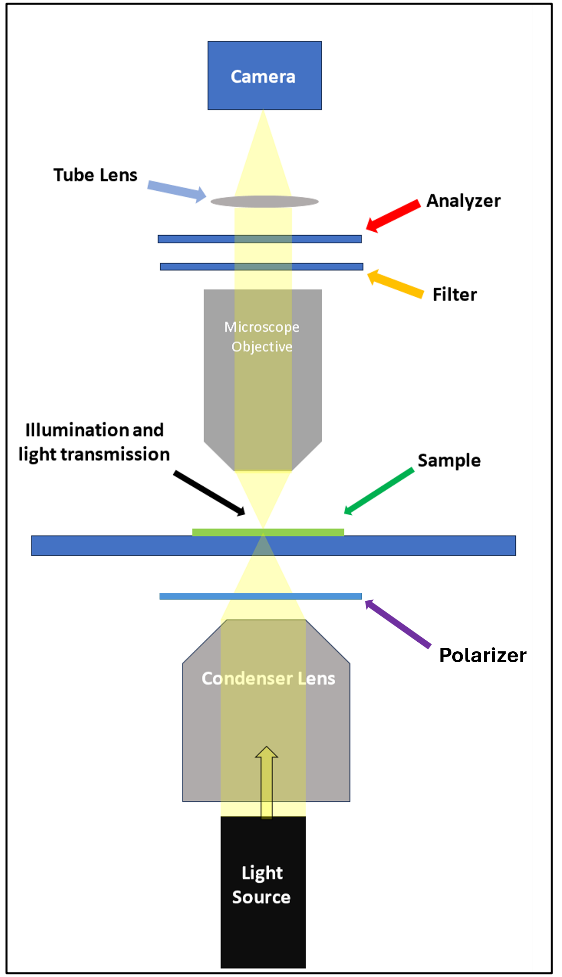
Polarized Light[3] :

- Ordinary light oscillates in all directions at a right angle to its propagation
- Polarized light is constrained to a specific direction of vibration
  - Plane Polarization: the electric vector vibrates in a single plane

Tool: Polarized Compound Microscope



https://www.olympus-lifescience.com/en/microscope-resource/primer/lightandcolor/polarization/



Research

Sample Set #3 (**June 17th**)

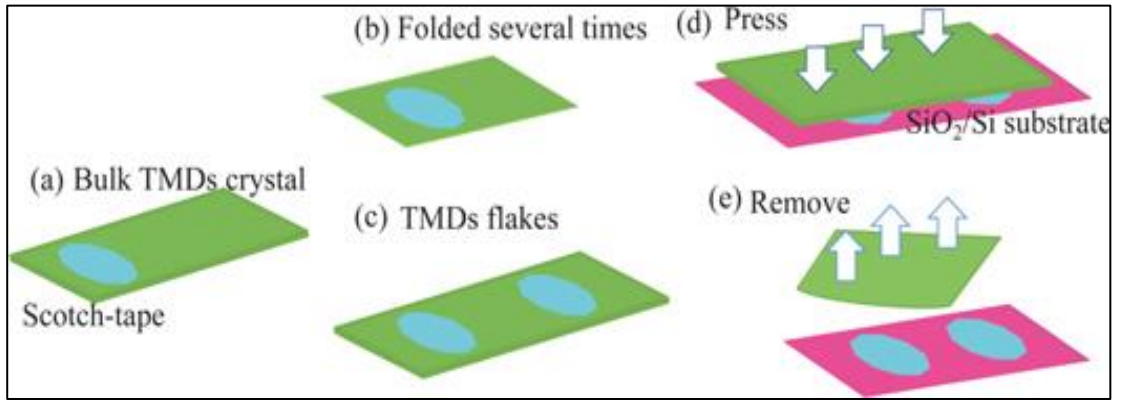
[exfoliated from Sample Set #2]

- Goal: Test ANPT response to exfoliation

Sample Set #4 (**June 26th**)

[Pen-written; var. concentrations; 30 microns/sec]

- Goal: Test effect various concentrations have on crystal growth



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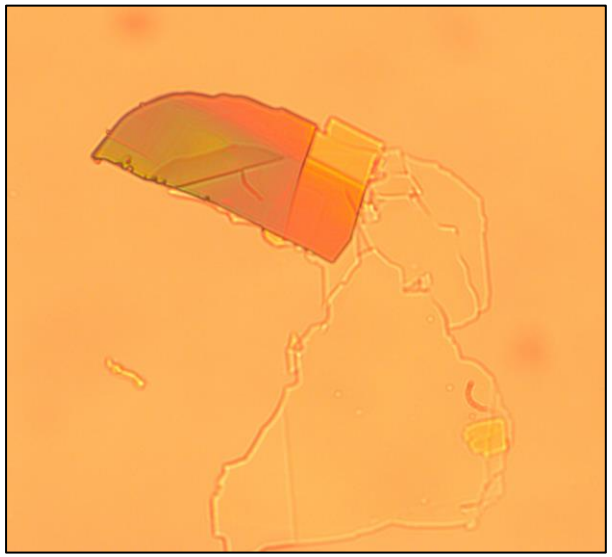
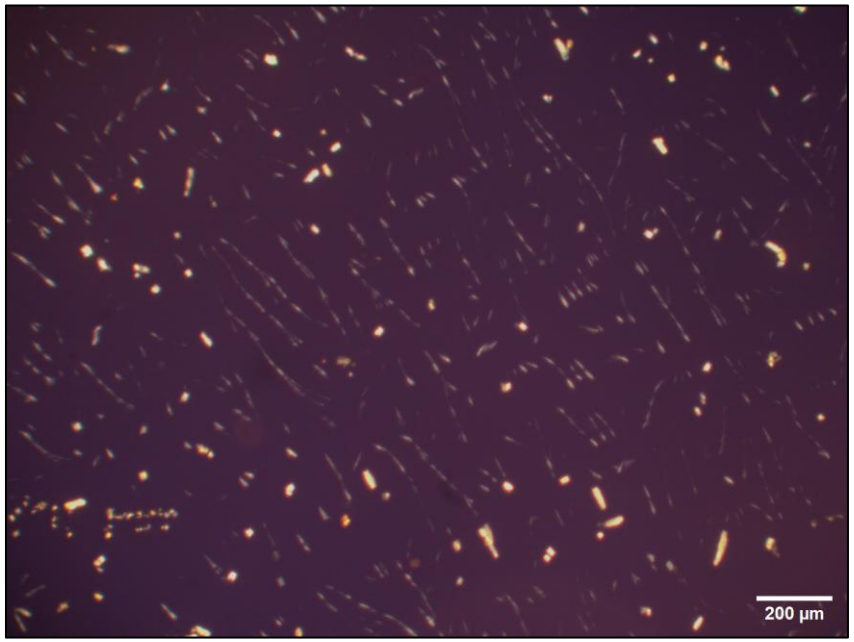
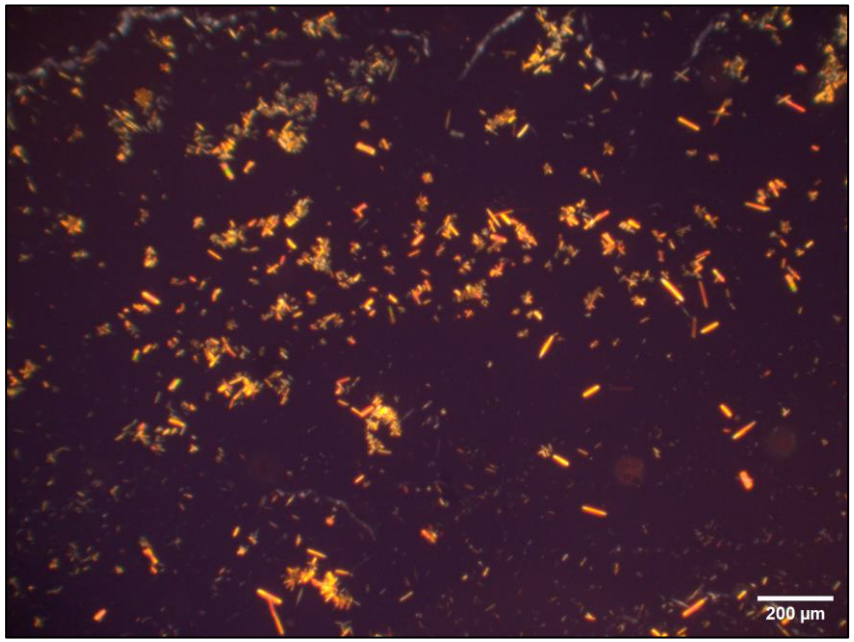




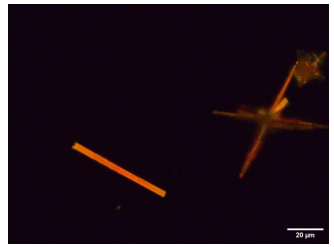
0.0266% Con

VS



0.1% Con.

(1)



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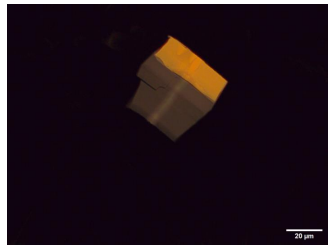
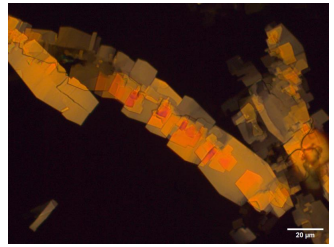


(3)



(4)