Covalent-Organic-Framework Polymerization and Crystallinity Study

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Research question & motivation

- **Covalent Organic Frameworks (COFs)**: a new class of crystalline and porous polymers constructed by covalently linking organic monomers into 2D or 3D ordered networks
- Due to their high surface-area-to-volume ratio, tunable pore size, and controllable chemical reactivity, COFs offer **unique functionality** for molecular separation, sieving, and catalysis applications.
- Despite their potential, however, COF **manufacturing** is still **poorly understood** due to **lack of insight into the reaction kinetics**. Some studies employ trial and error-based approaches, but these methods offer **insufficient control over crystallinity**, which is essential to transitioning these materials from bench-top scales to industrial space.
- **This research project aims to synthesize** these imine-linked COFs and **characterize** them under different growth parameters (temperature, catalyst concentration, etc.) using in-situ Raman Spectroscopy, X-Ray Diffraction, and Ultraviolet-Visible Spectroscopy, thereby **gaining insight into the kinetics of crystallization**.

Chemical Structure

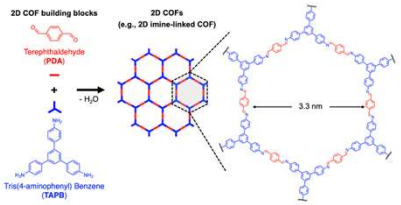


Figure 1: *Imine–COF and its monomers in the presence of (1,4–dioxane/mesitylene) and acetic acid*[1]

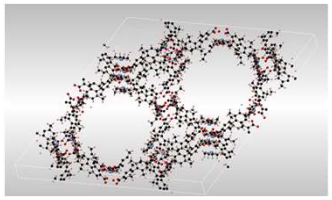


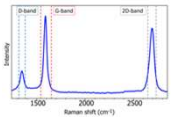
Figure 2: *An example of a COF structure (made in Crystal Maker)*

...corresponding to Raman peaks

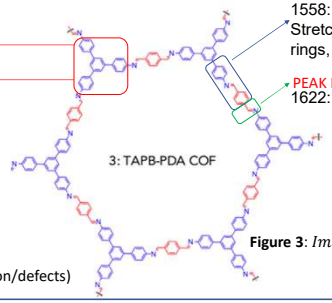
Benzene Domain

PEAK III 1588: multiple benzene rings stretching

PEAK I 1162: benzene ring C-H



G-band/1589 cm-1: Sp2 domain (in-plane vibration)
D-band/1325 cm-1: Sp3 domain (out of plane vibration/defects)



PEAK II
1558: newly formed C=N bonds
Stretching vibration between β- and γ-rings, and stretching of those two rings

PEAK IV
1622: C=N bonds

C=N Bonding

Figure 3: *Imine COF stucture and Raman pekas*[2]

Research methods

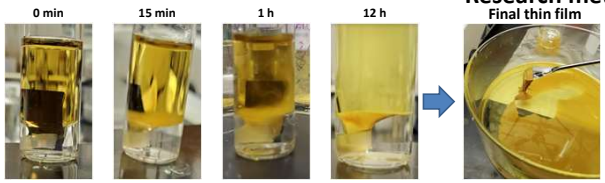
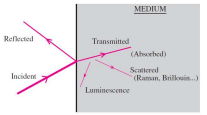


Figure 4: *Polymerization Process*[3]



$I = R + T + A$

$A = 1 - (R + T)$

Figure 5: *How UV Vis Spectroscopy works*[4]

Figure 6: *Raman Spectroscopy Setup*[5]

- Technique: determines the lattice vibrations to identify molecules in a material.
- Photons from a laser source interacts with the molecular modes of vibration.
- This causes phonon excitation which either up or down shifts the energy of the incident laser photons.
- These energetically altered photons are filtered, collected, and dispersed onto a detector.
- This energy level shift gives insight into the type of characteristic vibrations, and thus molecules, that exist in the material.

Additional results, references, and acknowledgments

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Findings and progress thus far

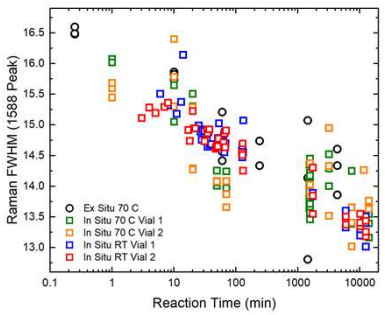

Figure 7: *Summary of TABP-PDA in-situ Raman Crystallinity Study*[6]

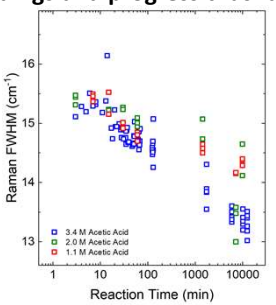

Figure 8: *In Situ Raman vs. Catalyst Concentration*

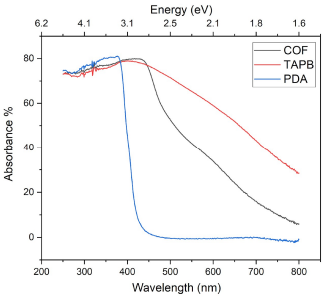

Figure 9: *UV-Vis Spectroscopy Measurement - Absorbance %*

As COF Raman peaks become sharper, indicating more distinct vibrational modes, the FWHM of the peaks decreases. Thus, **figure 7** and **8** indicate that crystallinity tends to improve as a function of increasing time and decreasing catalyst concentration. **Figure 9** shows the initial UV-Vis measurement for determining the bandgap of this COF, which can be viewed via the above barcode.

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