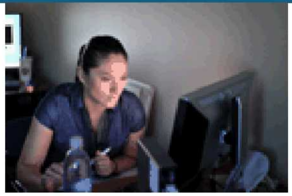
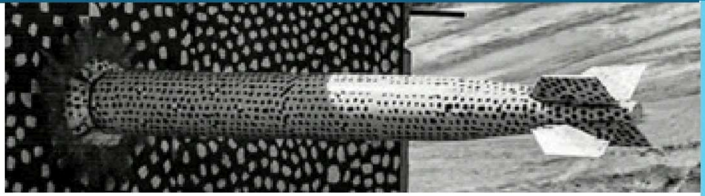
SAND2019-4046C

# Zirconium metal-organic framework functionalized plasmonic sensor





*PRESENTED BY*

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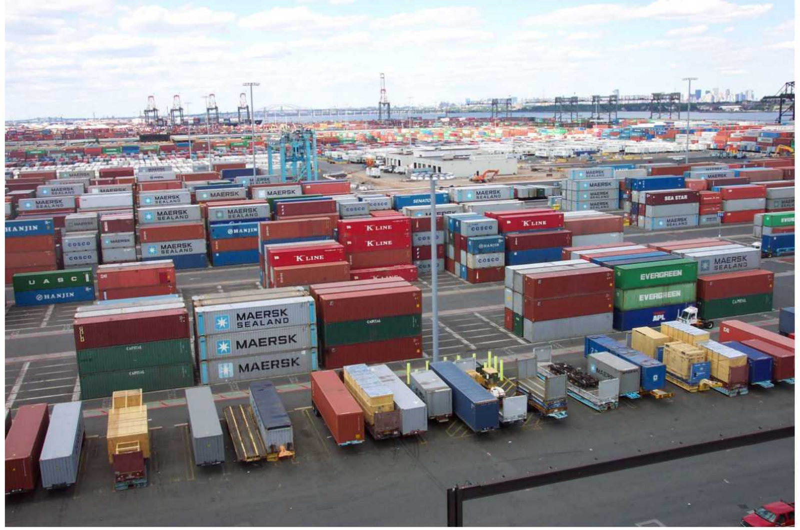
# Volatile Chemicals Exist In Everyday Life




Volatile chemicals remain a significant threat

- Military personnel
- Industrial processes
- Border/Port security
- Possible target locations for terrorism

A highly selective and ultra-sensitive sensor is desperately needed

# Approach

Sensing with Nanohole Arrays

Zirconium-based Metal Organic Frameworks

UiO-66 Synthetic Methods

MOFs on Gold

Thicker UiO-66 Films & XRD Confirmation

MOF Integration with NHAs

Experimental Setup

NHA Characterization

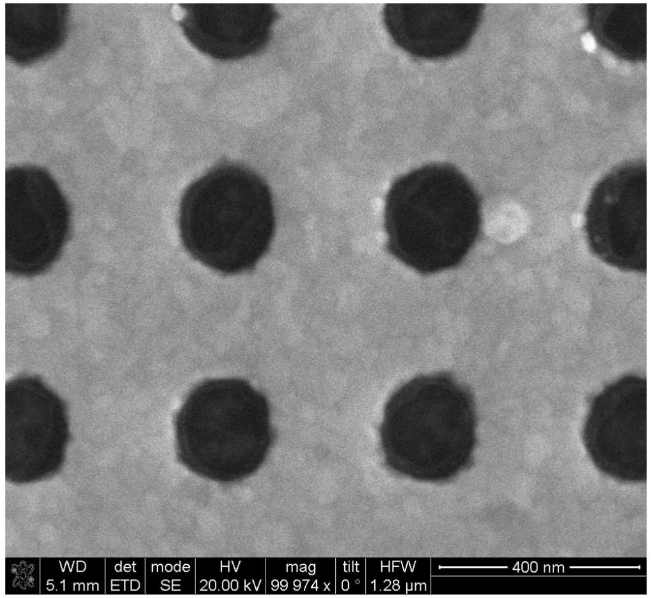
MOF Film Characterization with Surface Plasmon Polaritons

Methods of Detecting DMMP with MOFs

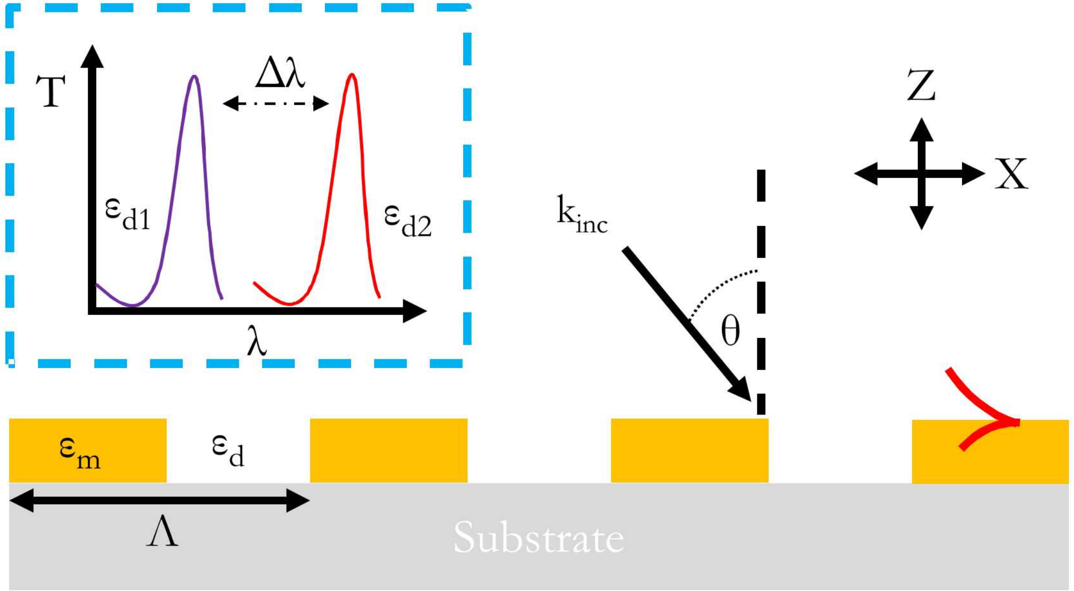
DMMP Results

Future Work

# Sensing with Nanohole Arrays




Extraordinary Optical Transmission (EOT)

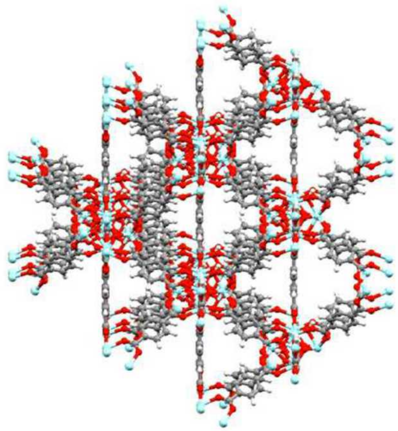


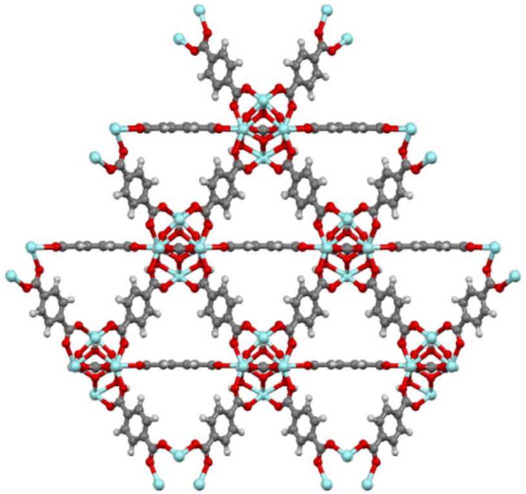

- Artificially structured/highly tunable
- Extremely sensitive to changes in the sensing volume
- Consistent and reproduceable results
- Scalable to wafer level production

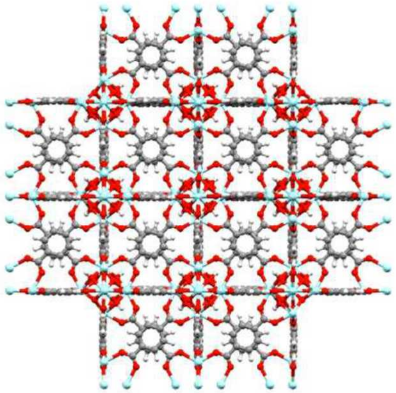
- Smaller molecules (gases) are challenging to detect
- Selectivity requires complex surface functionalization
- Metal/dielectric interface may not support surface functionalization

Is low-limit detection of small molecules feasible?

# Zirconium-based Metal Organic Frameworks (MOFs)







UiO-66

Crystalline coordination polymer:

- Micro/Nanoscale porosity (tunable)
- Extremely large surface area (1180-1240 $m^2/g$)
- Demonstrated sensitivity to chemical weapon agent (CWA)-simulant dimethyl methylphosphonate (DMMP)*

*Stassen et al. *Chemical Science*, 2016, 7 5827

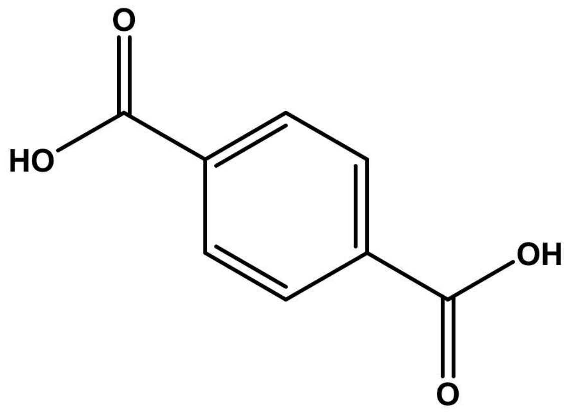
Would structural changes in MOFs be observable as a refractive index shift by a plasmonic transducer?

Can this be used as a new sensor architecture?

# UiO-66 Synthetic Methods

- There are many variations of the basic synthesis of UiO-66 in the literature
- Important parameters include reagent concentration vs solvent, use/stoichiometry of a monoacid capping agent, water concentration, and, for thin film growth, heating method (oven vs. microwave)
- We have explored four synthetic methods (Taddei et al., Miyamoto et al., Katz et al. and Fei et al.)
- The most successful methods for our purposes have been those reported by Taddei et al. and Miyamoto et al.

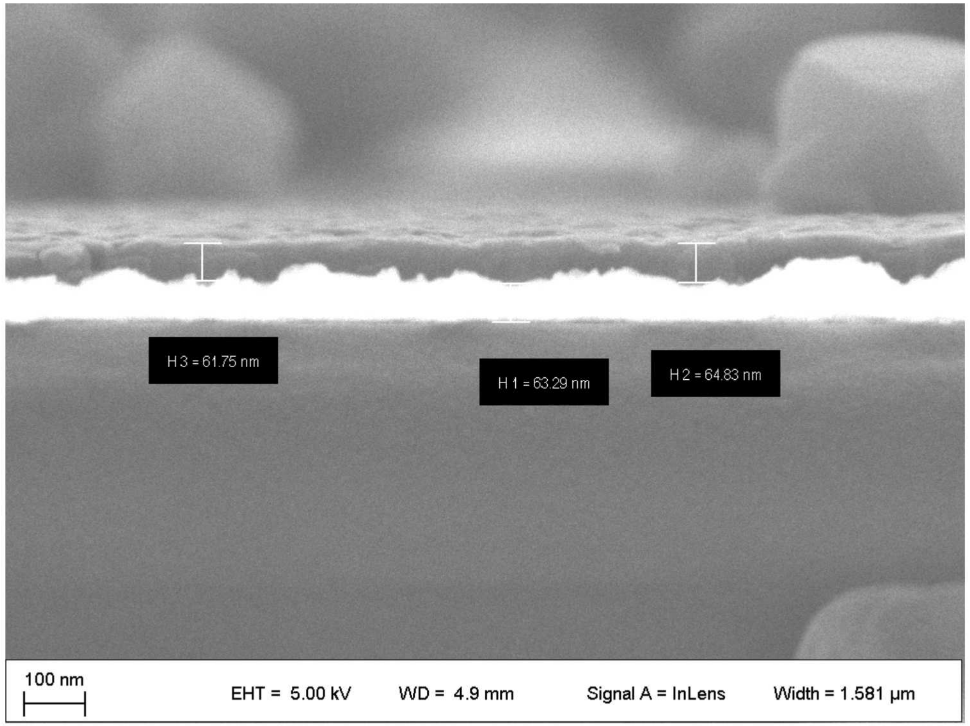
| Reagent/Condition | Miyamoto Method | Taddei Method |
|---|---|---|
| | mol/mol ratio vs $ZrCl_4$ | |
| $ZrCl_4$ | 1 | 1 |
| 1,4-benzenedicarboxylic acid | 1 | 1 |
| acetic acid | 80 | 30 |
| water | 0.2 | 6 |
| DMF | 250 | 110 |
| heating method | oven | microwave |
| duration/temp | 24 hrs/80°C | 30 min/120°C |




**1,4-benzenedicarboxylic acid (terephthalic acid)**

Taddei et al. *Dalton Trans.*, 2015, **44**, 14019
Miyamoto et al. *CrystEngComm*, 2015, **17**, 3422
Fei et al. *Chem Comm*, 2015, **51**, 66
Katz et al. *Chem Comm*, 2013, **49**, 9449

# MOFs on Gold



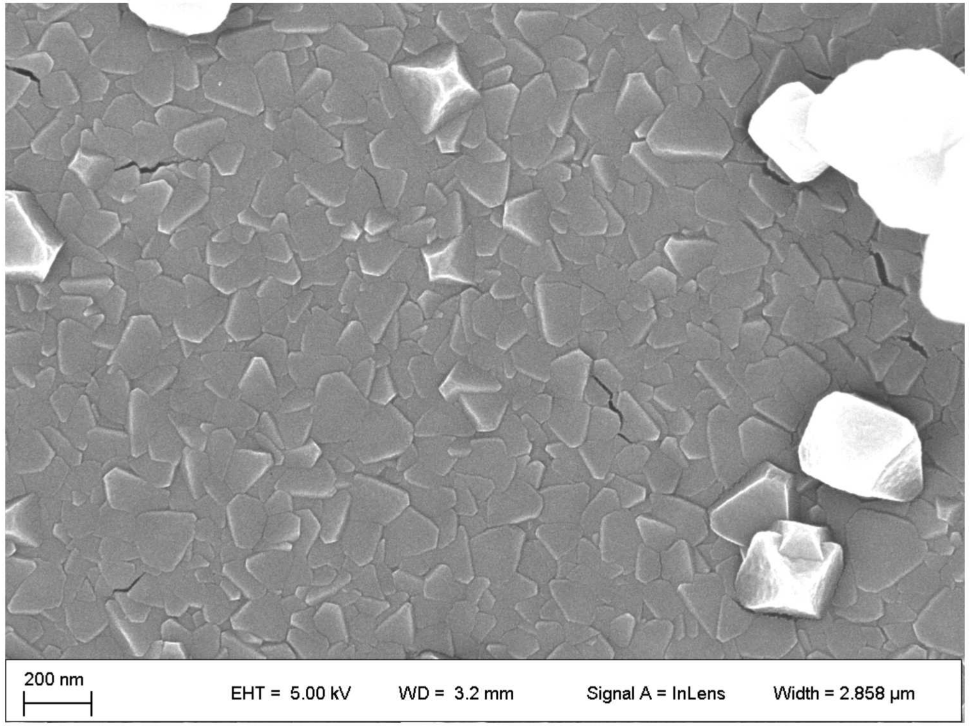

First demonstration of solvothermal growth of UiO-66 on Au surface

Uniform film thickness of 60-70 nm

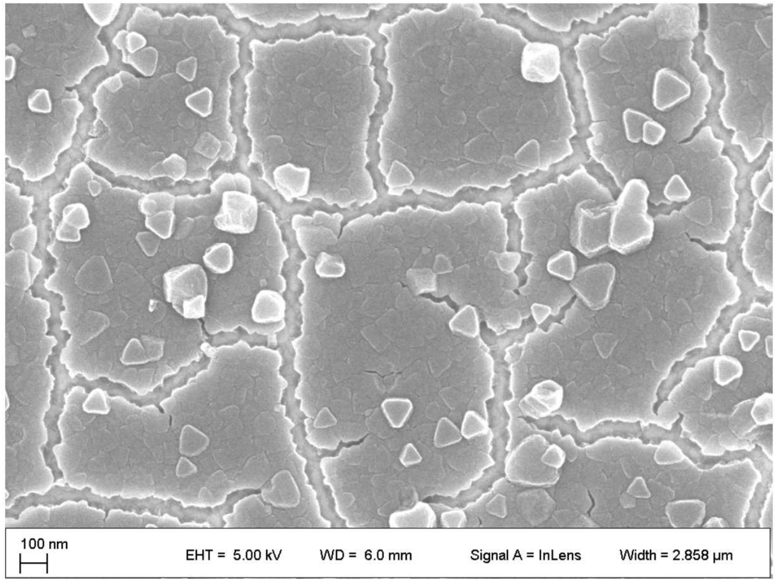
Intergrown base layer very promising!

Crystalline overgrowth observed:

- Mitigated with sonication
- Does not seem to interfere with sensing modalities



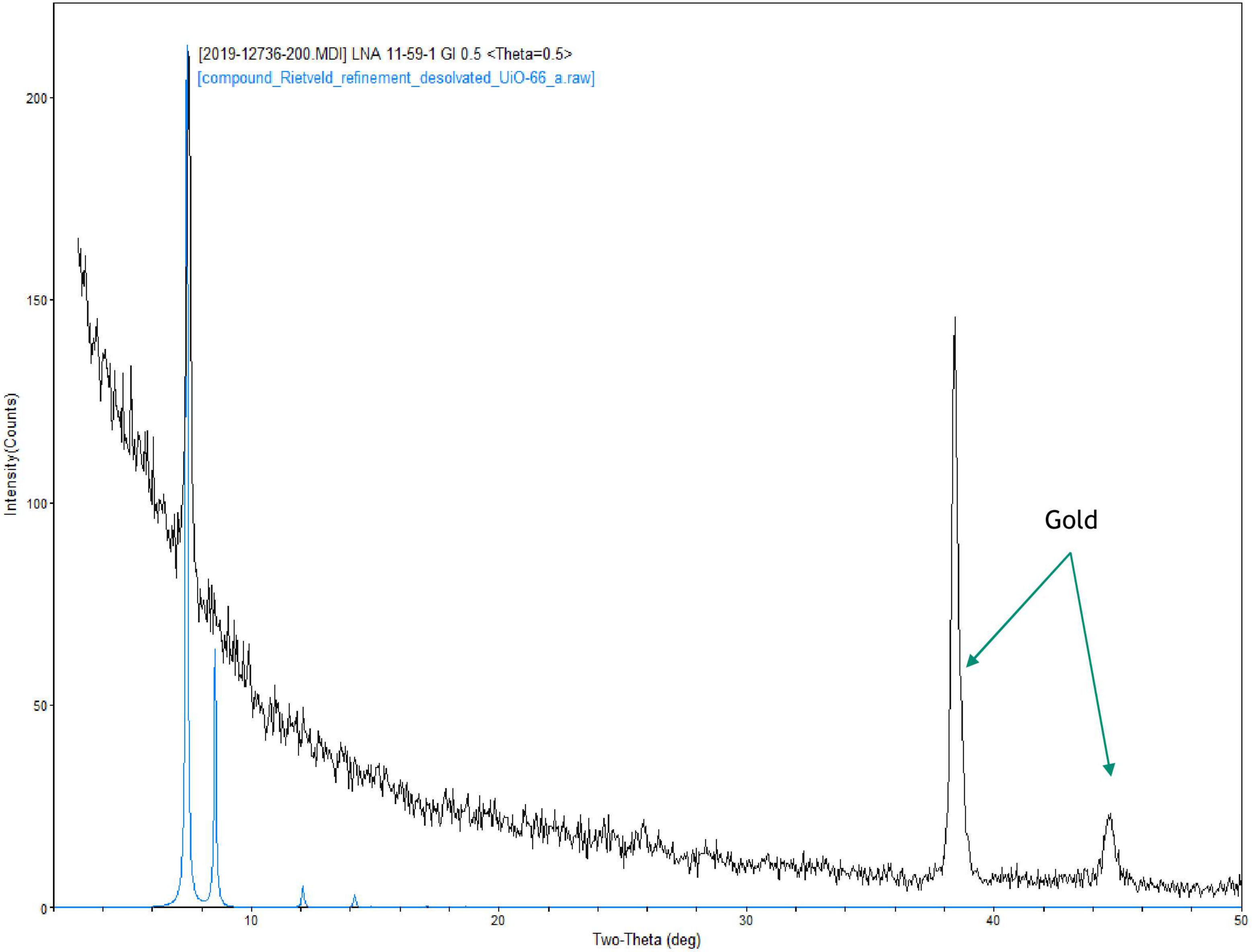
# Thicker UiO-66 Films & XRD Confirmation



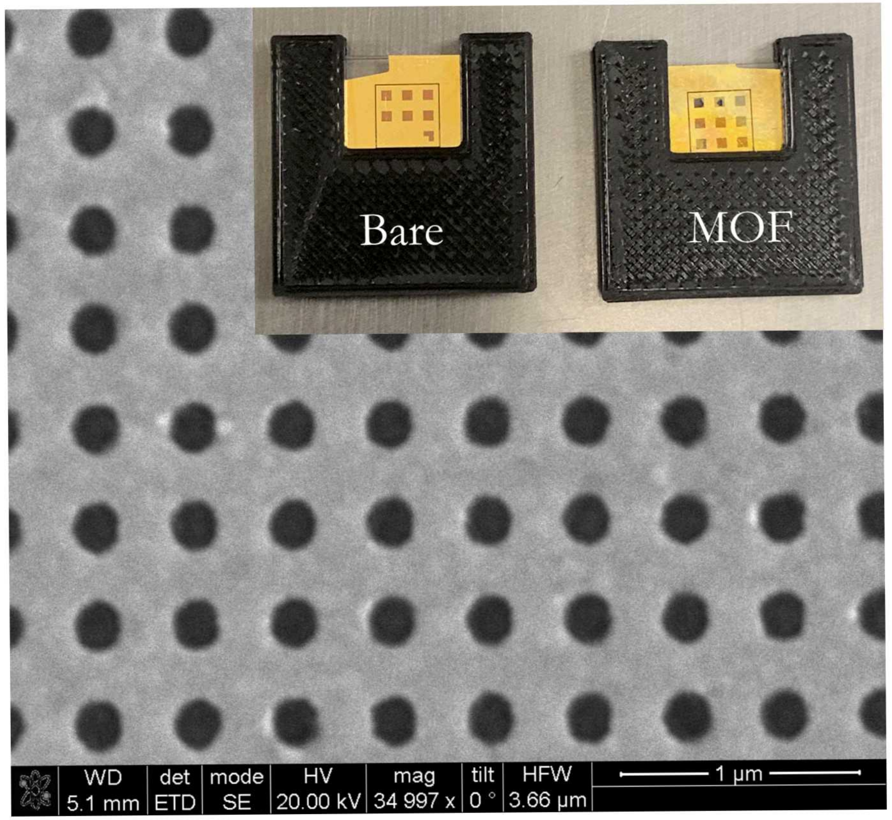

Thicker films of up to 200 nm show stress fracturing

Grazing incidence X-ray diffraction confirm strong <111> alignment as expected of UiO-66

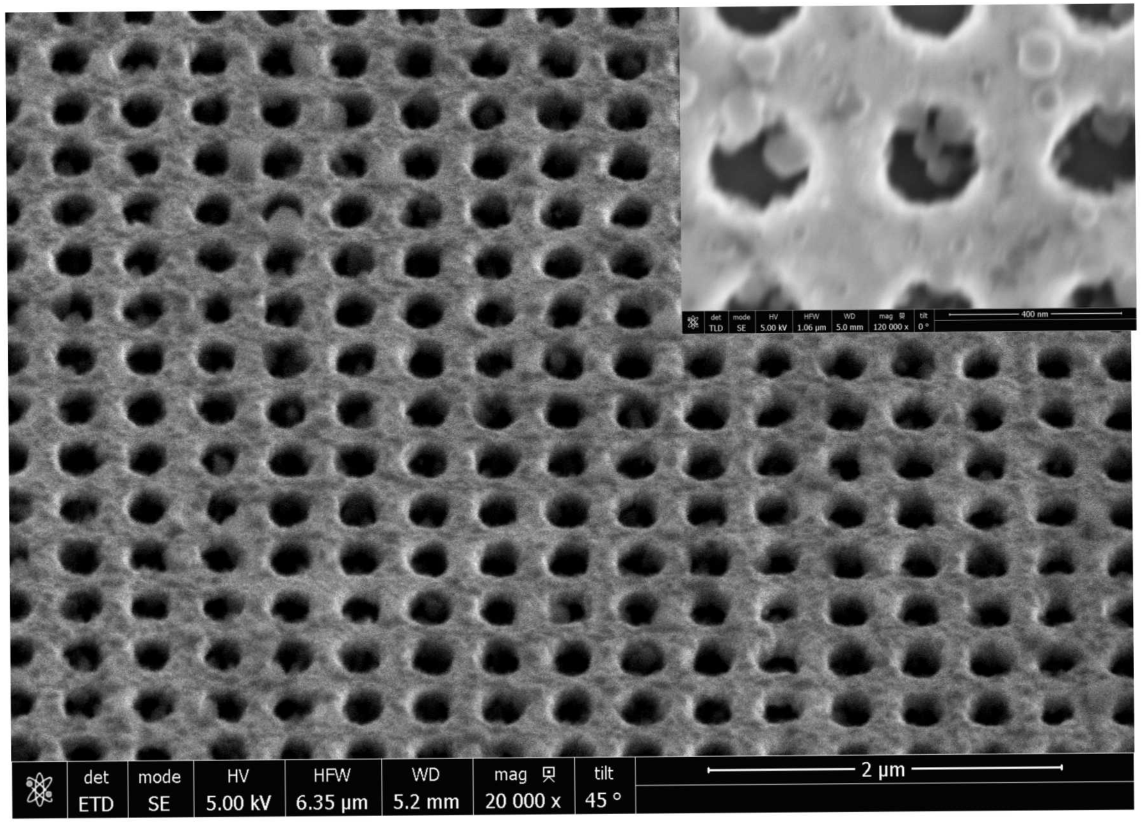
How well will thin film MOFs integrate with NHA structures?



# MOF Integration with NHAs




MOF Process

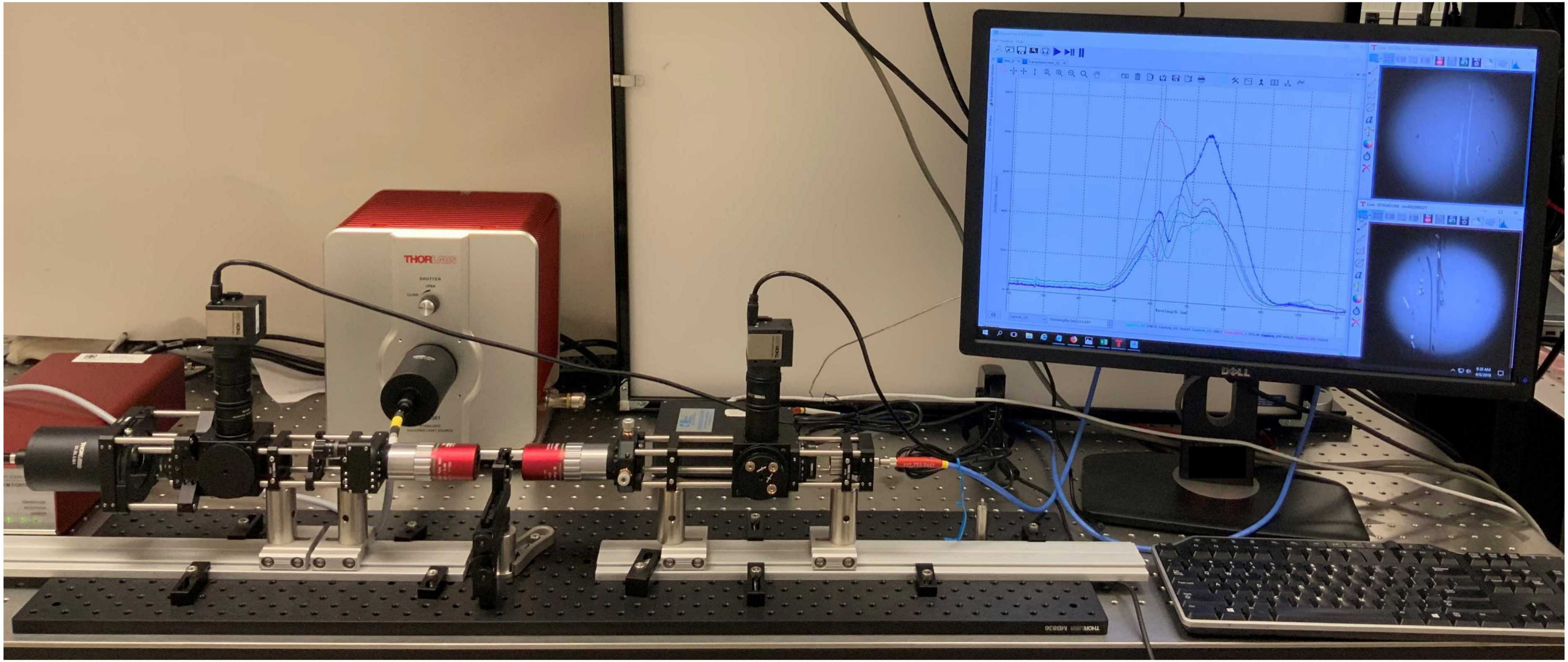



Obvious MOF thin film growth

Inset – Crystallites grown within nanoholes

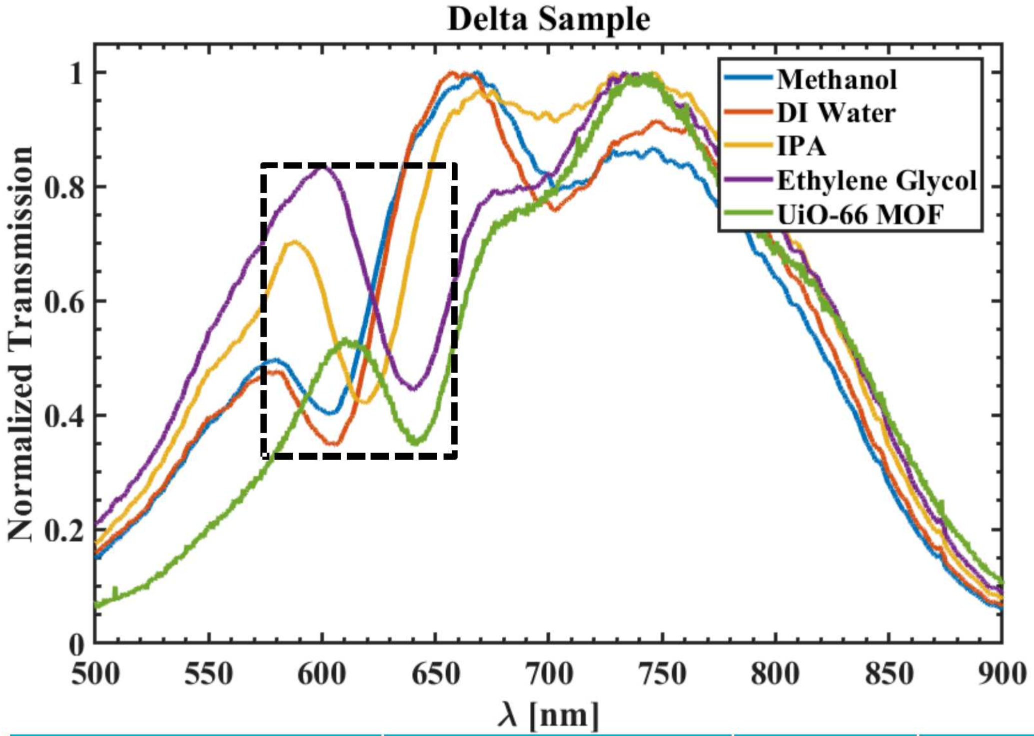
What can we learn about thin film UiO-66 from EOT spectra?

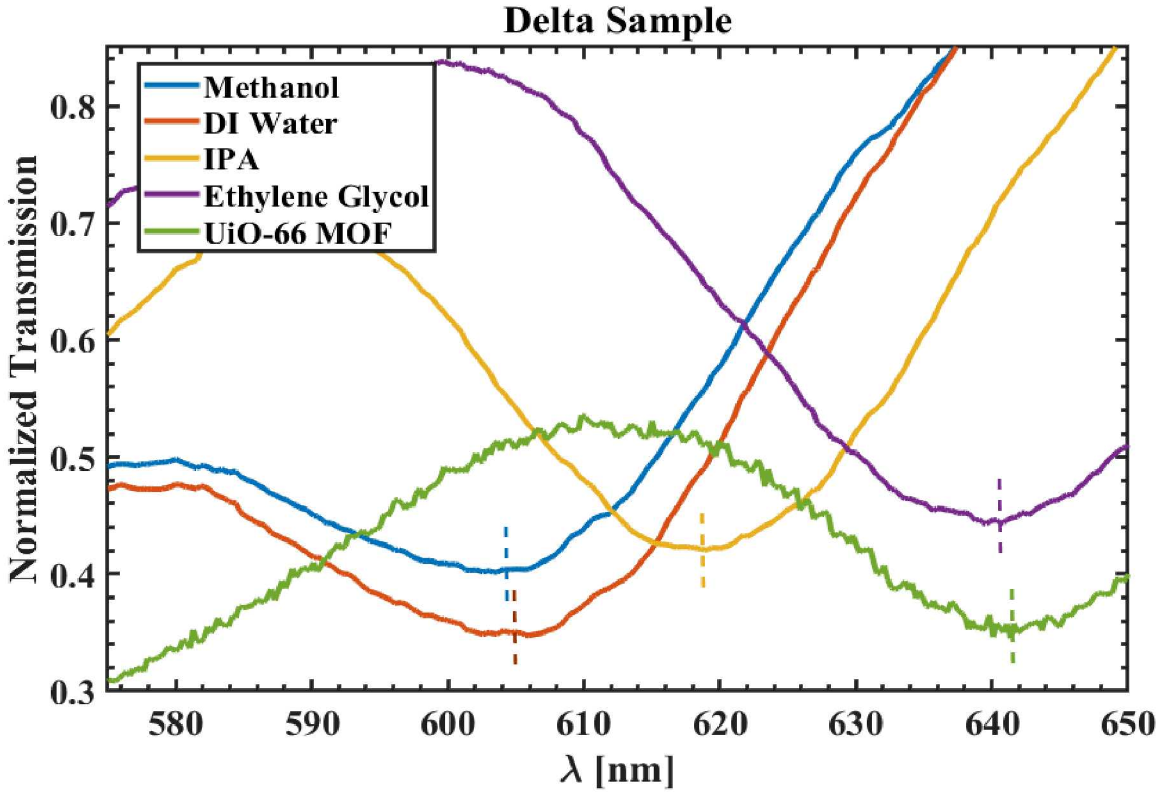
# Experimental Setup



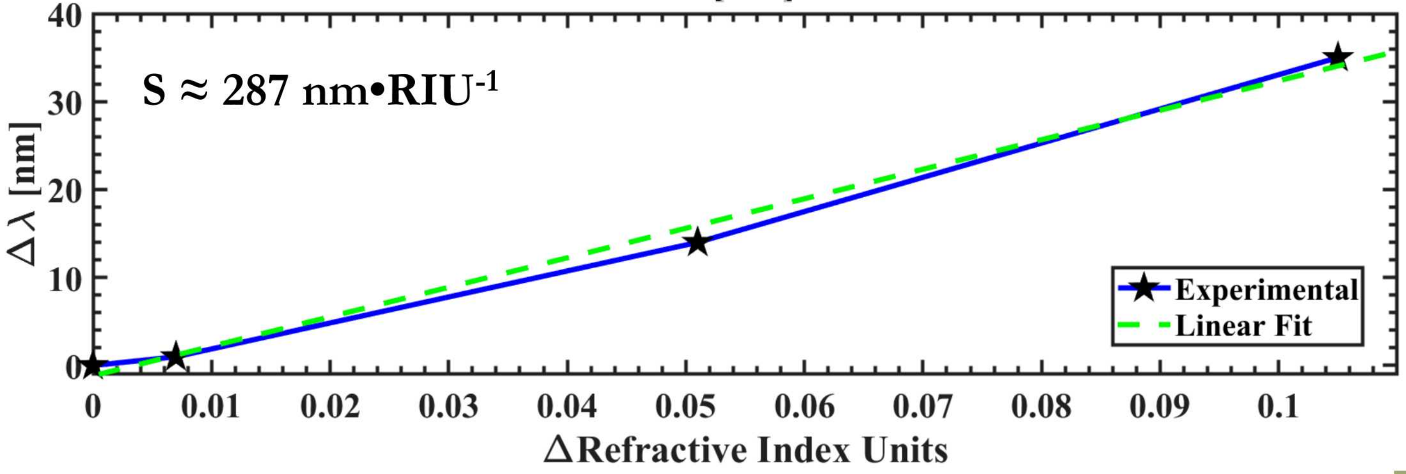

Excitation → Collection

# NHA Characterization

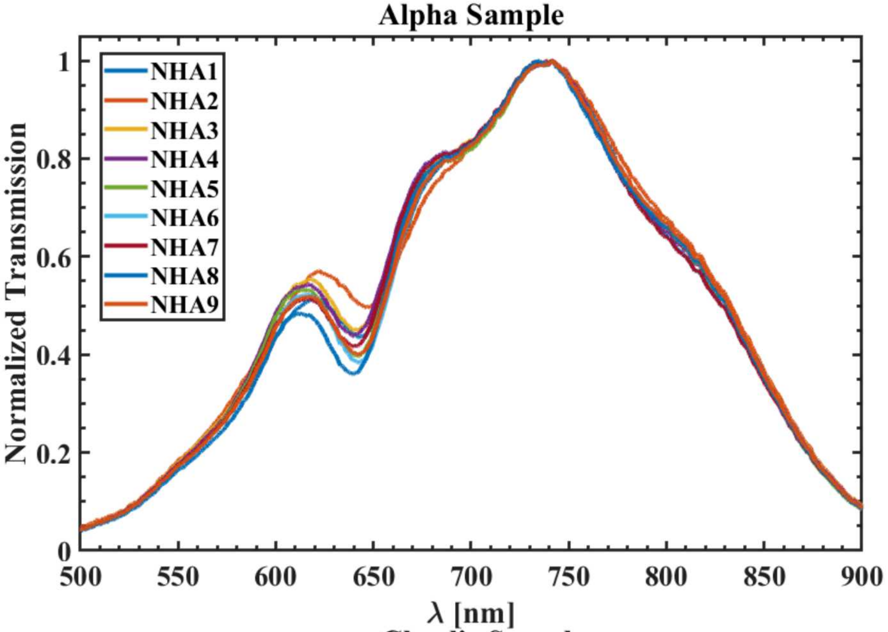


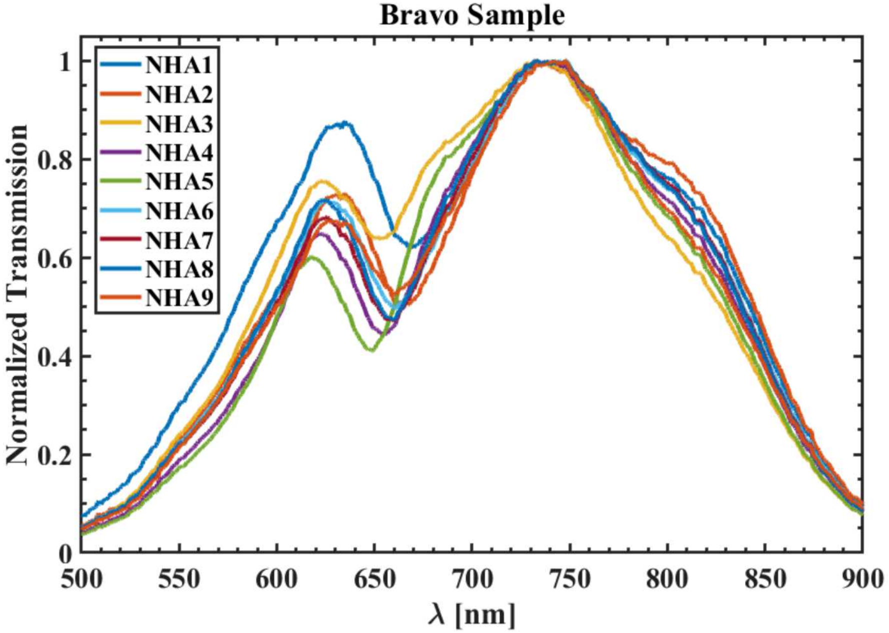




| Analyte | Refractive Index | $\lambda_{min}$ | Δλ |
|---|---|---|---|
| Methanol | 1.324 | 605 | - |
| DI Water | 1.331 | 606 | 2 |
| Isopropanol | 1.375 | 619 | 14 |
| Ethylene Glycol | 1.429 | 640 | 31 |
| MOF | 1.437 | 642 | 35 |



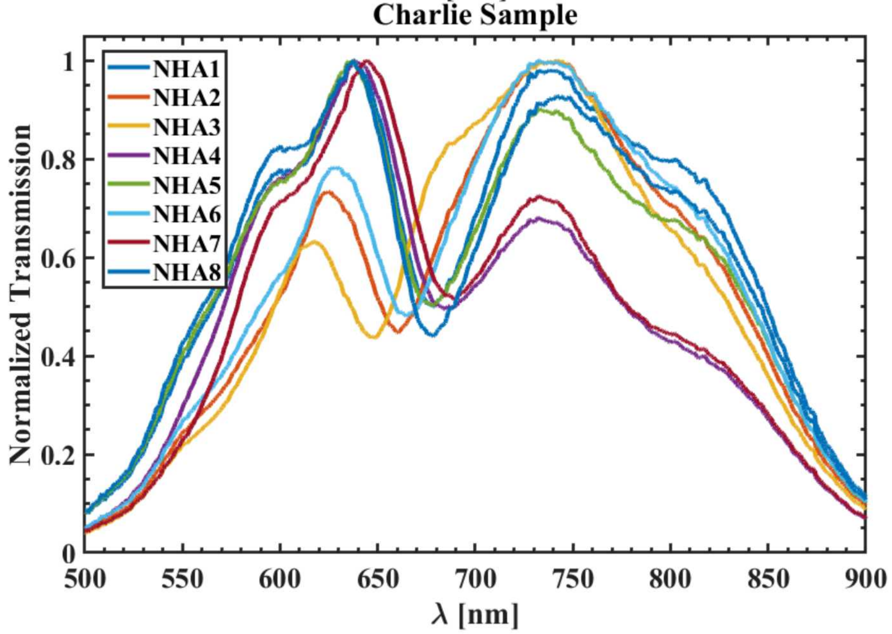
# MOF Film Characterization with Surface Plasmon Polaritons

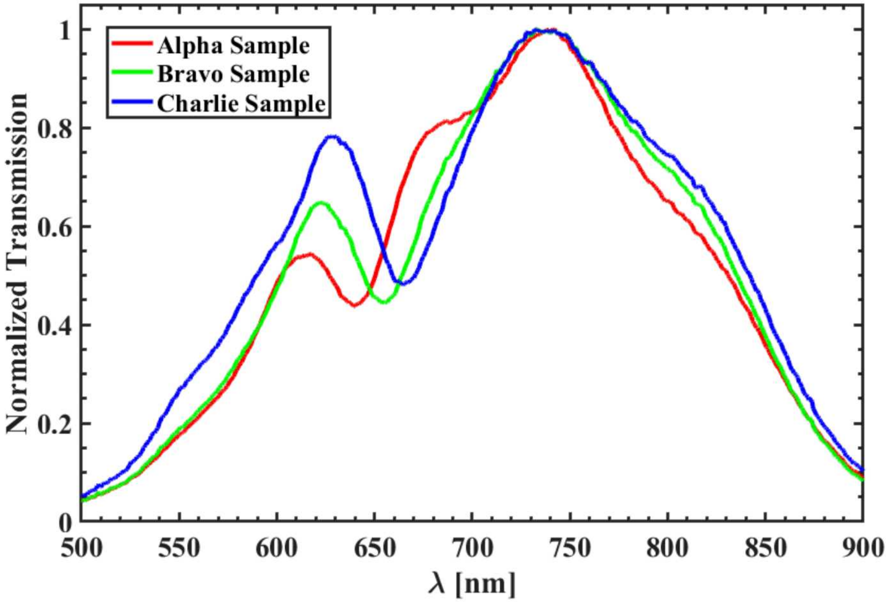



Film thickness variable from array to array and sample to sample

Alpha, Bravo, and Charlie samples were processed under the same MOF growth conditions



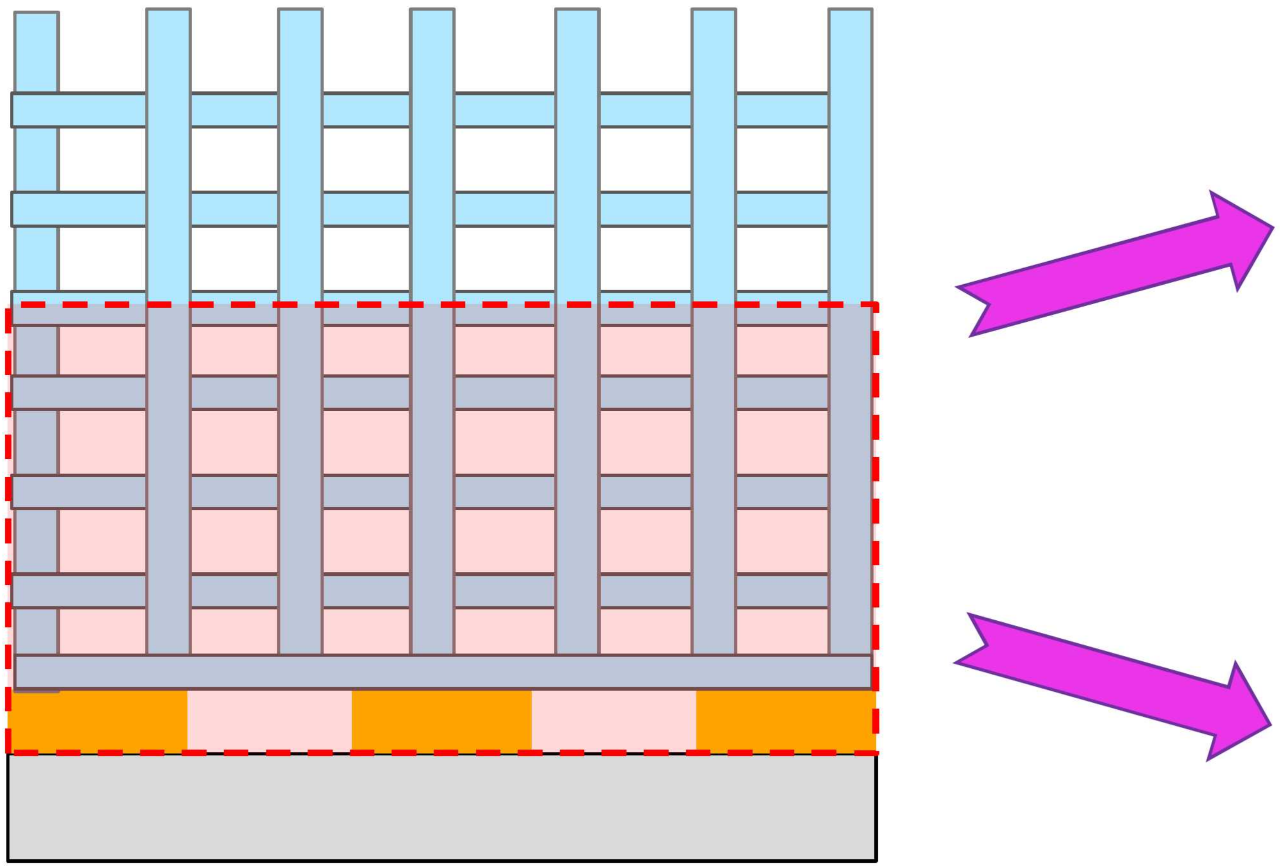




Alpha film growth process is promising and warrants further investigation

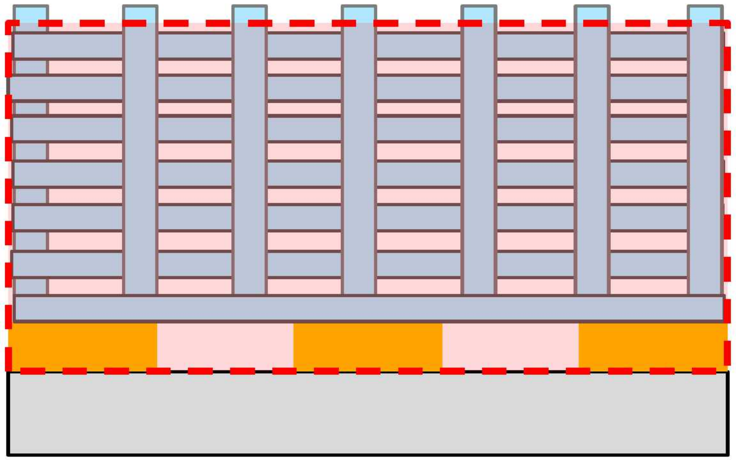
General agreement with expected spectral shape

# Methods of Detecting DMMP with MOFs

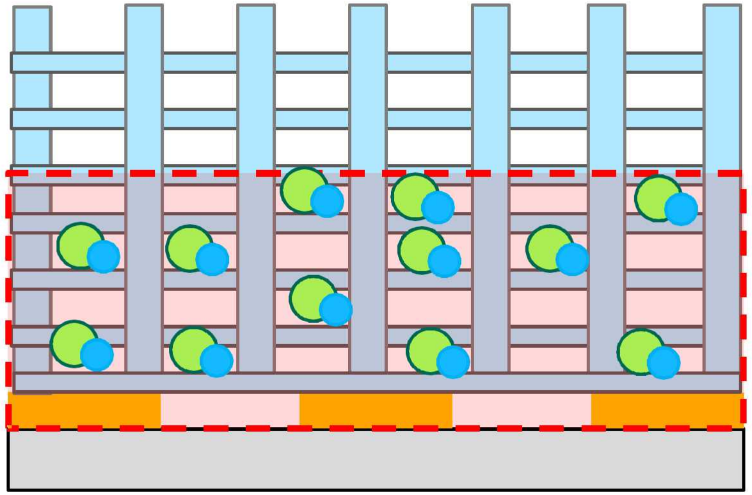
MOF Functionalized NHA



Framework Collapse

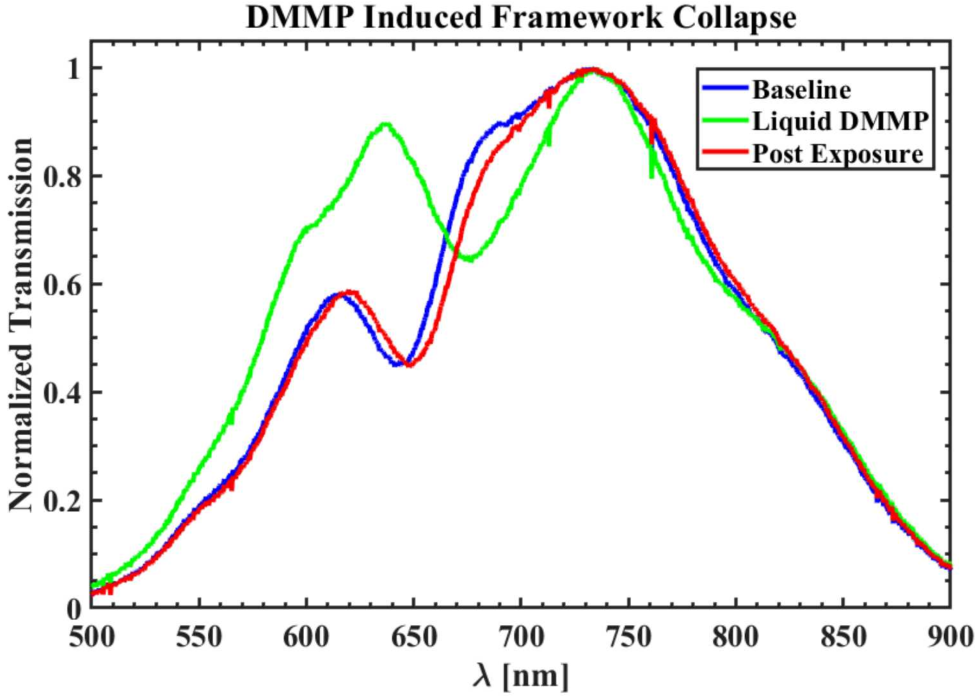


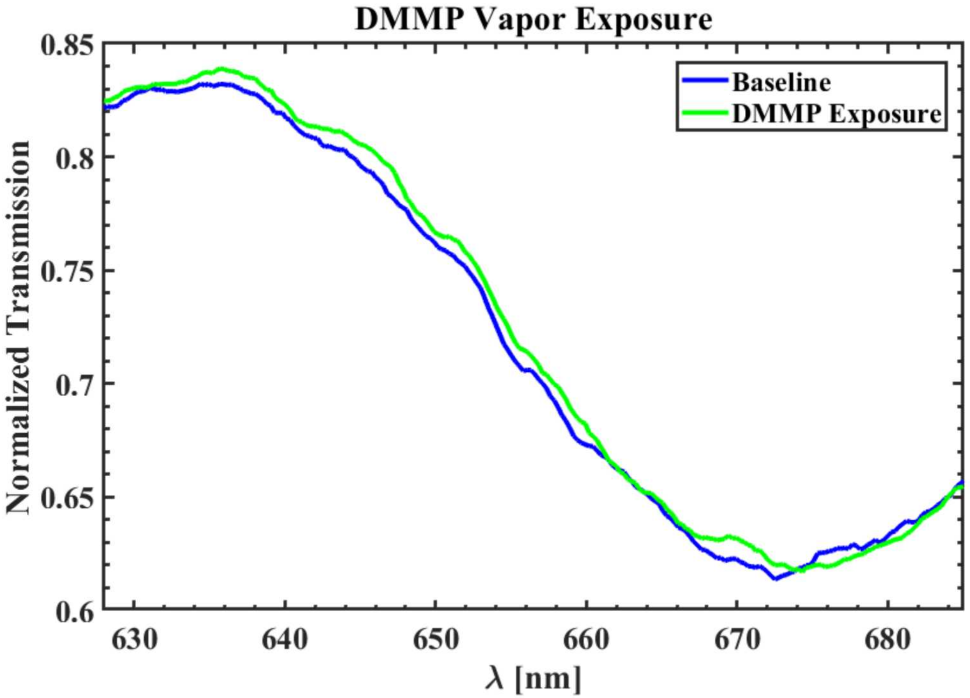
Sorber/Concentrator

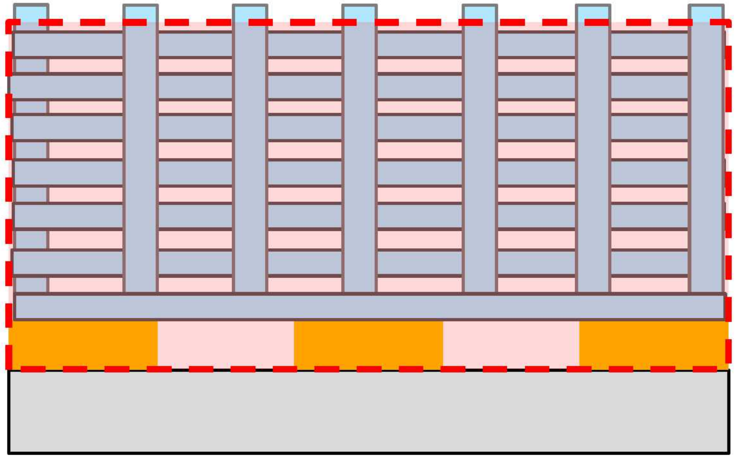


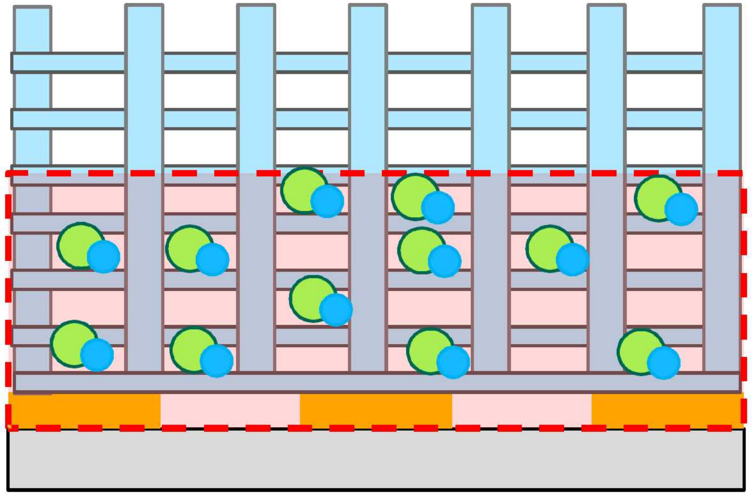
Both methods increase the effective refractive index within the sensing volume of the NHA. This change is observed by tracking changes to the EOT spectrum

# DMMP Results



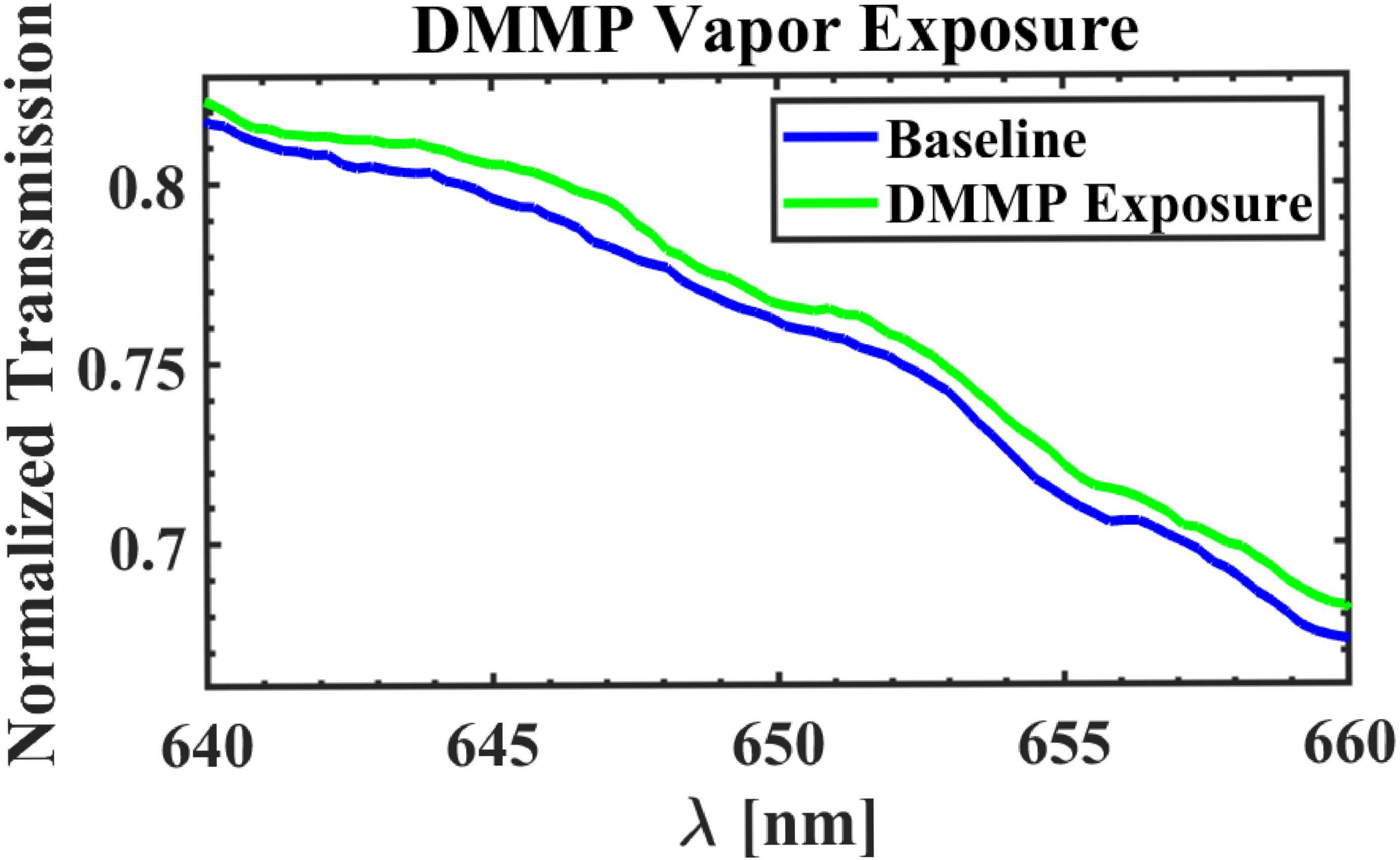


# Future Work

This work has confirmed DMMP can be detected with a MOF-functionalized NHA. However, this has been a qualitative confirmation. Our future work will focus on quantifying this sensing architecture:

- Optimize MOF film synthetic methods (thickness, porosity, uniformity)
- Investigate performance of current synthetic methods to atomic layer deposition methods
- Integrate a gas flow cell to control analyte/MOF interaction
- Flow varying concentrations of DMMP to fully characterize sensor responsivity
- Flow additional gases with DMMP to determine selectivity of MOF films

# Questions?


DMMP Vapor Exposure
Normalized Transmission
0.8
0.75
0.7
640
645
650
655
660
λ [nm]
Baseline
DMMP Exposure