SAND2014-0516C
National Nuclear Security Administration

# Molecular "Popoids"
## Assembling Functional Supramolecular Nanocrystal Films on Chemically-Modified Surfaces

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Sandia National Laboratories, Albuquerque, NM USA

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Electronic Materials and Applications 2014
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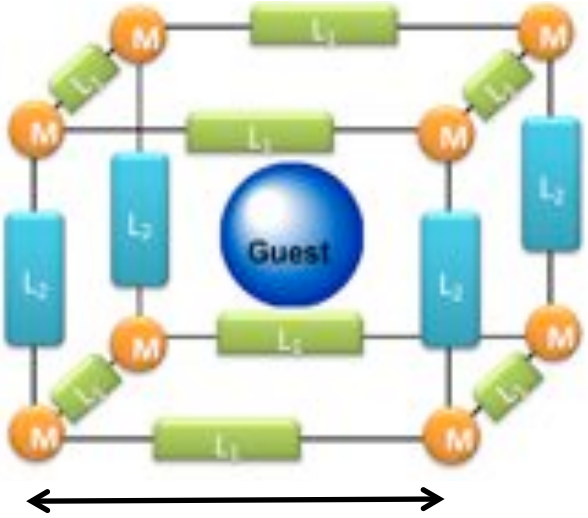
# What the Heck are Popoids?!

"Popoids" were a construction-based toy produced by Tomy in the 1980s…

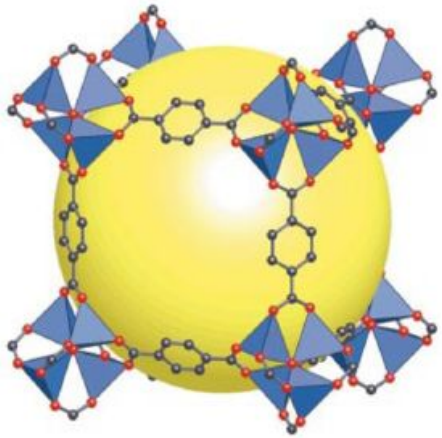
…batteries not included, nor required!

# Metal Organic Frameworks (MOFs): Supramolecular "Popoids"?




0.5-10nm

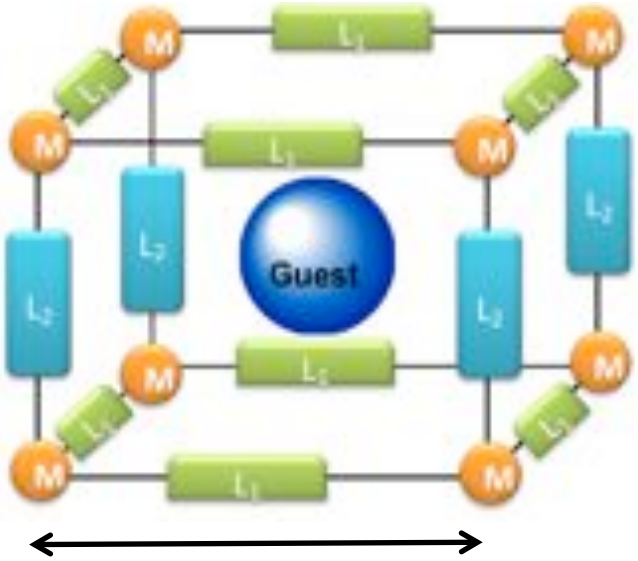
The modular character of the flexible linkers and plastic nodes in popoids suggest parallels to supramolecular materials such as metal organic frameworks.



# What are Metal Organic Frameworks?

## Metal Organic Frameworks (MOFs)

A subset of coordination polymers

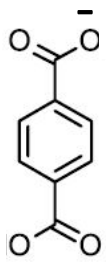
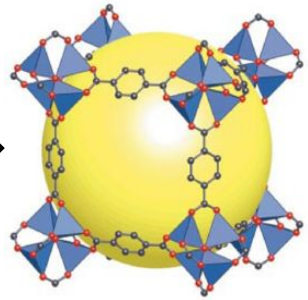



0.5-10nm

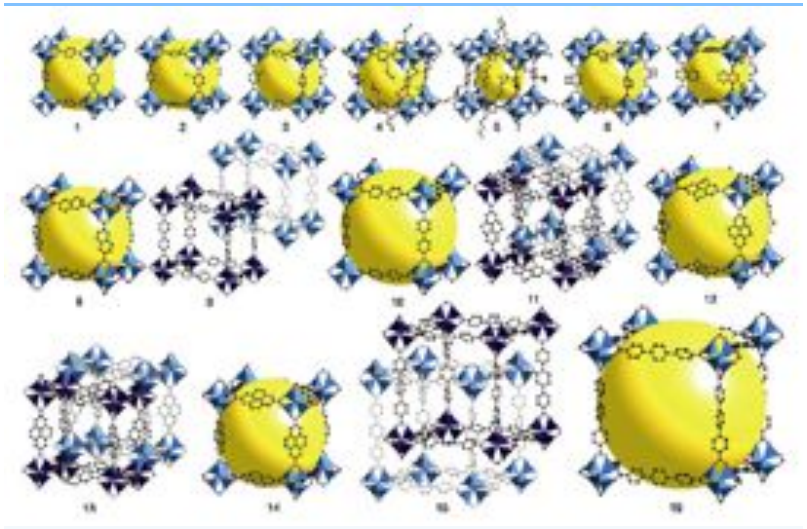
Crystalline MOF structures are composed of metal nodes (M), linkers ($L_1$) and pillars ($L_2$).

The nanoporous character of the MOF allows incorporation of molecular guests, organized on the nanoscale.

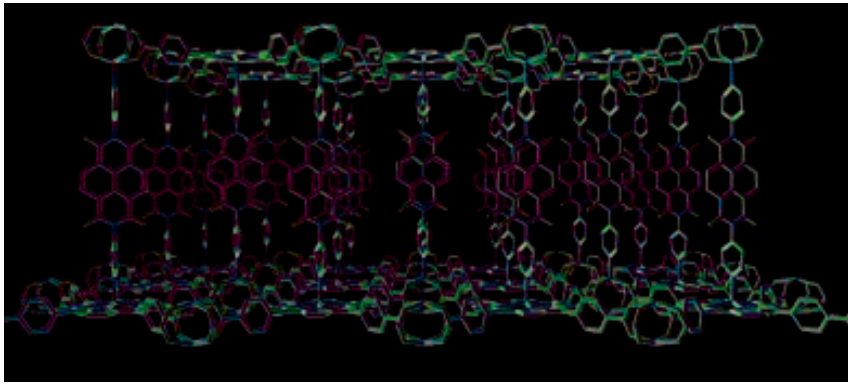
This chemically "modular" system allows for tuning of the structure, properties, and function of these materials.

$Zn^{+2}(NO_3)_2$ +  +  → 

# MOF Building Block Chemistry Determines Crystal Structure

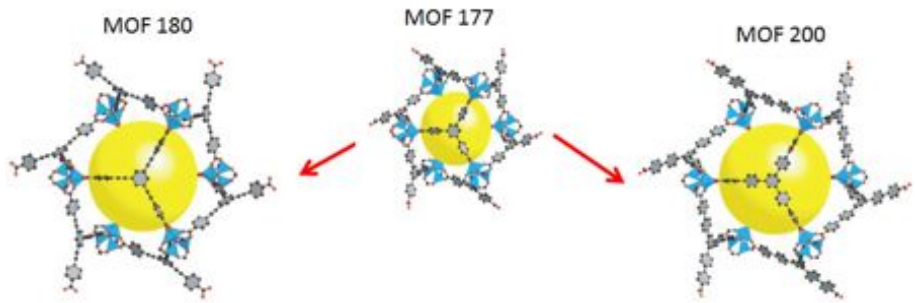


http://yaghi.berkeley.edu/research-MOF.html



Side view of PPF-18

Chung *et al*. *Crystal Growth & Design, Vol. 9, No. 7, 2009*

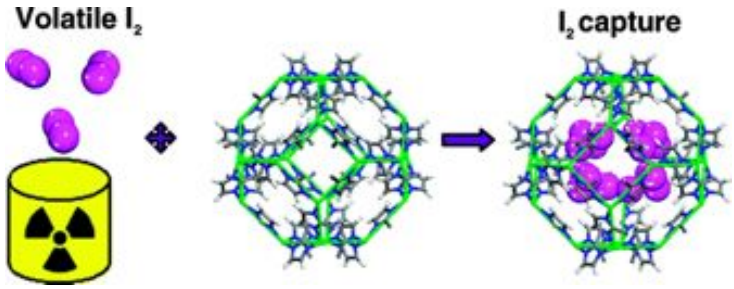



http://www.cchem.berkeley.edu/molsim/teaching/fall2011/CCS/Group7/structure.htm

Varying the "modular" composition of MOFs allows for tremendous flexibility of structure and function.

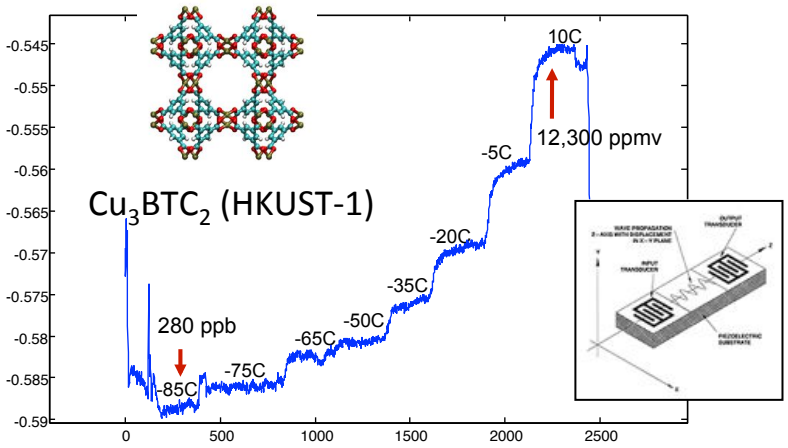
# MOF Applications Span A Wide Range of Fields

## Gas Sorption ($I_2$ capture)




*Sava, et al. JACS*, **2011**, *133* (32), pp 12398–12401

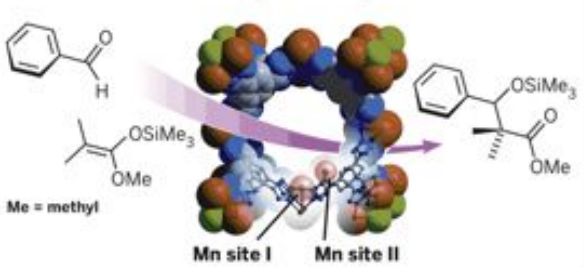
## Sensing ($H_2O$ sensing)




Robinson *et al*. *Anal. Chem.* **84** (2012), 7043

## Catalysis (Mukaiyama aldol synthesis)

Mn-BTT




Horike, *et al. JACS,* **2008**, *130* (18), pp 5854–5855

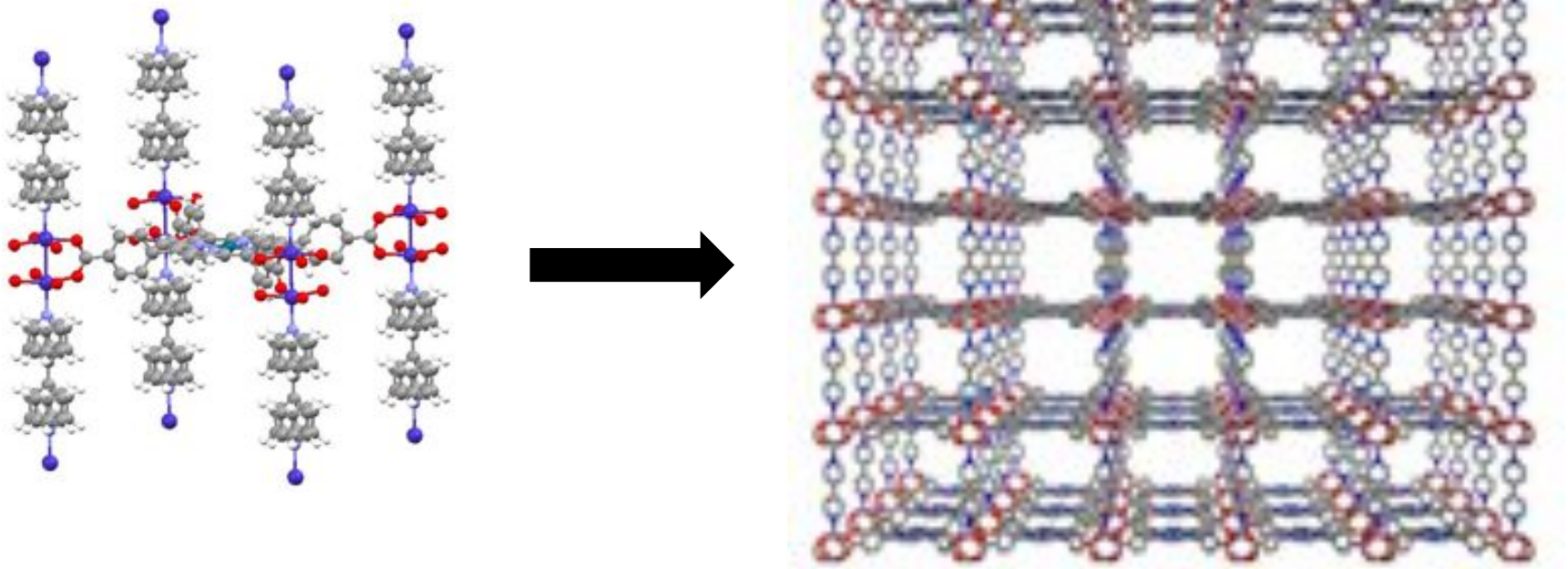
## Electronics/Optoelectronics

?

# Building Photoactive MOFs

## Consider Pillared Porphyrin Frameworks (PPFs)

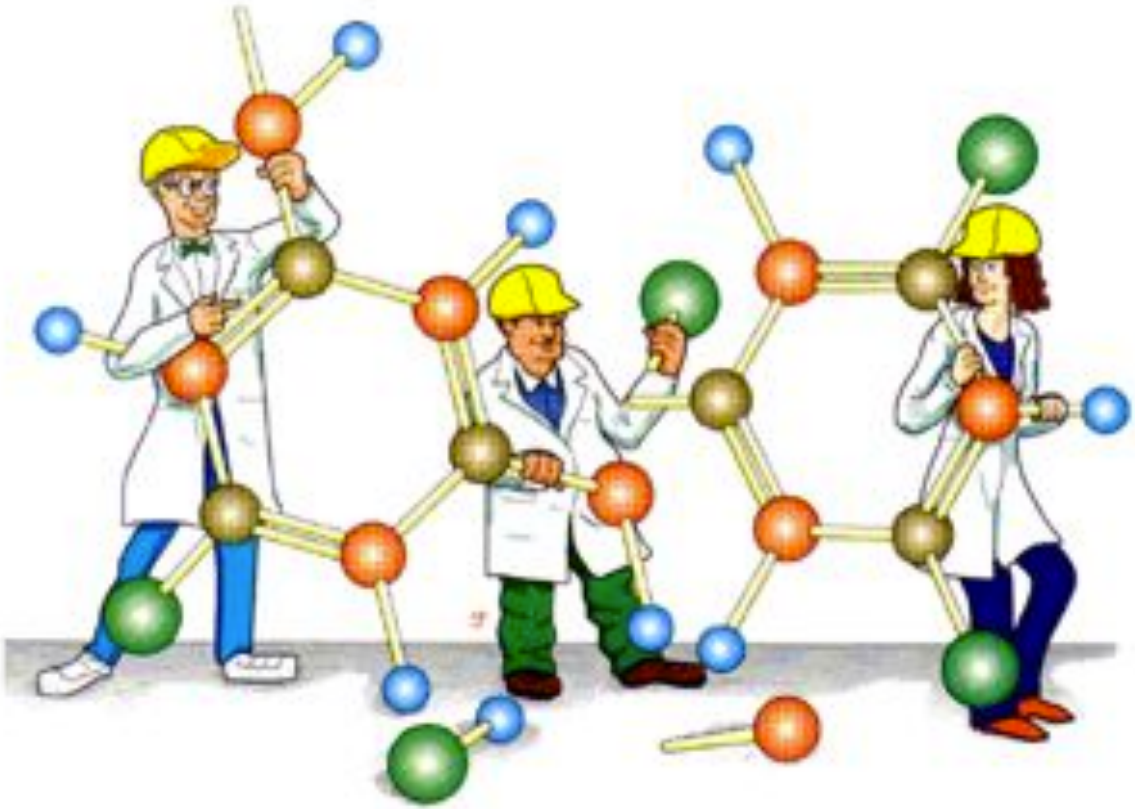
In PPF MOFs, transition metal cations coordinate the assembly of photoactive metalloporphyrins into sheets, stacked atop molecular pillars.



# Technical Challenge

*Can we nucleate and grow these functional materials on technologically-relevant surfaces (e.g., metals, oxides, etc.)?*

# Spoerke Lab Hard at Work…

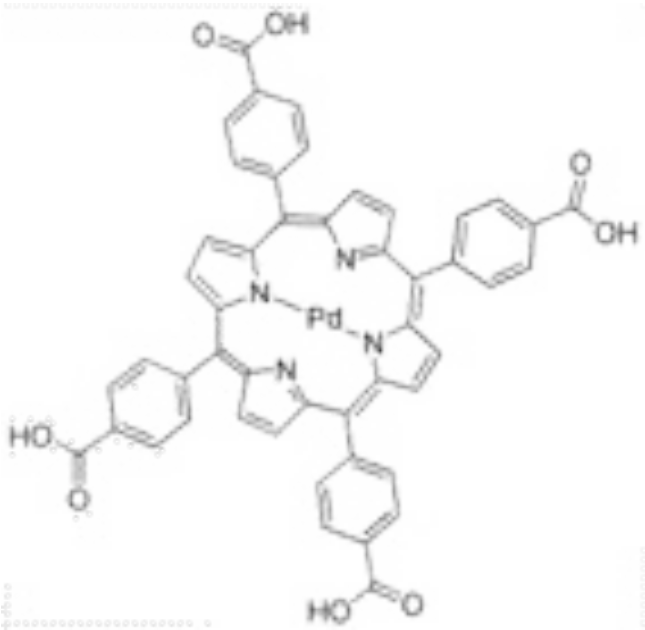


# PPF-5 Synthesis

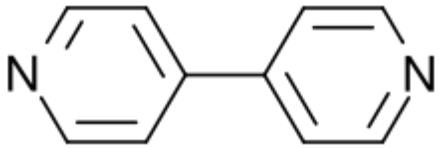
Palladium (II) meso-tetrakis(4-carboxyphenyl) porphine

$Co(NO_3)_2 \cdot 6H_2O$

4,4'-bipyridine



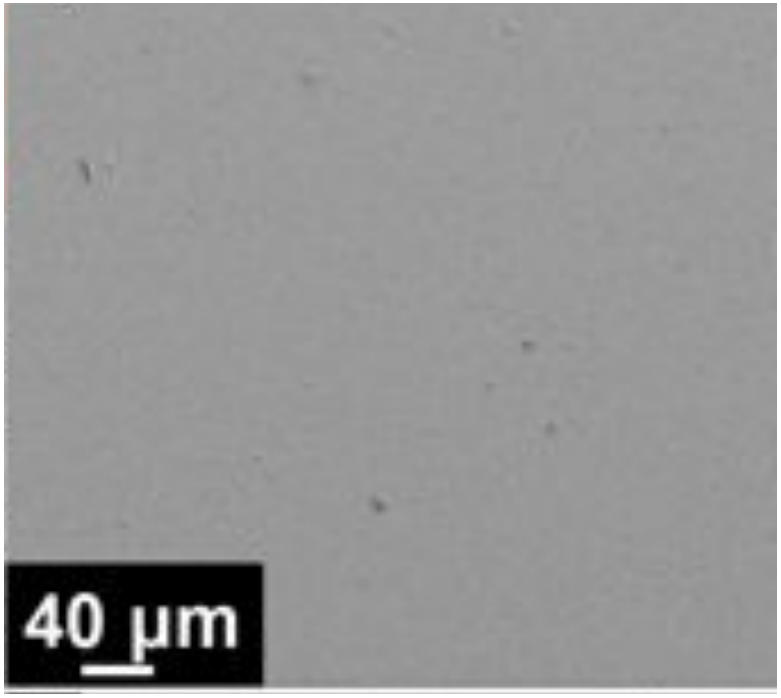

+ $Co^{2+}$ +



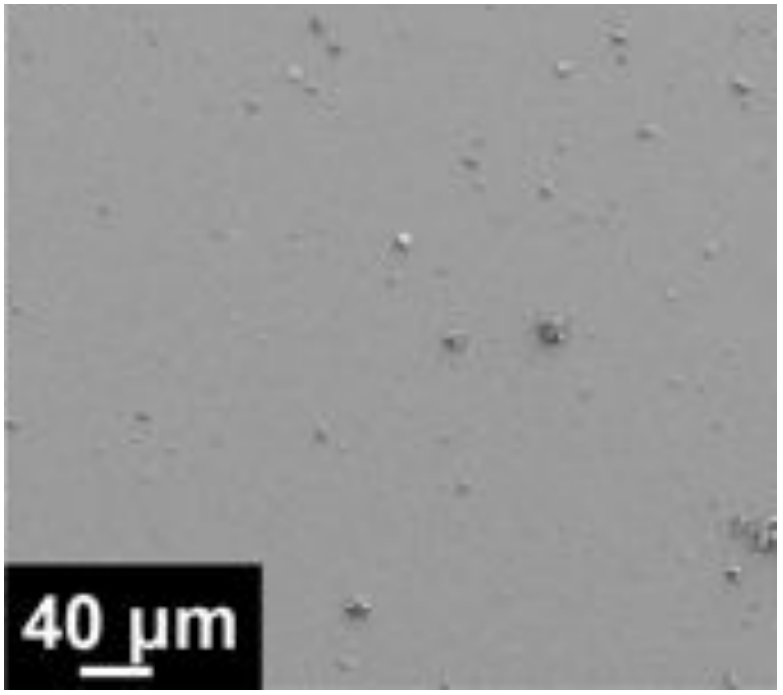

1. Combine reagents in 75% diethyl formamide (DEF), 25% ethanol.
2. Heat 24 hours at 80°C

# PPF-5 Thin Film Growth?

**PPF-5 growth on silicon**




**PPF-5 growth on ALD-titania**

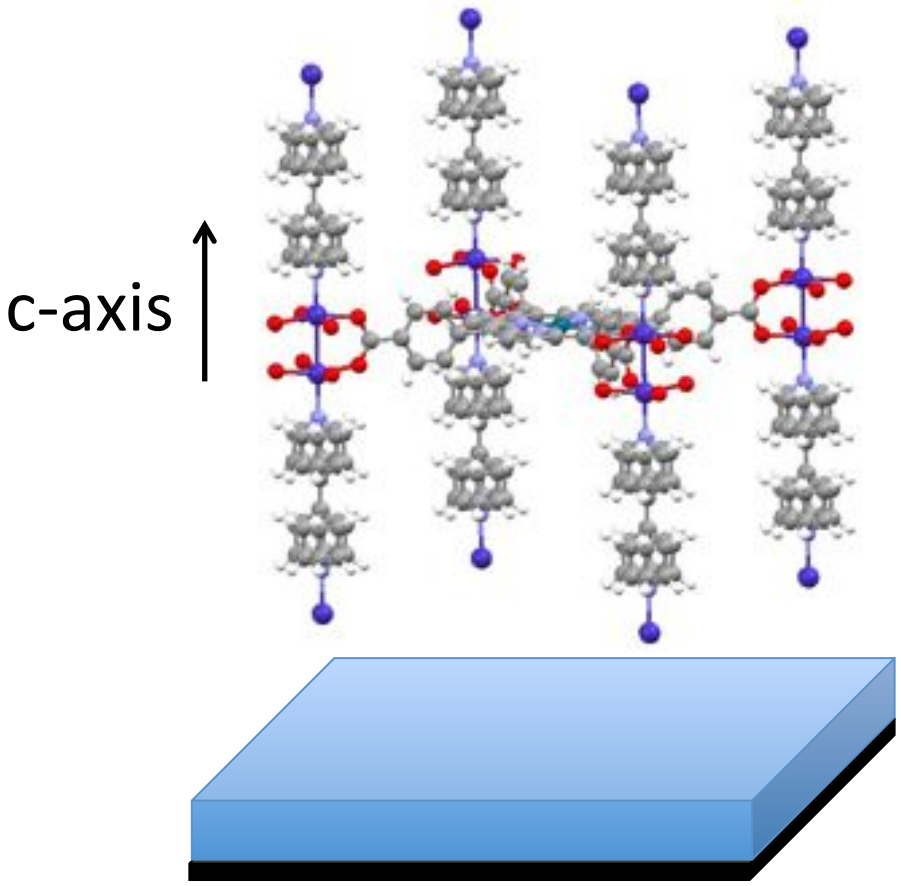


# Technical Challenge

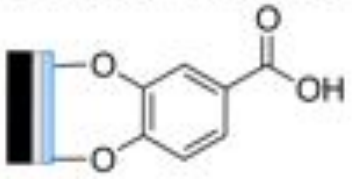
*Can we nucleate and grow these functional materials on technologically-relevant surfaces (e.g., metals, oxides, etc.)?*

Apparently not!

# Acidic Surface Functionalization

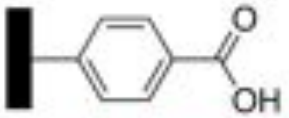



DHBA-modified titania



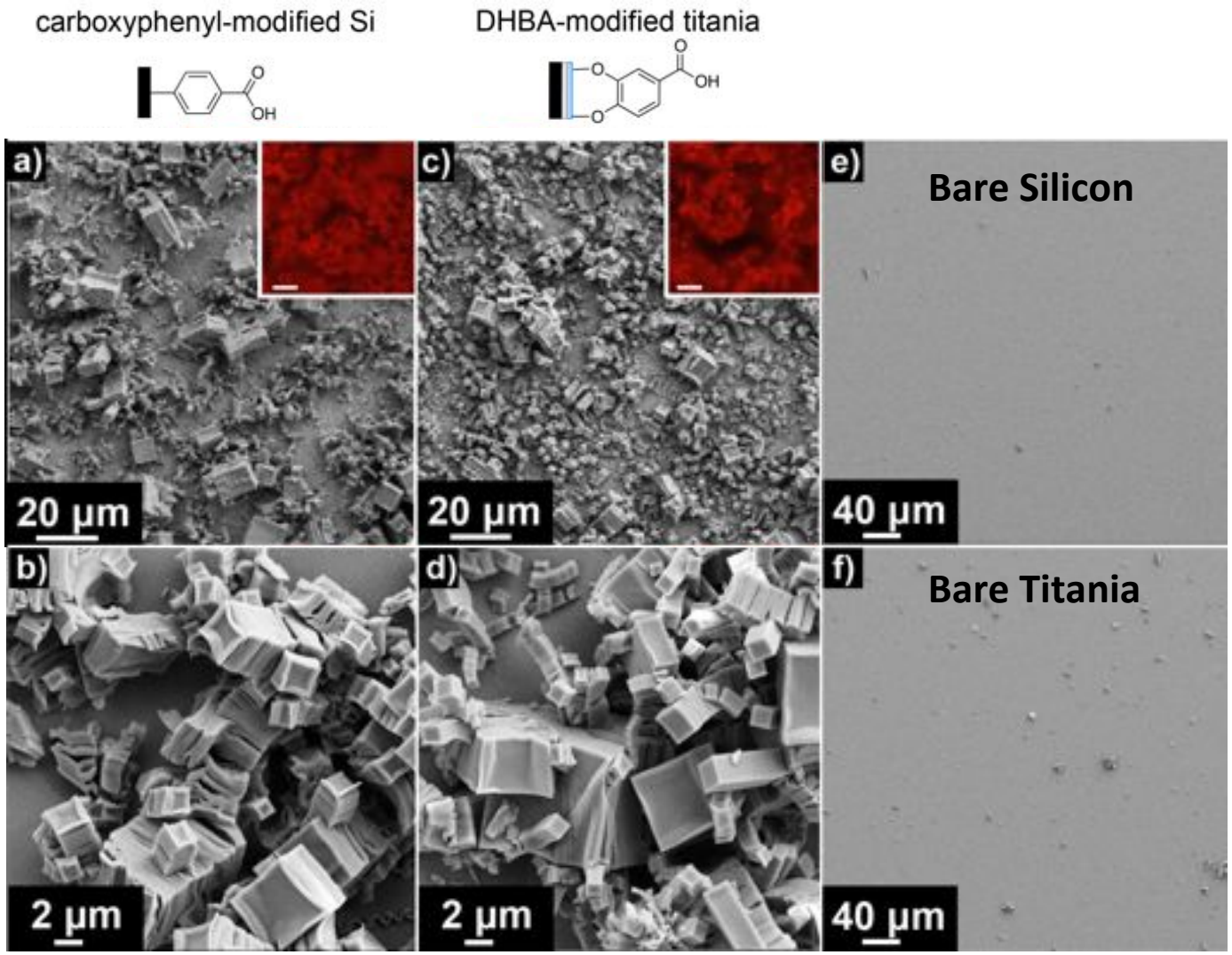

1. Deposit ~20nm titania on Si-wafer by atomic layer deposition (ALD)
2. Functionalize with 3,4-dihydroxybenzoic acid (DHBA)

carboxyphenyl-modified Si

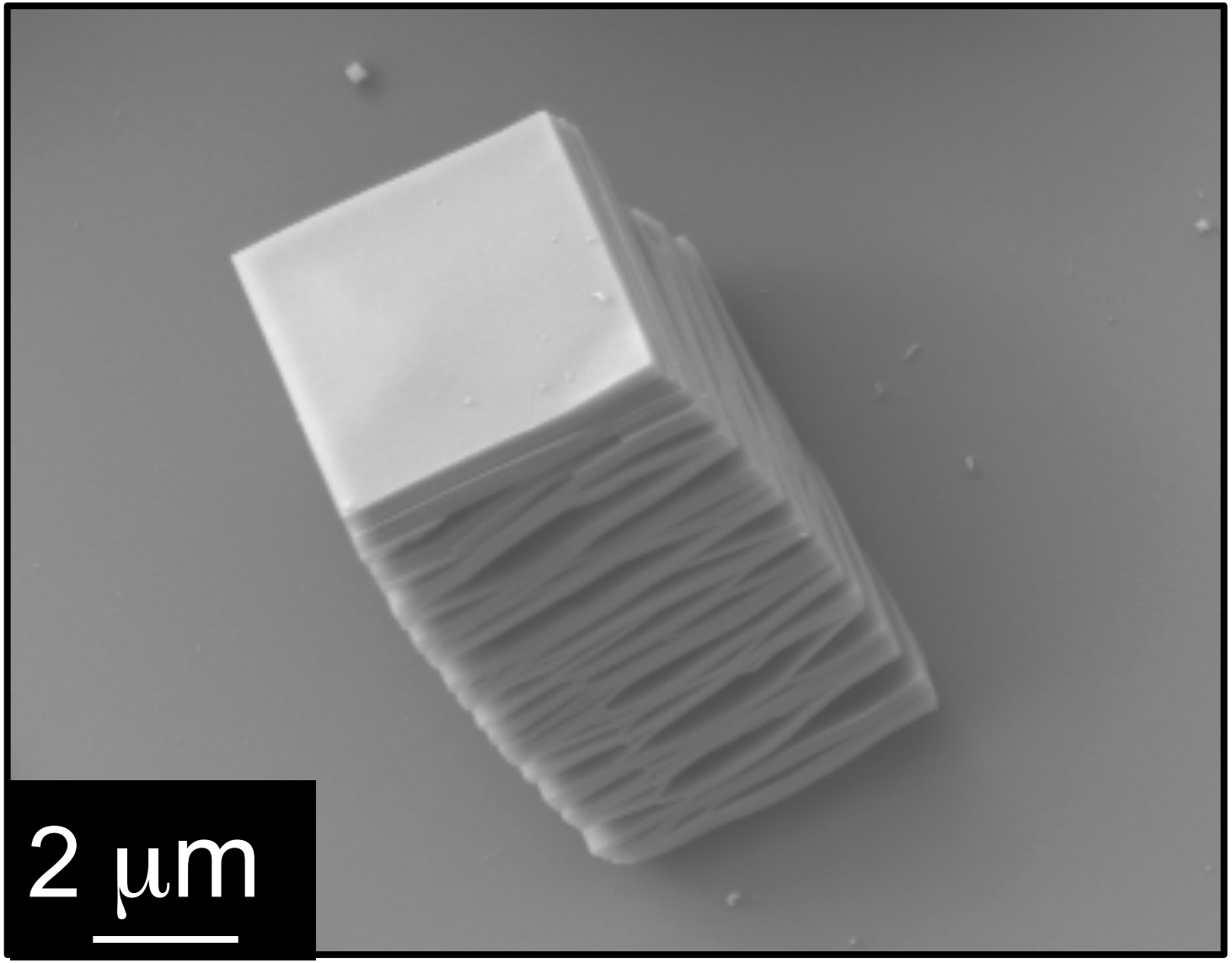



1. Remove native $SiO_2$ with 5% HF
2. Functionalize with p-carboxyphenyldiazonium tetrafluoroborate

# Acid Functionalization Promotes Dramatic Improvement in PPF-5 Nucleation



# PPF-5 Crystals Grow as “Nanostacks”

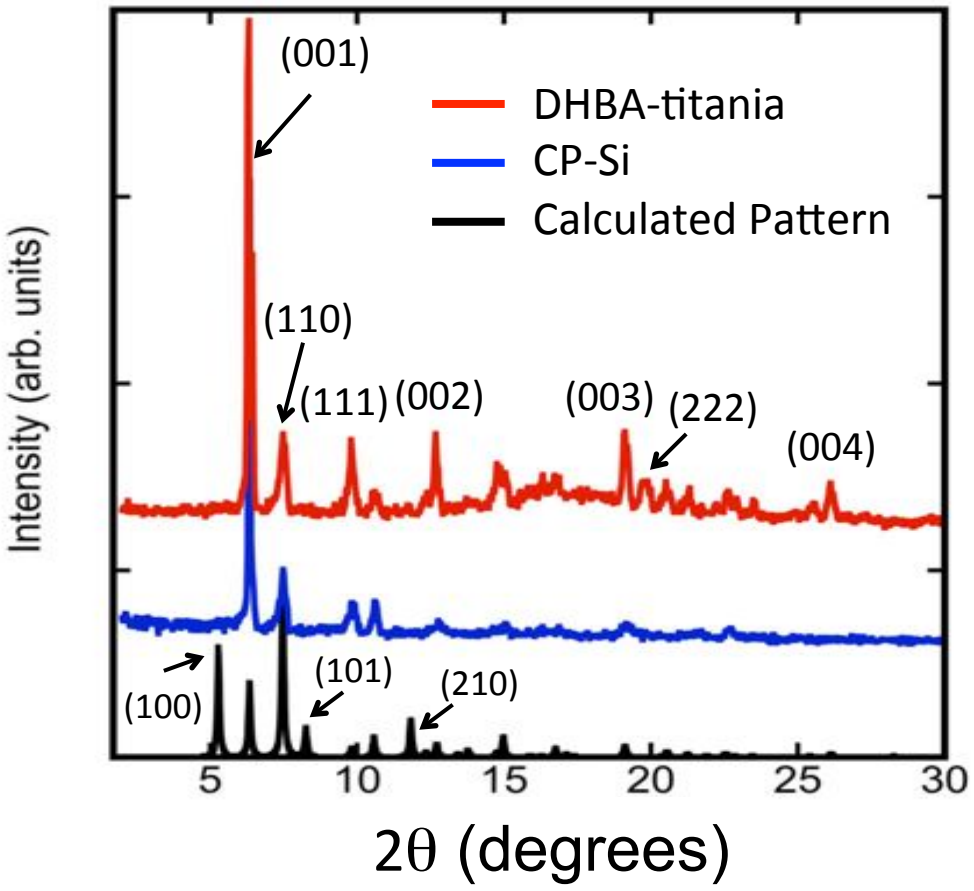


# Technical Challenge

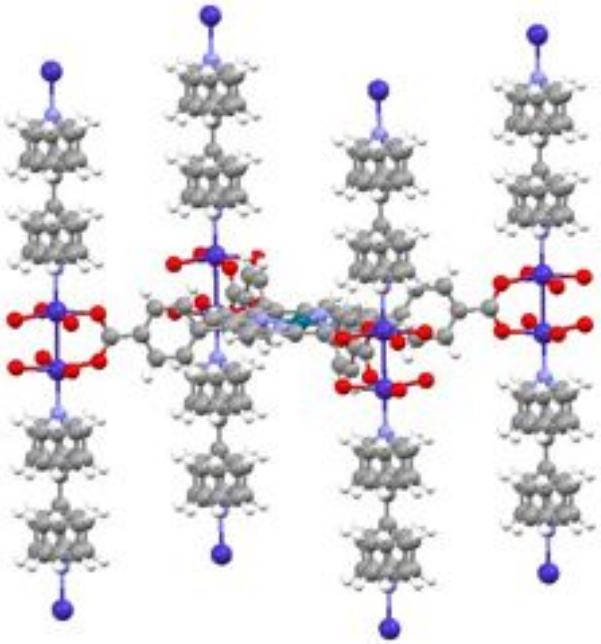
*Can we nucleate and grow these functional materials on technologically-relevant surfaces (e.g., metals, oxides, etc.)?*

Yes, if substrates are acid-functionalized!

# PPF-5 Crystallography



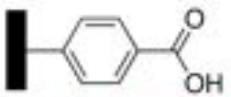

c-axis



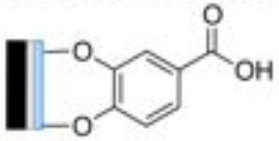
*XRD reveals considerable crystallographic orientation of acid-nucleated PPF-5.*

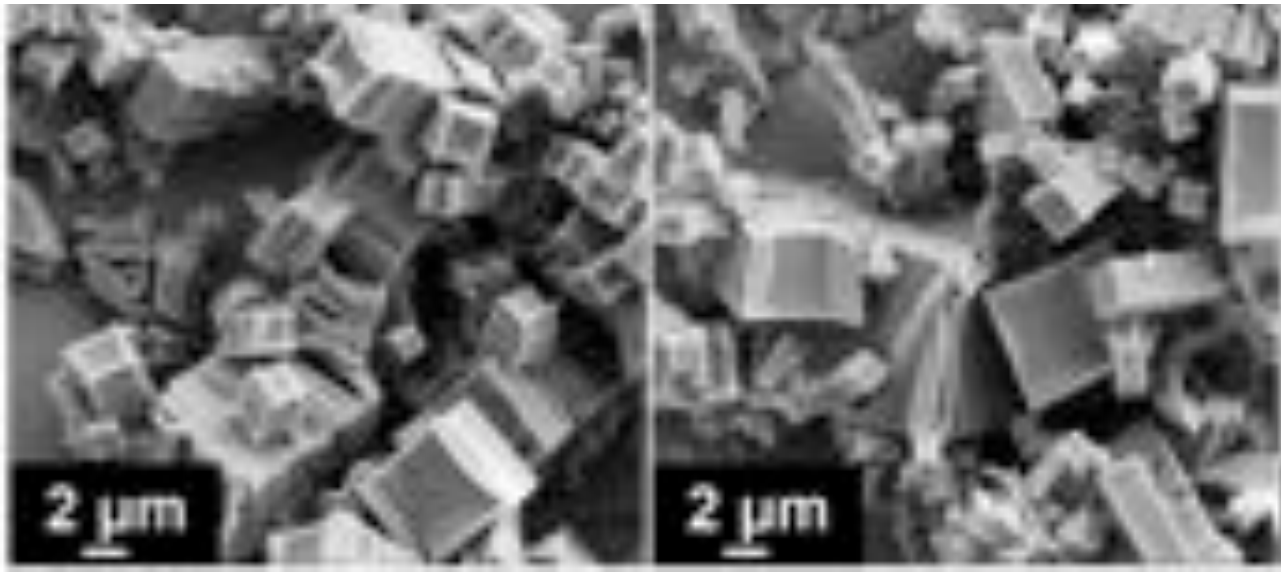
# Linking PPF-5 Diffraction and Morphology

carboxyphenyl-modified Si



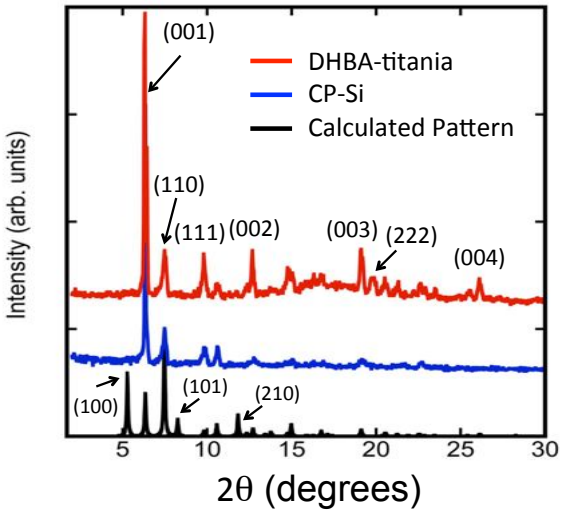

DHBA-modified titania



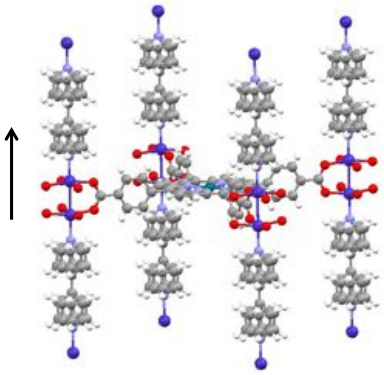




*Are these apparently jumbled crystal stacks really randomly oriented?*

# Linking PPF-5 Diffraction and Morphology



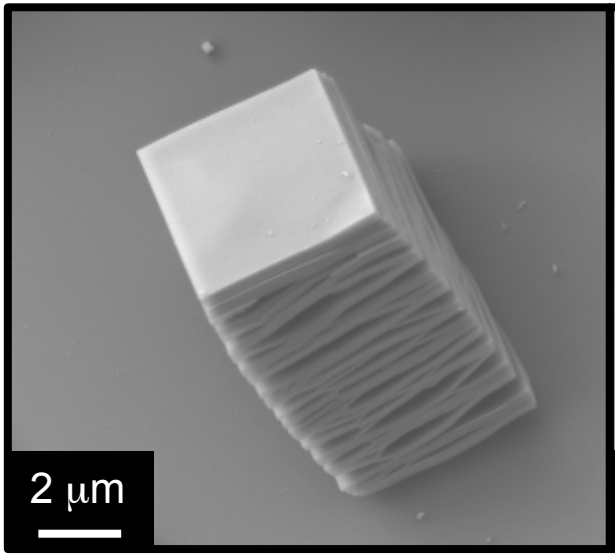

c-axis

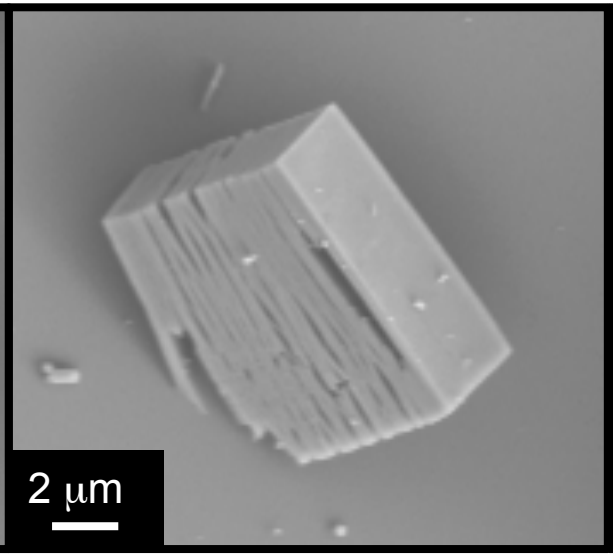


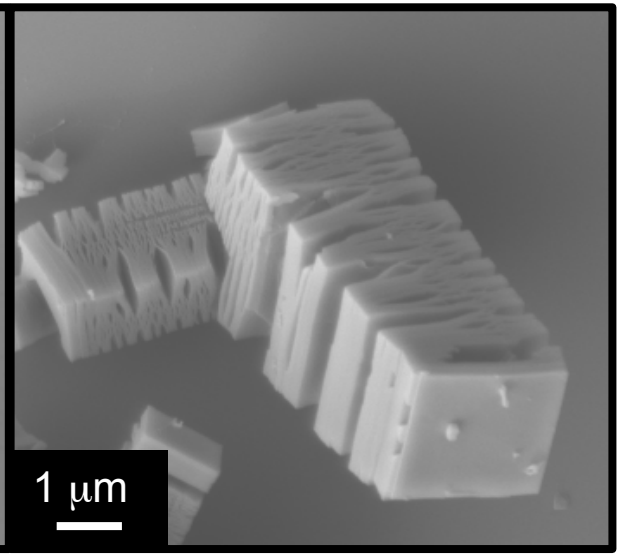
**Preferred Growth Directions:**

[001]
[111]
[110]

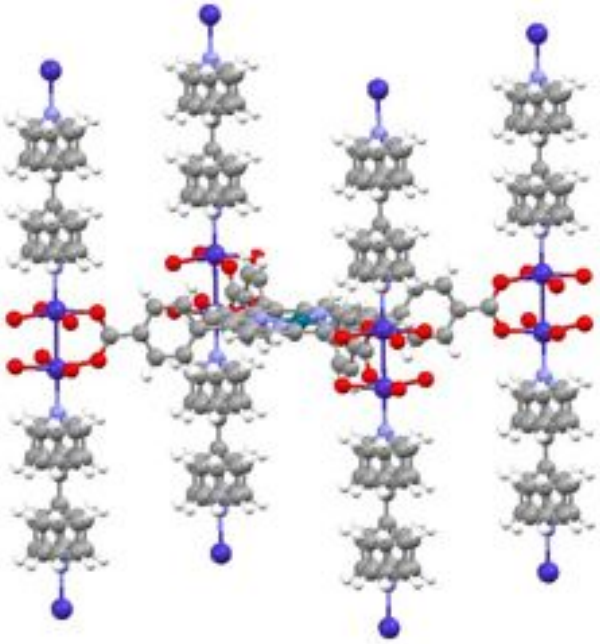
**[001]** **[111]** **[110],[111]**

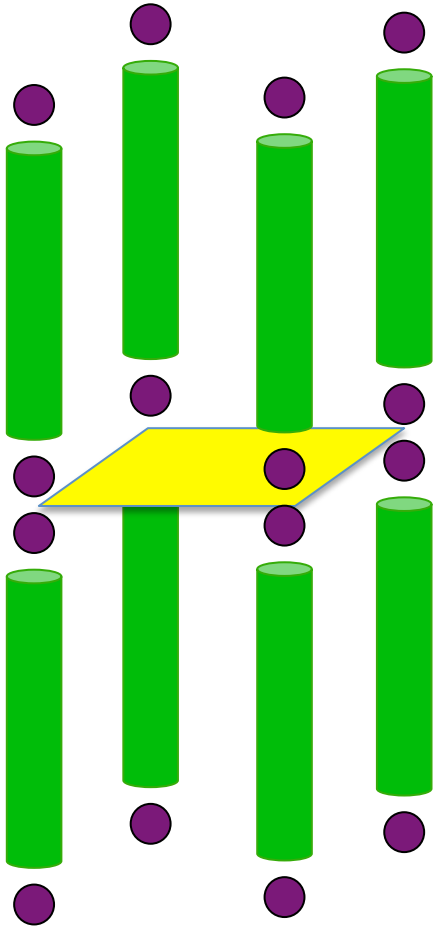


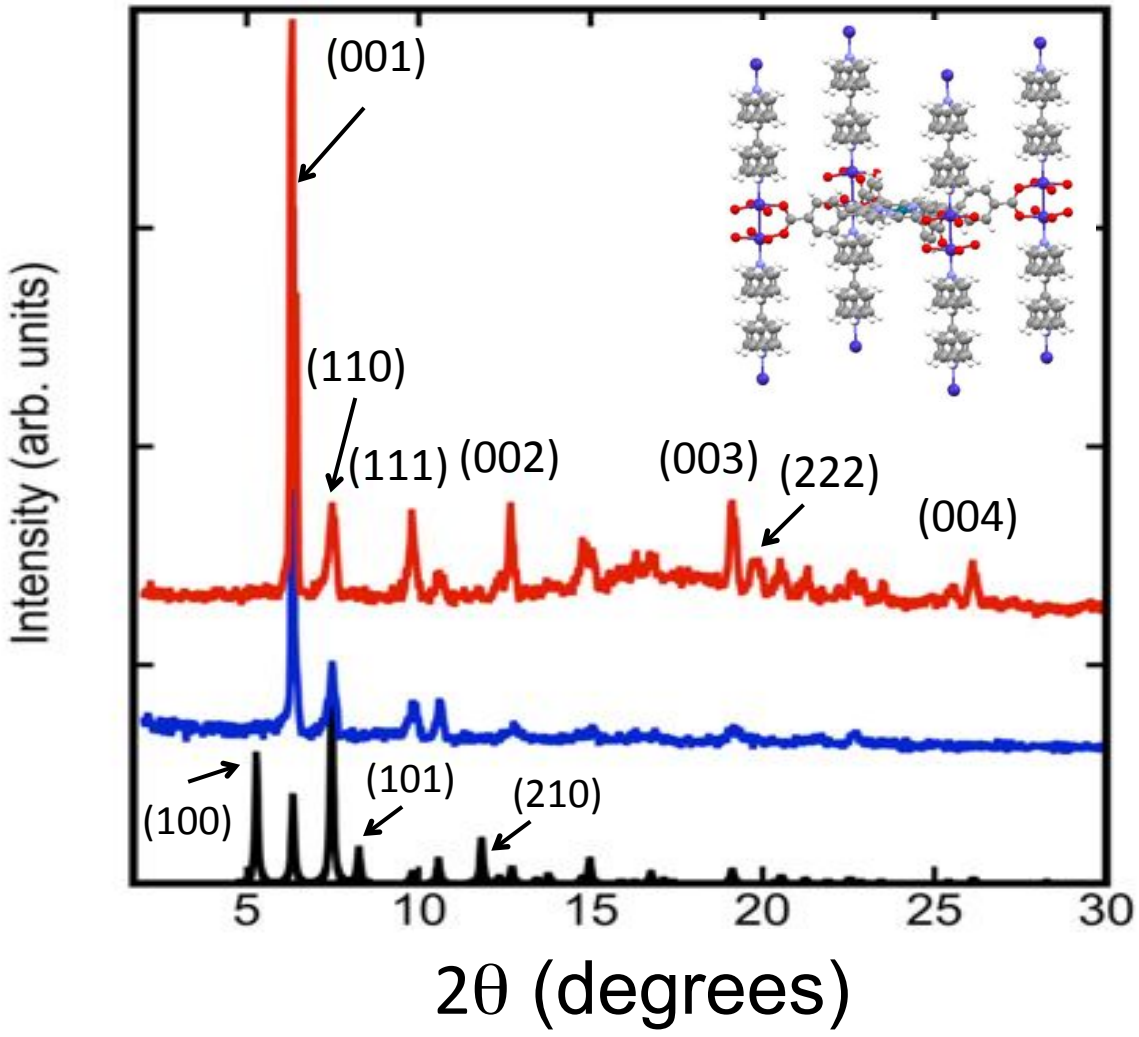



# Simplifying PPF-5





# PPF-5 Crystallographic Orientation



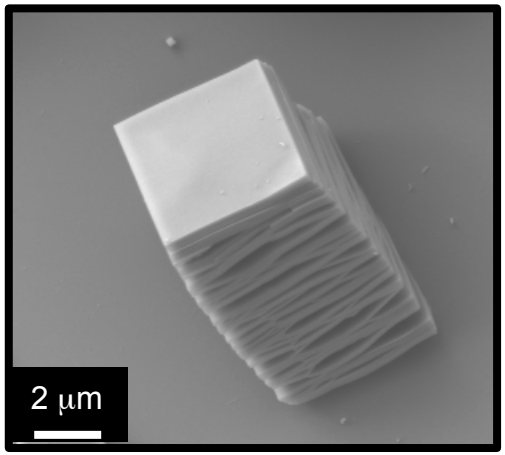

**Preferred Growth Directions:**

[001]
[111]
[110]

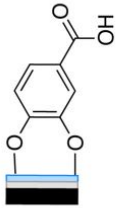
**Absent reflections:**

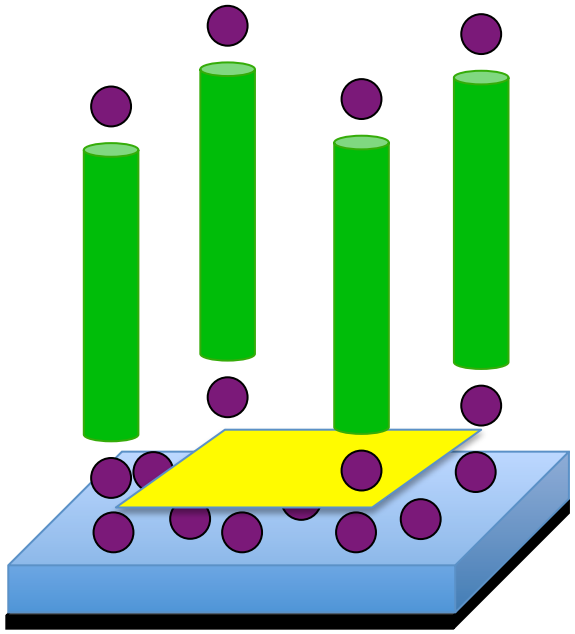
(100)
(101)
(201)

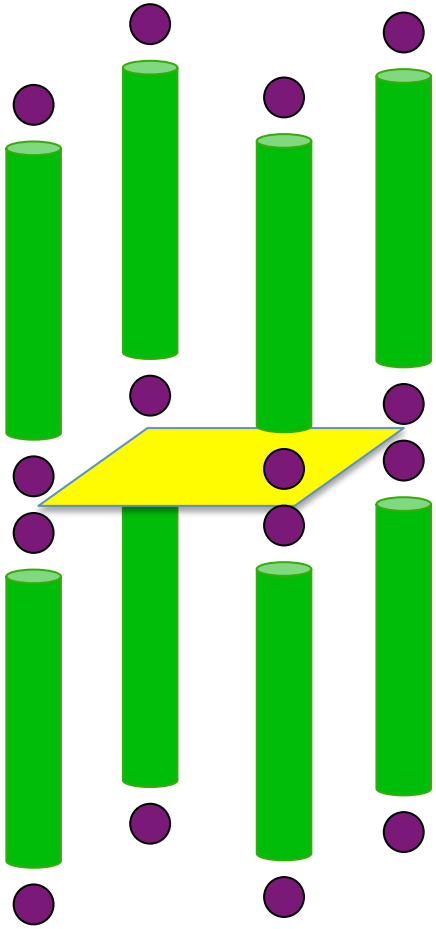
# Making Sense of PPF-5 Crystallography



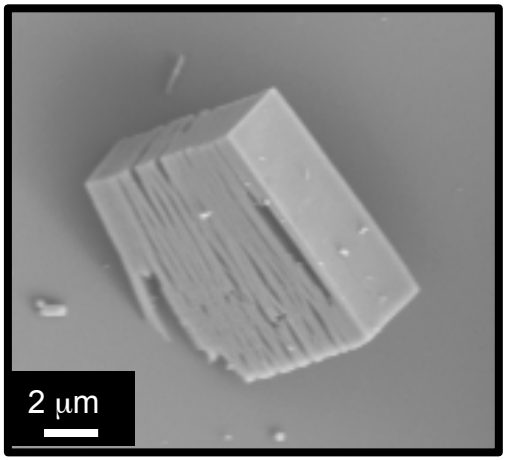

(001) Orientation



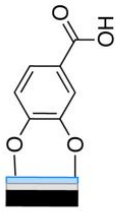



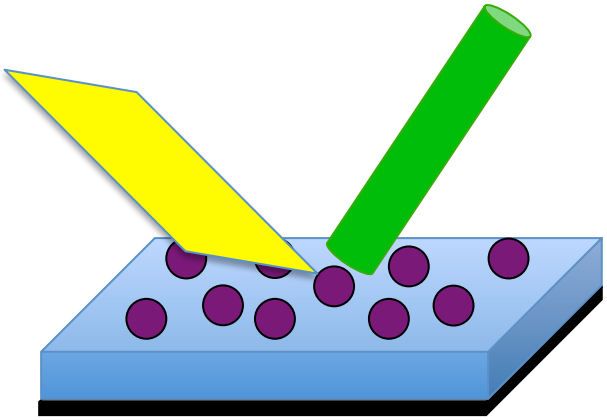


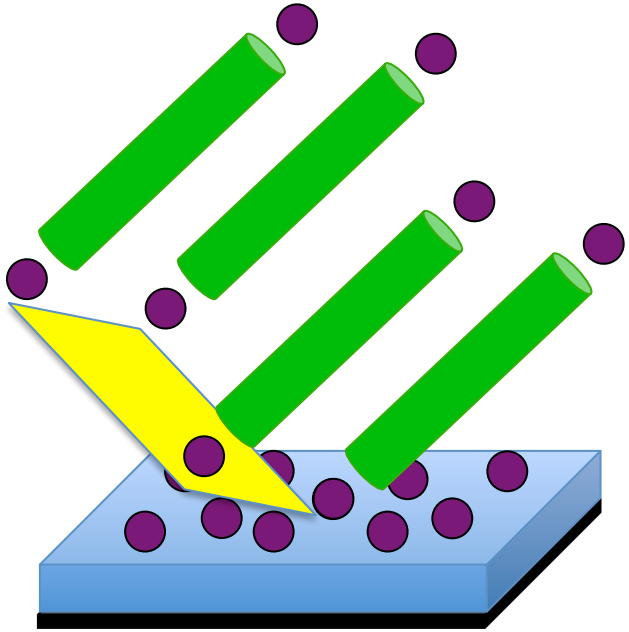
# Making Sense of PPF-5 Crystallography



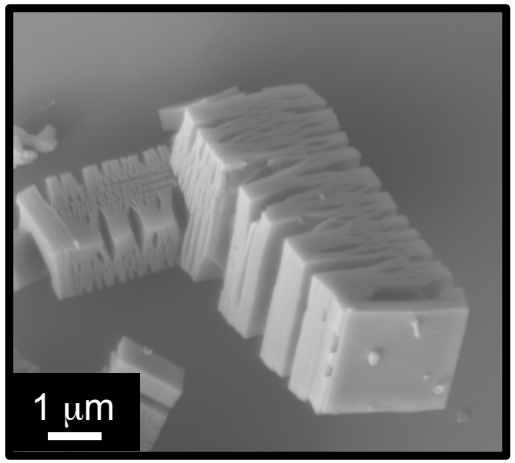

(111) Orientation



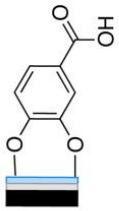



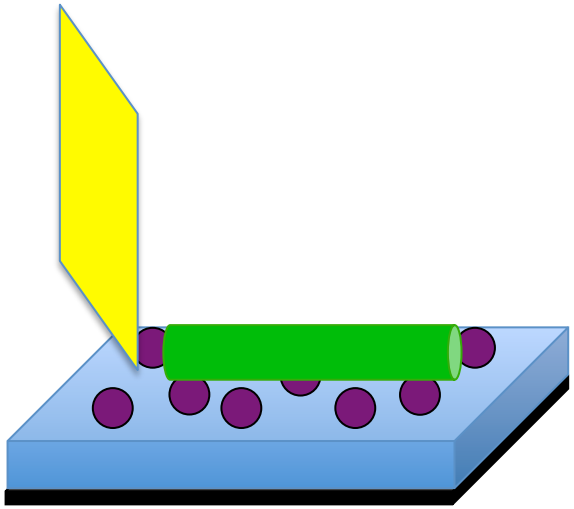


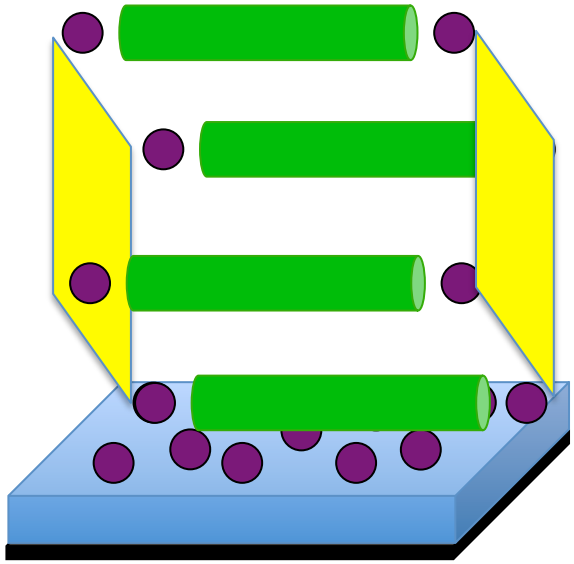
# Making Sense of PPF-5 Crystallography




(110) Orientation

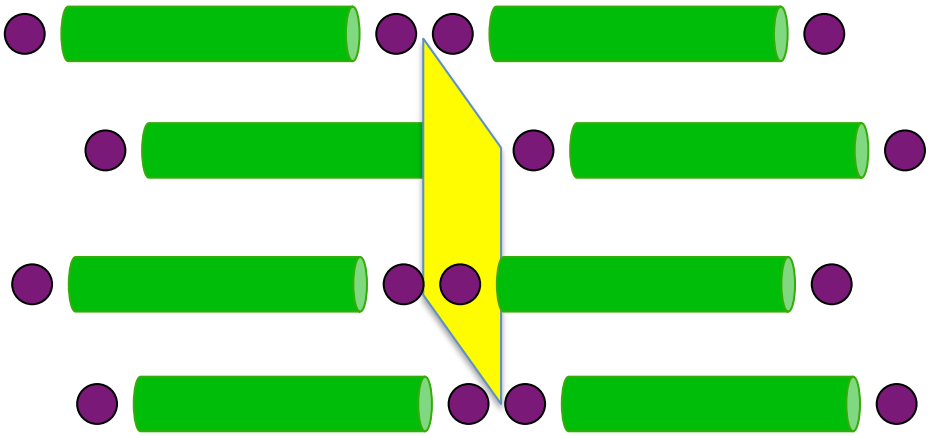


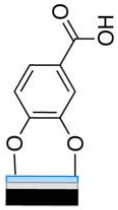



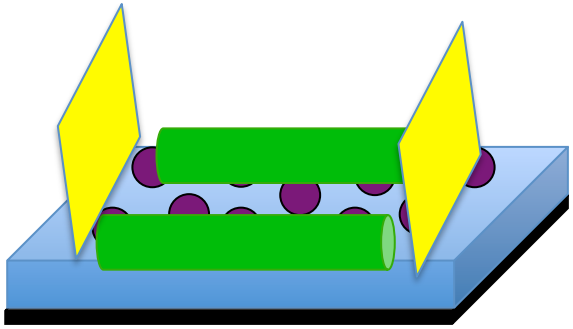


# Absent Reflections

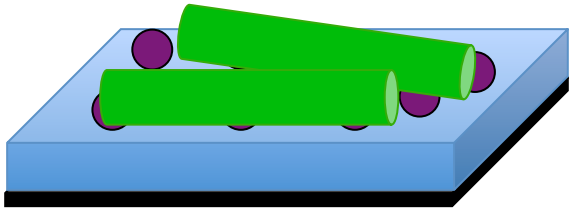
(100) is not observed…





Not likely…



Will not promote (100) growth…

# Wrapping Up…

- Porphyrin-based MOFs may be viewed as “modular” supramolecular structures:  popoids?
- Nucleation of these materials on “technological” surfaces would enable enhanced utility.
- Acid functionalization of silicon and titania surfaces promotes selective nucleation and growth of PPF-5 nanostacks.
- The modular nature of the linkers, cation nodes, and porphyrin paddlewheels leads to preferential crystallographic orientation.
- Similar surface-functionalization processes may be used to control the growth and orientation of other supramolecular materials on technological surfaces.

# Thanks!

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- **U.S. DOE Energy Efficiency and Renewable Energy (Sunshot)**
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# Backup Slides

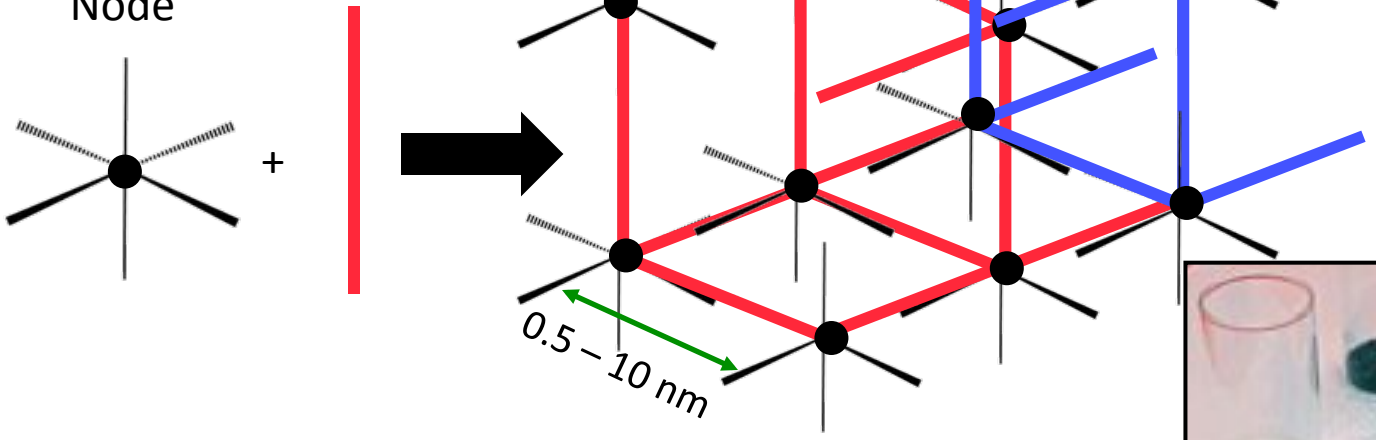
# What are Metal-Organic-Frameworks (MOFs)?

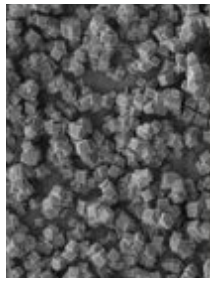
**A subset of "Coordination Polymers"**

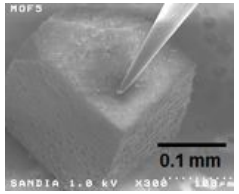
**Crystalline (therefore ordered), nanoporous structure**

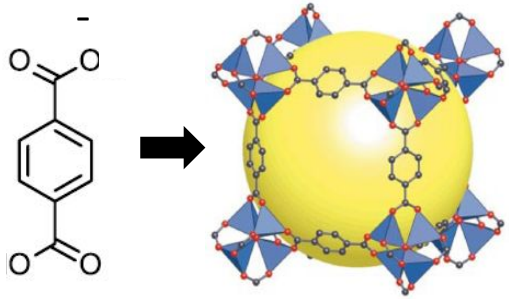
Metal "Node"

Organic "linker"

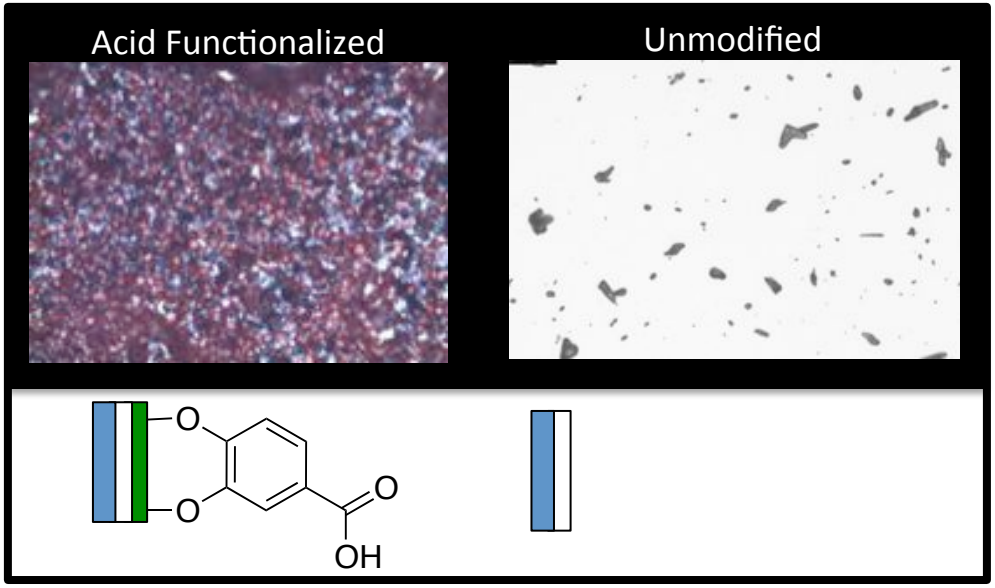





$Zn^{+2}(NO_3)_2$ + 

**Ultrahigh surface areas (record ~ 7000 $m^2/g$)**




D.V. Gough, et al. *ACS Appl. Mater. Interfaces* (2013) In review

# A new starting point for device applications: thin films

**In-situ methods**

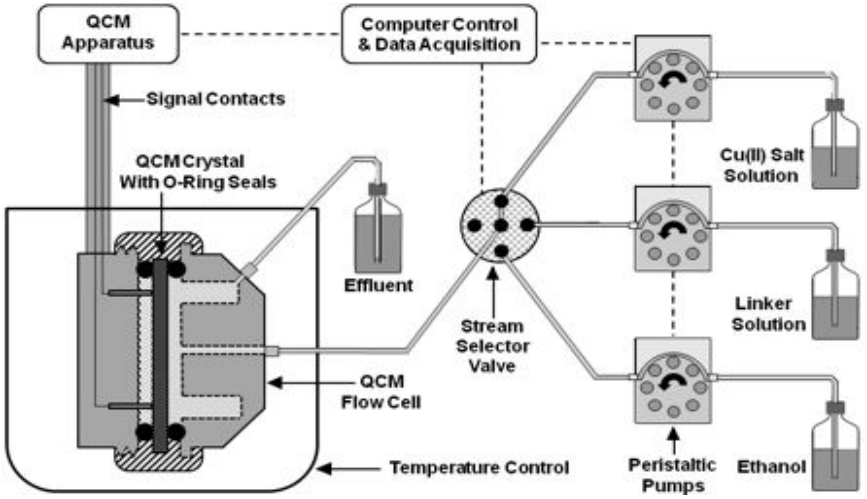
- Layer-by-layer (Fischer, Woell)
- Gel-layer (Bein et al. *Angew. Chem.* 2010)
- Electrochemical/redox (DeVoos *Chem.Mat.* 2009)

**Seeding methods**

- Nanocrystals
- Langmuir-Blodgett (Makiura et al. *Nat.Mat.*2010)

**Ex-situ methods**

- Colloidal synthesis (A. Demessence et al. *Chem.Comm.* 2009)




Schematic representation of automated MOF film growth/QCM capability

# Step-by-step synthesis of PPF-5