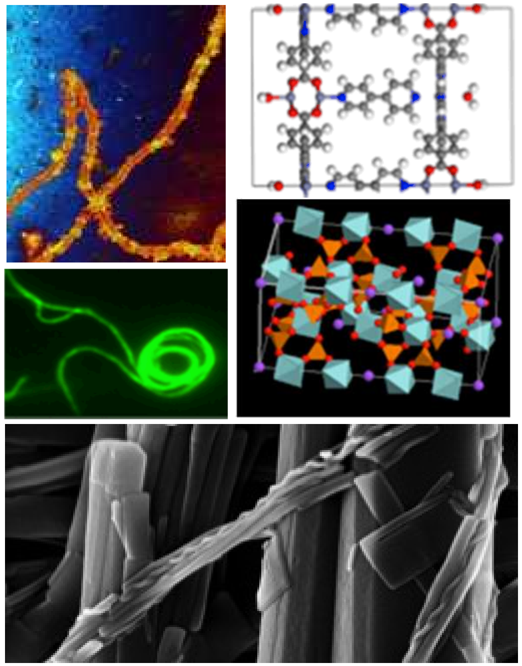

Thinking Small: Adopting Molecular Approaches to Tackle Big Problems

SAND2016-5299C

Erik D. Spoerke, Ph.D.

University of New Mexico
Student Research Day

April 16, 2016
Albuquerque, NM

Sandia National Laboratories

Exceptional service in the national interest

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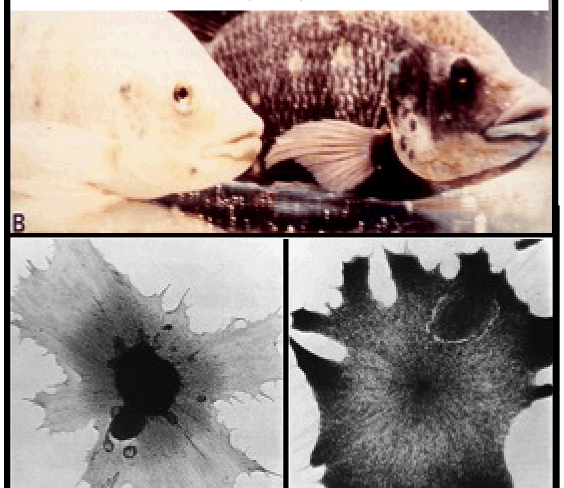
Discussion Roadmap…

- Bio-Inspiration for Bottom-up Assembly
- Adaptive, reconfigurable, and non-equilibrium materials assemblies
- Molecular engineering ion conducting ceramics
  - Na-batteries
  - Chemical Separations
- Molecular Materials for Solar Cells

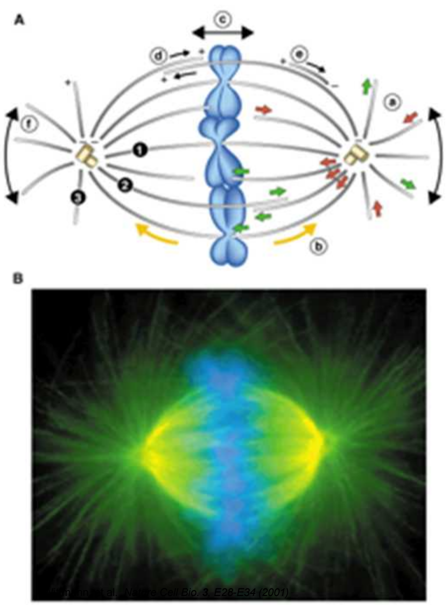
Microtubules (MTs) Impact a Huge Range of Biological Functions

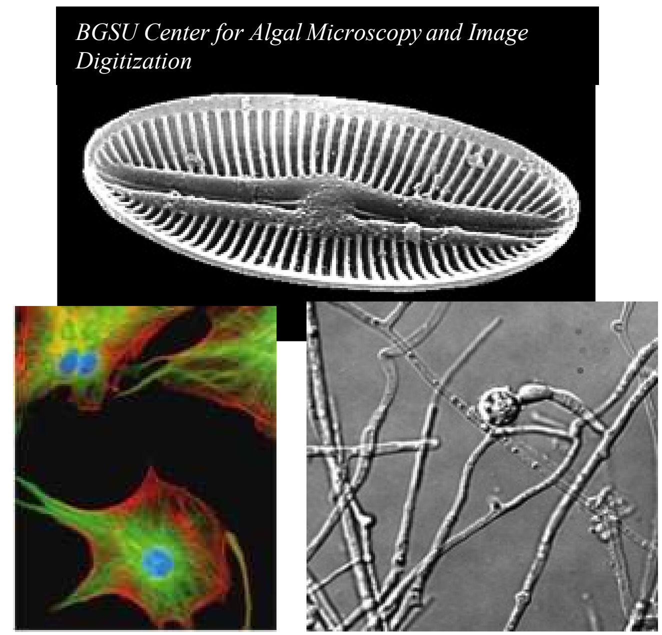
The remarkably diverse and highly scalable functions of microtubules are enabled by their dynamic, biologically programmable nanostructure and chemistry.

*L. Haimo and C. Thaler, BioEssays 16, 727-733 (1994).



Adapted from: http://wilkes-fs1.wilkes.edu/~terzaghi/BIO-226/lectures/24.html





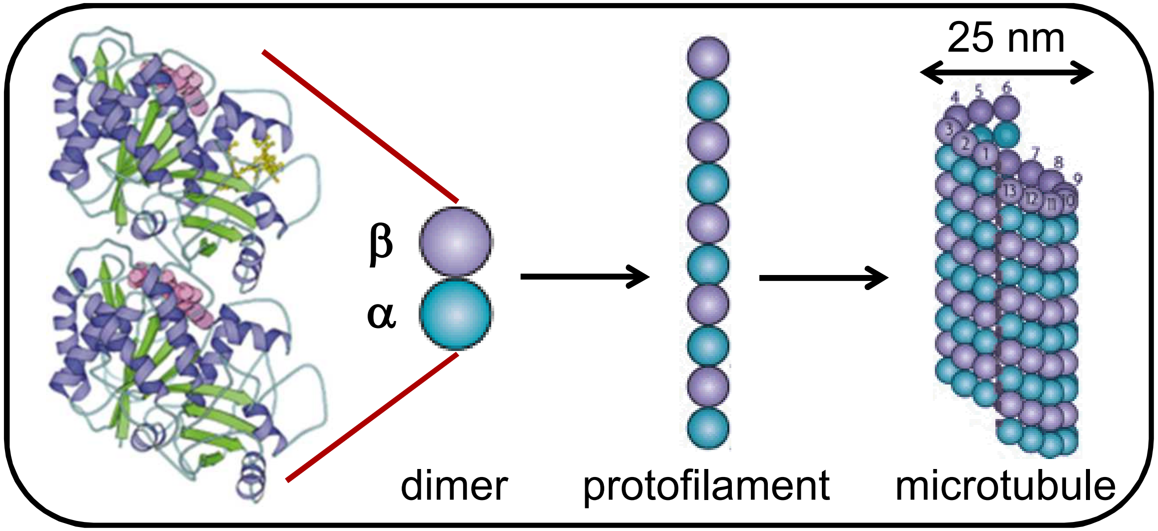
http://probes.invitrogen.com/

Adaptive reorganization of pigment granules in melanocytes

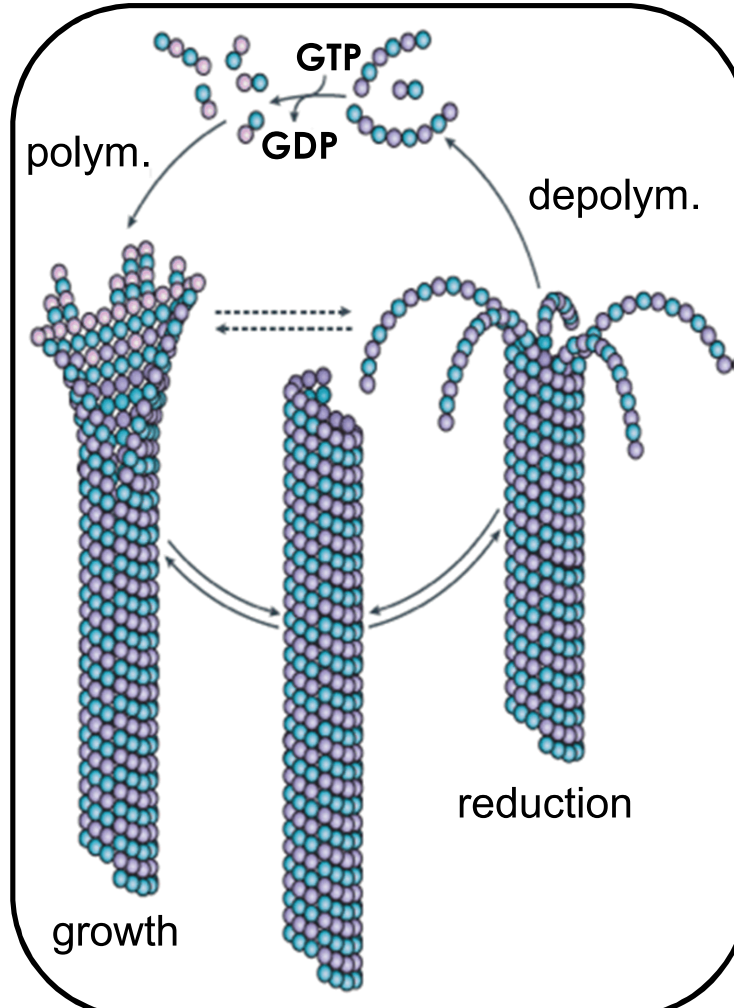
Chromosome positioning and separation during cell splitting

Trafficking of vesicles and macromolecule building blocks

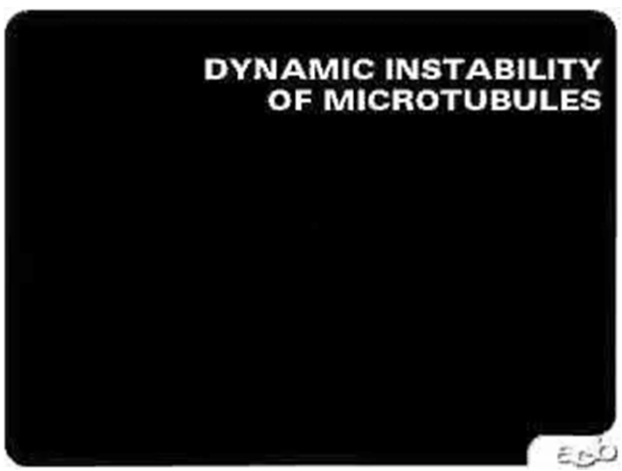
Microtubules: Dynamic, Organized Protein Assemblies



Akhmanova, A.; Steinmetz, M.O. *Nat. Rev. Mol Cell. Bio*. **2008**, *9*, 309.
Nogales, E. *Annu. Rev. Biochem*. **2000**, *69*, 277.



Akhmanova, A.; Steinmetz, M.O. *Nat. Rev. Mol. Cell. Bio*. **2008**, *9*, 309.

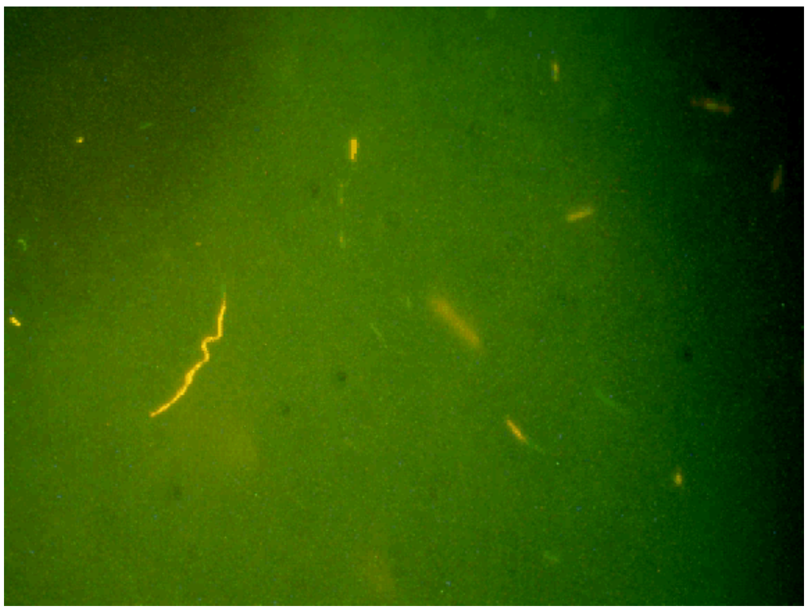


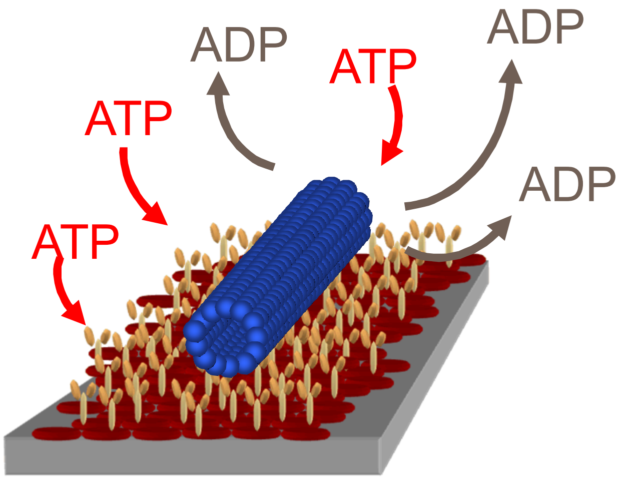
Our Challenge:

Exploit/mimic concepts central to MT form and function in synthetic materials to enable novel new materials behaviors.

Kinesin-based Nanocomposites

How can we use selective, dynamic cooperation between MTs and motor proteins to create nanocomposite assemblies?



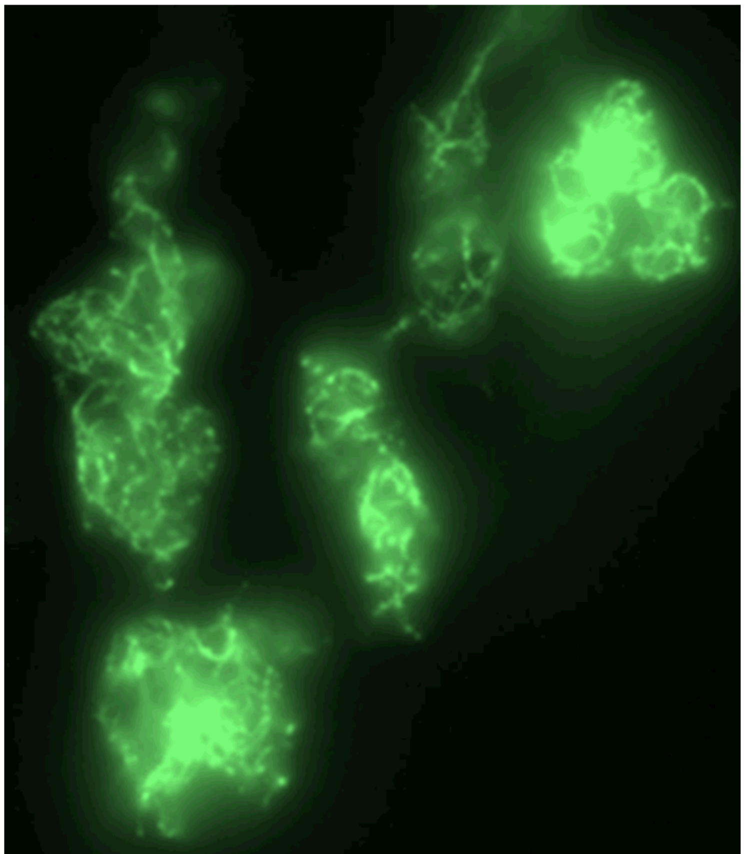


"Inverted (Gliding) Motility" relies on array of surface-bound inverted kinesins to capture and transport MTs over a surface.

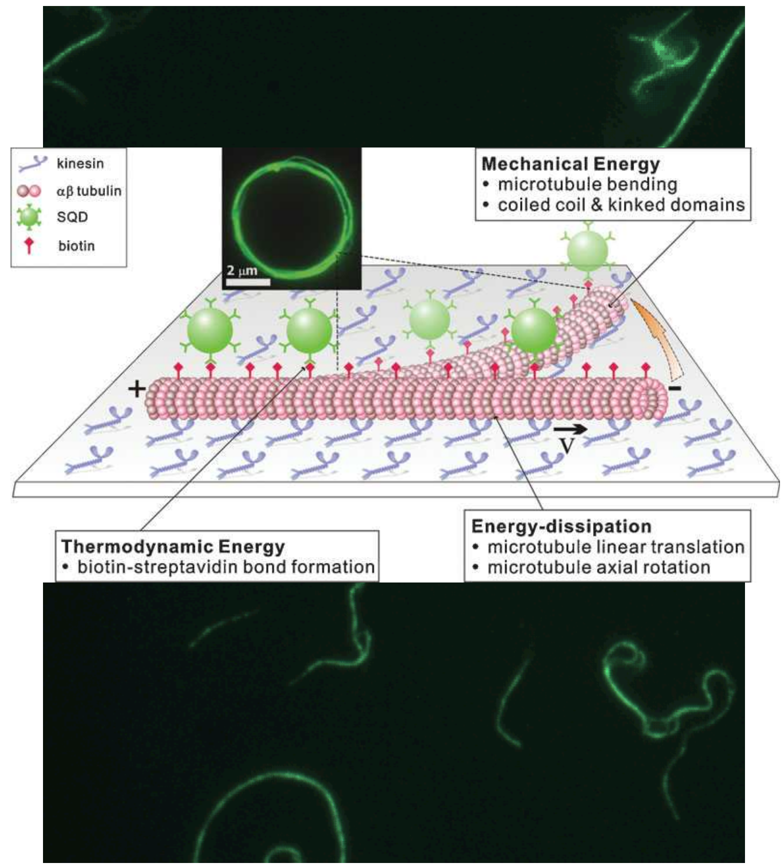
Influence of *Active* Assembly

When biotinylated MTs are combined with streptavidin linkers, active assembly has a profound impact on materials structure

Random Assembly

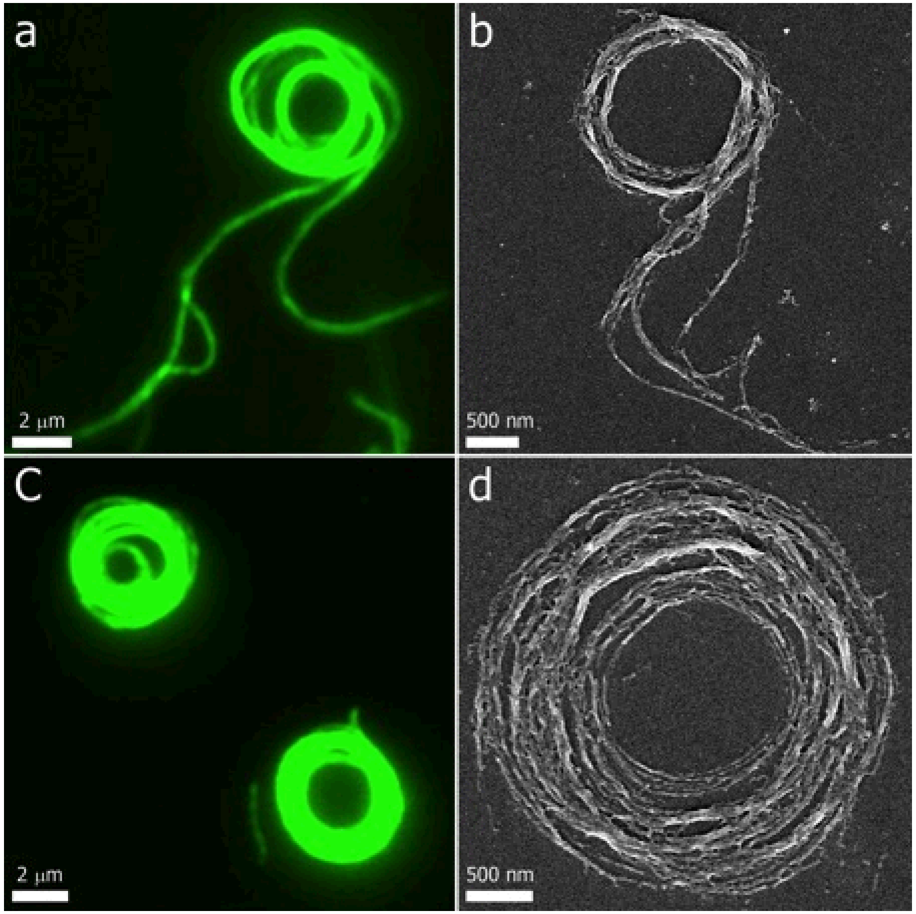


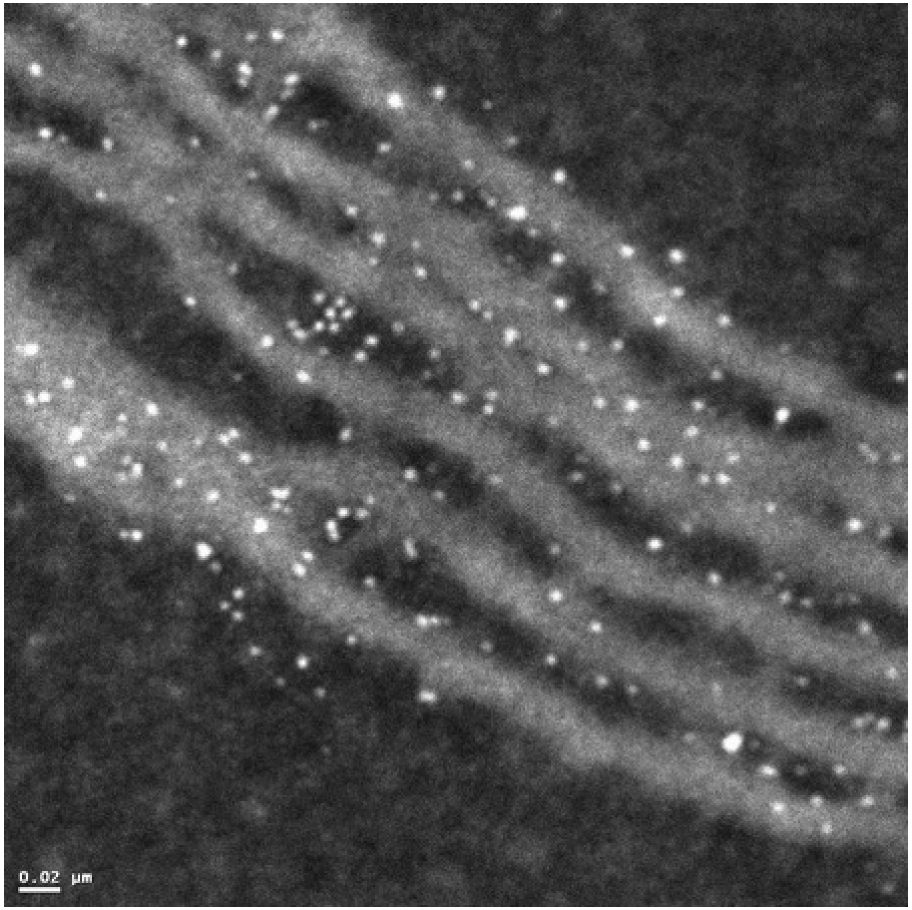
Kinesin-driven Active Assembly



Revealing Nanocomposite Structure

Electron microscopy reveals the local structure of MTs and SQDs in nanocomposite circles

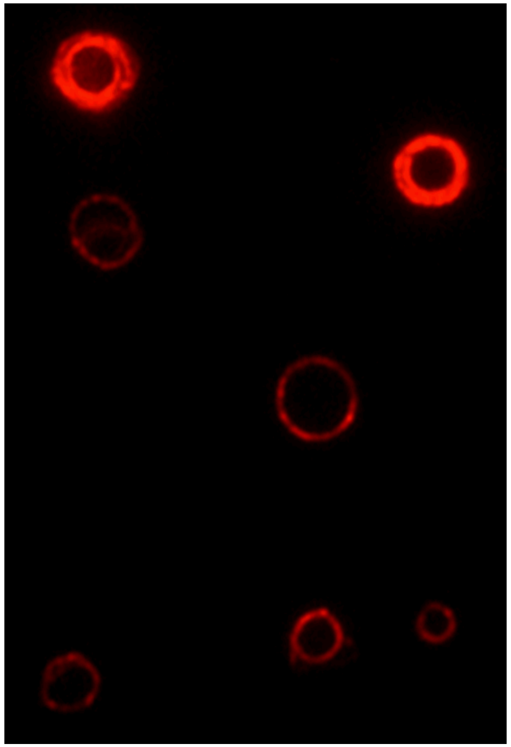




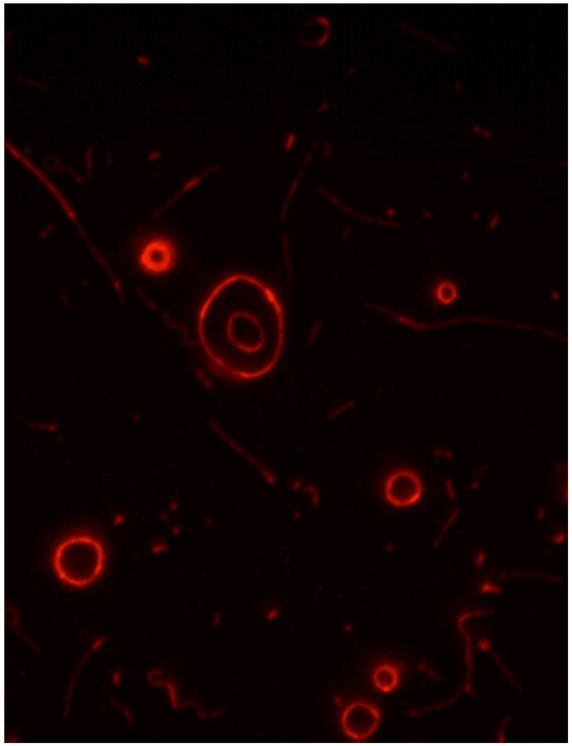
Dynamic Nanocomposite Diversity

Multiple materials/chemistries may be used to form MT ring nanocomposites.

Streptavidin-QDs

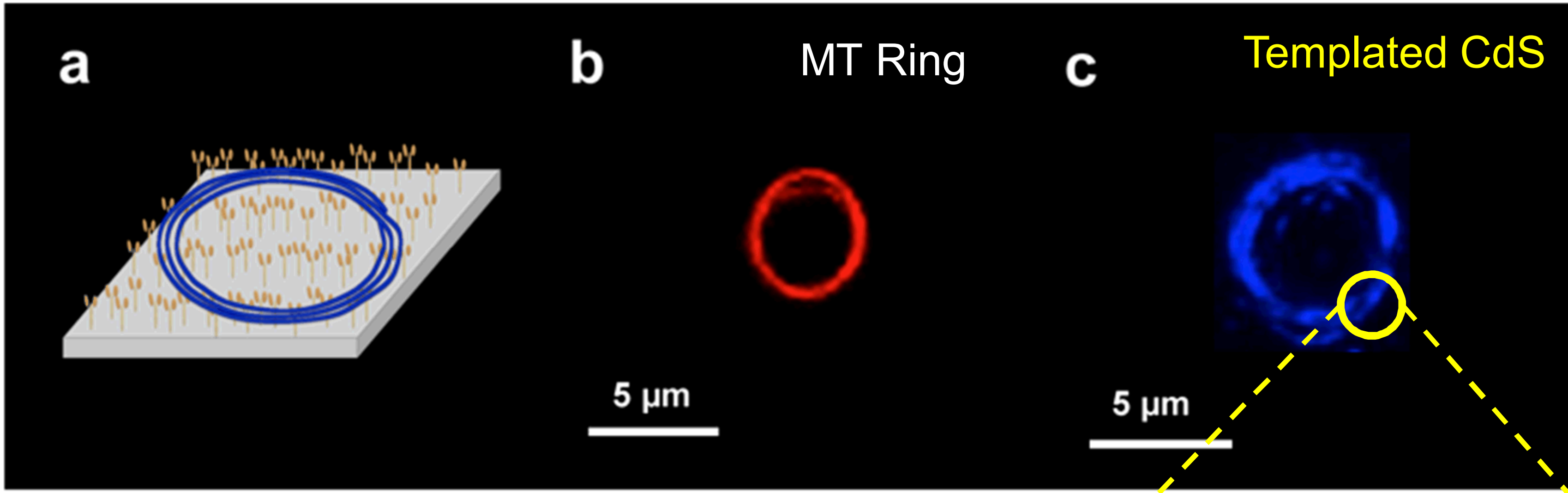


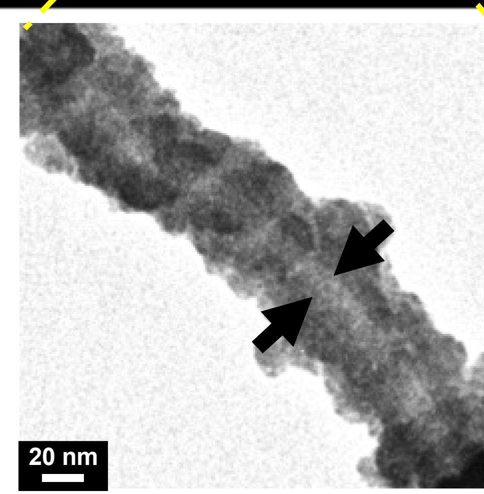
Streptavidin-SWNTs



Anti-biotin gold

Templating on Non-Equilibrium MT Structures

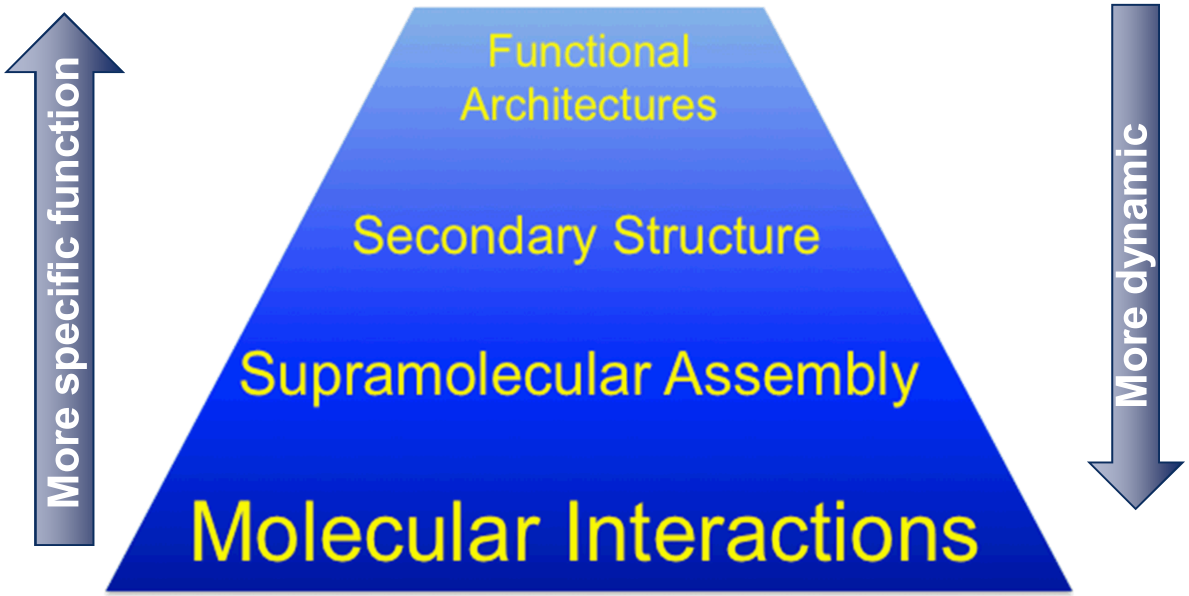




Incubation of MT rings with aqueous $Cd(NO_3)_2$ and thioacetamide leads to controlled templating of CdS nanotube rings.

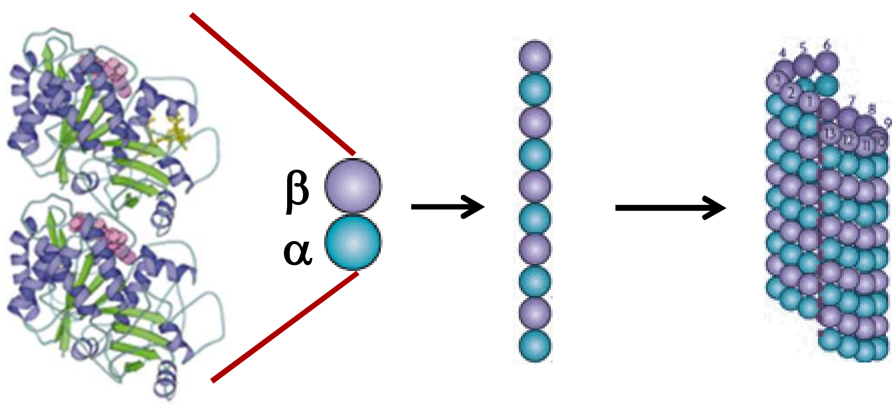
These structures are uniquely enabled through the use of non-equilibrium MT templates.

Hierarchical Molecular Assembly Applied to Microtubules

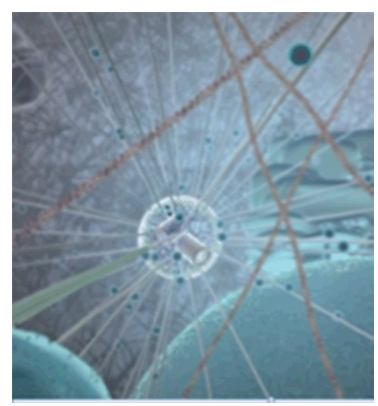


Dynamic assembly and organization of multi-functional microtubules follow a graded, hierarchical scheme.

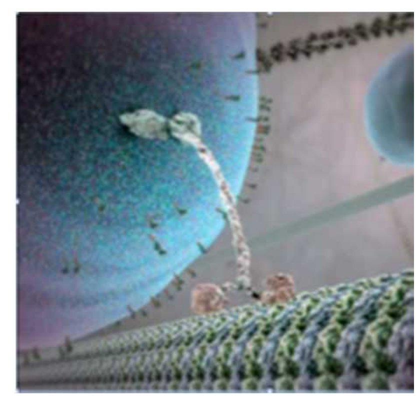
Dimer Protofilament Microtubule



Centrosome



Kinesin Motility



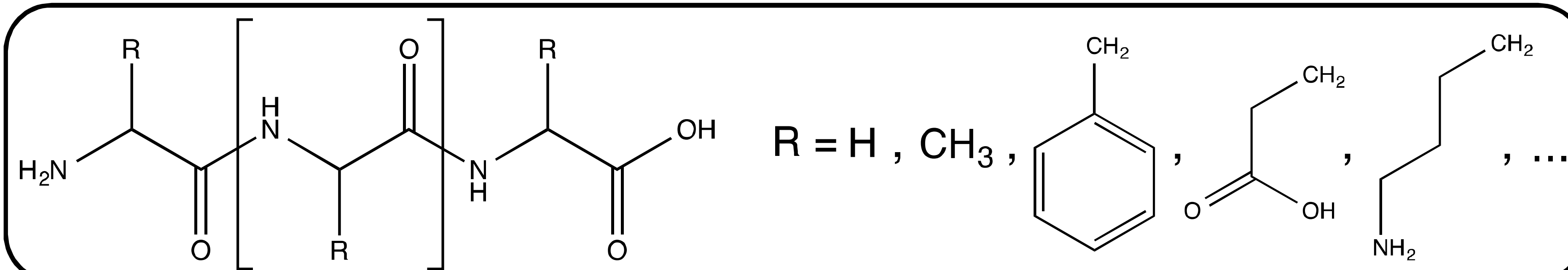
Key Dynamic Biomimetic Properties

- Multifunctional, *composite* building block structure (e.g., α/β heterodimer)
- Assembly dictated by cooperative interactions between solvent, additional building blocks, and secondary biomolecules (e.g., GTP)
- Assembled structure vulnerable to building block "change of state" (strain from GTP hydrolysis)
- Secondary interactions to control aggregate behavior of assemblies (MT organization into bundles, asters, etc.)

Peptides: Versatile Tools for Biomimetic Assembly

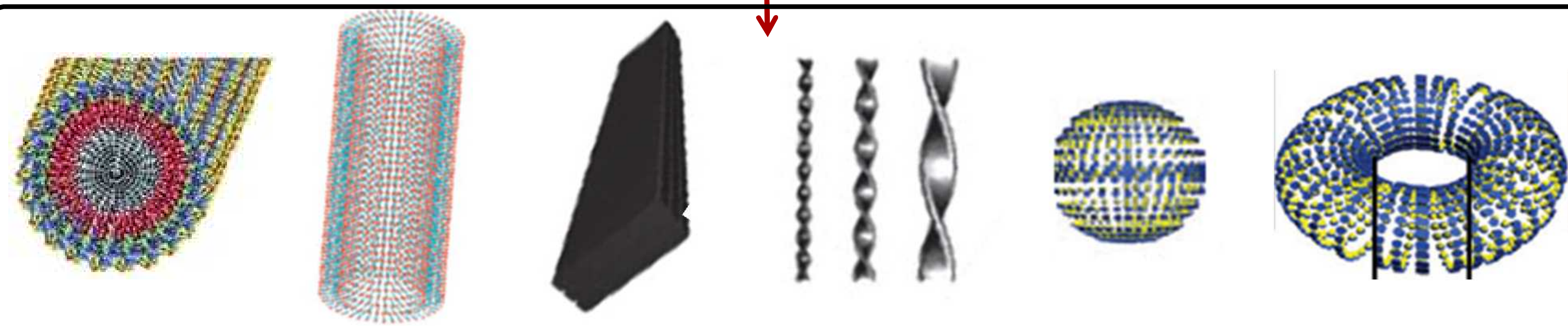
Sandia National Laboratories

A complex balance of interactions drives spontaneous self-assembly



electrostatic interactions | hydrogen bonding | aromatic stacking | hydrophobic interactions

chemical environment

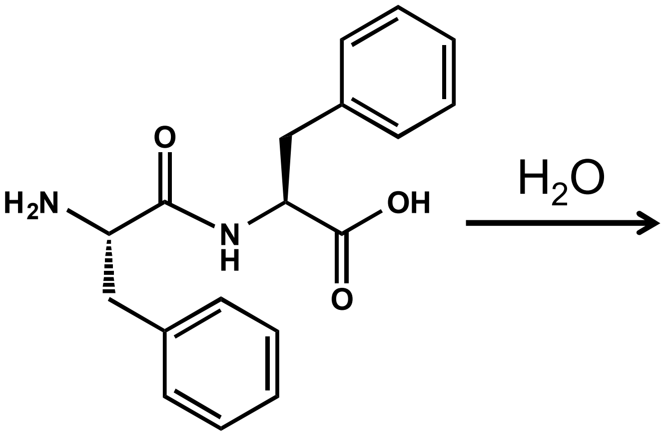


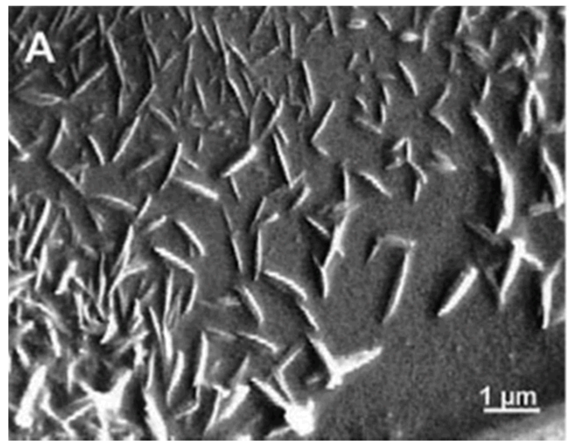
Hamley, I.W. *Soft Matter* **2011**, *7*, 4122; Zhao, X.; *et al. Chem. Soc. Rev.* **2010**, *39*, 3480.

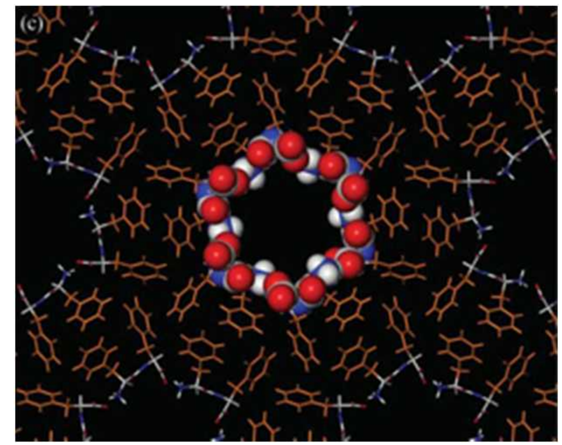
FF-Nanotube Formation

Di(phenylalanine) dipeptides will self-assemble into hierarchical nanotubes

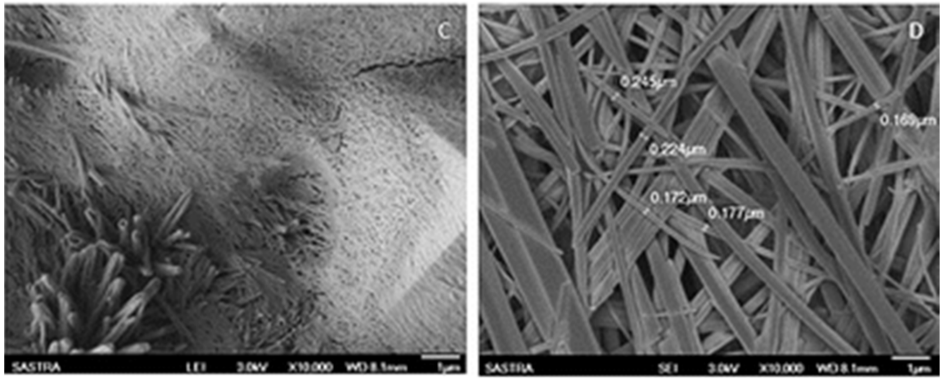
Nanotubes from di(phenylalanine)







Reches, M.; Gazit, E. *Science* **2003**, *300*, 625-627; Görbitz, C.H. *Chem. Comm.* **2006**, 2332-2334.

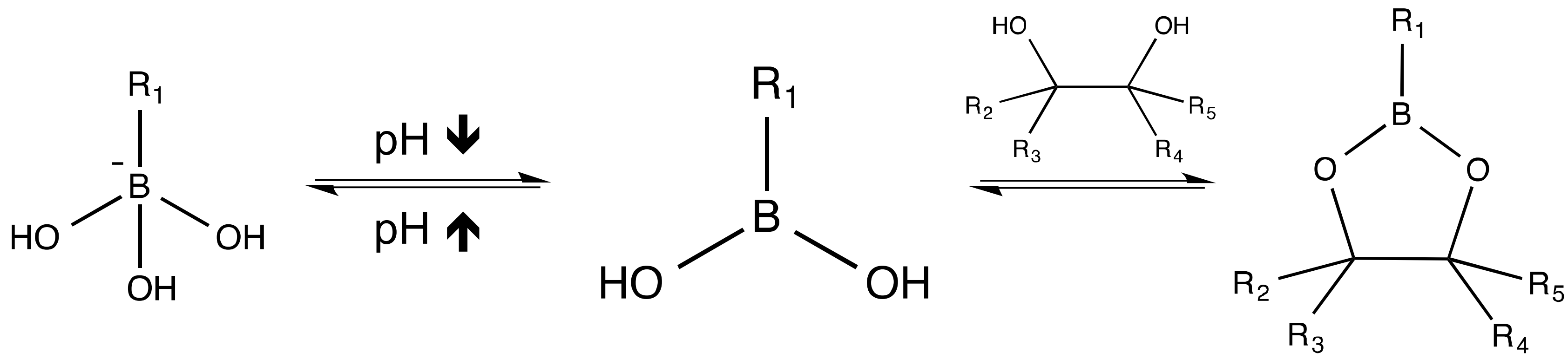


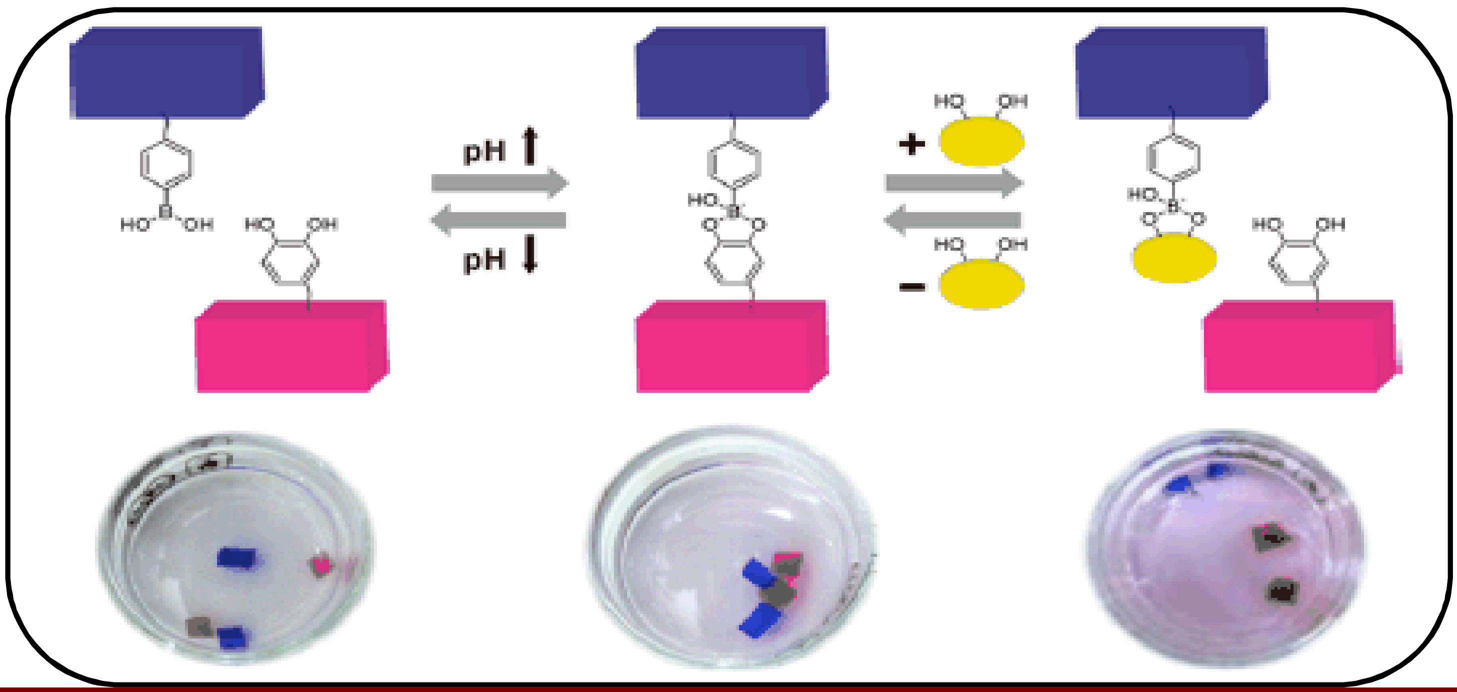
P. Kumaraswamy, et al. *Soft Matter*, **2011**,*7*, 2744-2754.

Scientific Challenge: *Can we modify this simple dimer building block for programmable self-assembly?*

Boronic Acids

Boronic acids provide potential for pH- and polyol-responsive behavior

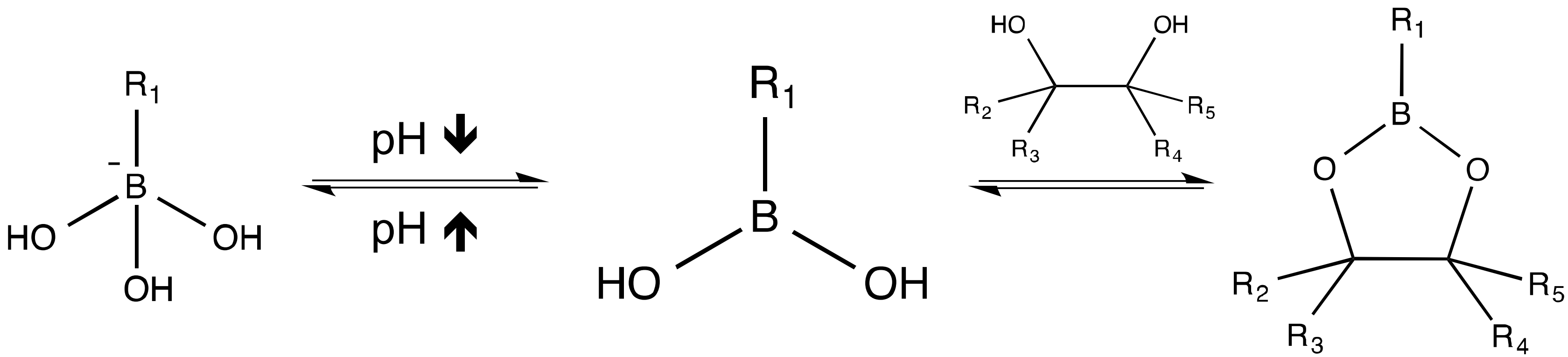




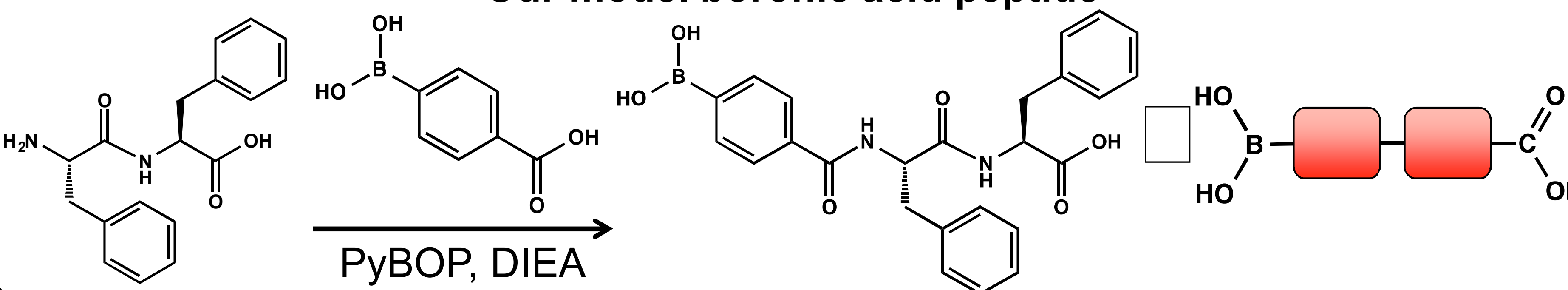
Nakahata, M.; *et al. ACS Macro Lett.* **2014**, *3*, 337-340.

A Simple Boronic Acid Peptide

Boronic acids provide potential for pH- and polyol-responsive behavior



Our model boronic acid peptide

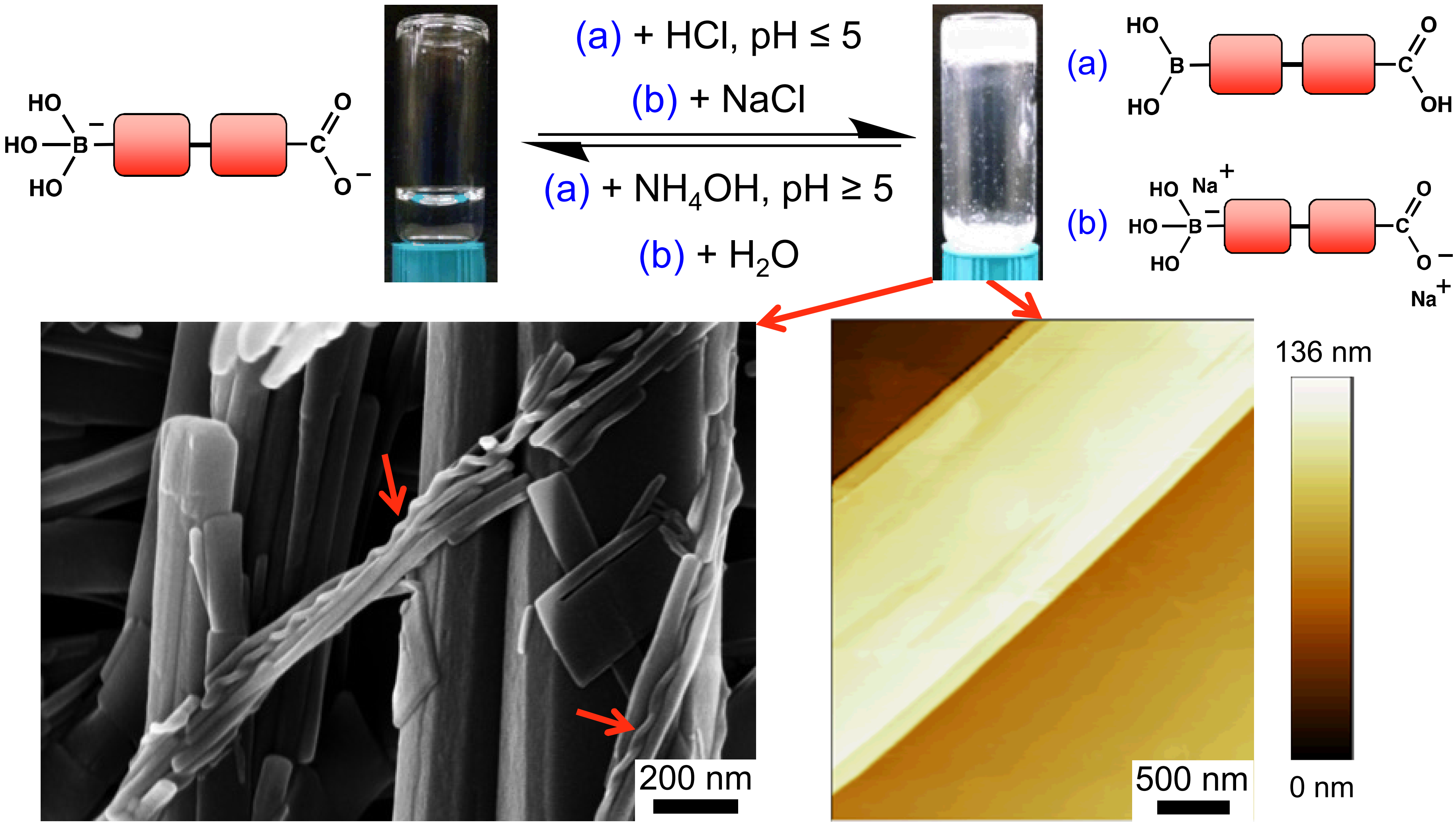


B.H. Jones, et al. *Tet. Lett.* (2015) **56** (42), 5731-5734.

B.H. Jones, et al. *Chem. Comm.* (2015) **51,** 14532-14535.

pH- and Salt-Responsive Self-Assembly

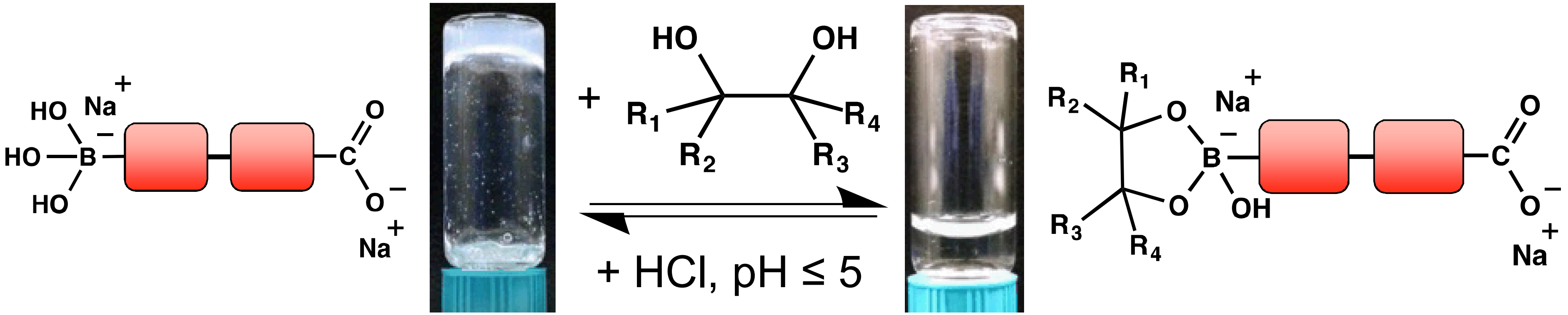
Nanoribbon assemblies are reversibly formed by ΔpH or Δionic strength

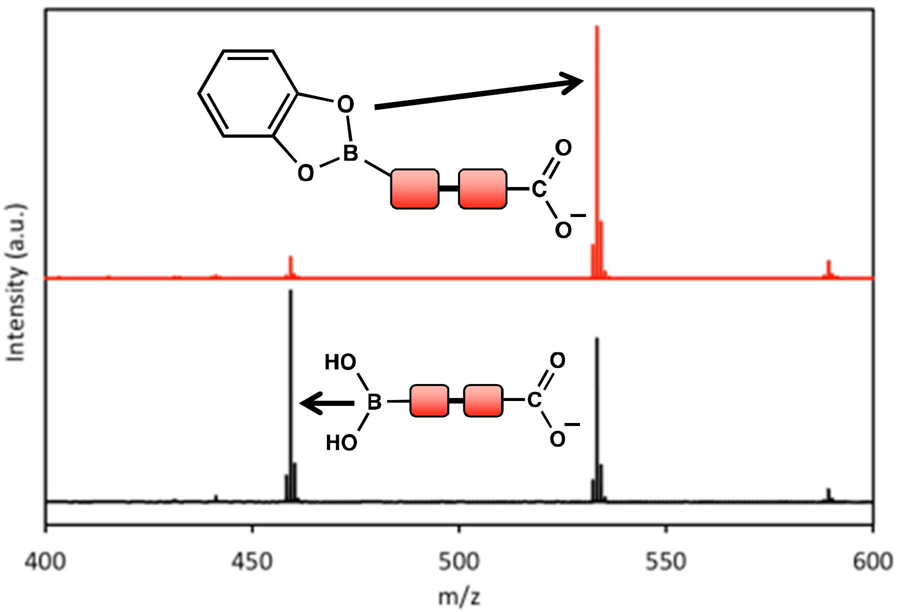


B.H. Jones, et al. *Chem. Comm.* (2015) **51,** 14532-14535.

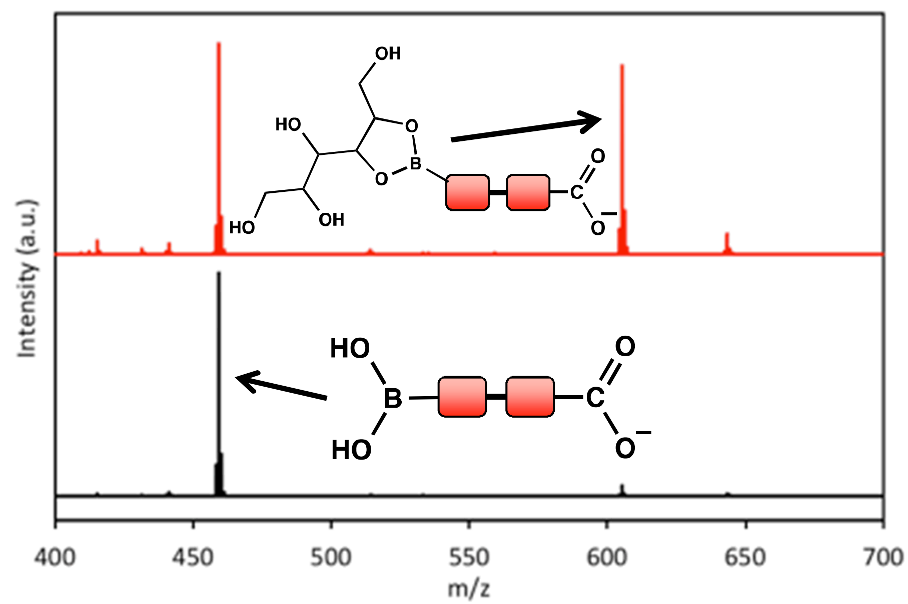
Saccharides/Polyols Induce Disassembly

Gel-sol transitions are triggered by addition of saccharides or polyols





[**catechol**]:[peptide] = 1:1 6:1



[**sorbitol**]:[peptide] = 1:1 6:1

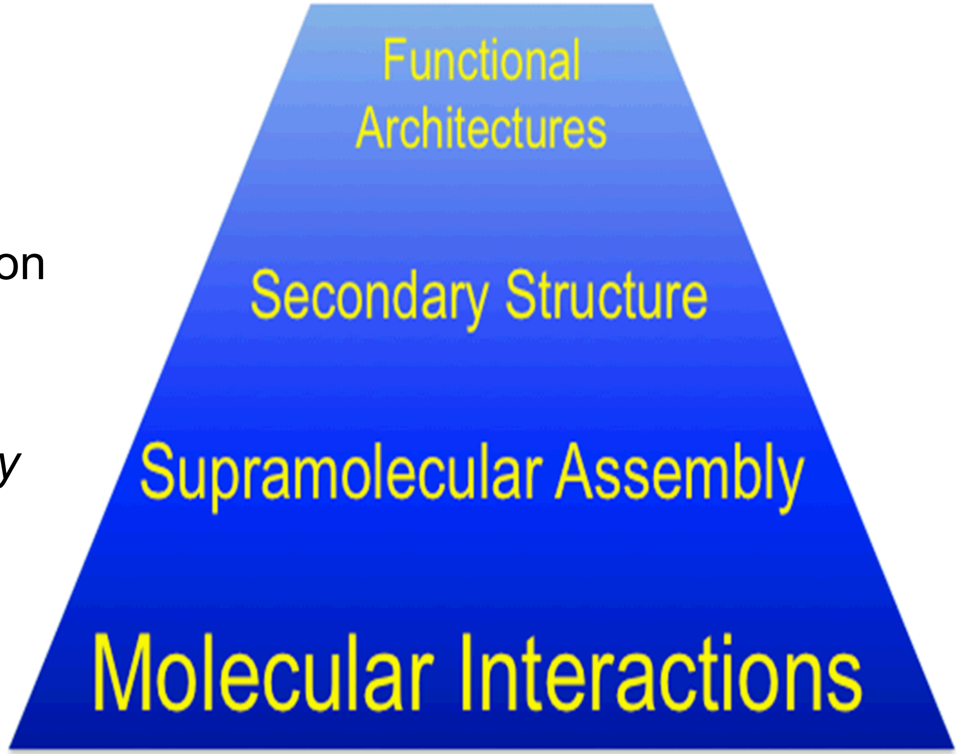
Biomimetic BFF Assembly

- Diol-based interactions facilitate tunable hydrogel integrity

- Inter-assembly interactions drive gelation

- Neutralization of electrostatics allows assembly (*interactions with diols to vary charge state reverses assembly)*

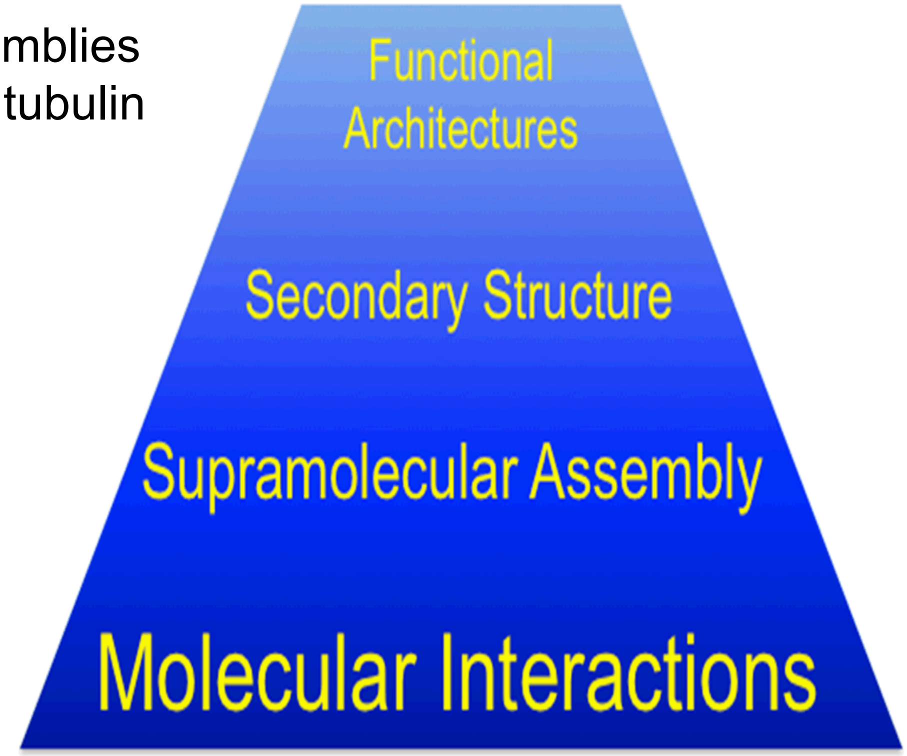
- Hydrogen bonding, π-stacking, molecular solvation, electrostatics (repulsion)



Take Home Messages

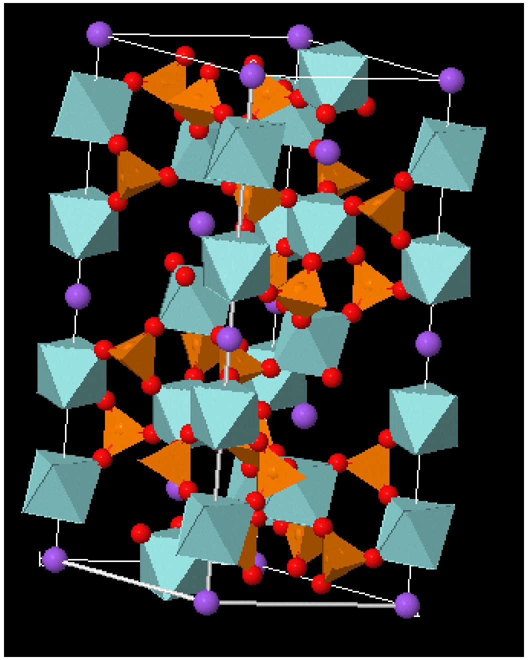
- ✓ MTs are complex, dynamic supramolecular nanostructures, formed as hierarchical assemblies through the collaborative interactions of α/β tubulin dimers and secondary biomolecules.

- ✓ Designing synthetic peptides with key aspects of composite, multifunctional building blocks, enables dynamic assembly mediated by
  - Change in charge state
  - Change in secondary molecular interactions
  - Changes in molecular conformation state



By incorporating fundamental biomaterial assembly principles into synthetic systems we stand to enable a wide range of new complex, functional, dynamic materials.

Tailoring Materials Chemistry for Improved Solid State Alkali Cation Conductors

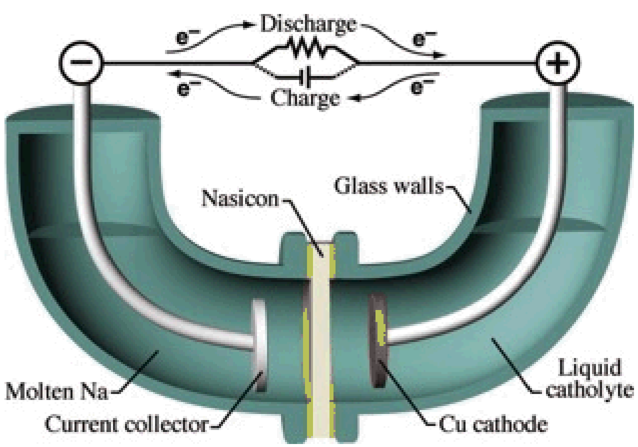


Sodium-based Battery Development

Technical Objective: Develop sodium-based battery chemistries for large scale energy storage

- Sodium-air
- Sodium-ion
- Low temperature sodium-sulfur
- Sodium-bromine: Na + ½ Br_2 ←→ Na^+ + Br^-
- Sodium-iodine: Na + ½ I_2 ←→ Na^+ + I^-
- Sodium-copper iodide: Na + CuI_2^- ←→ Na^+ +$2I^-$ + Cu(*s*)

$$Na \xrightarrow{discharge} Na^+ + e^-$$

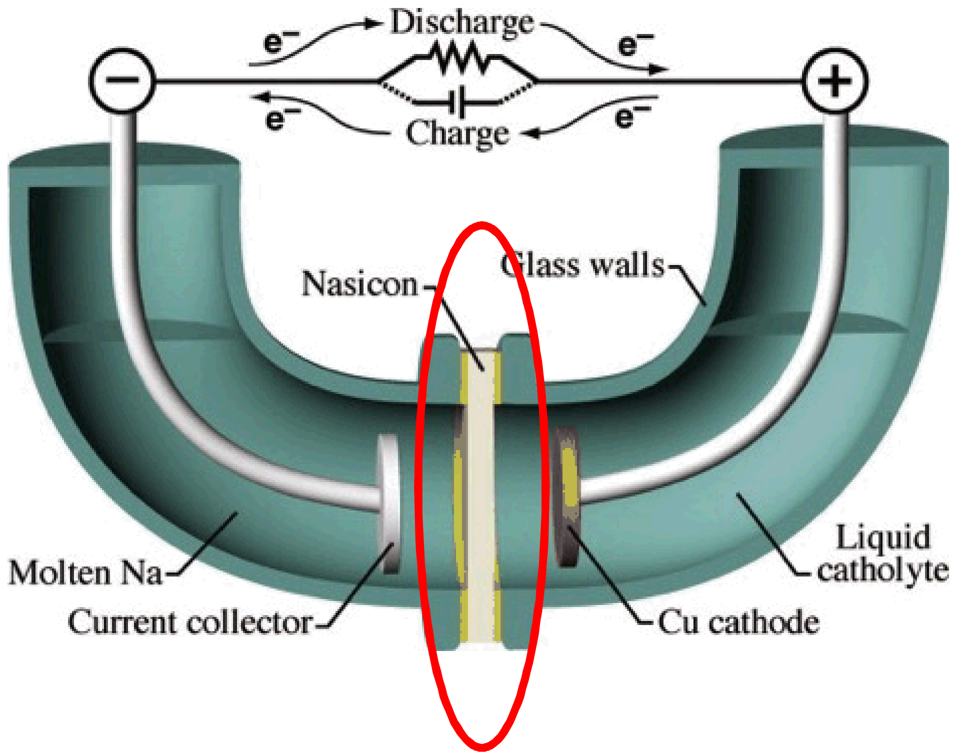


$$CuI_2^- + e^- \xrightarrow{discharge} Cu(s) + 2I^-$$

H. Zhu, S. Bhavaraju, and R. Kee. "Computational model of a sodium–copper-iodide rechargeable battery," Electrochimica Acta (2013).

Na-Based Batteries Depend on Ceramic Solid State Electrolytes

The ceramic separator is central to Na-battery performance!



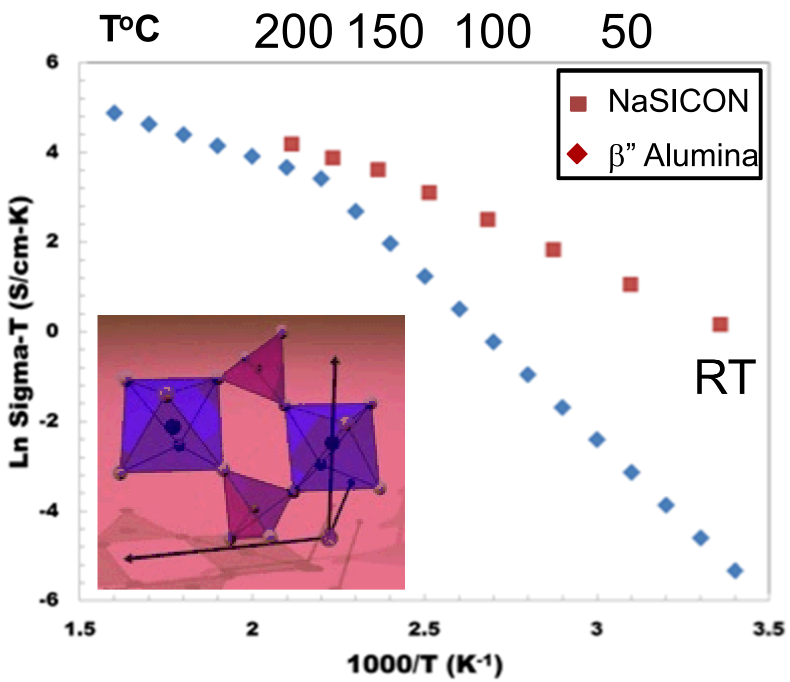
<u>Ceramic requirements:</u>

- Selective, high ionic conductivity
- High electronic resistivity
- Robust stability in extreme chemical environments
- Facile, low cost synthesis

NaSICON Ceramic Electrolytes

What is NaSICON? (Sodium (**Na**) **S**uper **I**onic **Con**ductor)

$Na_{1+x}Zr_2P_{3-x}Si_xO_{12} \xrightarrow{x = 2} Na_3Zr_2PSi_2O_{12}$ (NZSP)



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

Key NaSICON attributes:

- ✓ Selective, high ionic conductivity (> 10^{-3} S/cm at RT)
- ✓ High electronic resistivity
- Robust stability in extreme chemical environments
- ✓ Facile, low cost synthesis

These qualities all depend on the materials chemistry of the ceramic separator!

Data provided by Ceramatec, Inc.

Expanding NaSICON Utility: Alkaline Aqueous Environments

Sandia National Laboratories

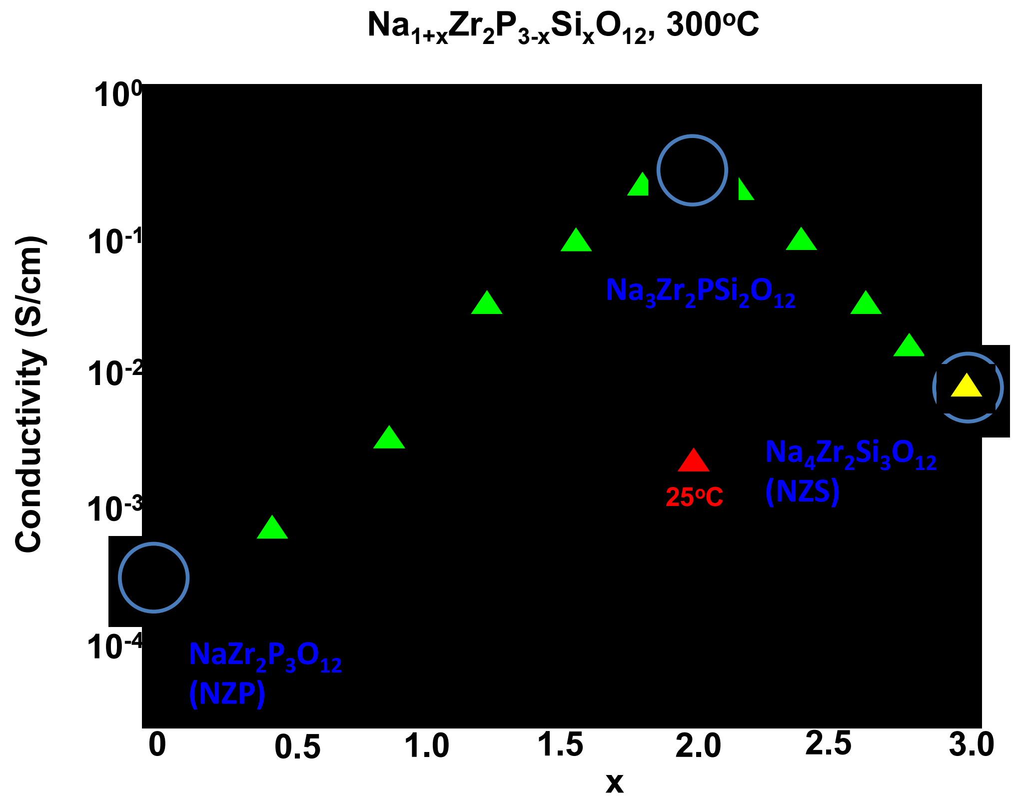
Promising low temperature conductivity opens the door to using NaSICON for aqueous chemistries…but there are challenges.

Alkaline Degradation:

- Si should be the weak link (Zr is point of attack for Si-free NASICON).
- Hydroxide attack on Si, Zr should increase 10x for each ΔpH of 1.

Step 1: Consider Si-free NaSICON

$NaZr_2P_3O_{12}$ (x=0)



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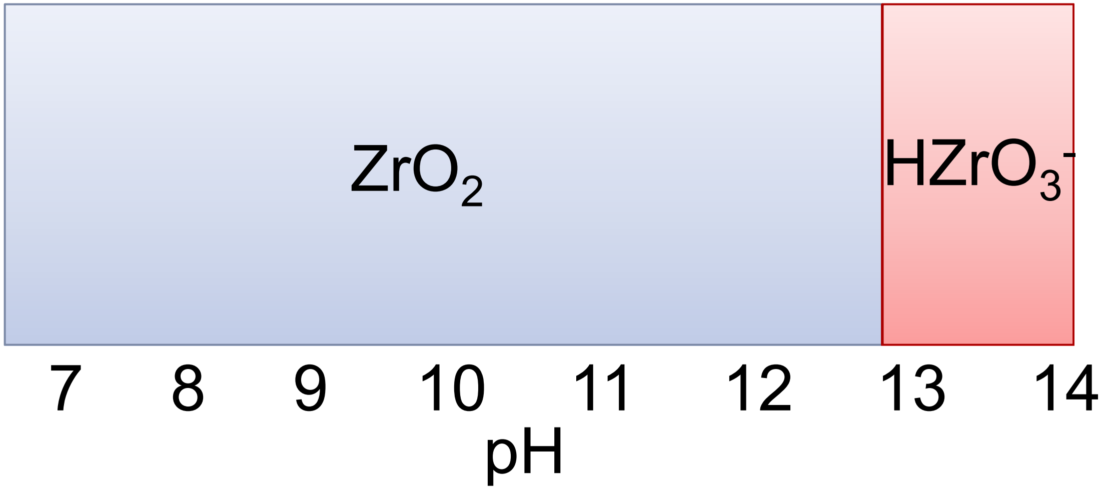
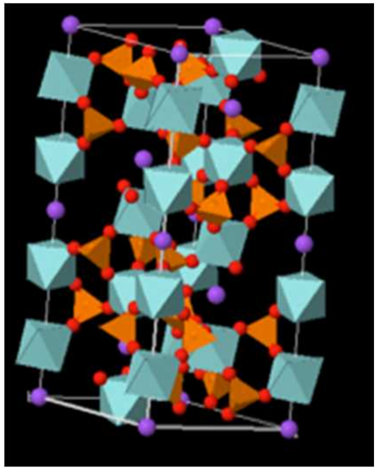


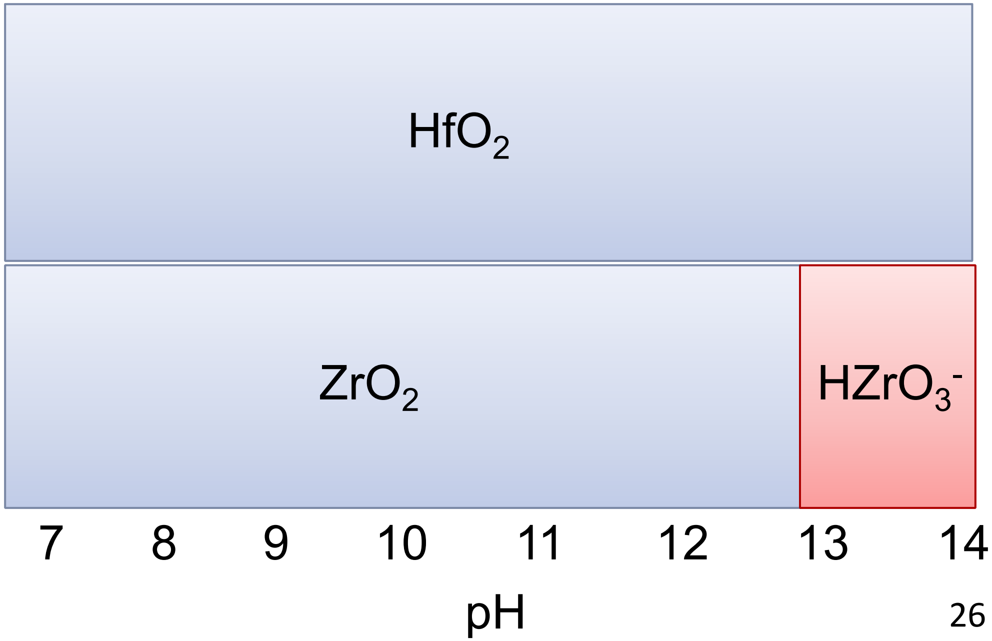
Strategy for Improved Aqueous Stability

What about Hafnium as a substitute for Zirconium in the octahedral sites of the NaSICON lattice?



- Both 4+ cations
- Ionic radii Hf: 0.85Å versus Zr: 0.86Å
- *<u>Potential dramatic improvement in stability</u>*

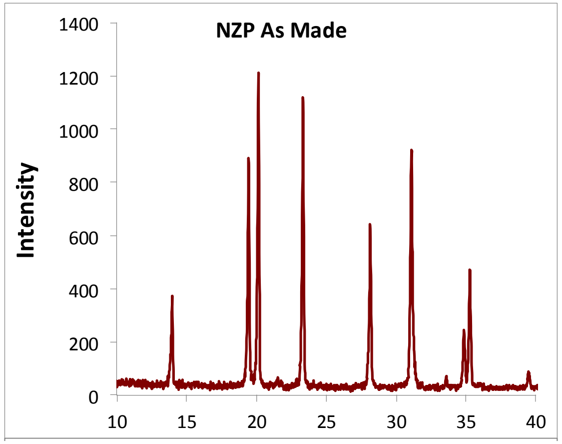
Hf-O bonds are expected to be more stable in alkaline environments…



Enhanced Alkaline Stability of Cation-Modified NaSICON

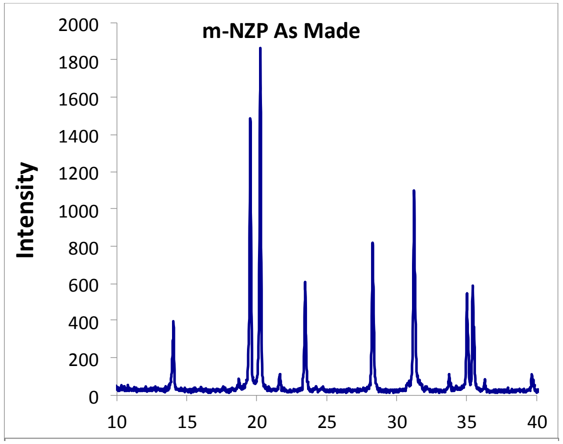
NZP

($NaZr_2P_3O_{12}$)



NHP

($NaHf_2P_3O_{12}$)



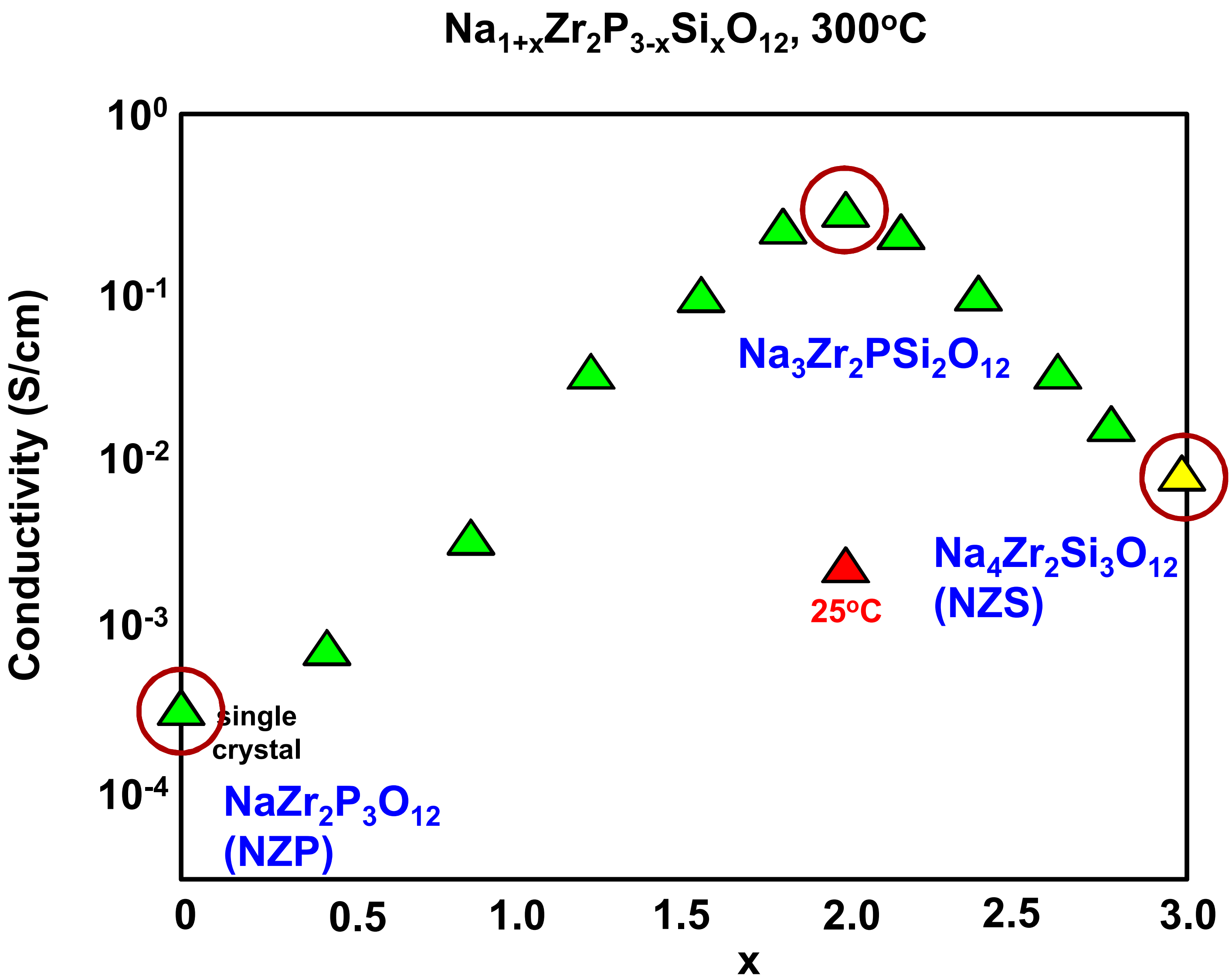
Synthesis:

- $NaH_2PO_4 \bullet H_2O$
- P_2O_5
- HfO_2 or ZrO_2

Fire at 1050C for 12 hours in ai

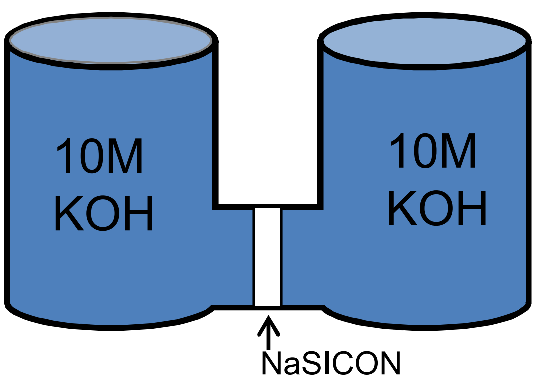
"As-synthesized" both NZP and the NHP show expected crystalline x-ray diffraction patterns.

Ionic Conductivity of NaSICON

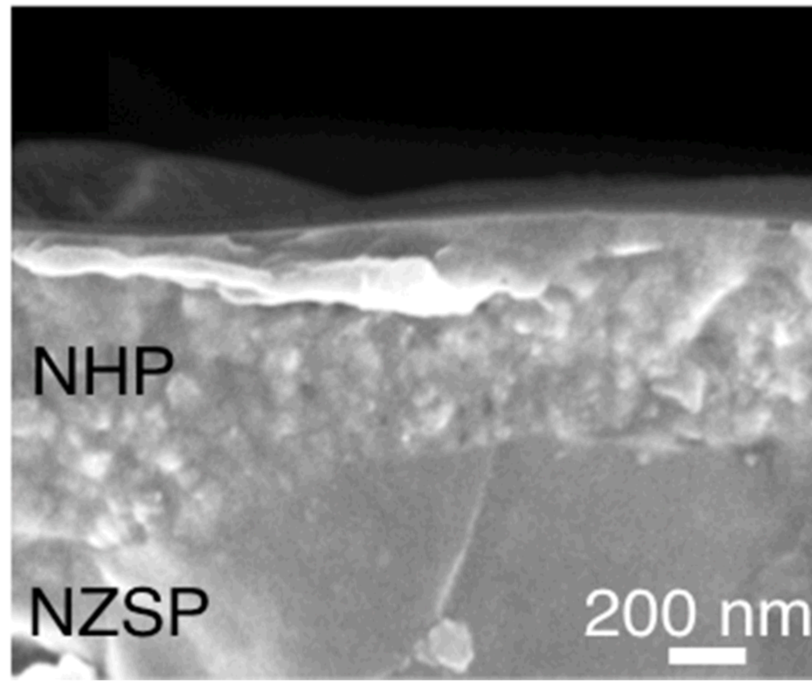


Translating NHP Stability to Protective Coatings

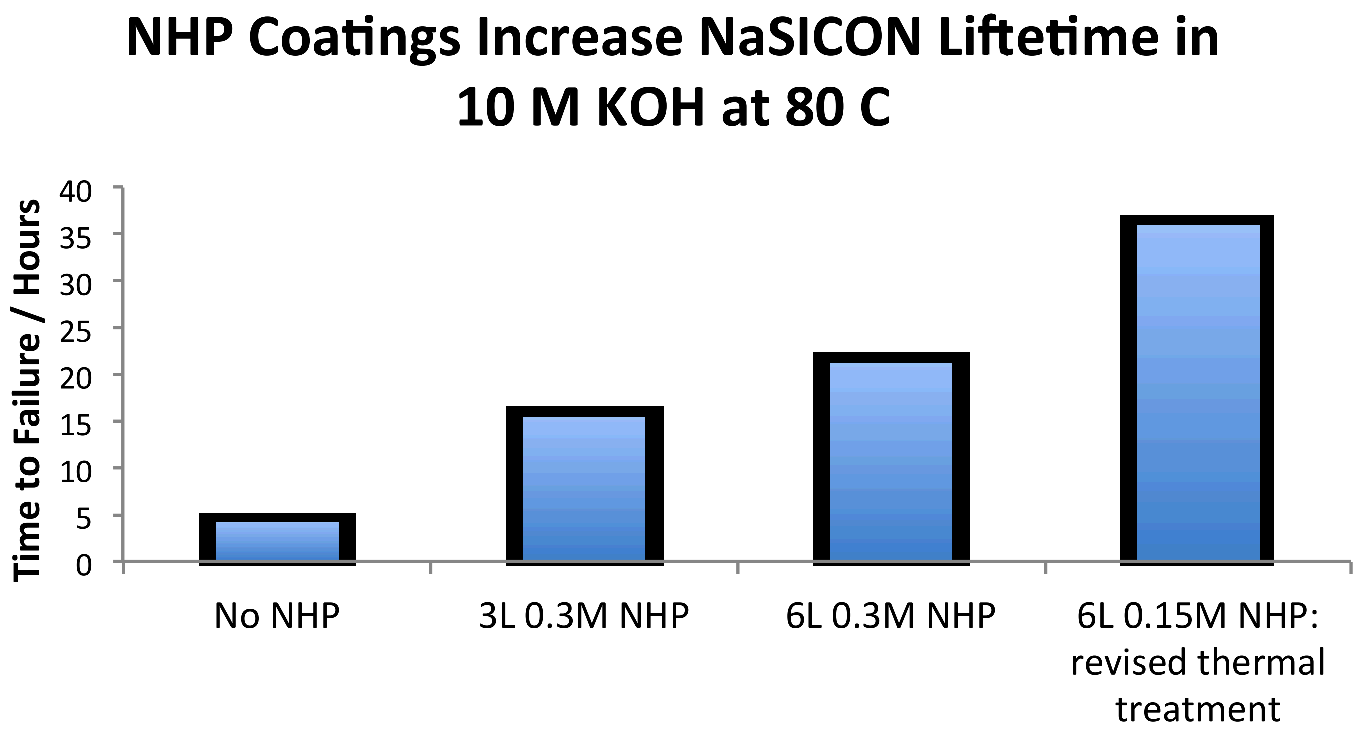
NZSP pellet after 24 hrs in 80°C 10M KOH.



NHP thin morphology on an NZSP NaSICON pellet (in cross-section)



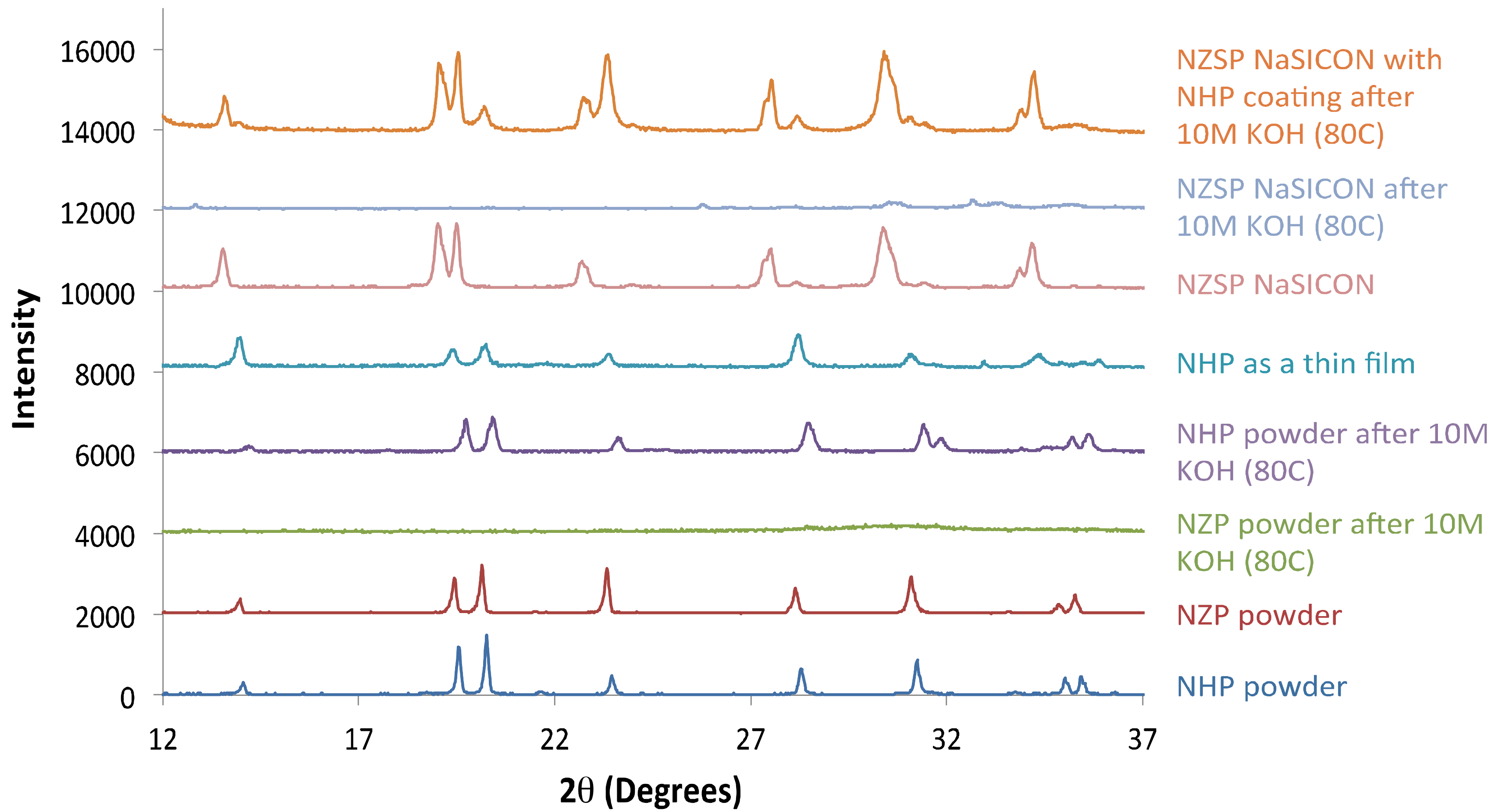
Summary of NHP-coated NaSICON Improved Alkaline Stability



Although thickness and processing conditions of sol-gel film matter, NHP coatings all clearly show improved resistance to alkaline degradation.

XRD Reveals Modified NaSICON Stability

X-ray diffraction illustrates alkaline stability of modified NaSICON and protective quality as a coating on NZSP NaSICON Materials

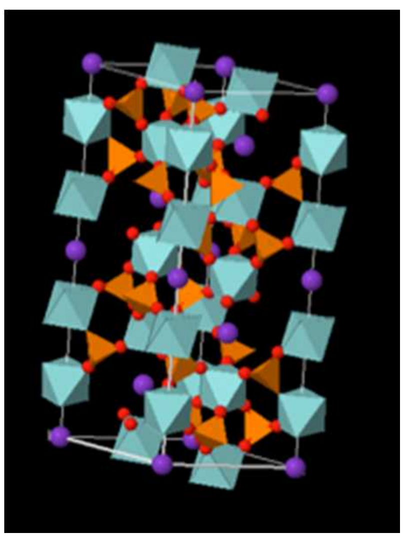


Modified NaSICON for Selective Isolation of Ionic Contaminants

A potassium-variant of NaSICON ($KZr_2P_3O_{12}$) provides a modified crystal structure to enable selective removal of Cs+ from contaminated LiCl-KCl molten salts used in the recycling of spent nuclear fuel.

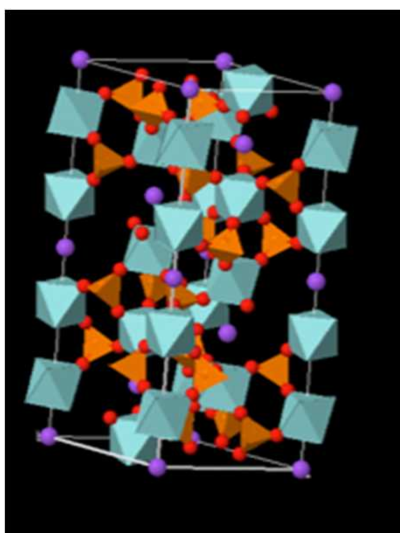
KSICON

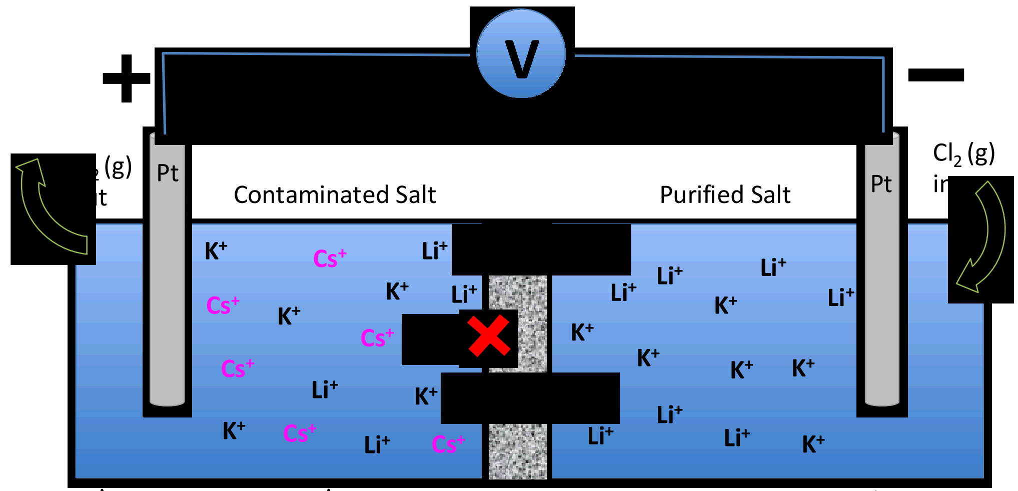
a = 8.71Å
b = 8.71Å
c = 23.89Å



NaSICON

a = 8.82Å
b = 8.82Å
c = 22.75Å





$2Cl^- \rightarrow Cl_2 + 2e^-$ $\quad$ $Cl_2 + 2e^- \rightarrow 2Cl^-$

Ion-selective ceramic

NaSICON Summary

What have we learned?

- NaSICON ceramics are promising solid state electrolytes for Na-based batteries.
- Low temperature conductivity of NaSICON is compatible with aqueous chemistries, but material stability challenges must be overcome.
- Modifying NaSICON structure with Hf improves alkaline stability of NaSICON.
- Application of NHP as a thin film “shield” provides improved NaSICON stability without sacrificing overall conductivity.

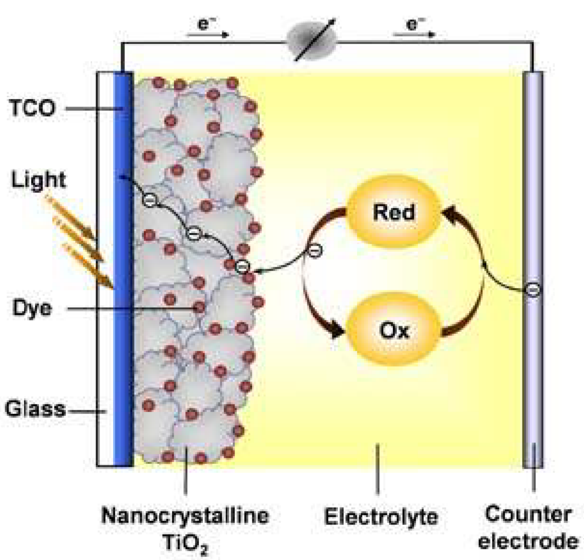
Continued modification of NaSICON materials chemistry may be used to refine the balance of NaSICON performance, durability, and application diversity.

Dye-Sensitized Solar Cells

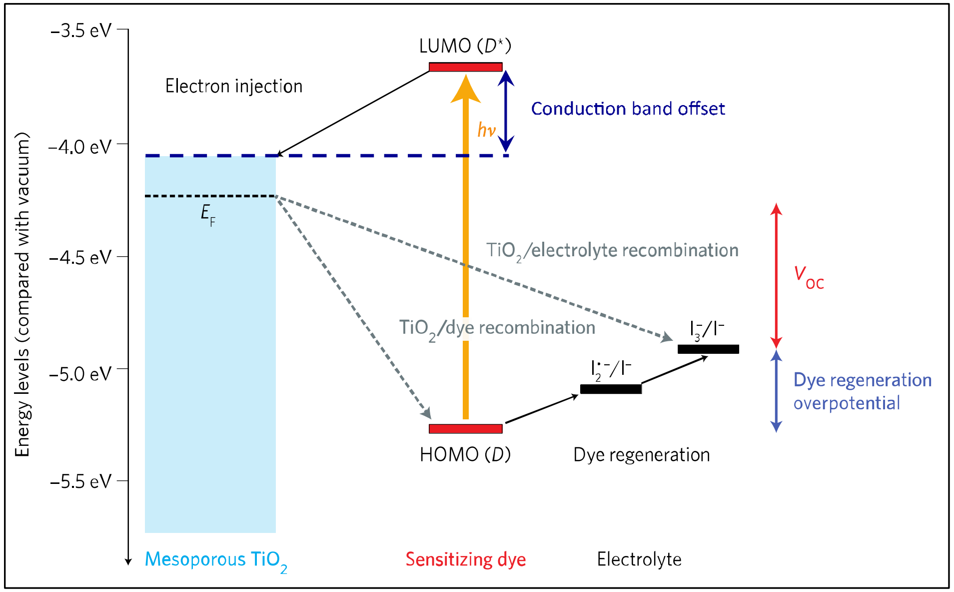
(O'Regan, B. & Grätzel, M. (1991). *Nature*, **353**, pp 737.)

World record is >15% efficiency…but there are still some critical challenges:

- Limited light harvesting
  - Spectral range
  - Dye concentration (*without dye aggregation)
- Carrier lifetimes
- Band offset overpotentials
- Stability/Reliability



http://staff.bath.ac.uk/pysabw/abwmod.html

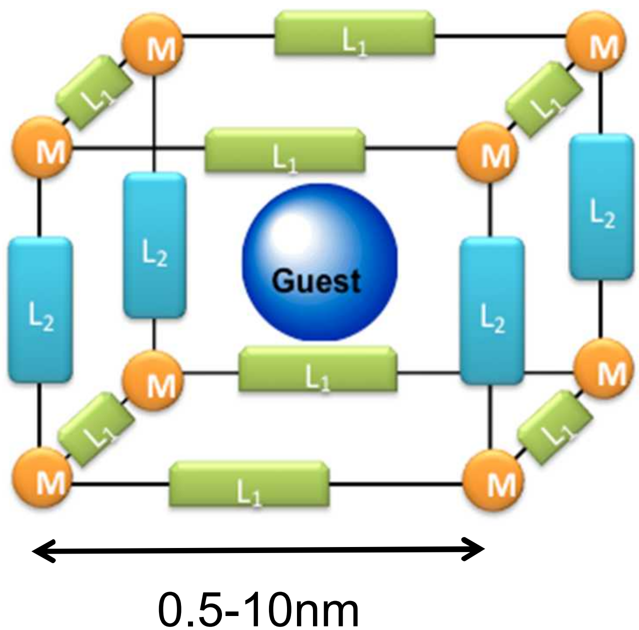


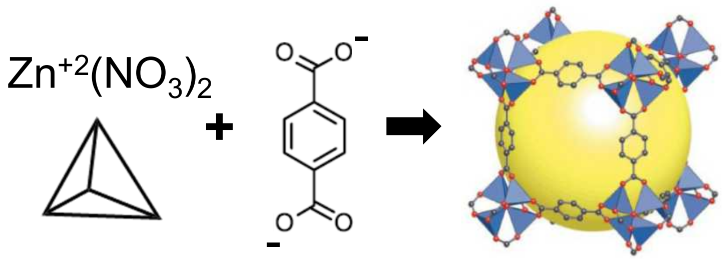
Adapted from B. Hardin, *et al*. (2012) *Nature Photonics*, **6**, 162-169.

What are Metal-Organic Frameworks?

Metal-Organic Frameworks (MOFs)

A subset of coordination polymers

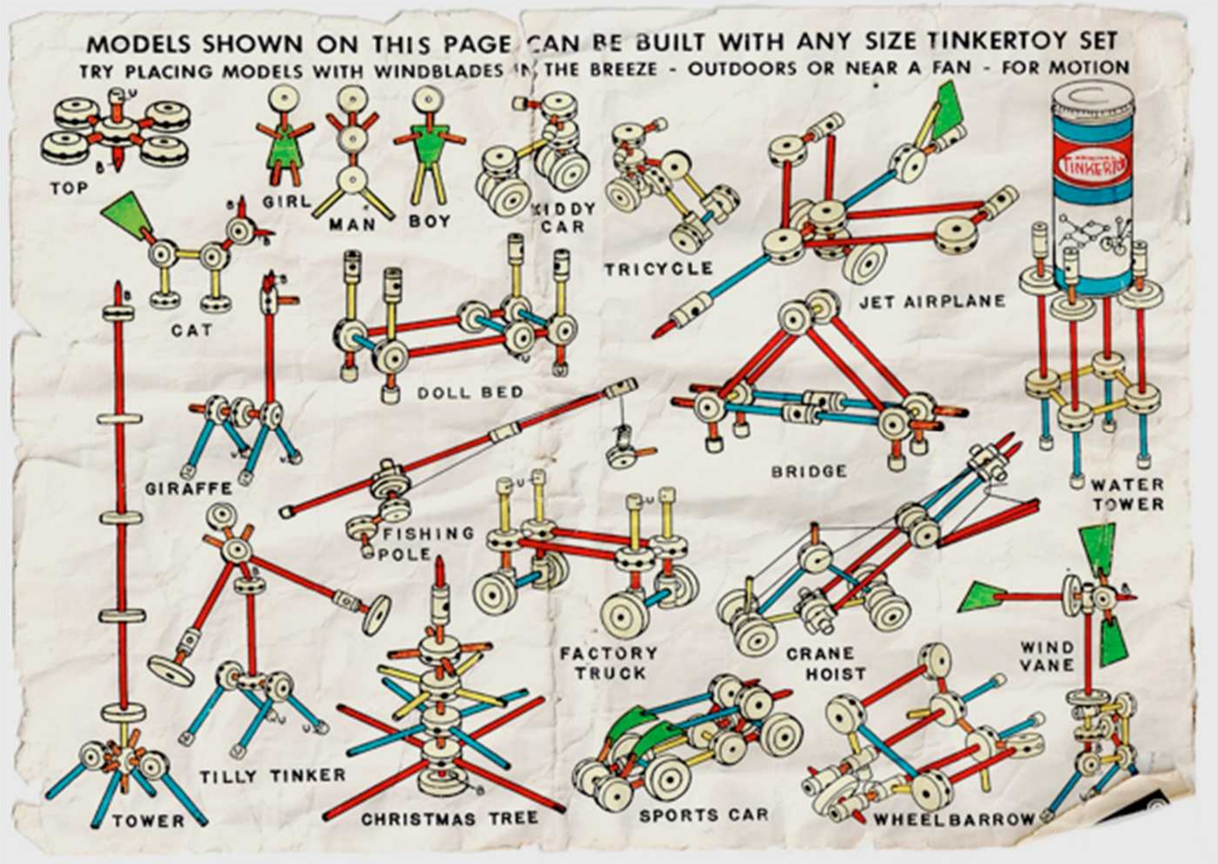




- Crystalline MOF structures are composed of metal nodes (M), linkers (L_1) and pillars (L_2).
- The nanoporous character MOFs allows incorporation of molecular guests, organized on the nanoscale.
- The highly ordered structure spaces and organizes linkers and pillars, producing unusual properties.
- This chemically "modular" system allows for tuning of the structure, properties, and functions of these materials.

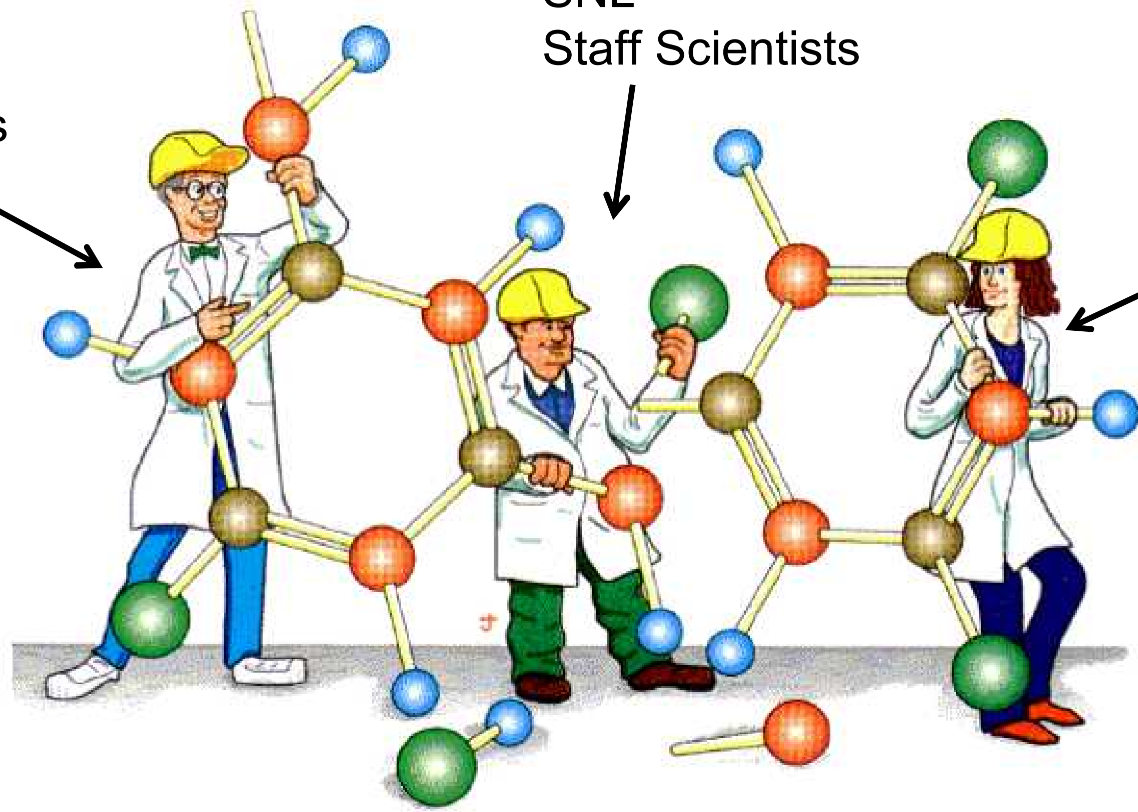
MOFs: Supramolecular "Tinker Toys"

MOFs are modular materials, diverse in form and function!



Realizing Supramolecular Materials

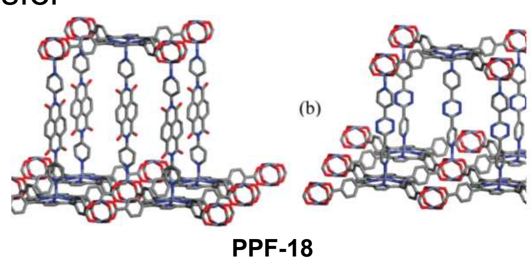
By manipulating and assembling these supramolecular building blocks we can tailor MOF structure and properties.



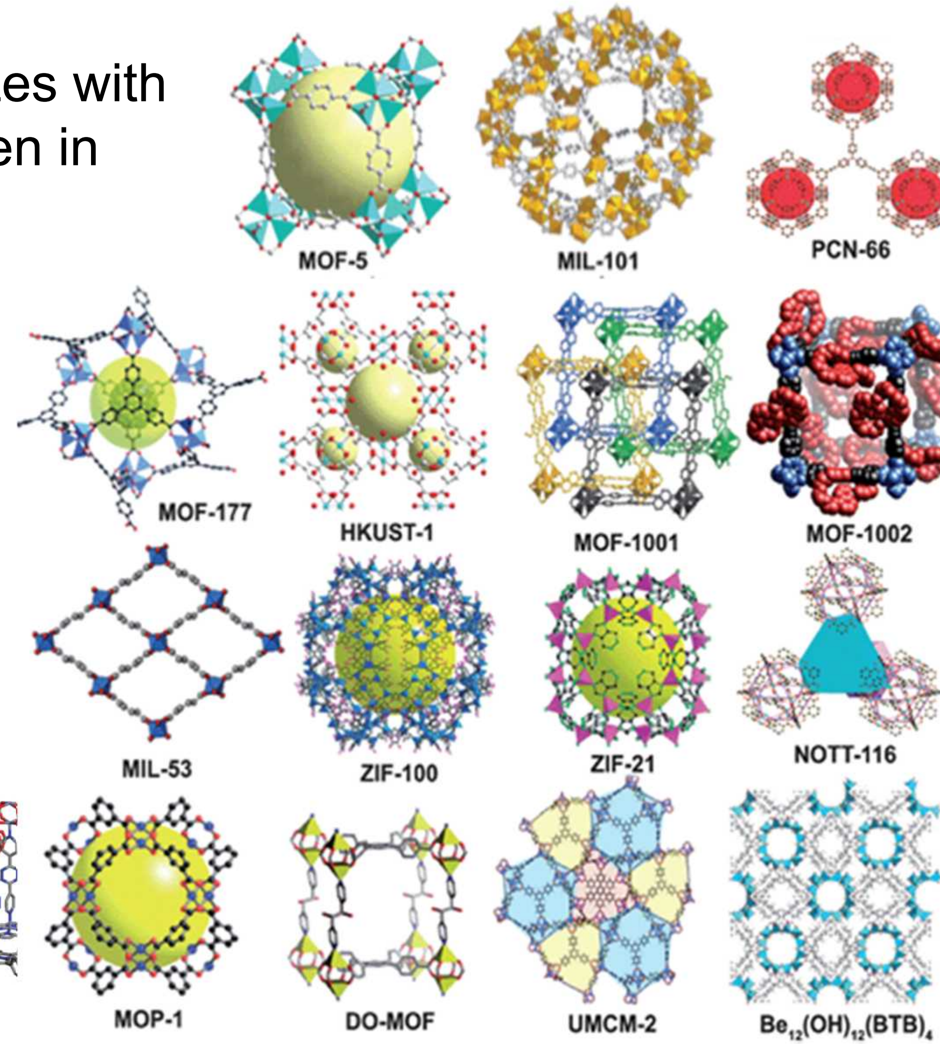
MOFs Properties

MOFs come in myriad shapes and sizes with varied chemistries and properties, often in unique combinations…

- Crystalline Order
- Nanoporosity (Guest/Host capability)
- Ultrahigh surface area (record ~ 7000 m^2/g)
- High chemical reactivity*
- Chemical, thermal, "irradiation" stability*
- Photoactivity*
- Charge/energy transfer*



Adapted from Chung, *et al.*[1]



Adapted from Xiang, *et al.*[2]

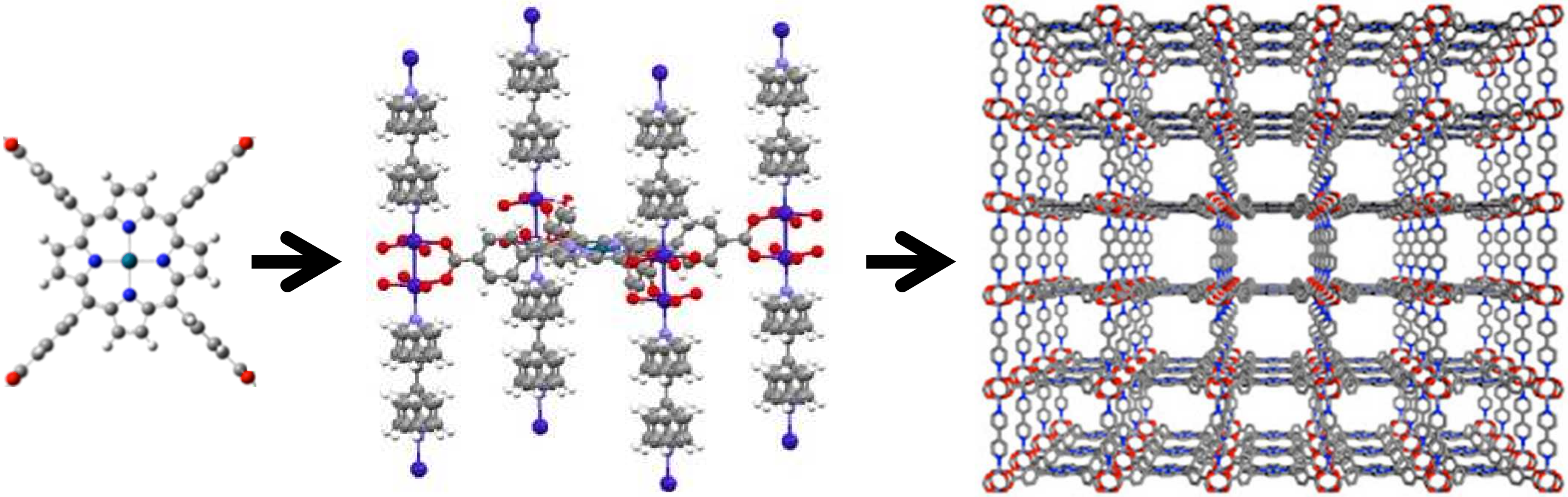
*MOF dependent

1) Chung *et al*. *Crystal Growth & Design, Vol. 9, No. 7, 2009*
2) Z. Xiang, et al. *Energy Environ. Sci.* (2010), **3**, 1469.

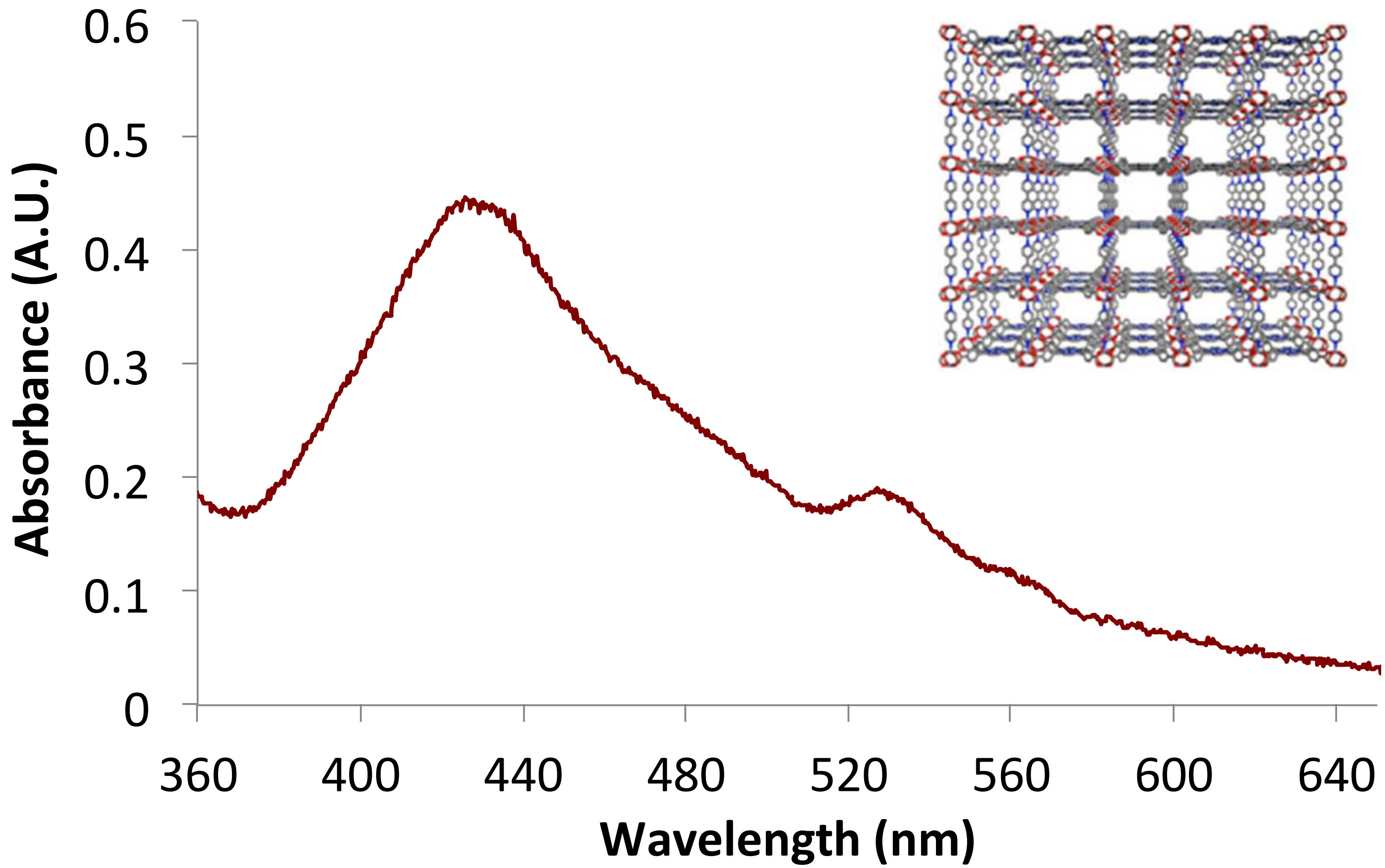
Building Photoactive MOFs

Consider Pillared Porphyrin Frameworks (PPFs)

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



PPF-5 Optical Absorbance

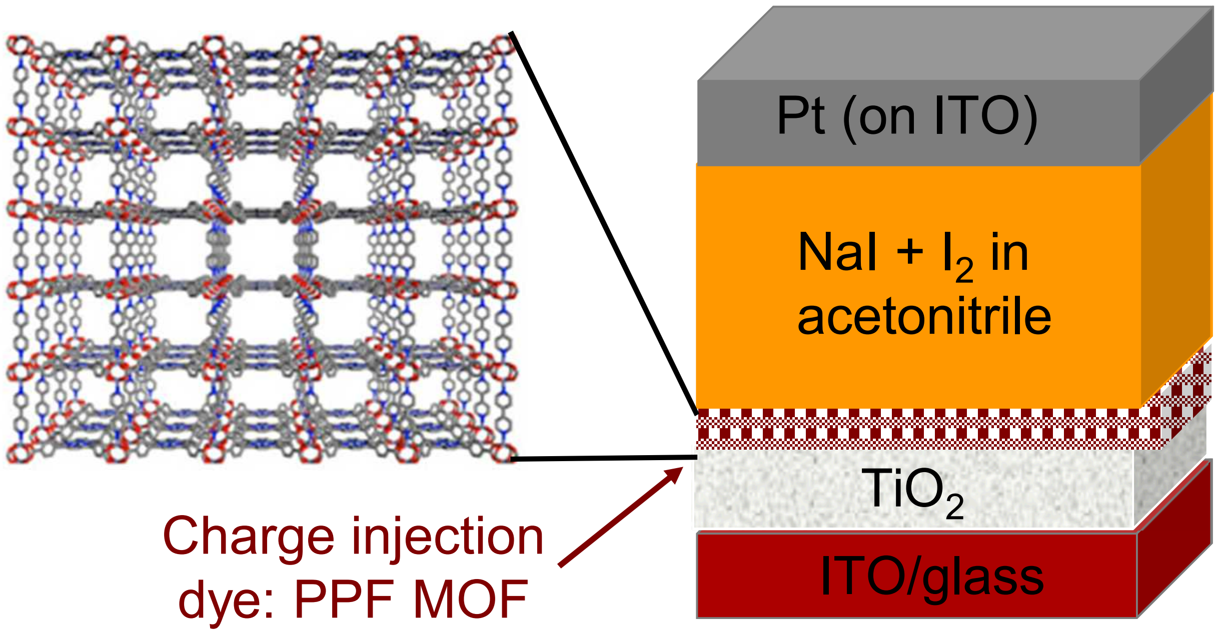


PPF-5 absorbs meaningful visible light.

Integration of PPF MOFs in DSSCs

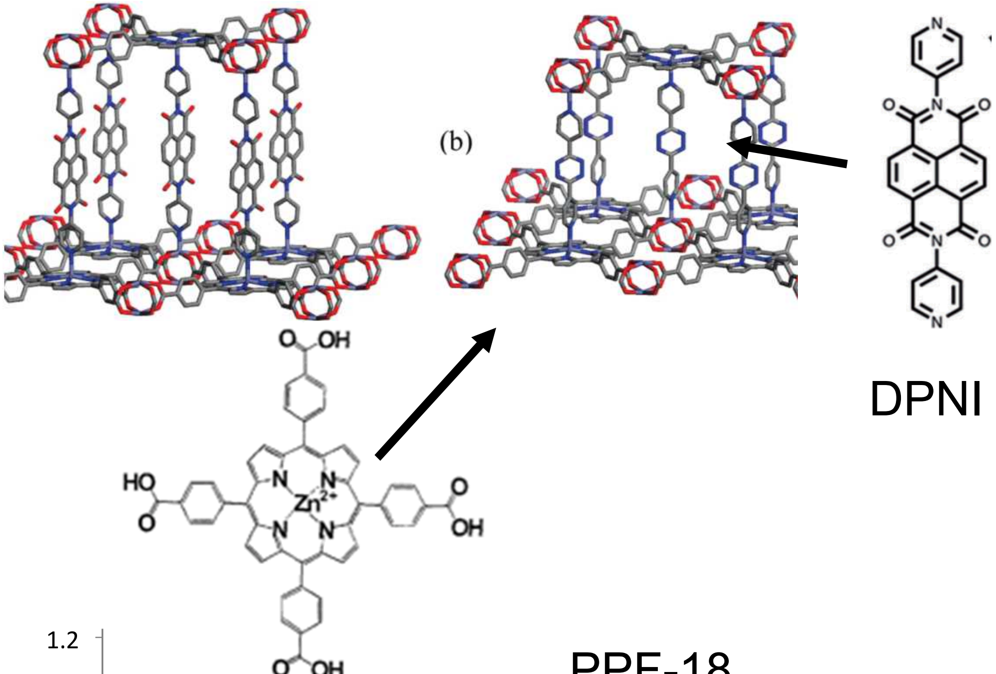
Potential advantages of PPF active layer:

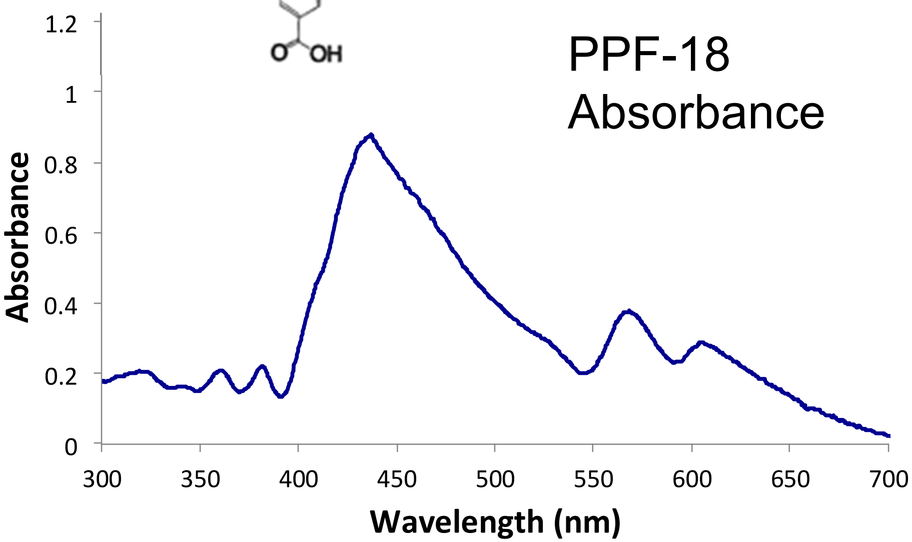
- Visible light absorption
- Ordered charge transport pathways
- Non-aggregated dye assembly
- Porosity for electrolyte access
- Promising photostability

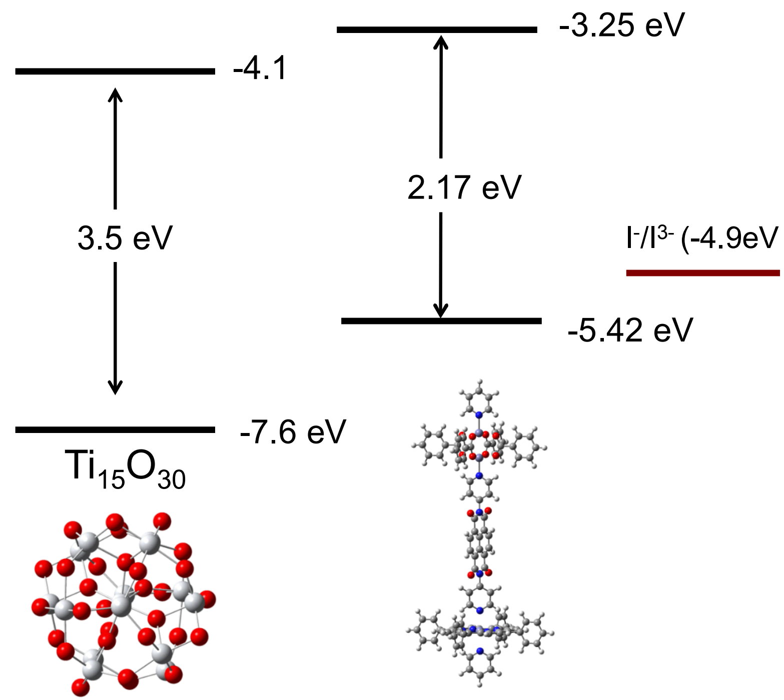


Challenge: Incorporating PPFs into DSSCs as active layer materials.

PPF-18…a Promising Candidate

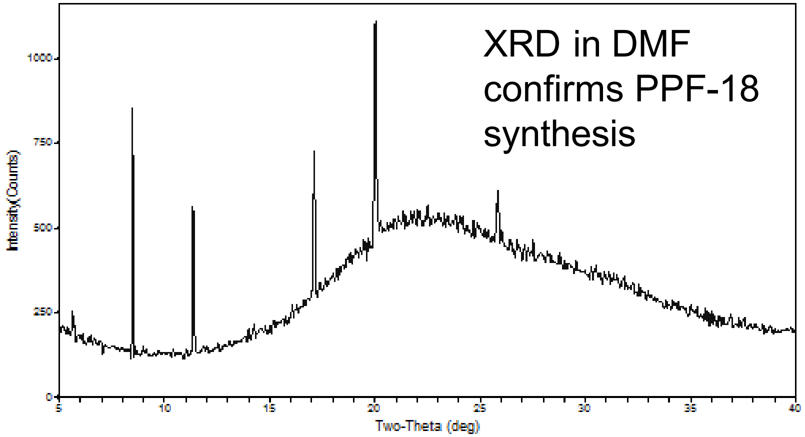






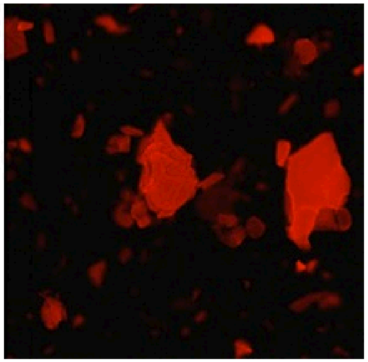
DFT predicts PPF-18 band alignment as slightly better than PPF-5…

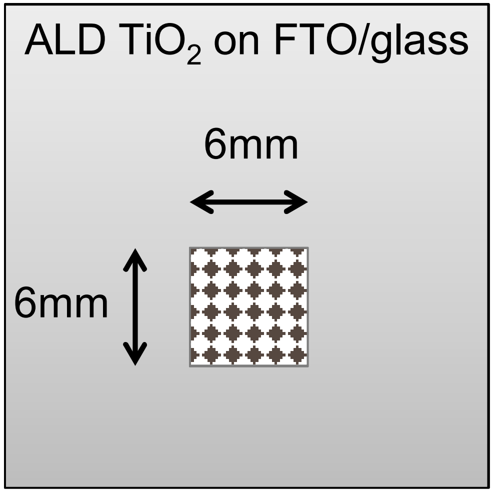
Assembling PPF-18 in a DSSC



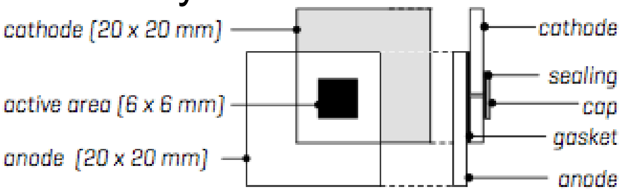
Solvothermal synthesis produces deep blue, crystalline PPF-18 particles.

PPF-18 Fluorescence (Green Excitation)





PPF-18 crystals were thoroughly washed with DMF, then chloroform, and dropcast out of chloroform onto a masked ALD TiO_2-coated substrate for device assembly.



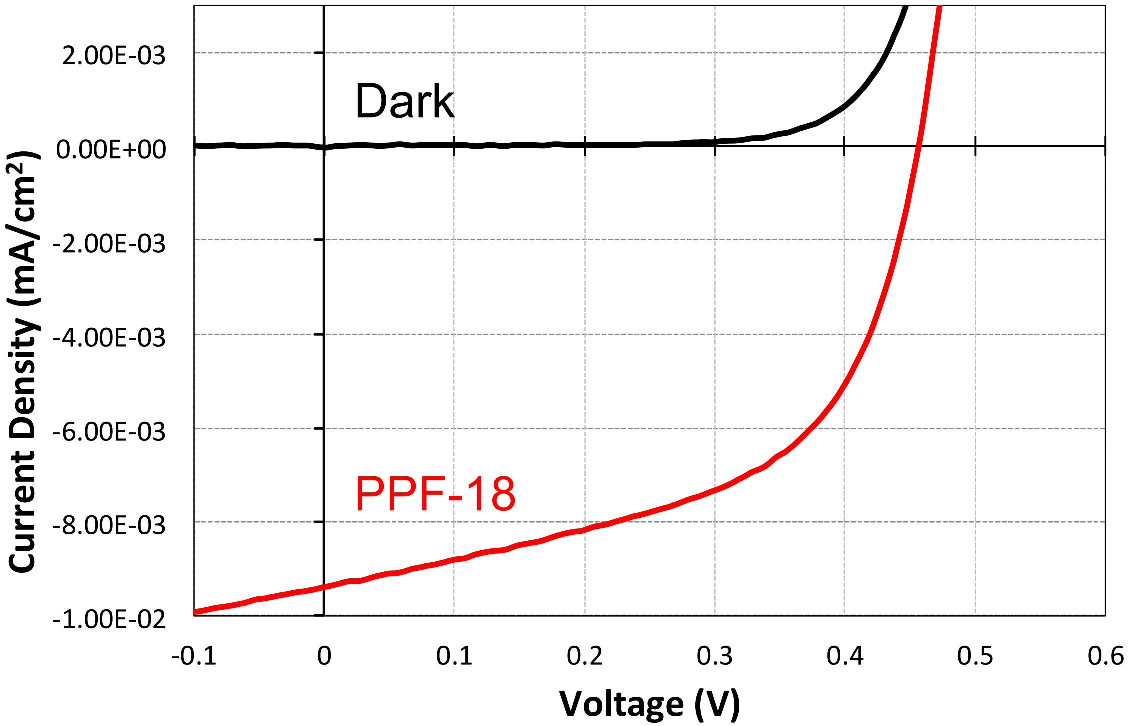
Solaronix, SA

Device Configuration and Details:

- Titania Working Electrode on FTO
- Pt nanoparticle counter electrode on FTO
- Iodolyte AN-50
- Surlyn gaskets and sealants

Performance of PPF-18 in a DSSC

DSSCs assembled from washed PPF-18 produces measurable photocurrent.



Averaged metrics:

V_{oc} (V) = 0.425 ± 0.029

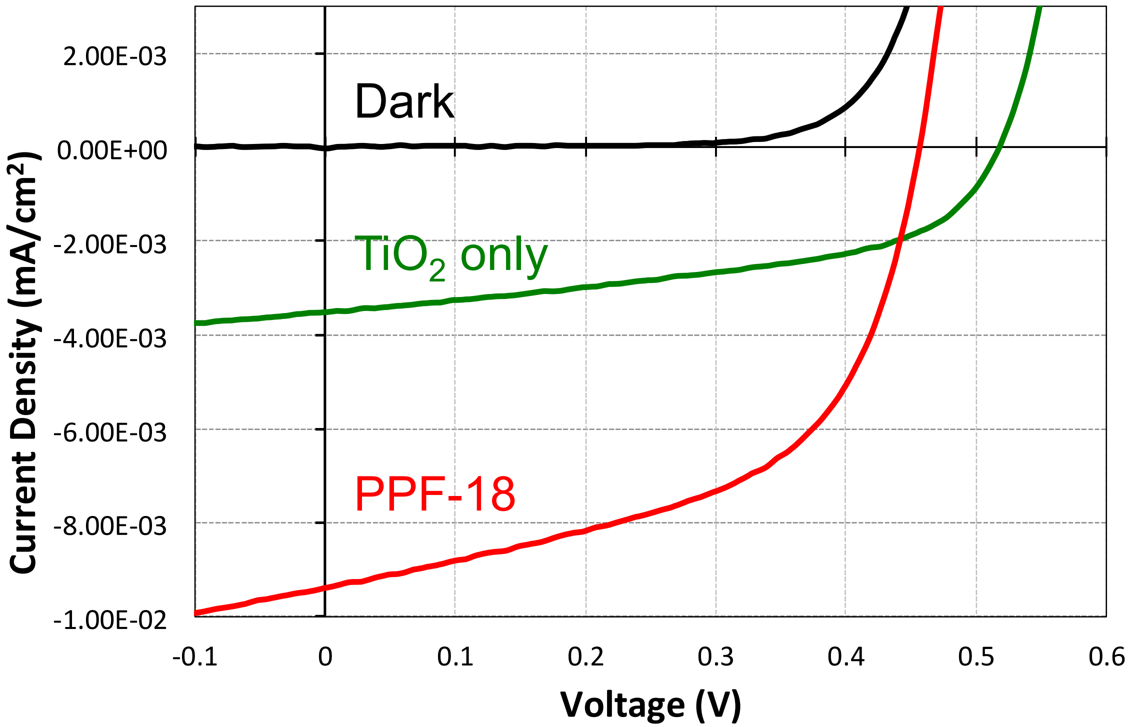
J_{sc} (mA/cm^2) = 0.00797 ± 0.0012

FF = 0.548 ± 0.014

η (%) = 0.00186 ± 0.000338

Negative Control: No PPF-18

Control experiments containing no PPF-18 produce reduced photocurrent.



Averaged metrics:

Voc (V) = 0.537 ± 0.023

Jsc (mA/cm^2) = 0.00410 ± 0.00090

FF = 0.486 ± 0.014

η (%) = 0.00107 ± 0.000233

Voc (V) = 0.425 ± 0.029

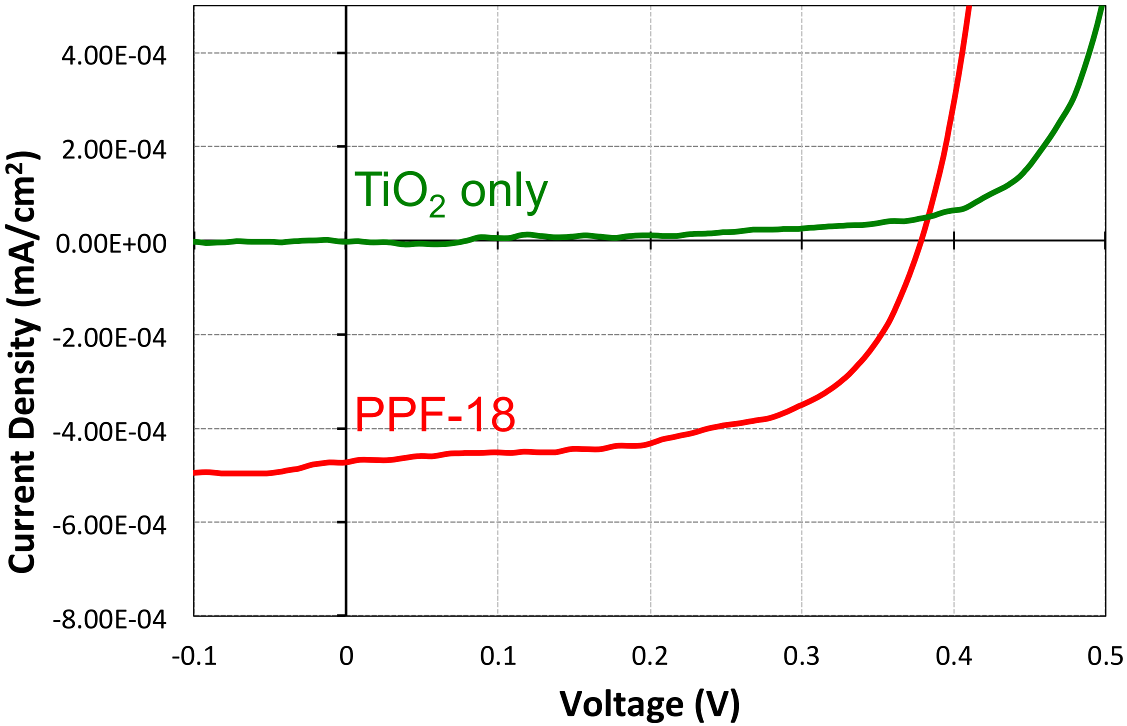
Jsc (mA/cm^2) = 0.00797 ± 0.0012

FF = 0.548 ± 0.014

η (%) = 0.00186 ± 0.000338

Confirming PPF Photocurrent with Green Light

Using a band pass filter (~490 nm) to remove UV excitation of TiO_2 still produces measurable photocurrent from PPF-18 DSSCs.



<u>Averaged metrics:</u>

Voc (V) = 0.370 ± 0.021

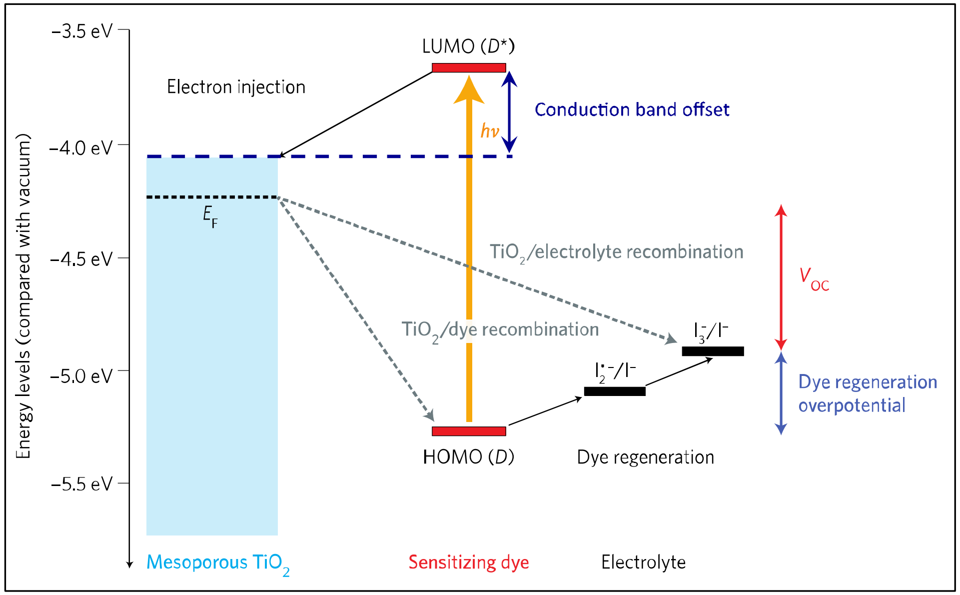
Jsc (mA/cm²) = 0.000377 ± 0.00011

FF = 0.62 ± 0.018

What Next?

How to build on this initial demonstration?

- Improve interfacial loading on TiO_2
- Optimize band alignments to reduce loss in potential
- Increase spectral range of absorber
- Consider Guest-host interactions
- Explore stability/reliability



DSSC Summary

- MOFs are highly porous, multifunctional composites crystals, assembled from "modular" molecular building blocks.
- PPF-18 incorporated into a DSSC yields measurable photocurrent, attributable to the absorbers in the MOF.
- Tuning of MOF composition, structure, and interfaces with TiO_2 are expected to improve DSSC device performance.
- This preliminary demonstration shows that this electrochemical configuration is a feasible platform to explore the diversity of MOF chemistry in solar applications.

MOFs introduce enormous diversity and opportunity for the development of new, interesting, and potentially very effective photoactive materials!

Acknowledgements

Microtubules:
Dr. Haiqing Liu
Marlene Bachand
Judy Hendricks
Bridget Connor
Dr. George Bachand

Synthetic Peptides:
Dr. Brad Jones
Alina Martinez
Jill Wheeler
Dr. David Wheeler

Ion Conductors:
Jill Wheeler
Dr. Leo Small
Dr. Paul Clem
Dr. Jon Ihlefeld
Dr. Harlan Brown-Shaklee

MOF-DSSCs:
Dr. Mark Allendorf
Dr. Michael Foster
Dr. Vitalie Stavila
Jill Wheeler
Dr. Dara Gough
Dr. Tim Lambert

Characterization:
XRD – Dr. Mark Rodriguez
SEM – Bonnie McKenzie
TEM – Dr. Dara Gough
Mass Spec – Lance Miller

Funding Acknowledgements

- Active assembly and reconfigurable materials work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, Biomolecular Materials Program (KC0203010).
- NaSICON battery work was funded by the U.S. Department of Energy Office of Electricity Delivery and Energy Reliability.
- Chemical separations work was funded by the U.S. Department of Energy Office of Nuclear Energy under the Fuel Cycle Research and Development Program.
- MOF-DSSC work was funded by the U.S. DOE Energy Efficiency and Renewable Energy (Sunshot): Next Generation PV II and III and the Sandia Laboratory Directed Research and Development Program.

OFFICE OF ELECTRICITY DELIVERY & ENERGY RELIABILITY

SunShot U.S. Department of Energy

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

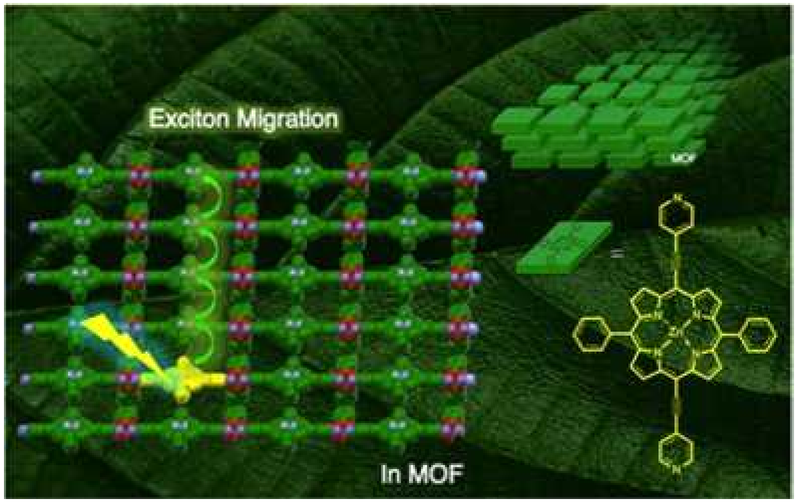
NNSA National Nuclear Security Administration

Backup Slides

Building Photoactive MOFs

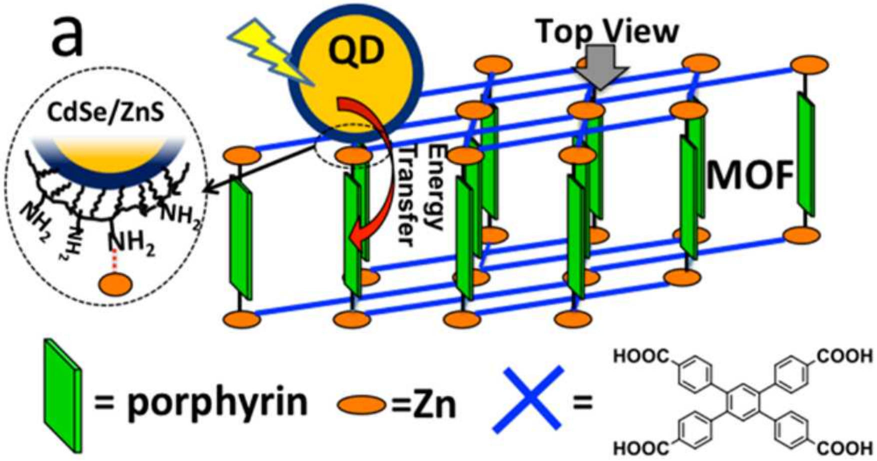
Energy transfer is viable in porphyrin-based MOFs

Fast exciton transport between porphyrins



H.-J. Son, *et al. JACS* (2013) **135**. 862-869.

Energy transfer between MOFs and semiconductors



S.Jin, *et al. JACS* (2013) **135**. 955-958.

Precedents for using porphyrins in DSSCs…

1. Kay and Grätzel, J. Phys. Chem. (1993) **97**, 6292.
2. Walter, et al. J. Porphyrins and Phthalocyanines. (2010) **14**, 759.
3. M. J. Griffith and A. J. Mozer (2011), Available from: http://www.intechopen.com/books/solar-cells-dye-sensitized-devices/porphyrin-based-dye-sensitized-solar- cells