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Sandia National Laboratories

MOF@ALD: A New, Integrated Materials Platform to Improve Dye-Sensitized Solar Cells

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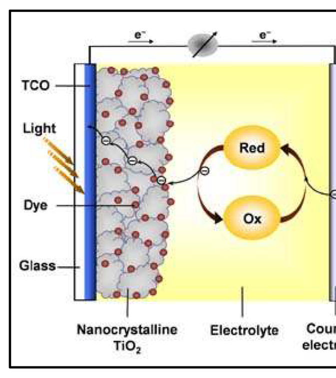
Technical Problem

Dye-Sensitized Solar Cells (DSSCs)

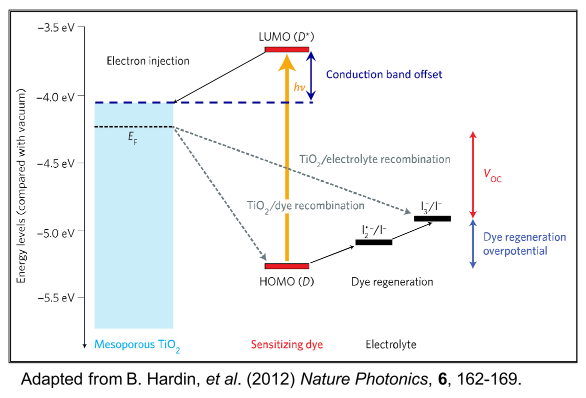
(O'Regan, B. & Grätzel, M. (1991). *Nature*, **353**, pp 737.)

DSSCs have re-emerged as a promising PV technology with world record efficiencies >15%…but there are still some critical challenges:

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



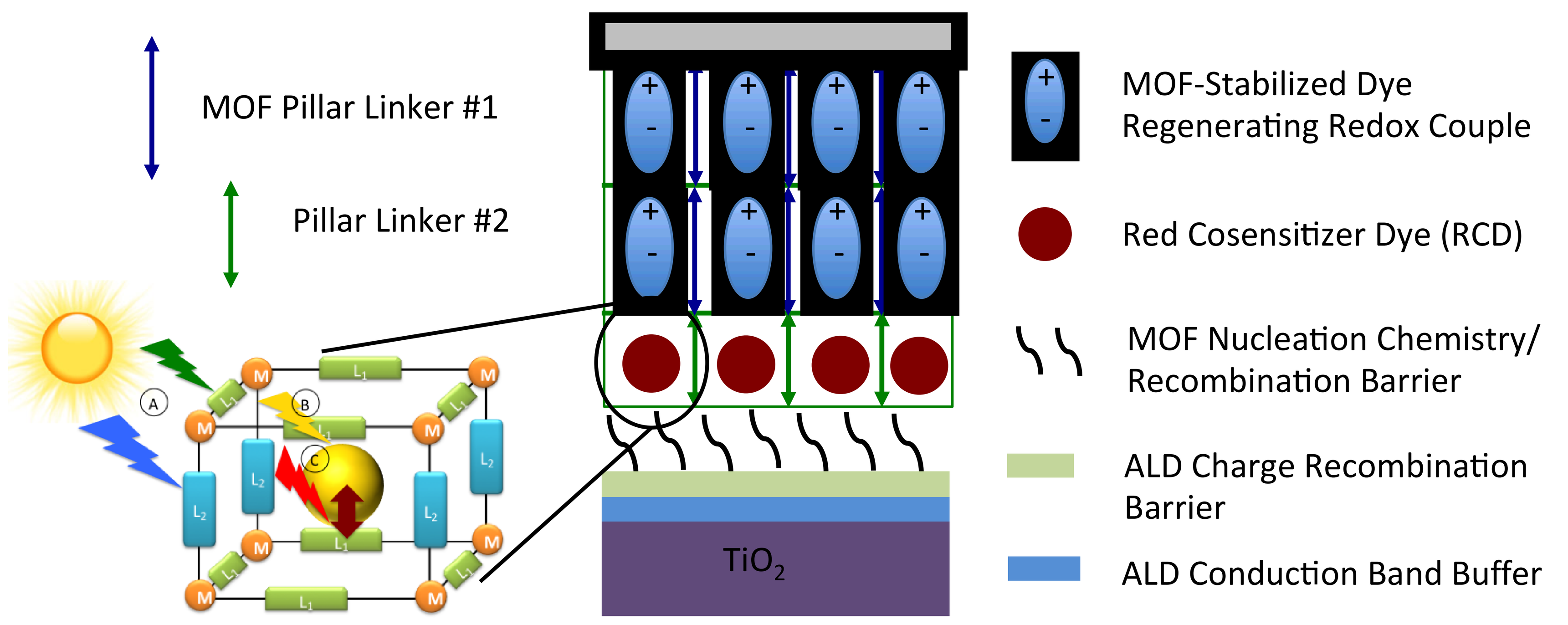
http://staff.bath.ac.uk/pysabw/abwmod.html



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

Our challenge: Can we use molecular design of materials and interfaces to improve DSSCs?

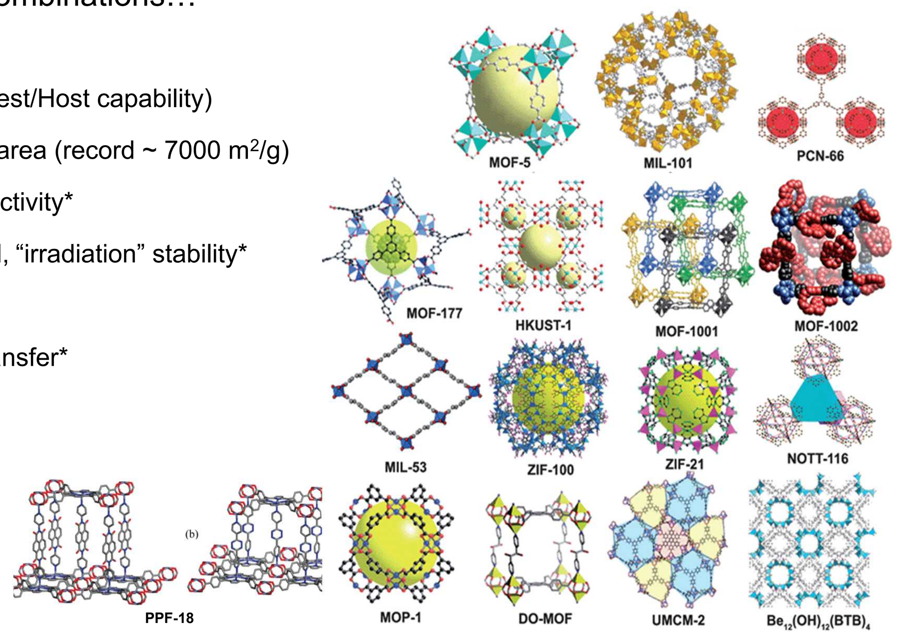
Approach



MOF Selection and Development

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*



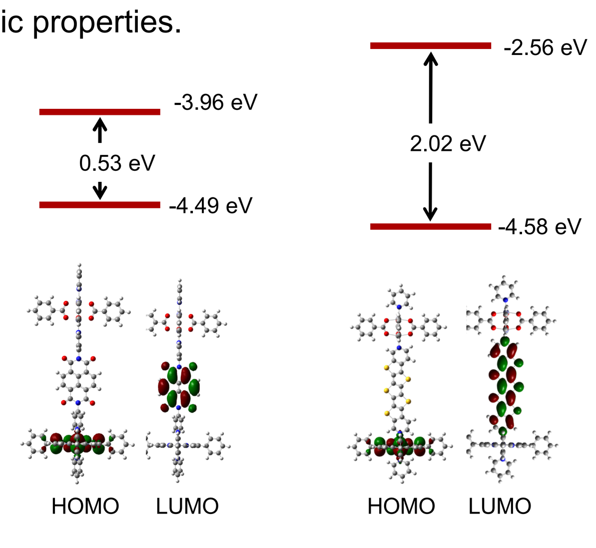
*MOF dependent

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

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

Density Functional Theory (DFT) simulations can be used to predict the optoelectronic band structure of different MOF structures.
These studies not only help identify suitable candidate MOFs, but can also help predict how modifications of the modular MOF structure can be used to tune the optoelectronic properties.

Varying organic pillars

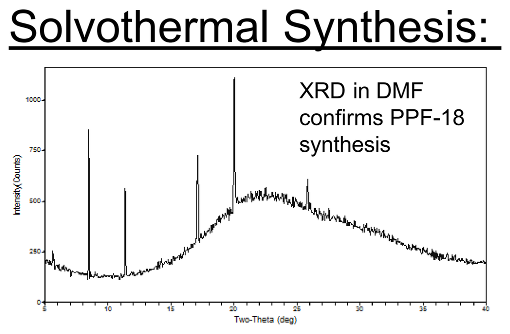


2D periodic optimization - DFT(B3LYP/ CEP-31G)

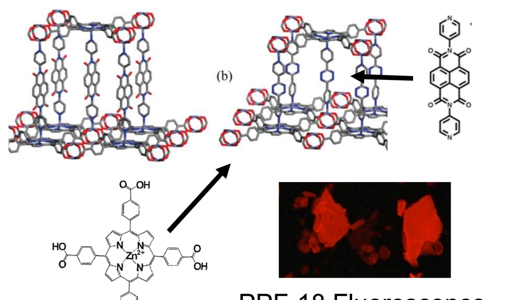
Results and Accomplishments

MOF Synthesis

Solvothermal Synthesis:

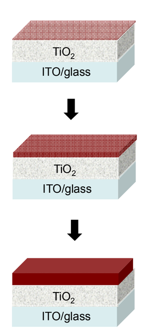


Solvothermal synthesis produces deep blue, crystalline PPF-18 particles that fluoresce red under visible light excitation.



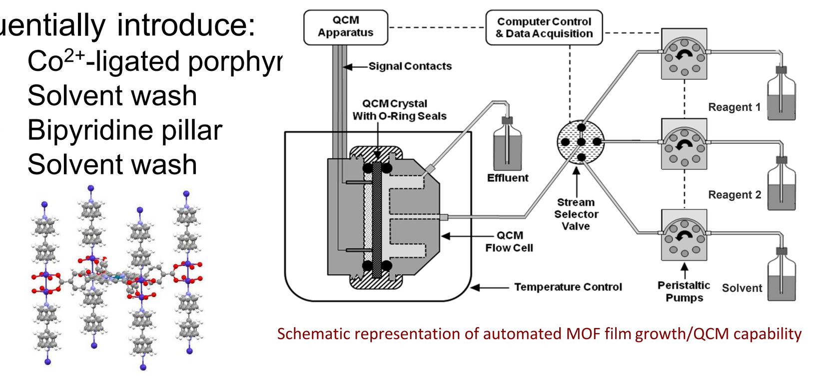
PPF-18 Fluorescence (Green Excitation)

Layer-by-Layer Synthesis (Stavila)

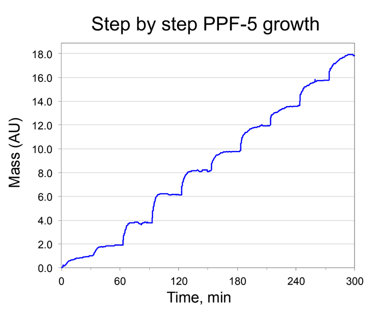


Sequentially introduce:

- Co^{2+}-ligated porphyr
- Solvent wash
- Bipyridine pillar
- Solvent wash

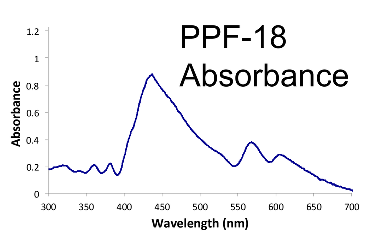


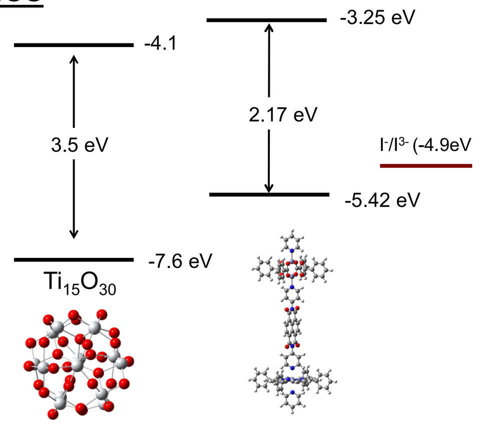
Schematic representation of automated MOF film growth/QCM capability



PPF-n MOF Properties

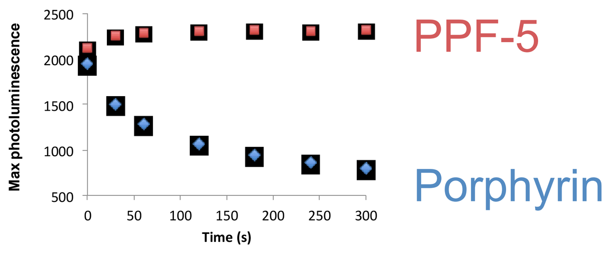
Visible light absorbance and expected reasonable band alignment for a DSSC.





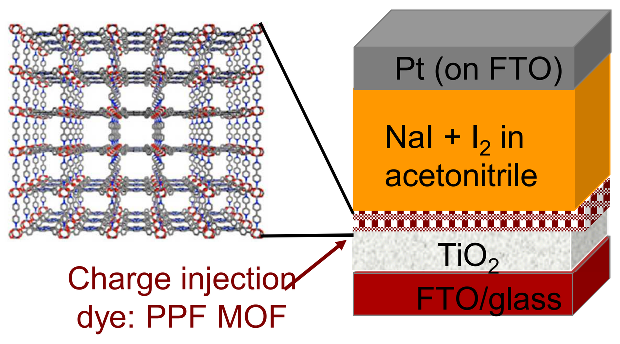
DFT(M06-2X/6-31G)

PPF-5 also shows remarkable photostability, relative to the free porphyrin linker, potentially important for optimal DSSC performance.

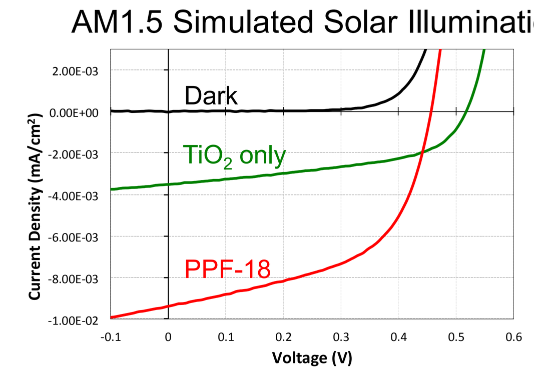


DSSC Performance

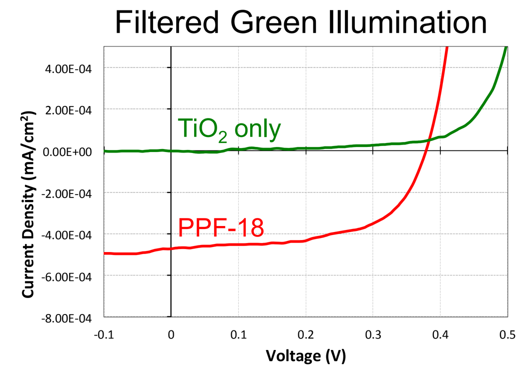
Solvothermal PPF-18 was washed to remove free absorber and deposited on planar anatase TiO_2 (grown by ALD).



AM1.5 Simulated Solar Illumination



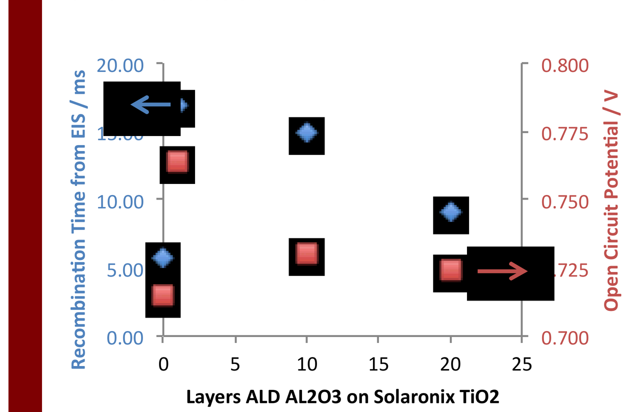
Filtered Green Illumination



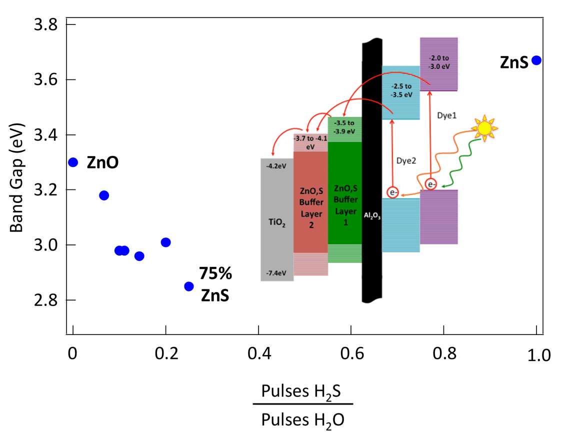
Initial test cells show measureable photocurrent from MOF-based DSSCs! Green light illumination confirms the source of the photocurrent is from the porphyrin used to make the MOF.

ALD Interfacial Coatings

ALD-deposited Al_2O_3 barrier coatings show increased carrier lifetime (decreased recombination) and increased Voc.



ALD-deposited conduction band "buffer" layers with tunable band gaps will mediate charge transfer from MOFs to TiO_2.



Moving Forward

How to build on this initial work?

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

Impact and Mission Relevance

Through this integrated, molecular materials approach, we expect to be able to improve many of the issues limiting DSSC large-scale utilization:

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

If successful, the ultimate improvements in PV technology realized stand to directly impact and dynamic and versatile energy infrastructure, which directly ties to several Sandia programmatic priorities:

- Sandia's Secure and Sustainable Energy Future Mission Area
- Power on Demand Research Challenge
- Materials Science Research Foundation Thrusts
  - Control of Energy Mass and Charge Transfer
  - Developing New Materials - Next Generation Materials for Electronics and Optoelectronics

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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SunShot U.S. Department of Energy

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT