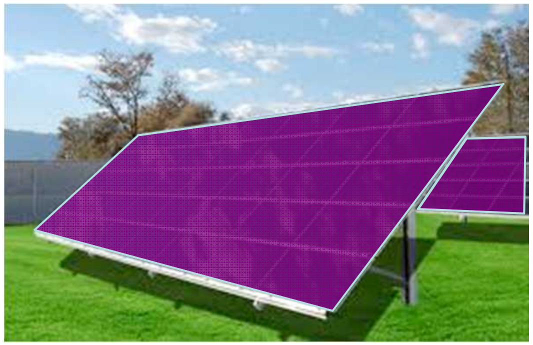
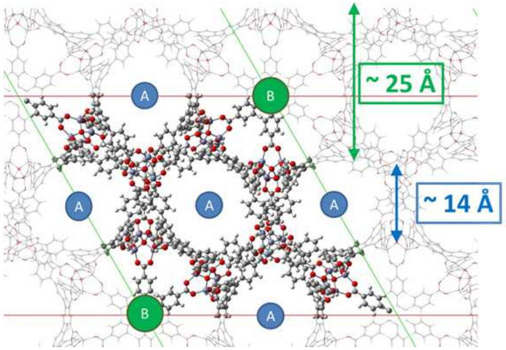
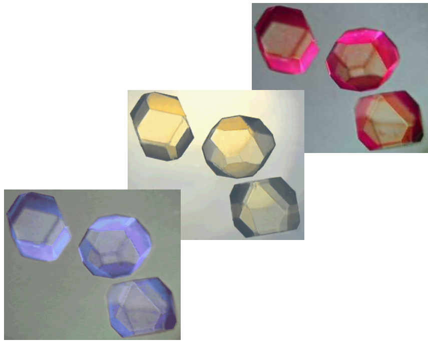
SAND2015-0142C

Exceptional service in the national interest

Sandia National Laboratories





Solar MOFs: Supramolecular Materials to Enable Next Generation Dye-Sensitized Solar Cells

Erik D. Spoerke

Leo Small, Steven Wolf, Jill Wheeler

Michael Foster, Vitalie Stavila, Kirsty Leong, and Mark D. Allendorf

Energy Materials Nanotechnology 2015 on Photovoltaics

SunShot U.S. Department of Energy

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

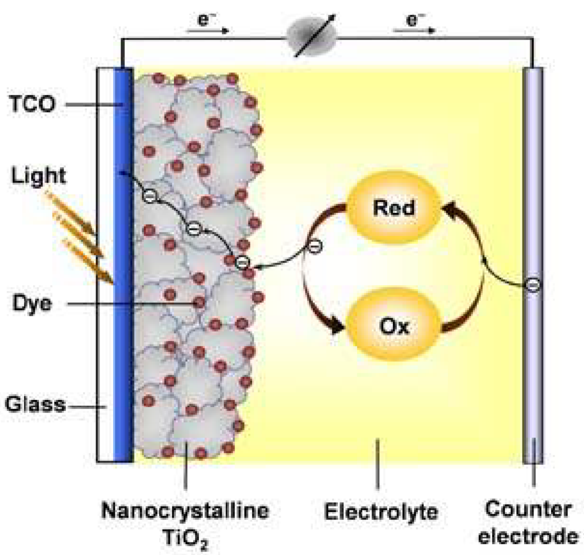
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

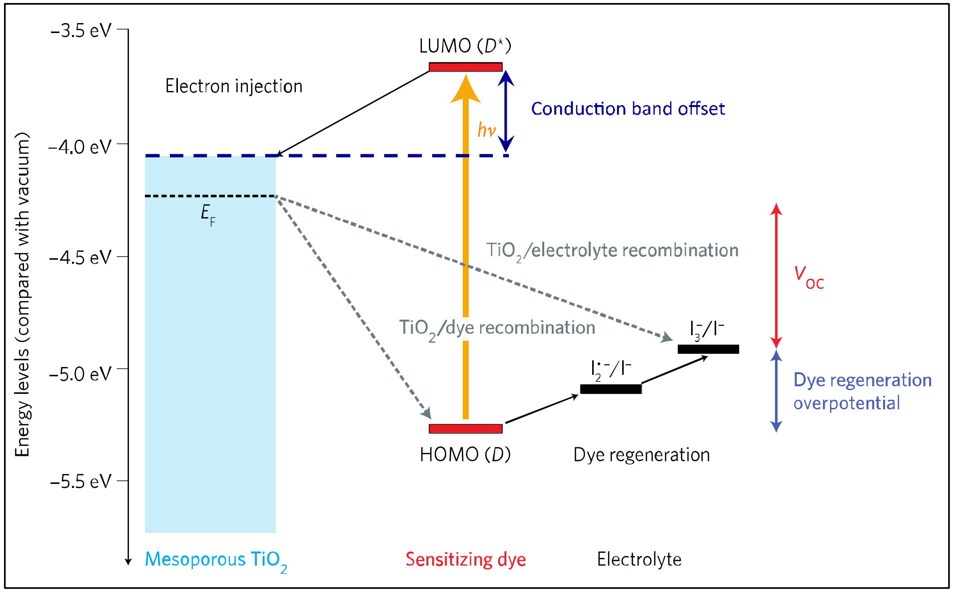
Dye-Sensitized Solar Cells

(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





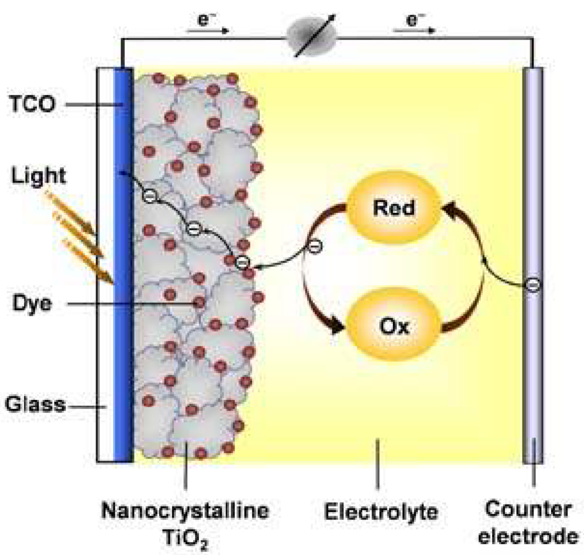
http://staff.bath.ac.uk/pysabw/abwmod.html

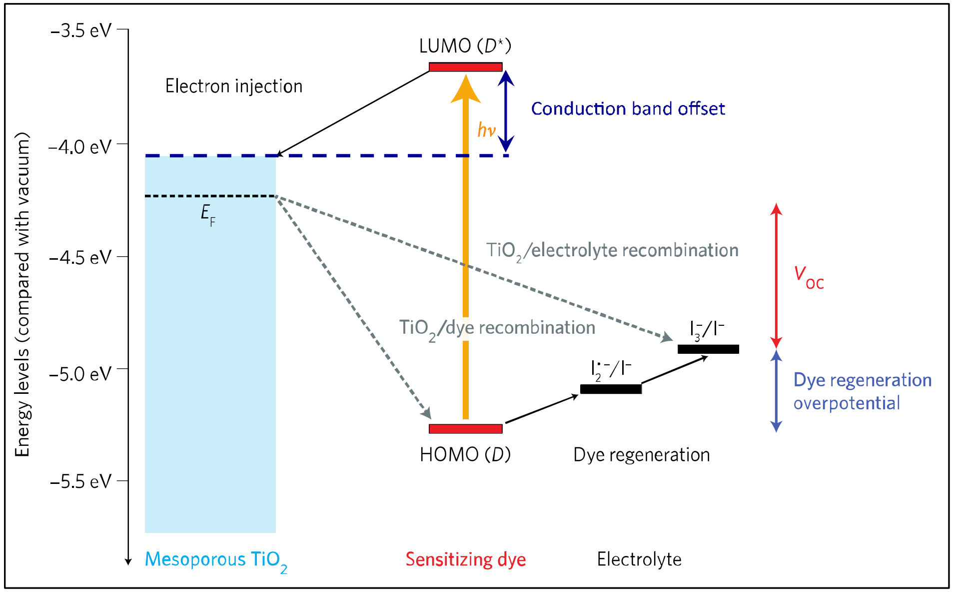
Technical Challenge

Dye-Sensitized Solar Cells

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

Can we use Metal-Organic Frameworks (MOFs) to address these challenges?



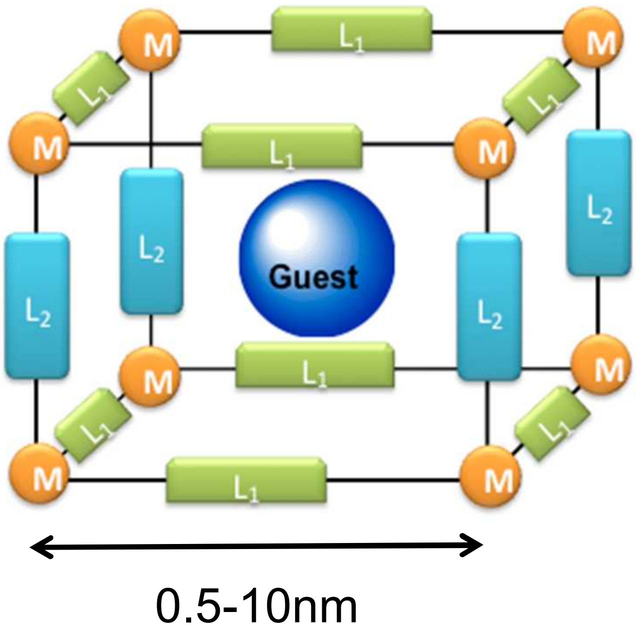


http://staff.bath.ac.uk/pysabw/abwmod.html

What are Metal-Organic Frameworks?

Metal-Organic Frameworks (MOFs)

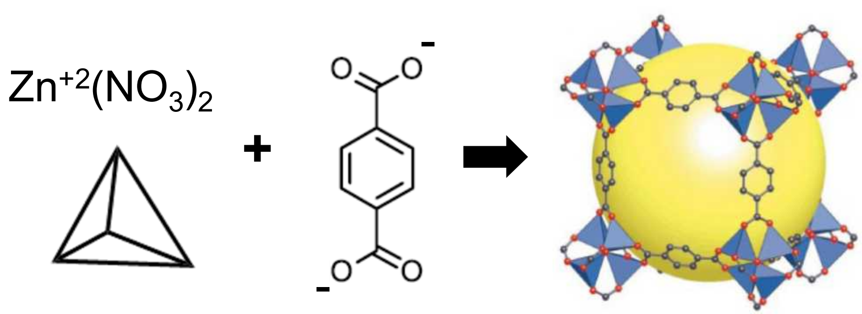
A subset of coordination polymers



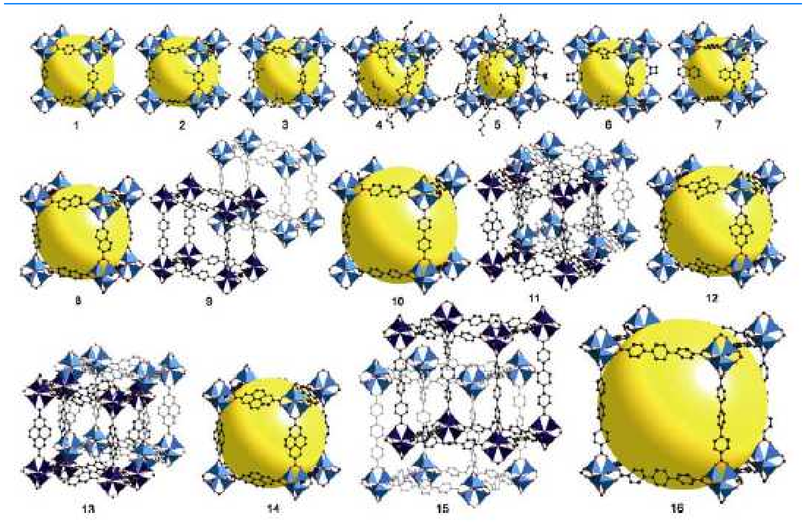
Crystalline MOF structures are composed of metal nodes (M), linkers (L_1) and pillars (L_2).

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

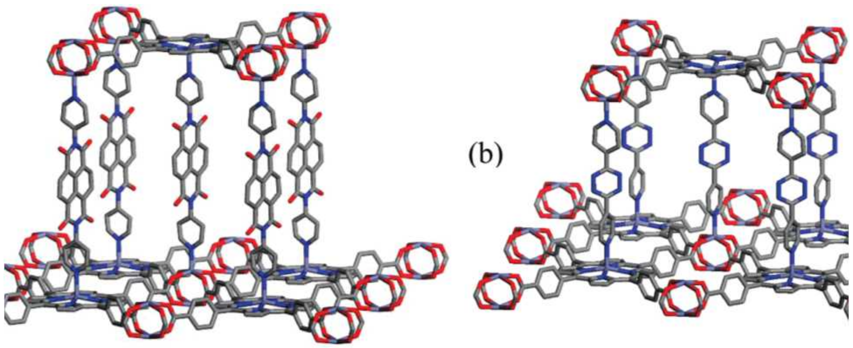
This chemically "modular" system allows for tuning of the structure, properties, and function of these materials.



MOF Building Block Chemistry Determines Crystal Structure

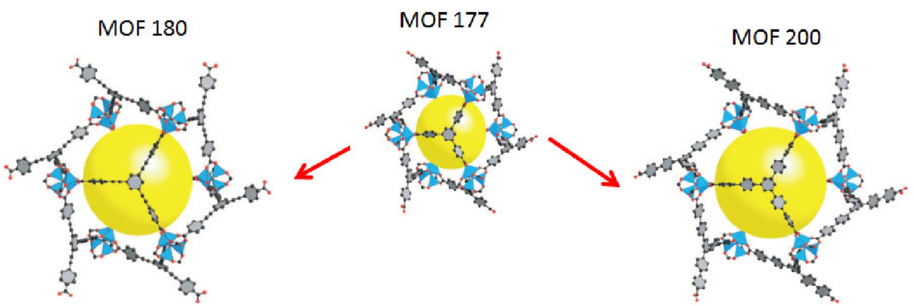


http://yaghi.berkeley.edu/research-MOF.html



Side view of PPF-18

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

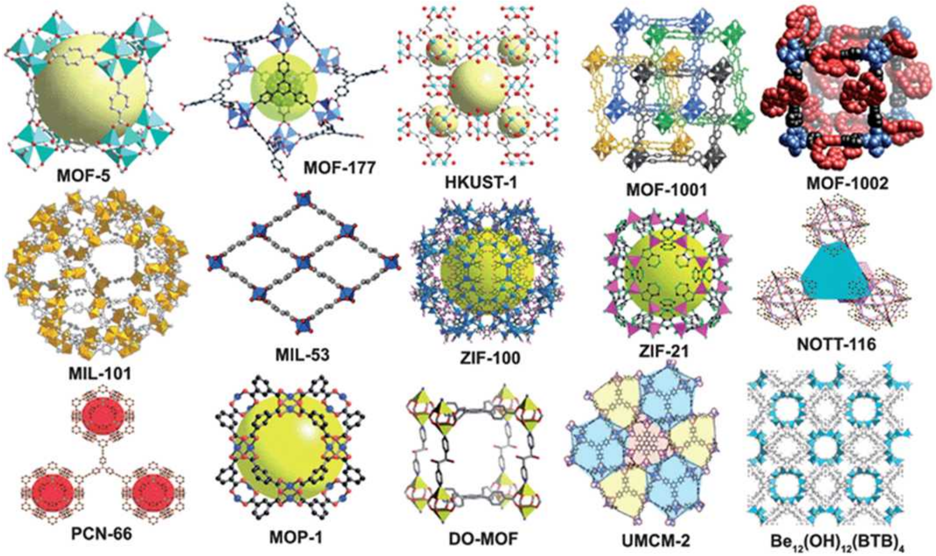


http://www.cchem.berkeley.edu/molsim/teaching/fall2011/CCS/Group7/structure.htm

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

MOF Properties

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



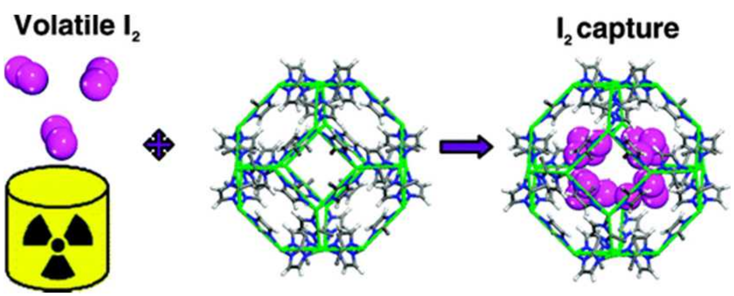
*MOF dependent

Z. Xiang, et al. *Energy Environ. Sci*. (2010), **3**, 1469.

MOF Applications Span A Wide Range of Fields

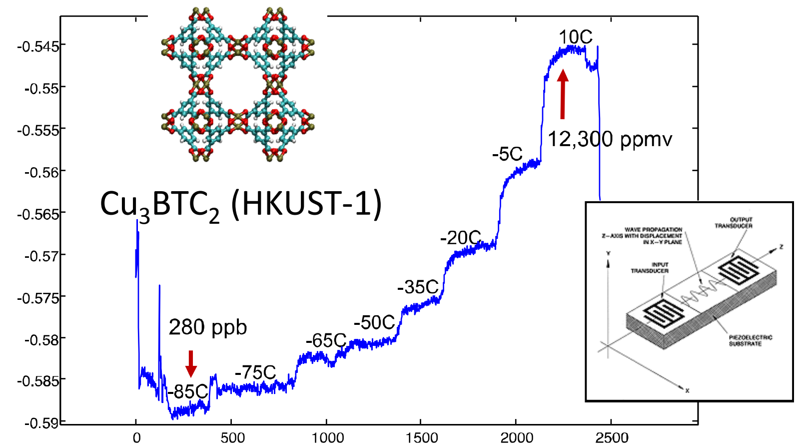
Sandia National Laboratories

Gas Sorption (I_2 capture)



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

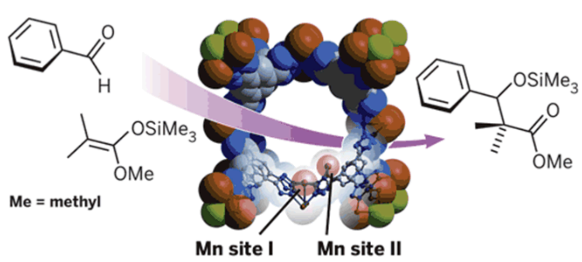
Sensing (H_2O sensing)



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

Catalysis (Mukaiyama aldol synthesis)

Mn-BTT



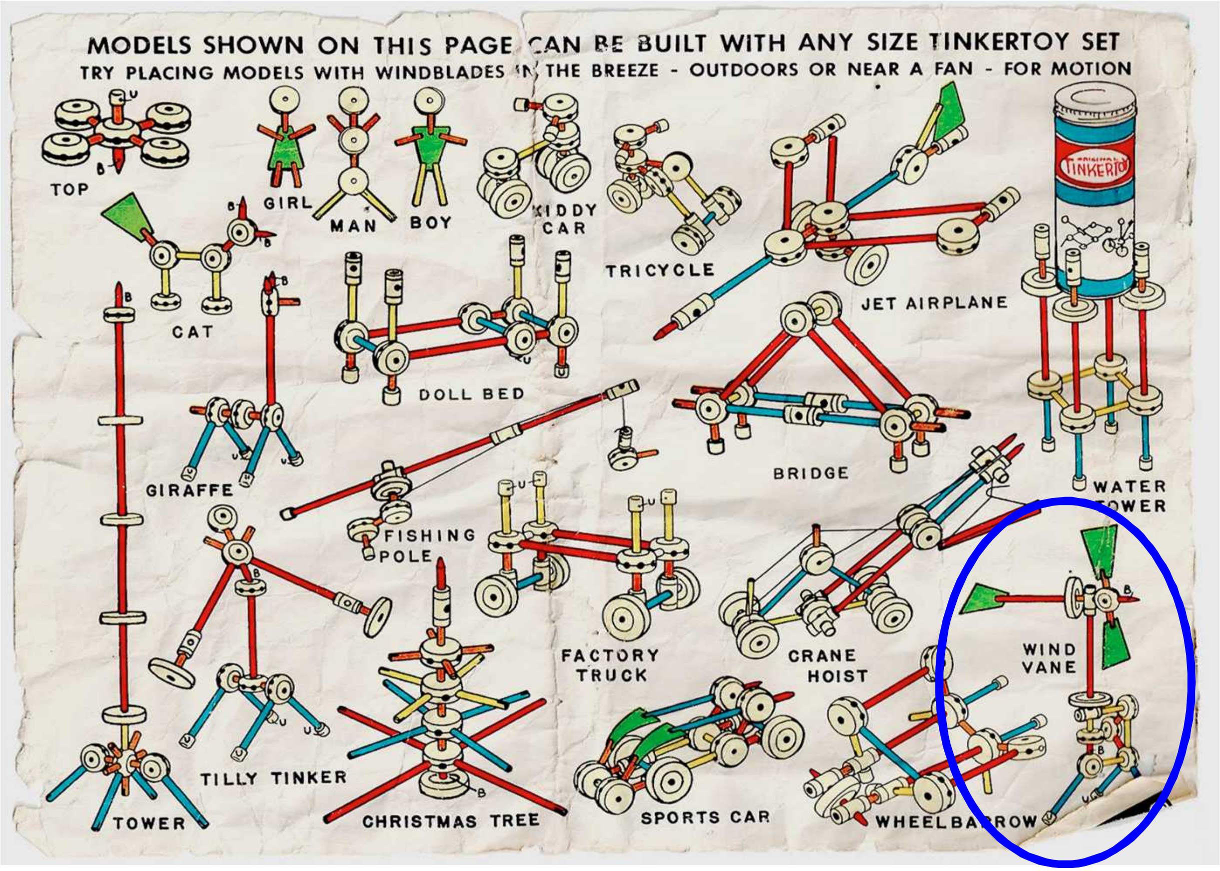
Horike*, et al. JACS,* **2008**, *130* (18), pp 5854–5855

Electronics/Optoelectronics

?

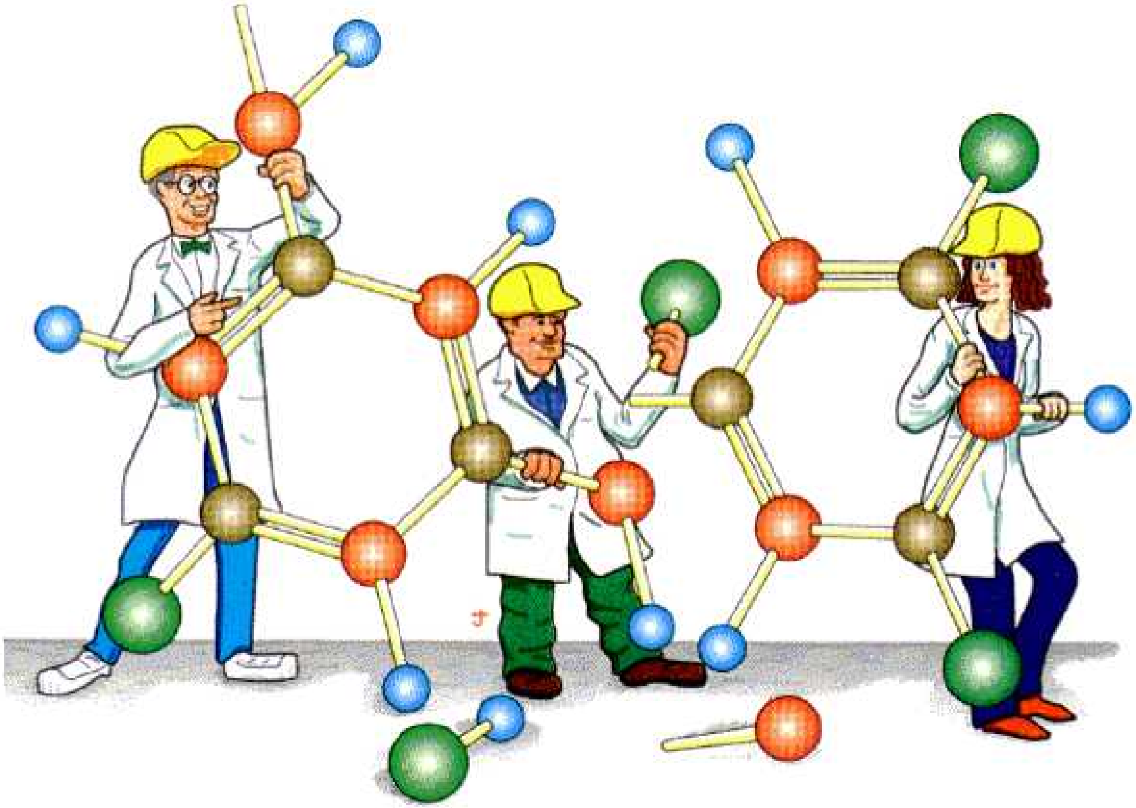
MOFs: Supramolecular "Tinker Toys"

A modular materials system for renewable energy?

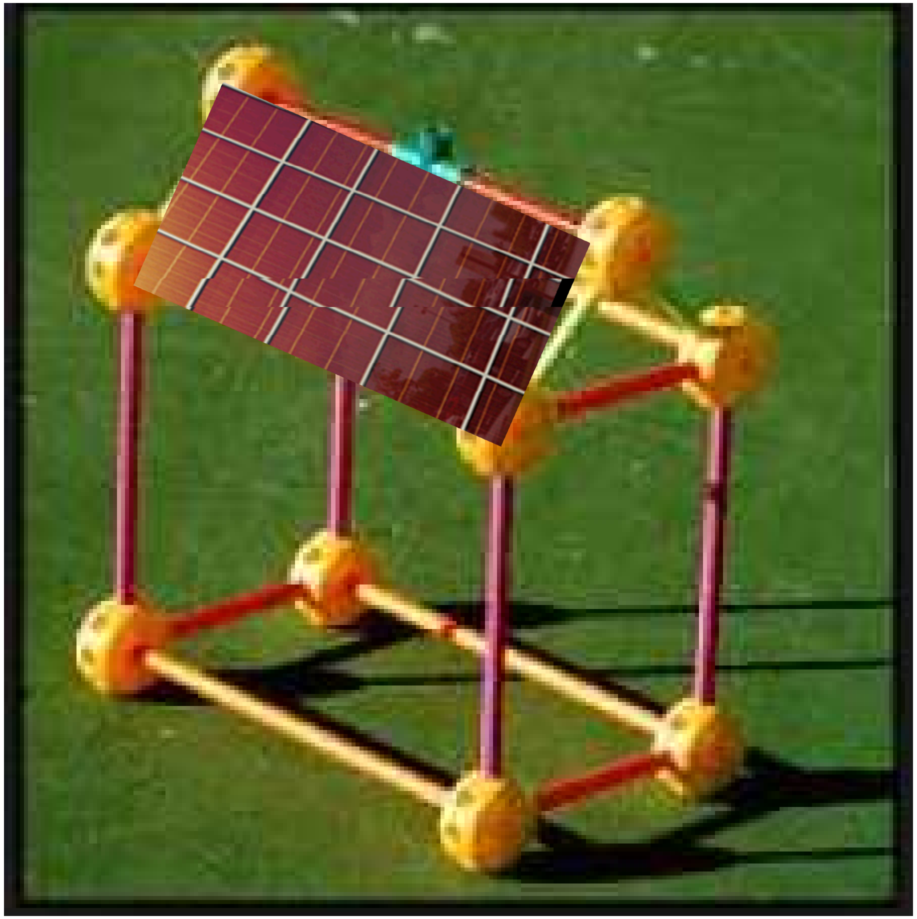


Realizing Supramolecular Materials…

Can we manipulate and assemble these supramolecular building blocks to improve DSSCs?



Merging "Modular" Chemistry and Photovoltaics…

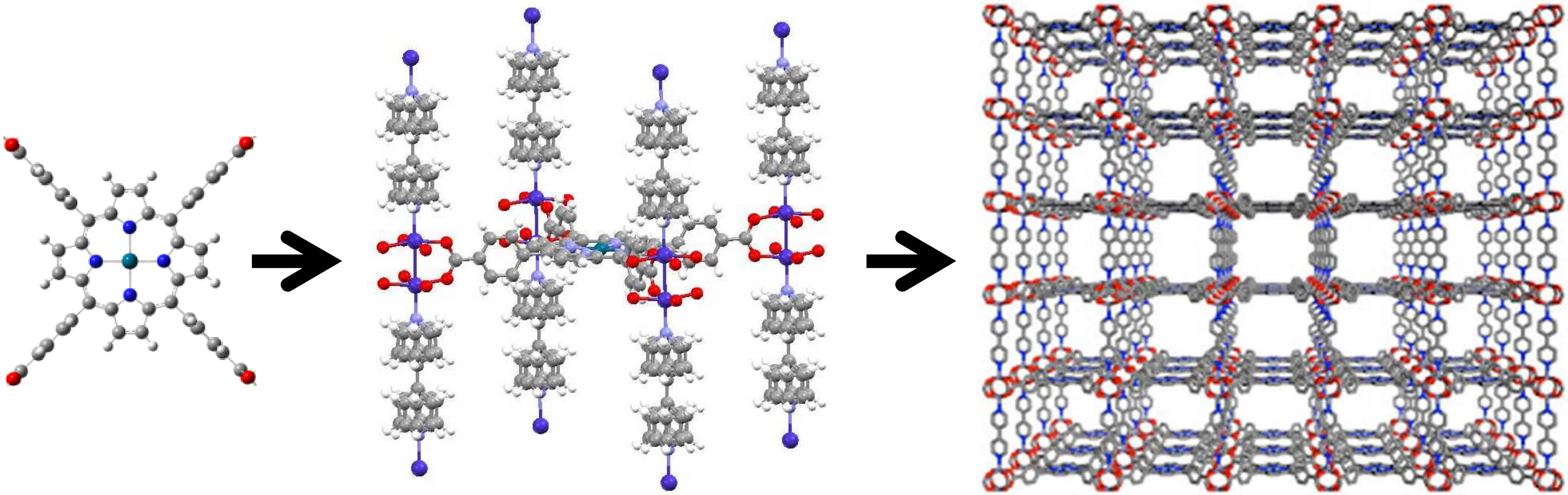


Building Photoactive MOFs

Consider Pillared Porphyrin Frameworks (PPFs)

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

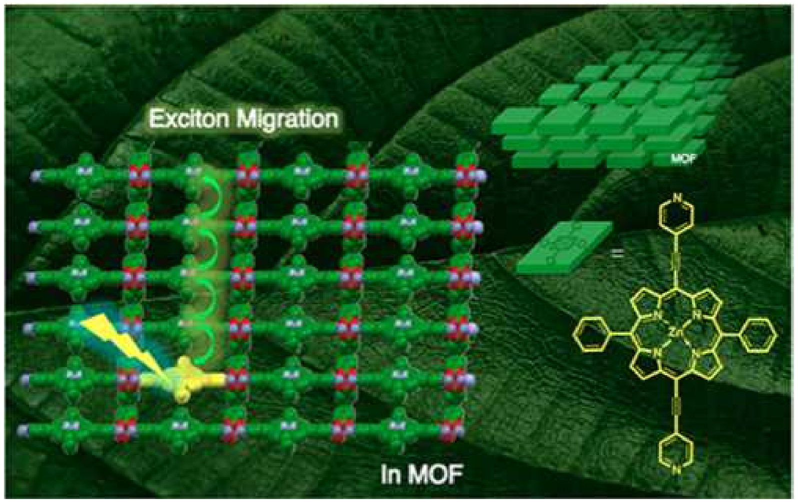
PPF-5



Building Photoactive MOFs

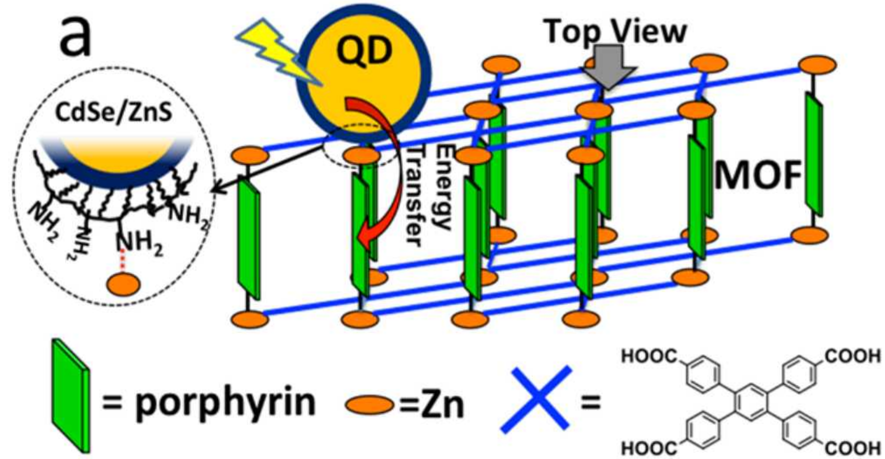
Energy transfer is viable in porphyrin-based MOFs

Fast exciton transport between porphyrins



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

Energy transfer between MOFs and semiconductors

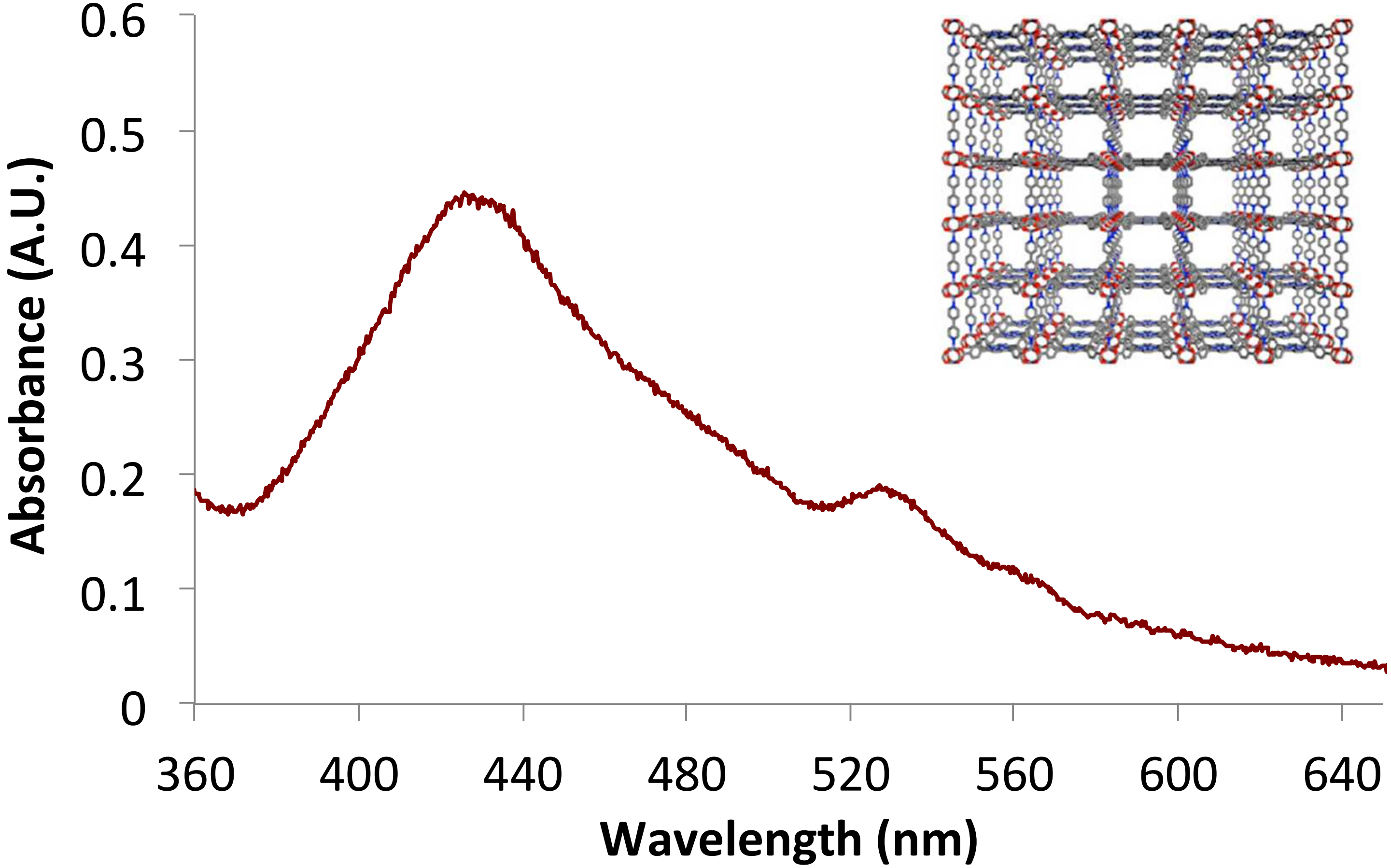


S.Jin, *et al. JACS* (2013) **135**. 955-958.

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

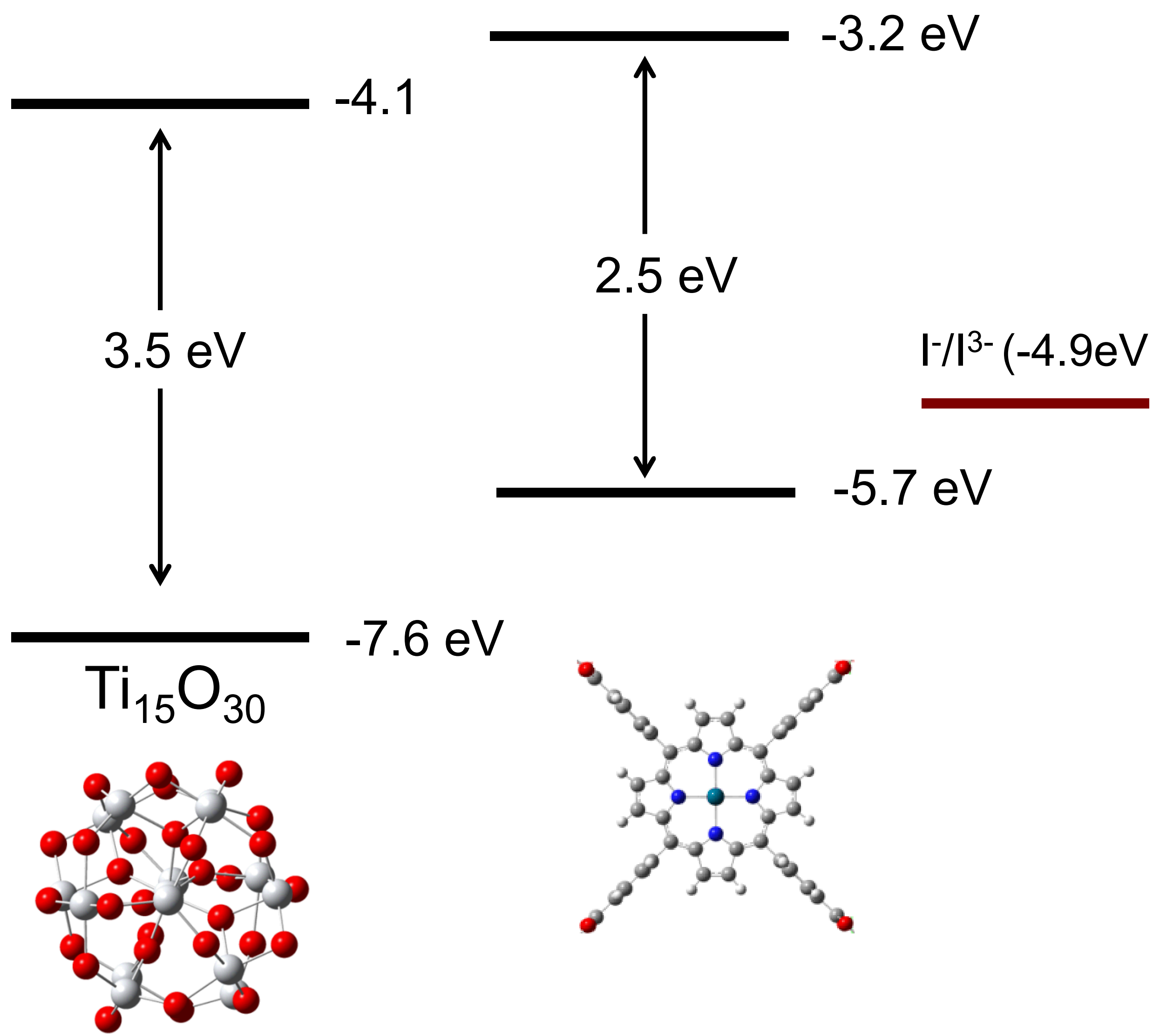
PPF-5 Optical Absorbance



PPF-5 absorbs meaningful visible light.

DFT Predictions of Band Alignment

Density Functional Theory (DFT) predicts reasonable band alignment between the PPF-5 porphyrin and a TiO_2 electron acceptor.



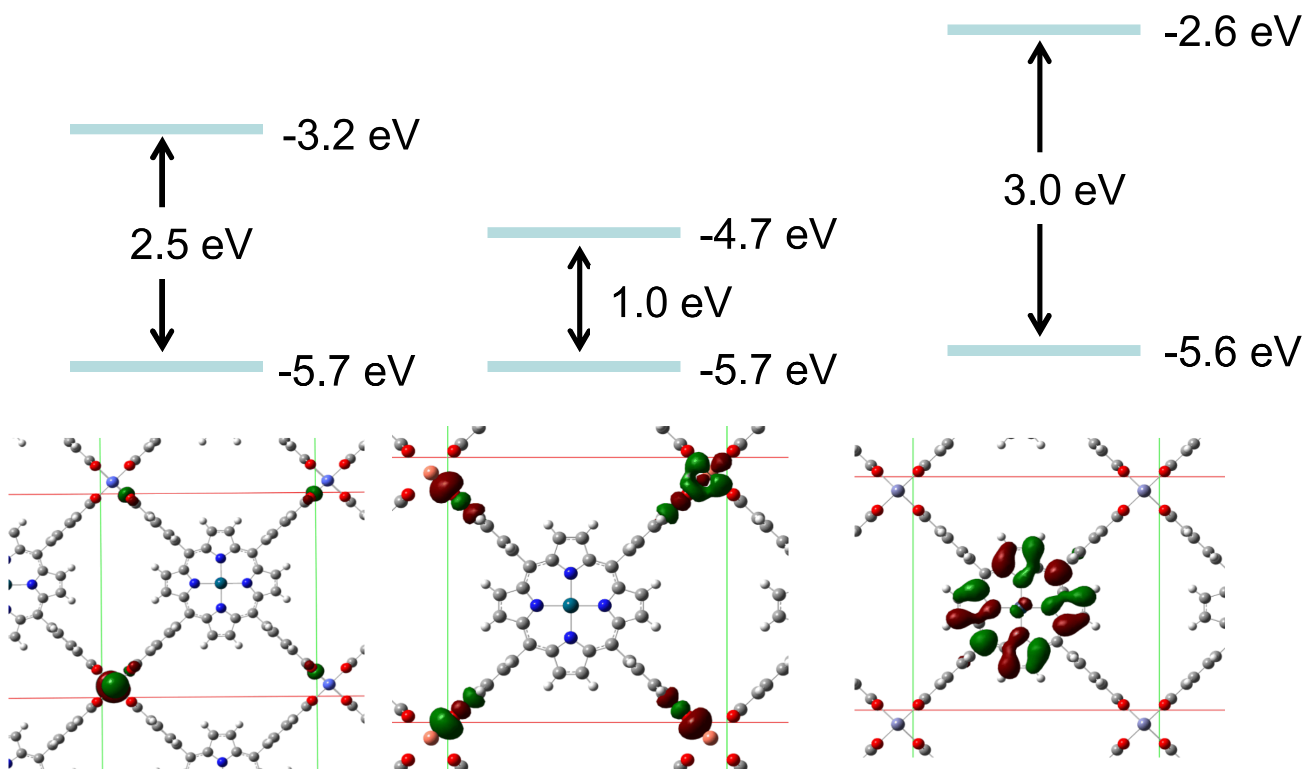
TiO_2 Molecular Clusters
DFT (B3LYP/LanL2DZ)

PPF-5 2D
DFT(B3LYP/ CEP-31G)

Band Structure Tailoring

Density Functional Theory (DFT) simulations show that by varying the composition of PPF molecular building blocks, it is possible to tune the electronic band structure of these MOFs.

<u>Varying transition metal ions</u>



LUMO Pd porphyrin - Co layer

LUMO Pd porphyrin - Cu layer

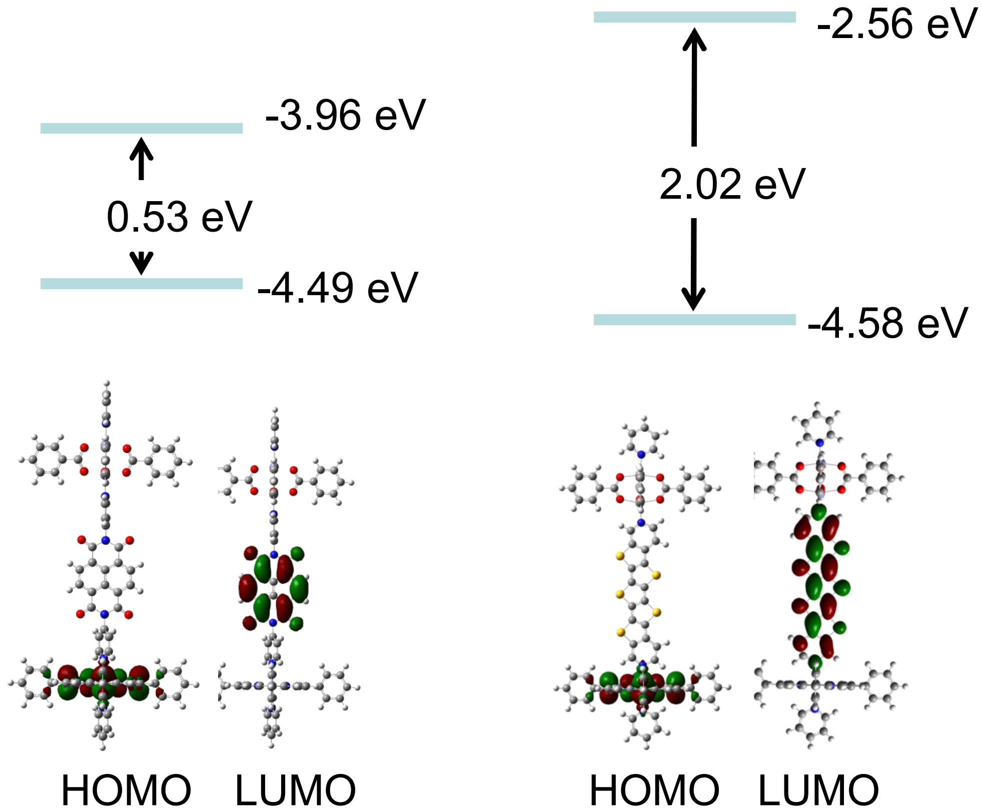
LUMO Pd porphyrin - Zn layer

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

Band Structure Tailoring

Density Functional Theory (DFT) simulations show that by varying the composition of PPF molecular building blocks, it is possible to tune the electronic band structure of these MOFs.

<u>Varying organic pillars</u>

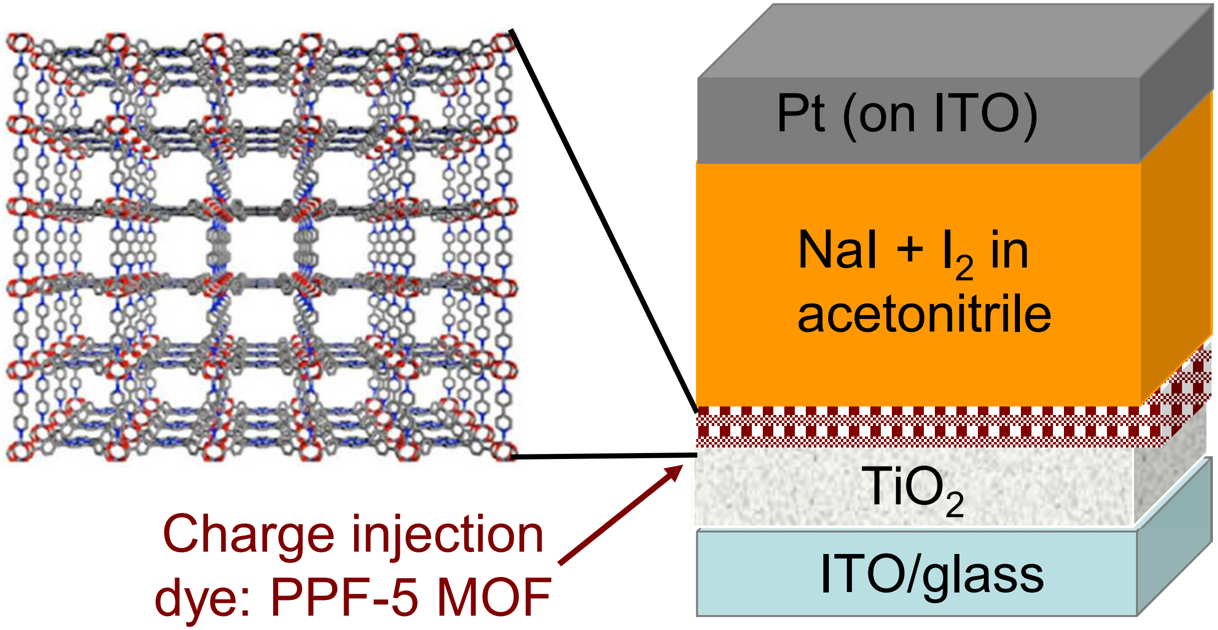


2D periodic optimization - DFT(B3LYP/ CEP-31G)

Integration of PPF-5 in DSSCs

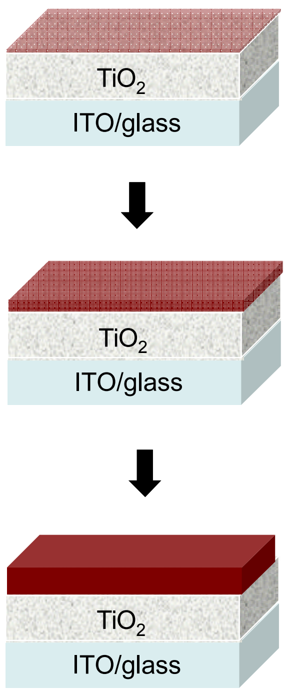
Potential advantages of PPF-5 active layer:

- Visible light absorption
- Reasonable, potentially tunable band alignment
- Ordered charge transport pathways
- Non-aggregated dye assembly
- Porosity for electrolyte access

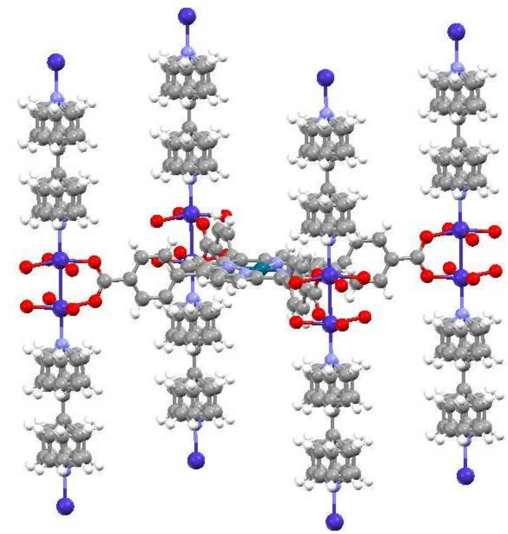


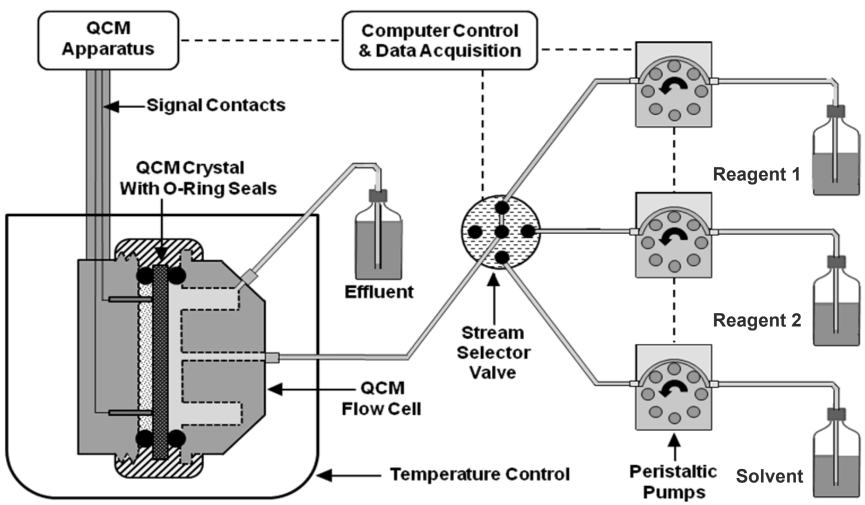
Can we grow PPF-5 onto the TiO_2 anode for integration into a "standard" DSSC configuration?

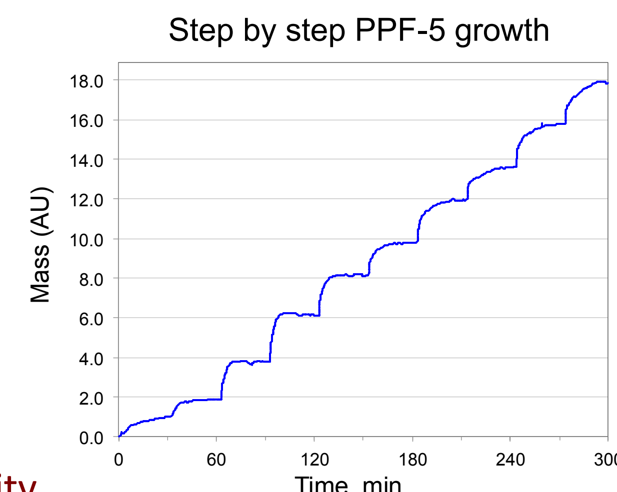
Layer-by-Layer MOF Growth



1. Deposit/anneal TiO_2 nanoparticle slurry (DeGussa P25) on ITO/glass
2. Pretreat TiO_2 with Co^{2+}
3. Sequentially introduce
   - Co^{2+}-ligated porphyrin linker
   - Solvent wash
   - Bipyridine pillar
   - Solvent wash



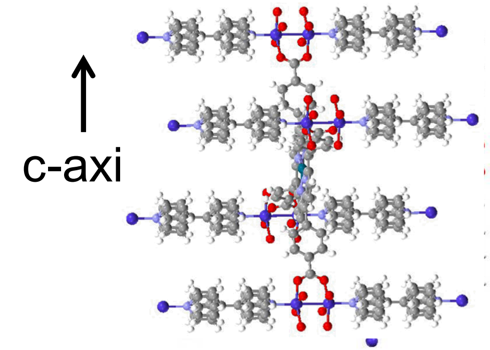


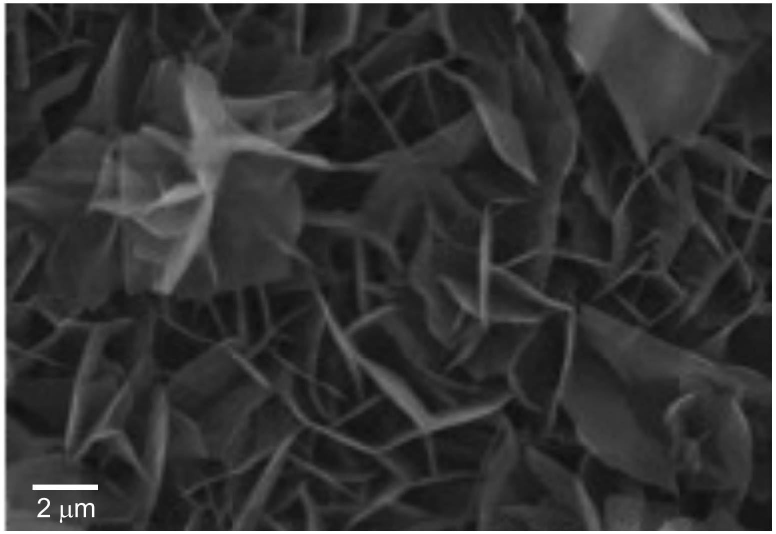


Schematic representation of automated MOF film growth/QCM capability

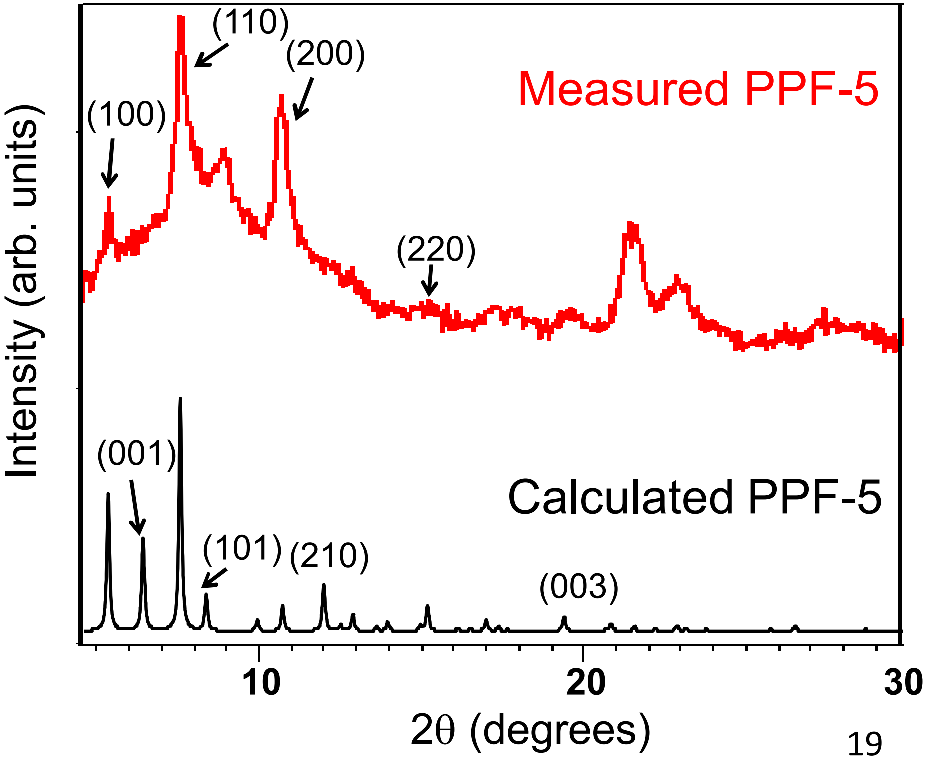
Characterization of PPF-5 Films on TiO_2/ITO

LBL-growth produces a porous array of PPF-5 crystals exhibiting crystallographic orientation on the TiO_2 surface.





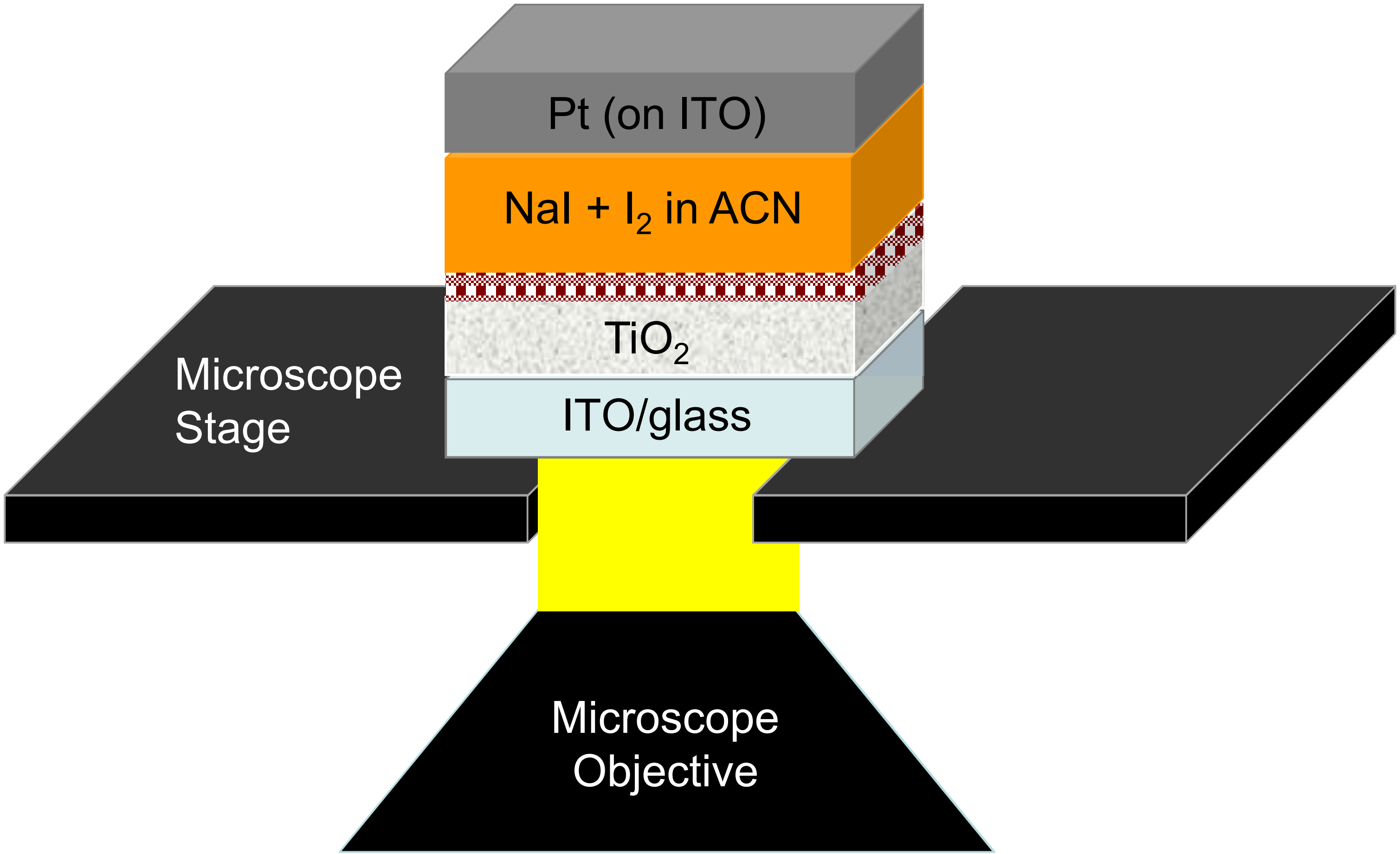
Scanning electron micrograph shows PPF-5 "platelets" extending off the TiO_2 surface.



Vitalie Stavila

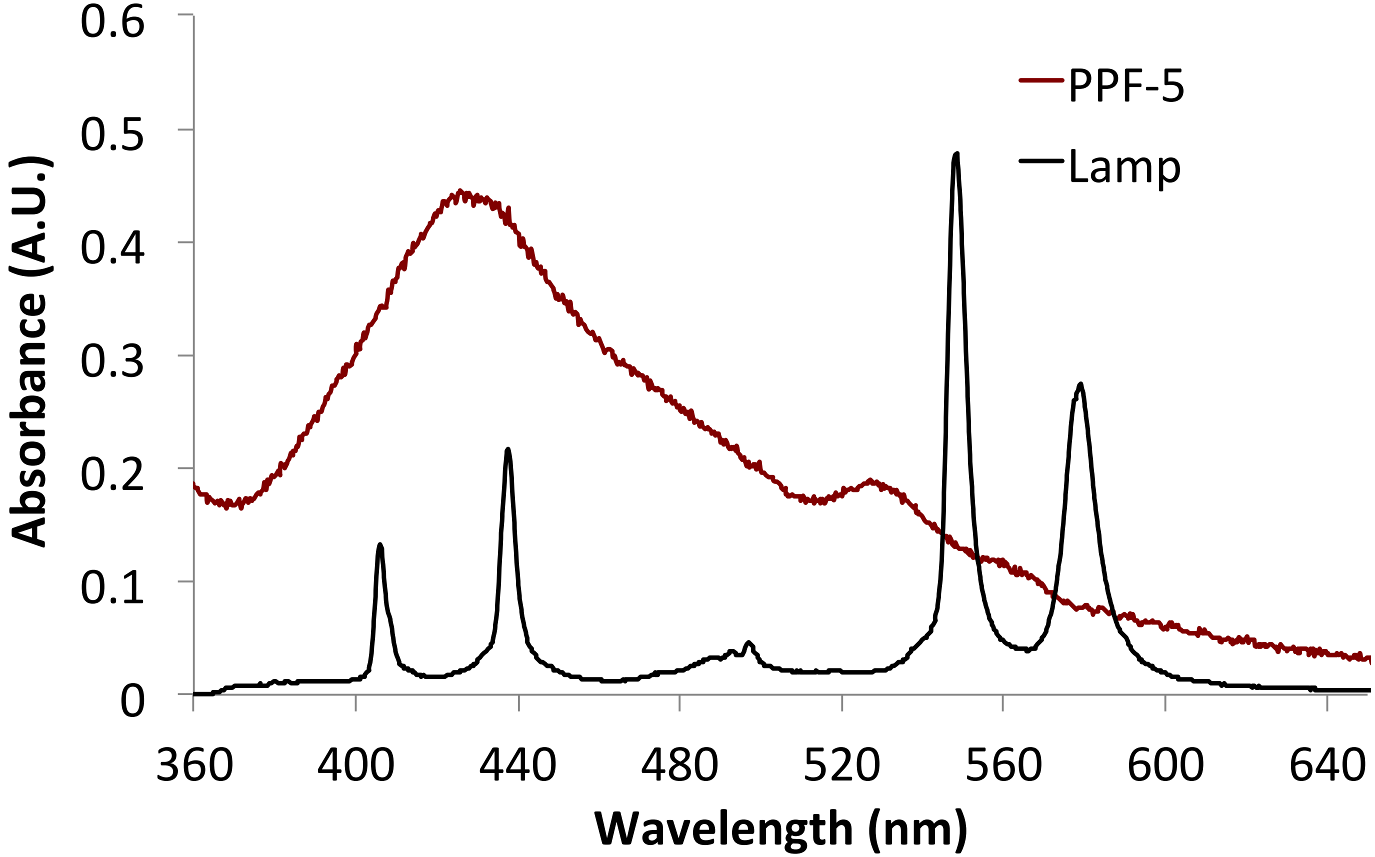
PV Measurement Setup

DSSC devices assembled and tested on microscope stage with UV-filtered Hg-arc lamp.



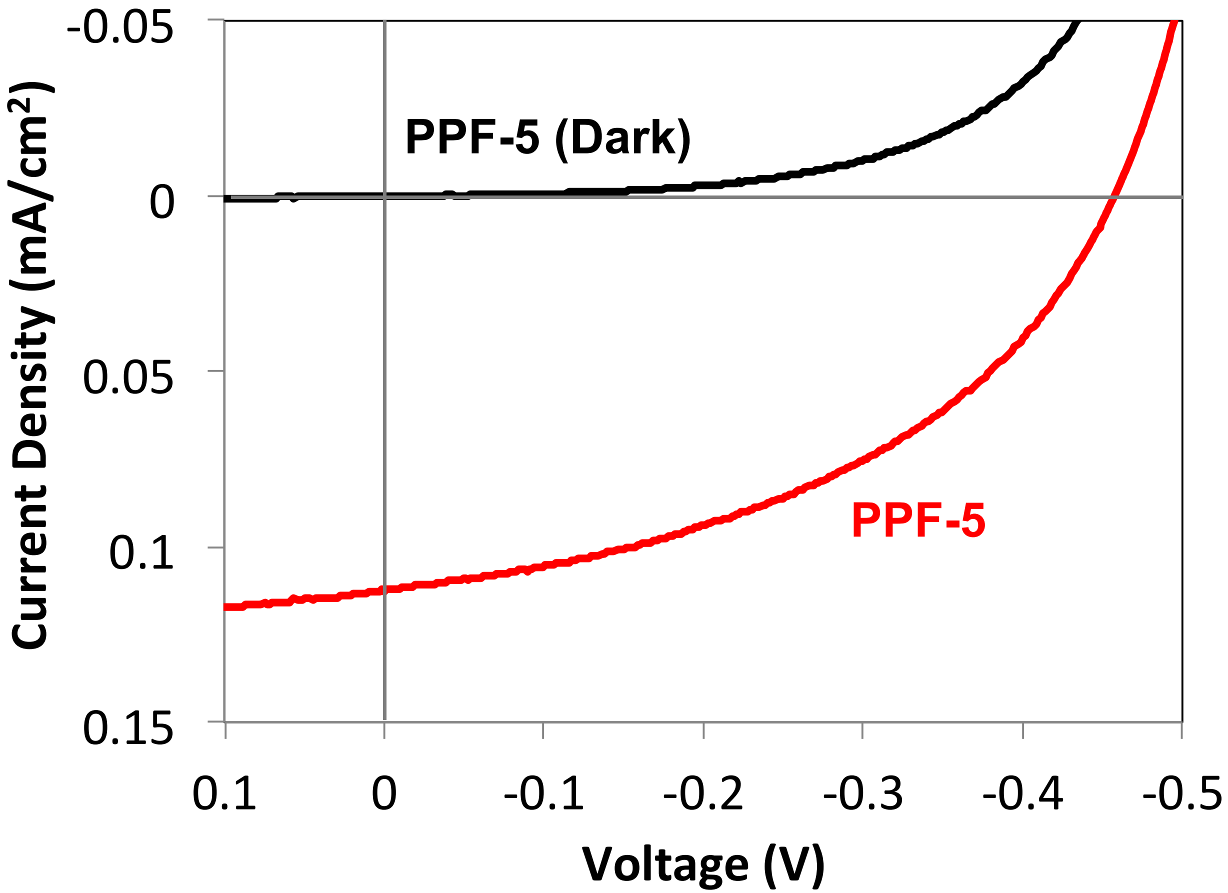
PPF-5 Optical Absorbance

PPF-5 absorbance aligns reasonably UV-filtered Hg-arc lamp.



Performance of PPF-5 in a DSSC

PPF-5 DSSC produces measurable photocurrent!



Averaged metrics:

Voc (V) = 0.452 ± 0.029

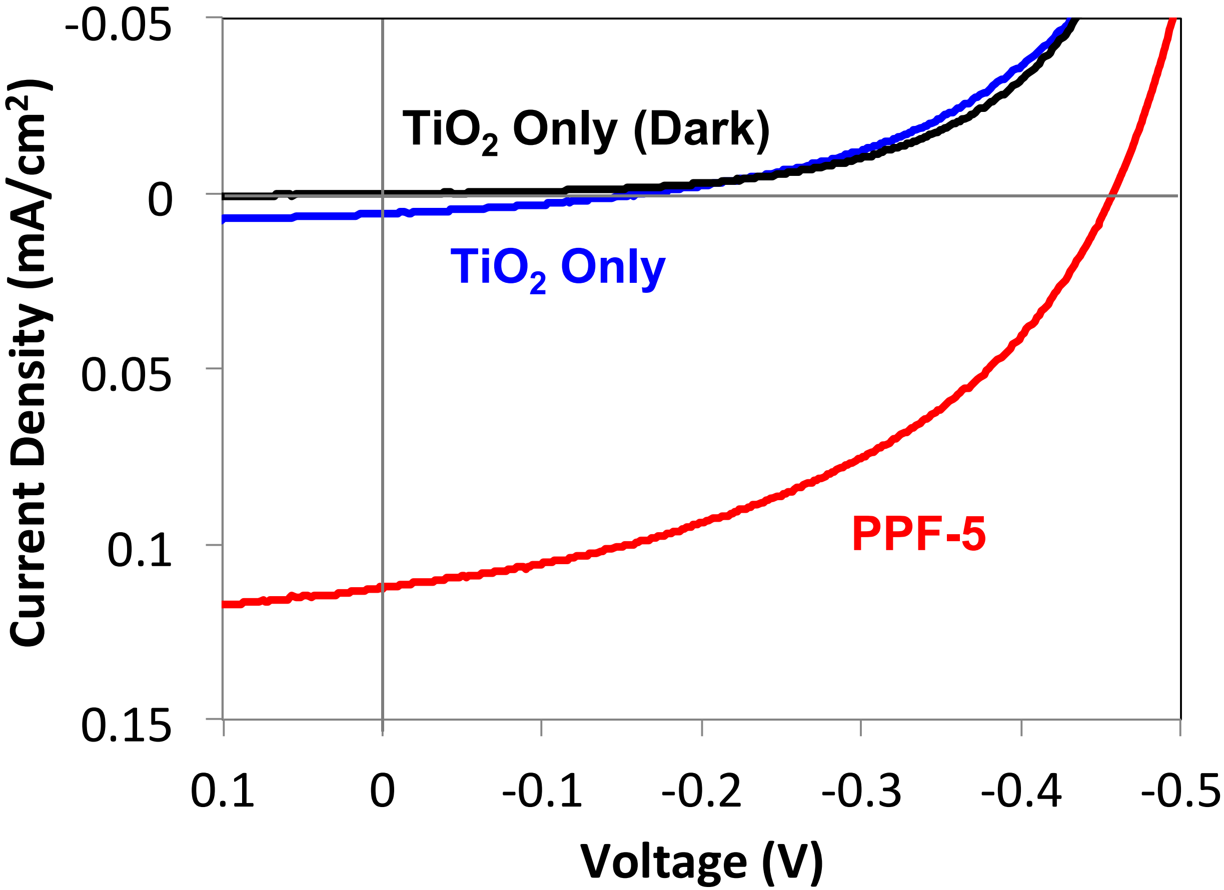
Jsc (mA/cm^2) = 0.097 ± 0.014

FF = 0.47 ± 0.031

η (%) = 0.026 ± 0.0038

Negative Control: No PPF-5

Control experiments containing no PPF-5 produce negligible photocurrent.



In the absence of dye:

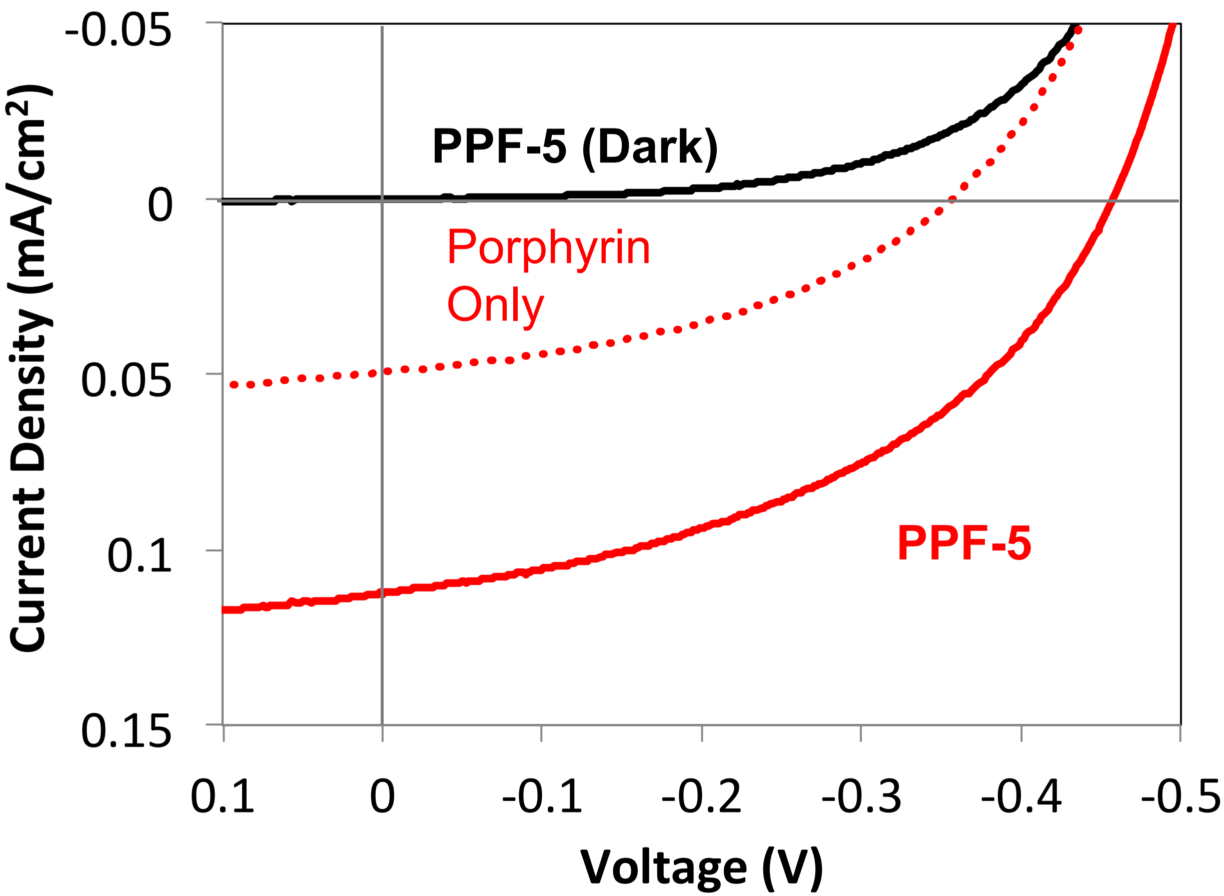
Voc (V) = 0.16

Jsc (mA/cm^2) = 0.0058

FF = 0.31

η (%) = 0.000378

Performance of PPF-5 in a DSSC



Averaged metrics:

Voc (V) = 0.401 ± 0.057

Jsc (mA/cm^2) = 0.061 ± 0.017

FF = 0.45 ± 0.039

η (%) = 0.015 ± 0.0073

Voc (V) = 0.452 ± 0.029

Jsc (mA/cm^2) = 0.097 ± 0.014

FF = 0.47 ± 0.031

η (%) = 0.026 ± 0.0038

Wrapping up

Sandia National Laboratories

- MOFs are highly porous, multifunctional composites crystals, assembled from "modular" molecular building blocks.
- Grown by Layer-by-Layer processes, *PPF-5 integrated into DSSC devices can serve as a functional active absorber*!
- Tuning of MOF composition and structure 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.

This is just the beginning!

Acknowledgements

Sandia National Laboratories

Sandia (Albuquerque)
Jill S. Wheeler
Dr. Dara Van Gough
Steven Wolf
Dr. Leo Small
Bonnie McKenzie

Sandia (California)
Dr. Michael Foster
Dr. Vitalie Stavila
Dr. Kirsty Leong
Dr. Mark D. Allendorf

Funding

- U.S. DOE Energy Efficiency and Renewable Energy (Sunshot)
- Sandia Laboratory Directed Research and Development Program

SunShot U.S. Department of Energy

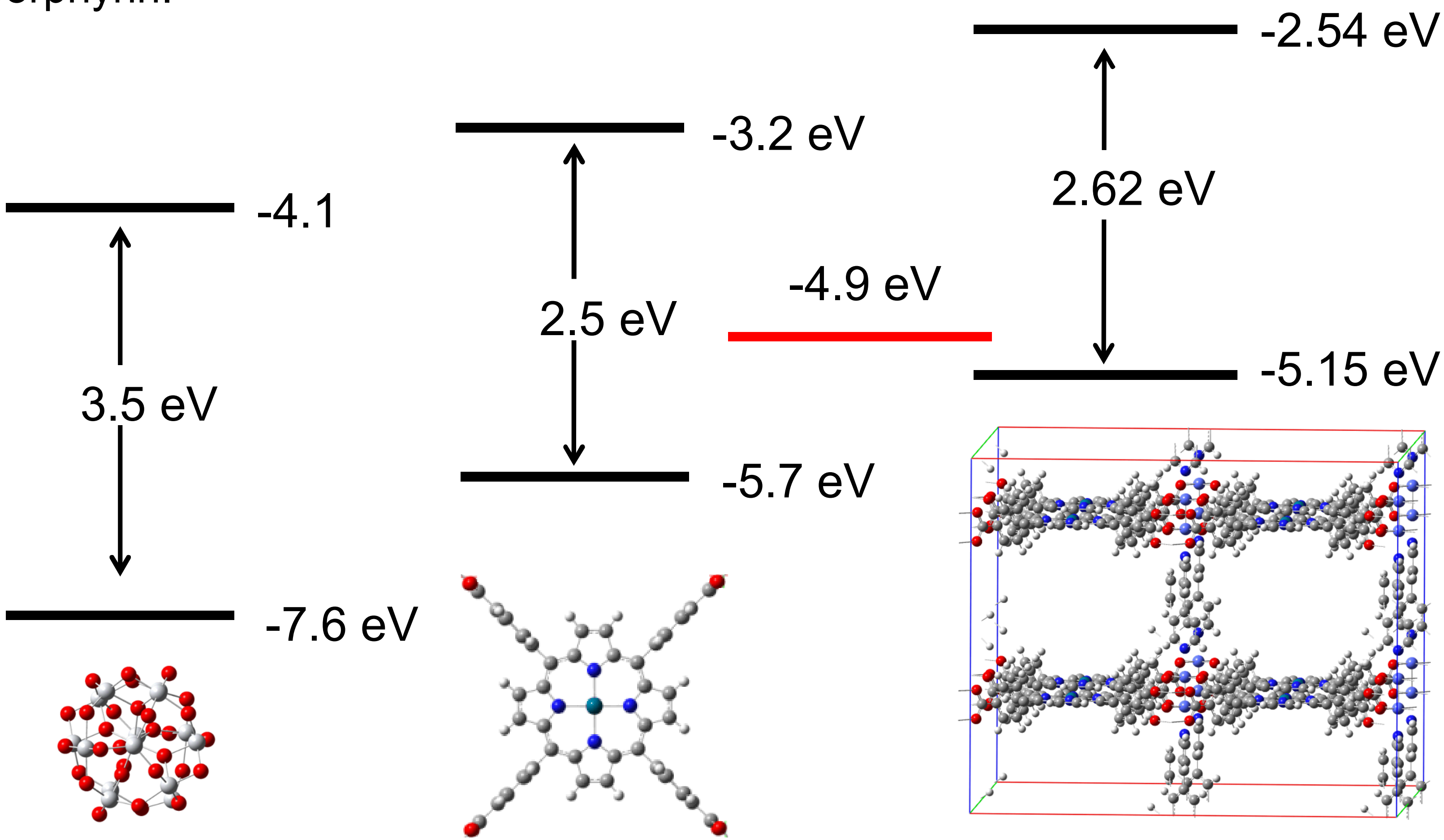
LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

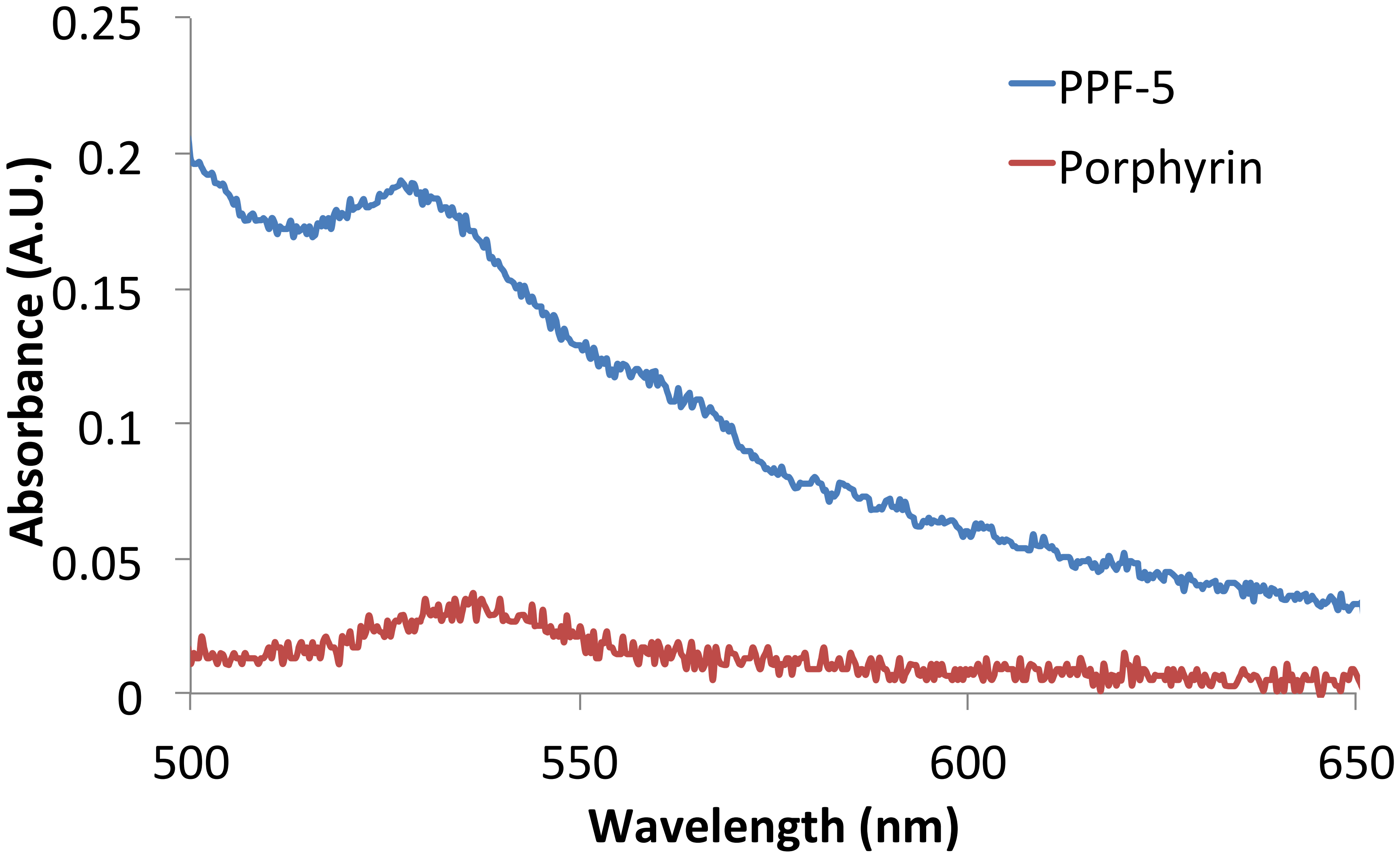
Backup Slides

DFT Predictions of Band Alignment

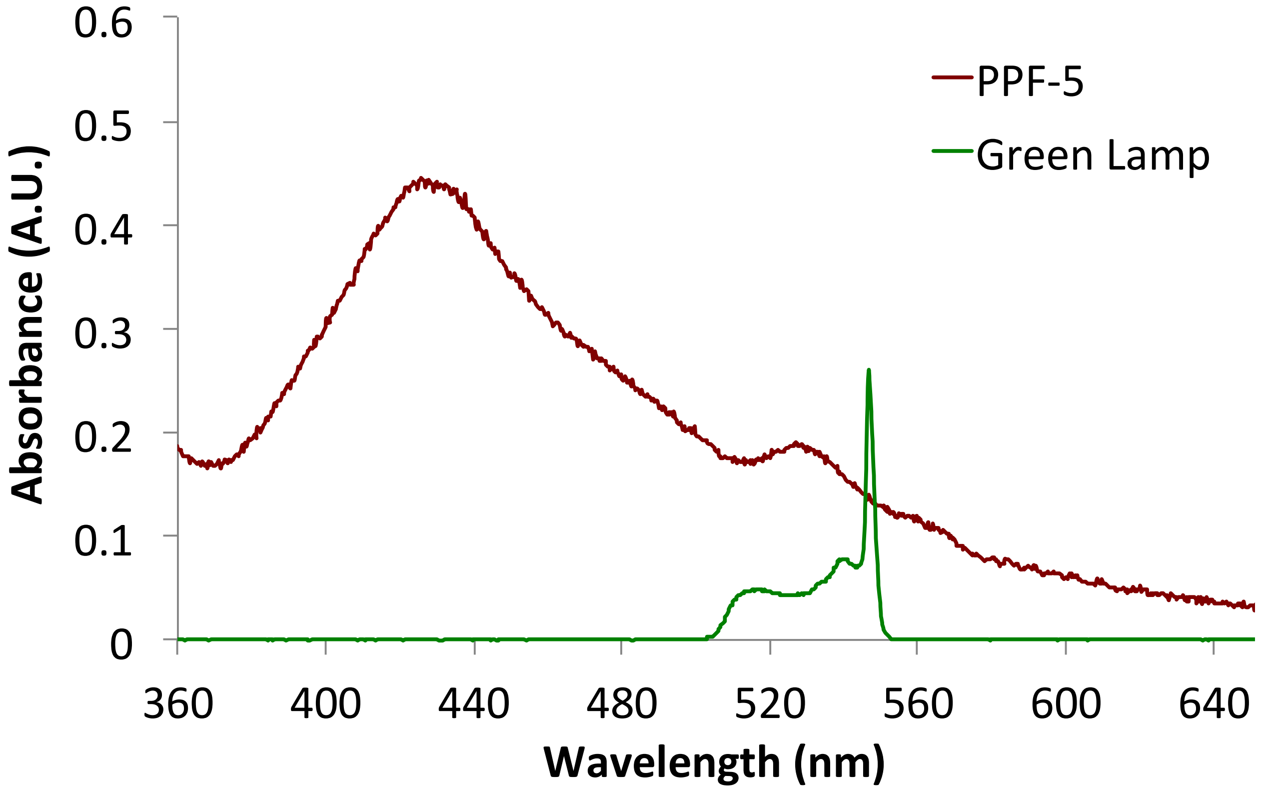
Density Functional Theory (DFT) predicts a shift in band alignment of PPF-5 relative to the Pd-porphyrin.



Absorbance Changes in PPF-5



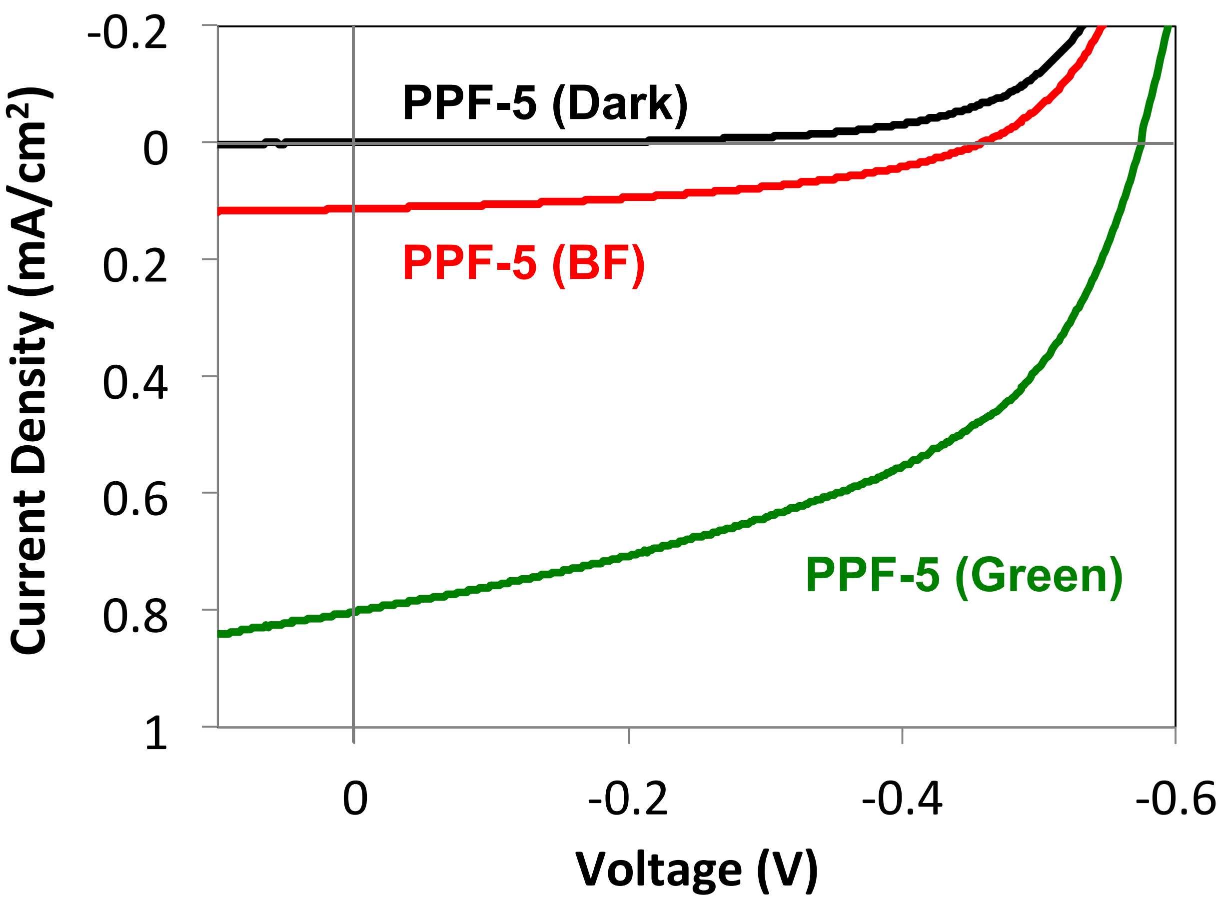
Optical “Cheating”



PPF-5 absorbance aligns reasonably with Hg-arc lamp.

Enhancing PPF-5 Performance with Green Light

Selective excitation with Green light produces enhanced photocurrent, confirming contribution from PPF-5 absorber.



Averaged metrics:

Voc (V) = 0.452 ± 0.029

Jsc (mA/cm^2) = 0.097 ± 0.014

FF = 0.47 ± 0.031

Voc (V) = 0.563 ± 0.018

Jsc (mA/cm^2) = 0.73 ± 0.083

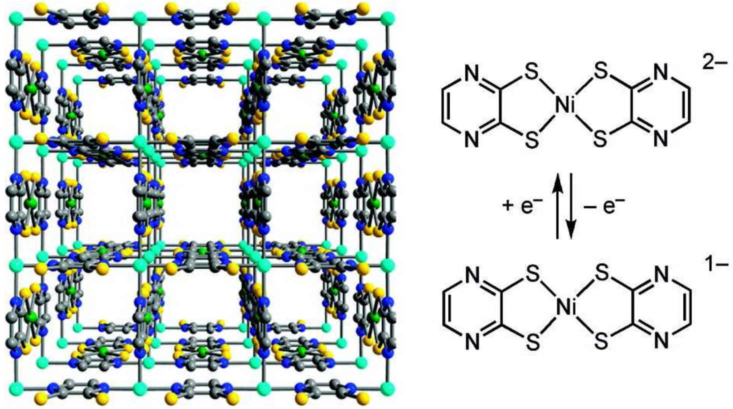
FF = 0.537 ± 0.07

Electrically conducting porous MOFs are rare

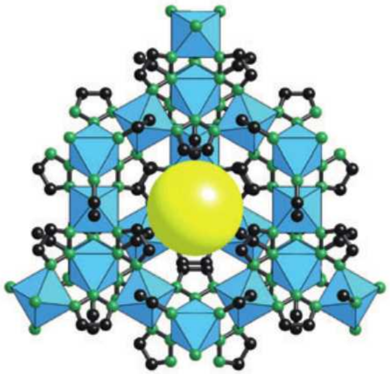
- **p-type Cu-Ni Dithiolene MOF**
  - First semiconducting, porous MOF
  - Conductivity increases with oxidative doping
  - Original Cu-Cu version is not porous (*Inorg. Chem.* 2009, 48, 9048)

- **Other examples**
  - MET-3 (Fe-triazolate MOF)
  - Mn(thiophenol) MOF: (−Mn−S−)∞ Chains

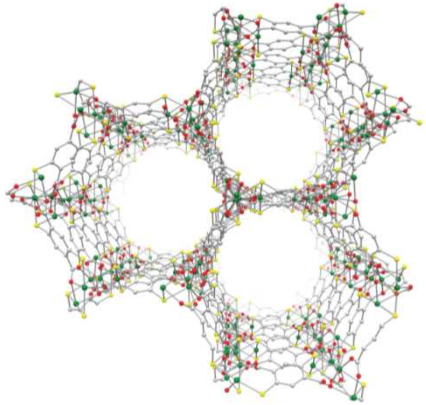
- **Strategies for conducting MOFs:**
  - Charge delocalization
  - 2^{nd}- and 3^{rd} row transition metals
  - Redox-active ligands (e.g., TCNQ)
  - Soft ligands (e.g. S-containing molecules)



Y. Kobayashi et al. *Chem. Mater.* 2010, 22, 4120



MET-3 (Fe)
Gándara et al.
Chem. Eur. J. 2012, 18, 10595

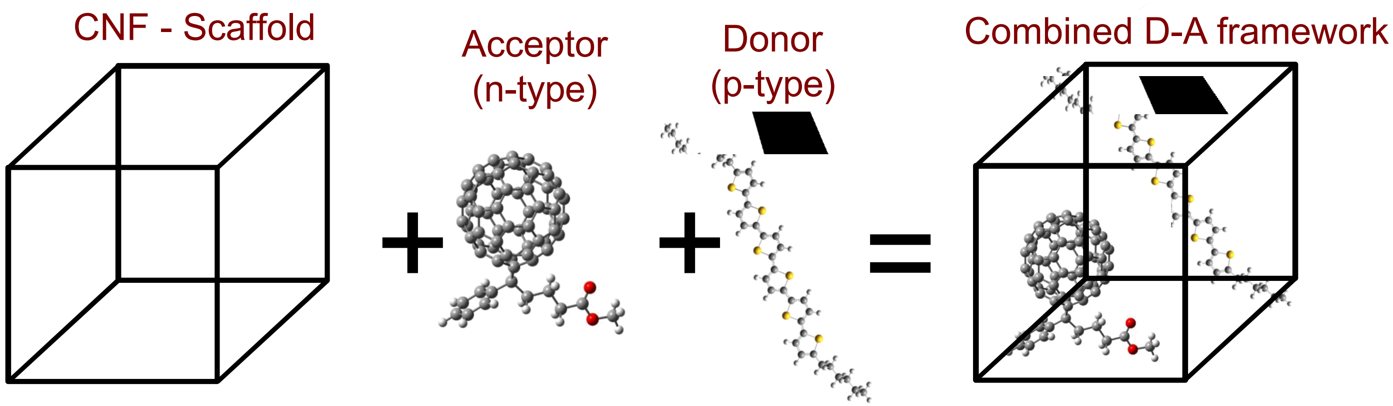


Mn(thiophenol) MOF
L. Sun et al.
J. Am. Chem. Soc. 2013, 135, 8185

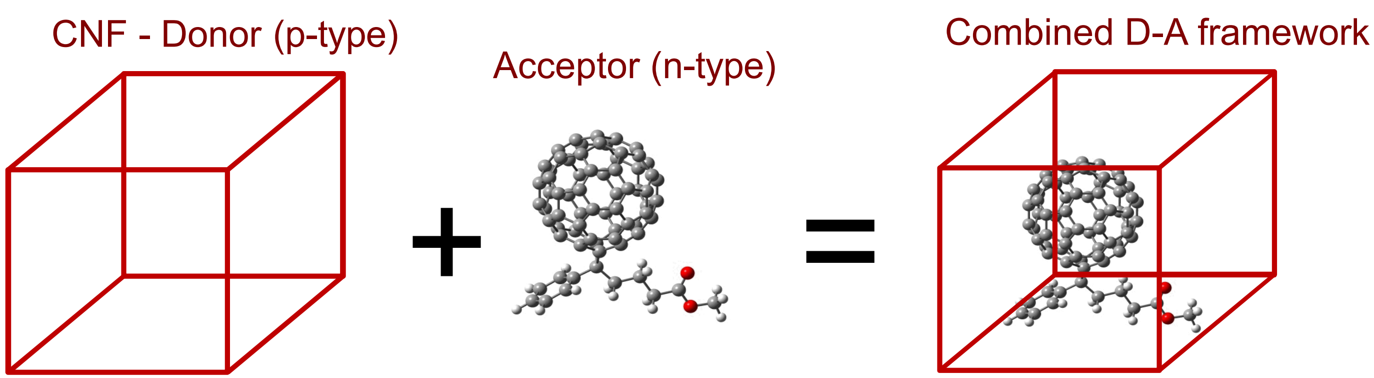
A. Talin, et al., *Science* (2013) In review.

Composite MOF Scaffolds for OPV

Passive Scaffolds - the CNF simply functions to order the donor/acceptor materials and plays no active role in the PV energy conversion process.

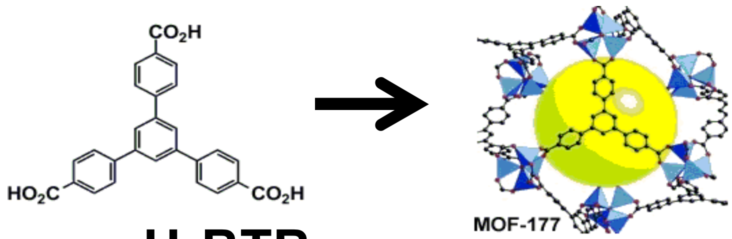


Active Network – the CNF is designed to play an active role in the PV energy conversion process by functioning as the donor or acceptor material.

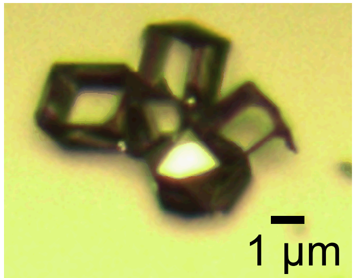


MOF177: A Passive Scaffold for D-A Assembly

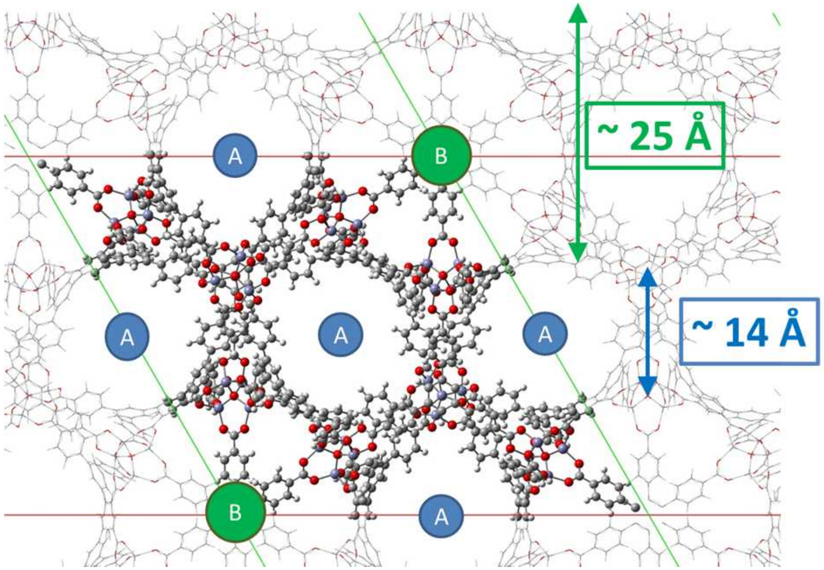
$Zn(NO_3)_2 \bullet 6H_2O + H_3BTB \longrightarrow$ MOF-177



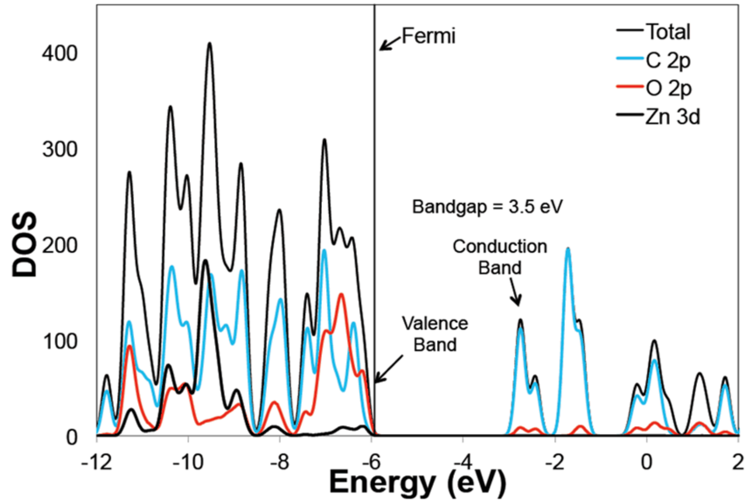
H_3BTB



Optical image of MOF-177 crystals.



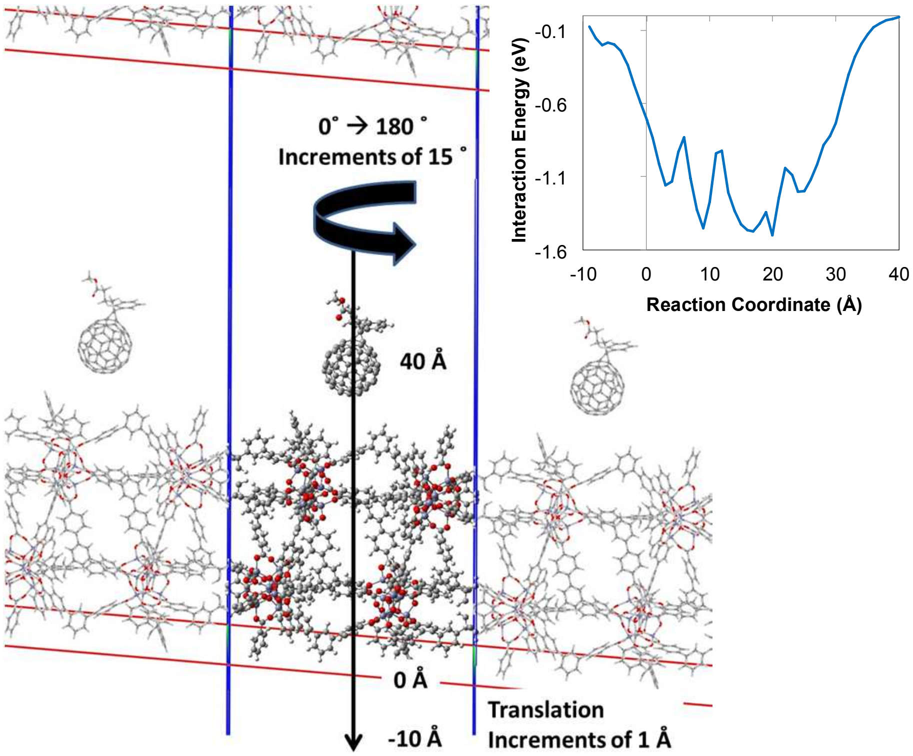
MOF-177 – sites “A” and “B” denote unique cavities; DFTB optimized structure.

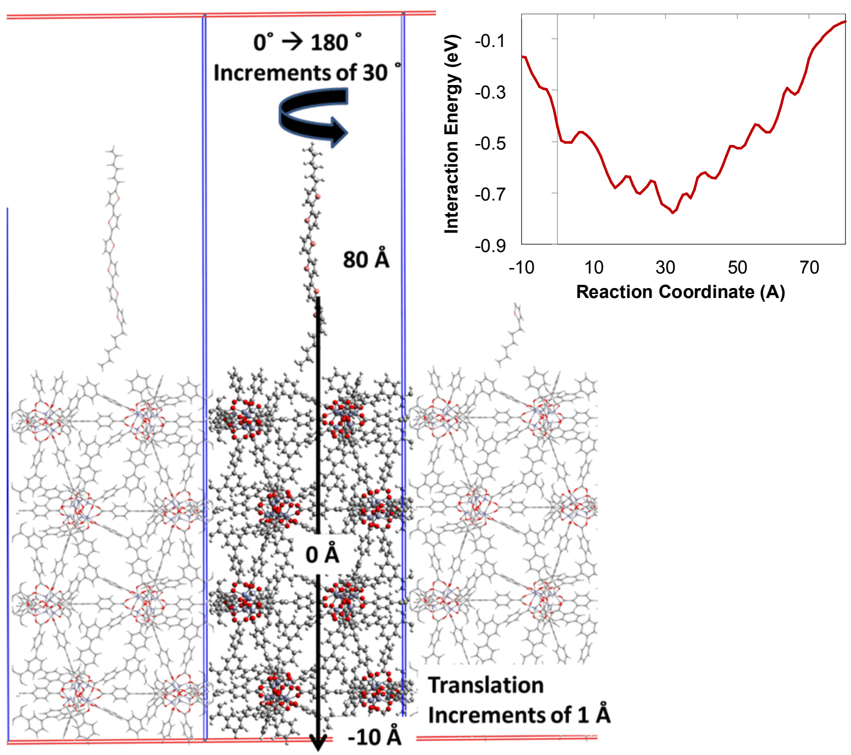


Partial Density of States (PDOS) - Density Functional Tight-Binding (DFTB) calculations of MOF-177.

Predicting Guest Infiltration

Density Functional simulations show that infiltration of both PCBM (A) and Sexithiophene (D) in MOF177 are enthalpically favored.

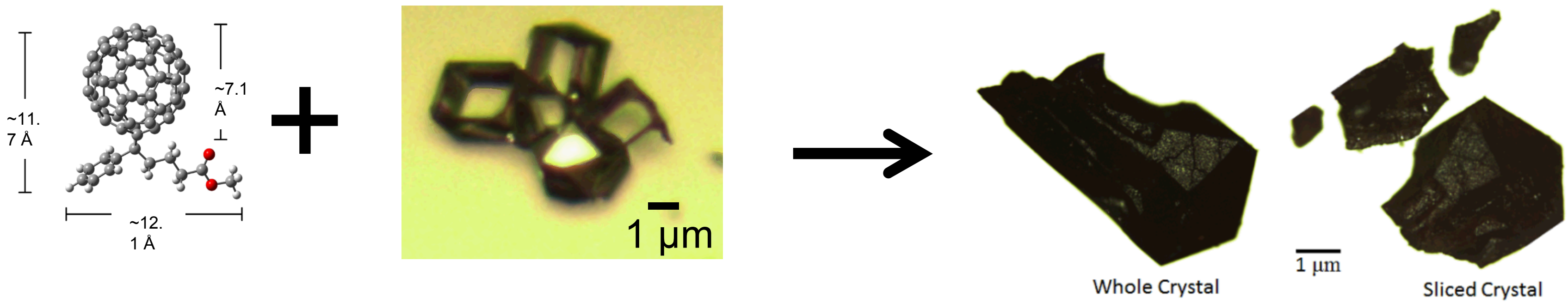


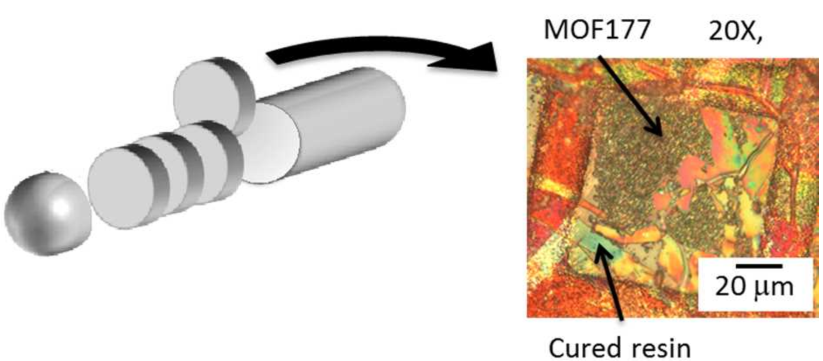


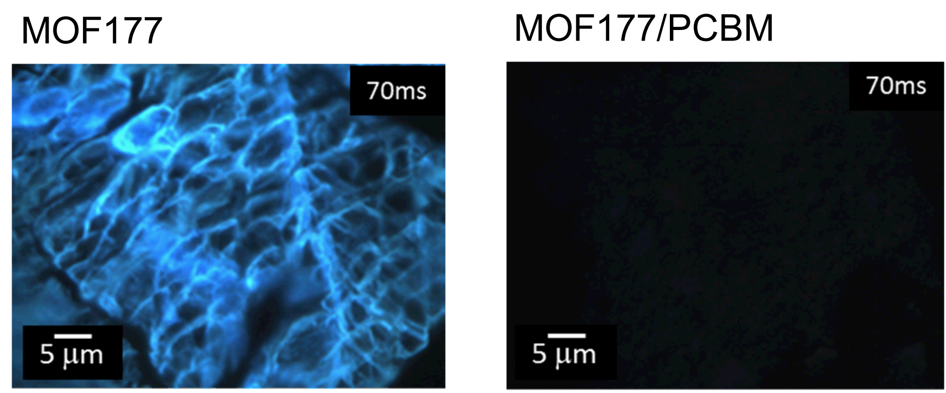
>600 structures generated for each case; 10 step geometry optimization performed to remove close contacts. Interaction energies determined using Density Functional based Tight Binding (DFTB) method.

PCBM Integration into MOF177

Incubation of MOF177 crystals in concentrated PCBM solutions leads to PCBM infiltration





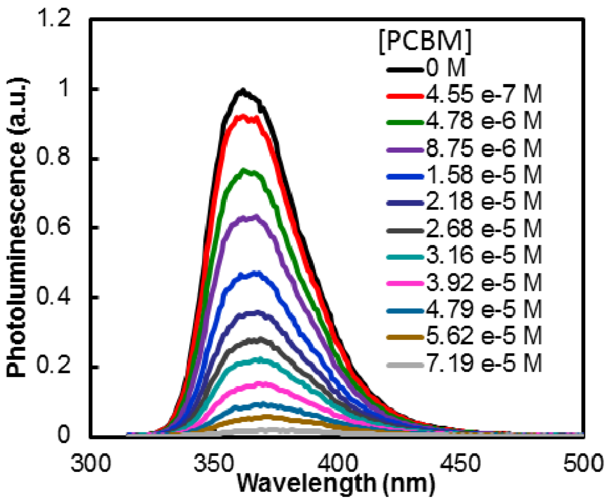


Ex: 330-385nm; Em filter: 420nm

Spectroscopic characterization of PCBM@MOF177 cross-sections shows significant quenching of MOF177 fluorescence.

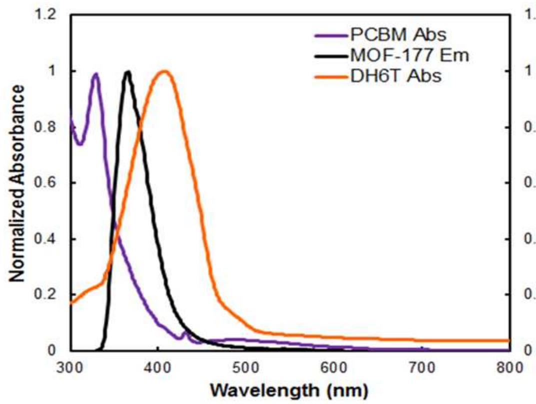
Introduction to MOFs

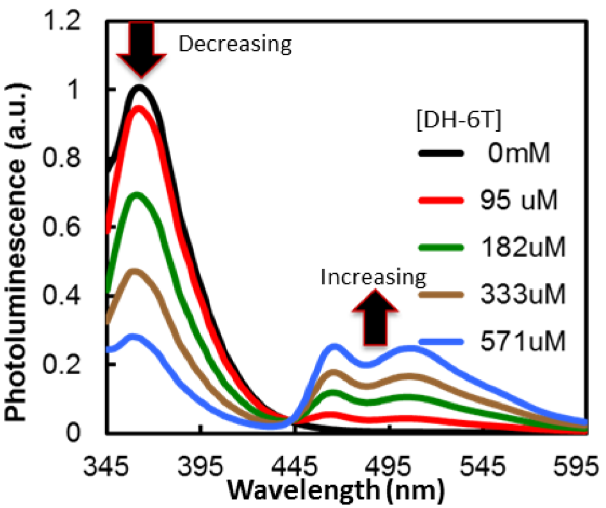
Spectral characterization reveals complex energy transfer between MOF177, PCBM, and DH6T



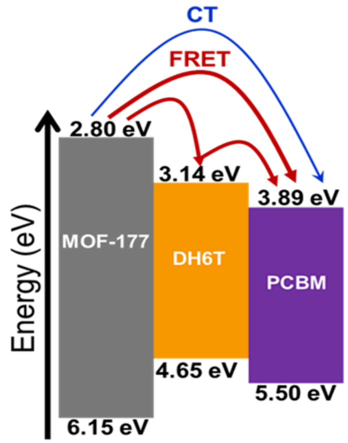
MOF177 and DH-6T are quenched by PCBM.

Spectral overlap between DH-6T, PCBM, and MOF177 inform multiple optoelectronic relationships.





MOF177 transfers energy to DH-6T.

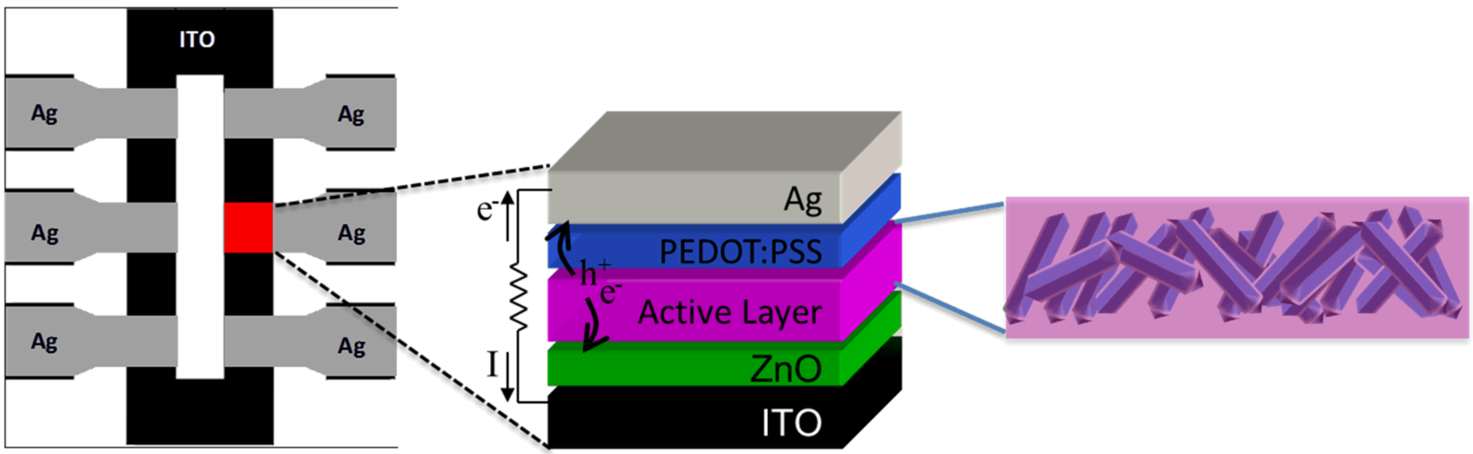


MOF177, DH6T, &PCBM band alignment predicted by SCC-DFTB

K. Leong, et al. J. Mater. Chem. (2014) ***In press***.

Device Integration

PCBM@MOF177 were incorporated into hybrid OPV active layers to evaluate the influence of MOF templating on PV performance.

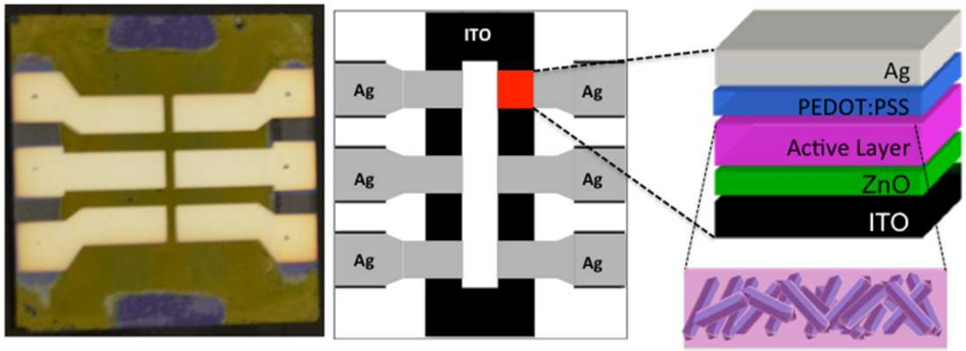


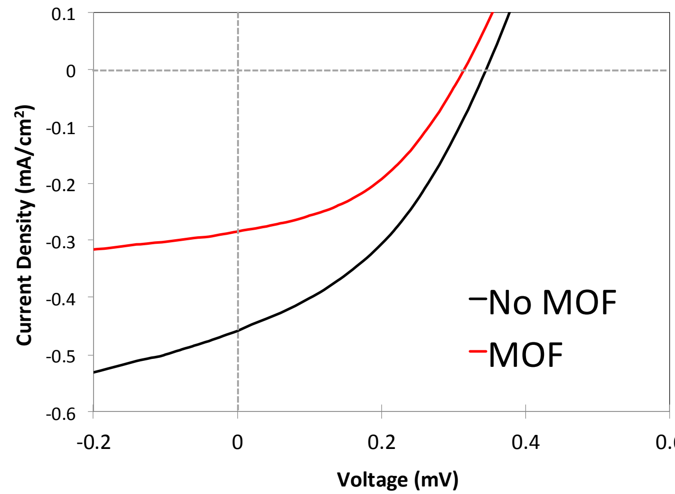
Patterned ITO and silver electrodes create controlled $0.1 cm^2$ active areas.

Inverted device configuration

Infiltrated (e.g., oligothiophene, PCBM) MOF177 particles incorporated into polythiophene active layer.

Device Testing





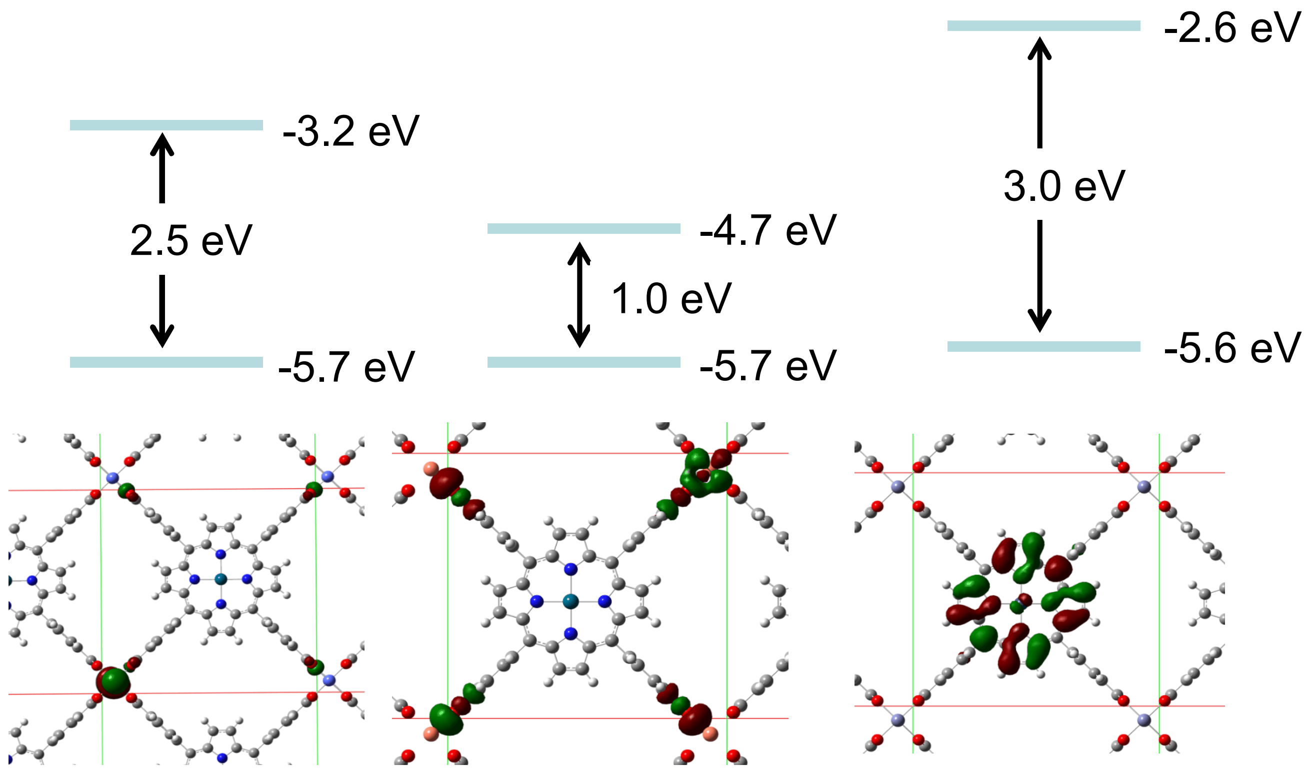
	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	Efficiency (%)
With MOF177	320 +/- 23	0.290 +/- 0.018	40 +/- 0.3	0.04 +/- 0.003
P3HT Alone	340 +/- 26	0.460 +/- 0.029	39 +/- 1.9	0.06 +/- 0.01

PV testing with 1 sun illumination shows reduced current, possibly from reduced active volume or charge trapping in suspended PCBM@MOF177 composites.

Band Structure Tailoring

Density Functional Theory (DFT) simulations show that by varying the composition of PPF molecular building blocks, it is possible to tune the electronic band structure of these MOFs.

<u>Varying transition metal ions</u>



LUMO
Pd porphyrin - Co layer

LUMO
Pd porphyrin - Cu layer

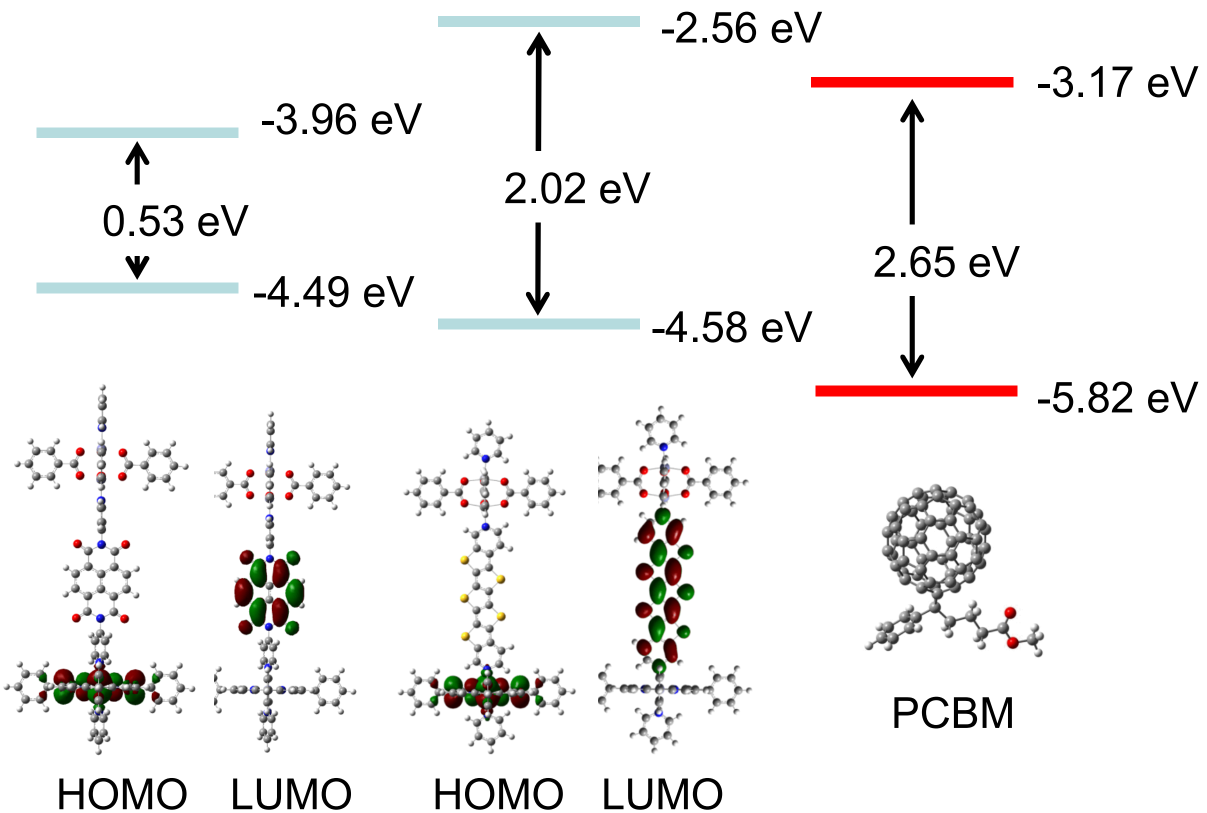
LUMO
Pd porphyrin - Zn layer

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

Band Structure Tailoring

Density Functional Theory (DFT) simulations show that by varying the composition of PPF molecular building blocks, it is possible to tune the electronic band structure of these MOFs.

<u>Varying organic pillars</u>

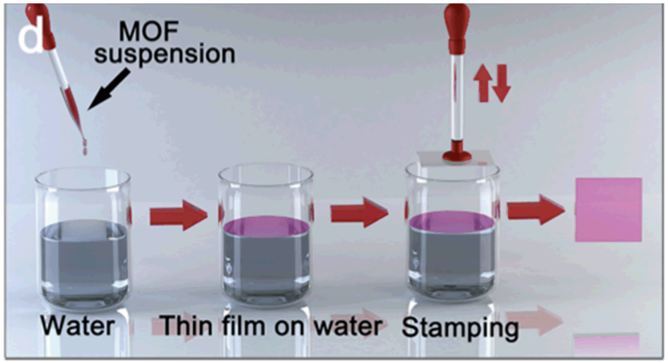


2D periodic optimization - DFT(B3LYP/ CEP-31G)

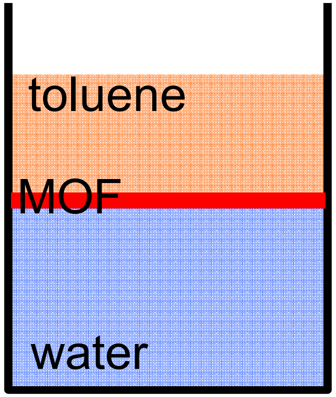
Revisiting Layered Growth

Sandia National Laboratories

Can we deposit a thicker active layer to increase our current?

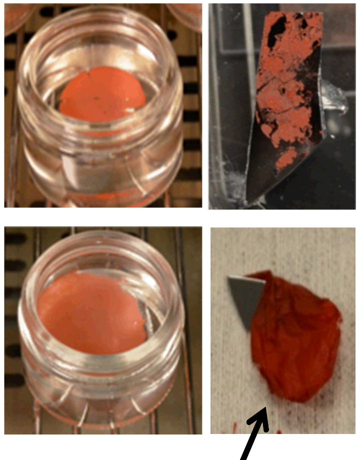


G. Xu, et al., *JACS* 2012, 134, 16524



Stamped onto OTS/APS-treated Si (toluene + acetone, 1:4)

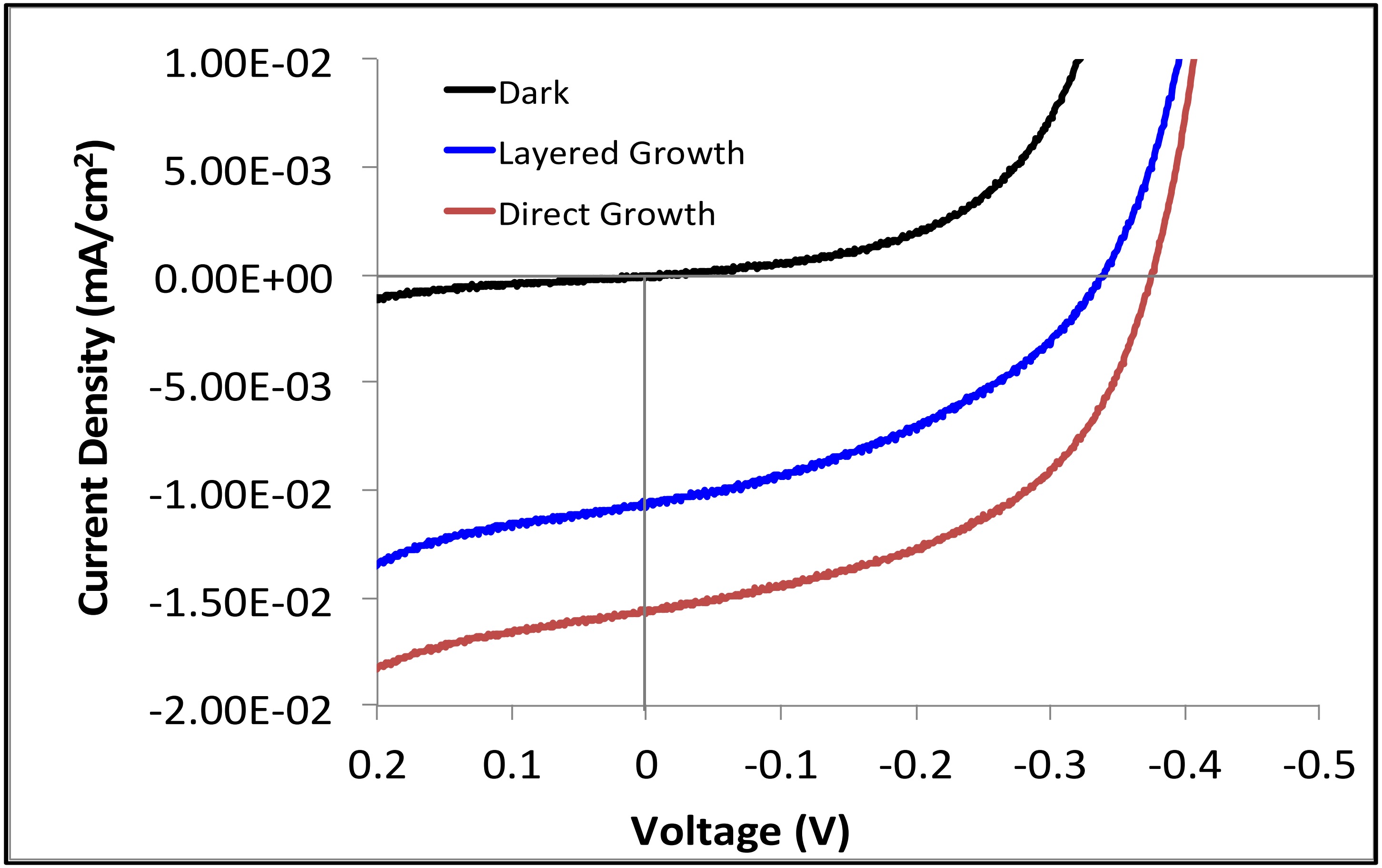
Untouched on water surface for 48 hours (toluene + acetone, 1:4)



Self-supporting film!

PPF-5 Integration is Important!

PPF-5 grown directly on TiO_2 yields greater PV response than PPF-5 deposited by layered growth



Key Materials Considerations

Requirements for efficient OPV system:

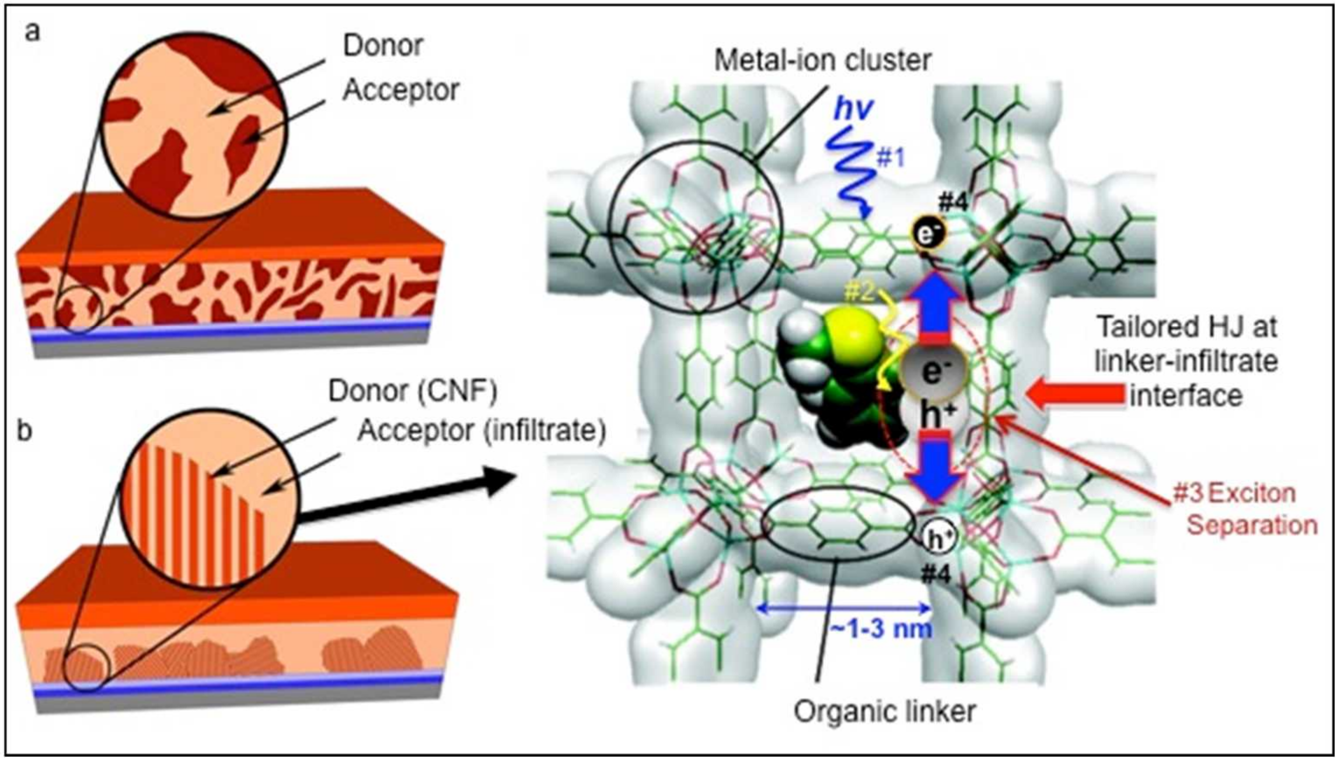
- Good p-type absorber
- Short exciton diffusion distances
- Ordered molecular charge separation interfaces
- Proper band alignment (D-A interface) for charge separation/transfer
- Facile incorporation into device architectures!

A Supramolecular Approach to PV Integration

Order vs. disorder: creation of nano-heterojunctions

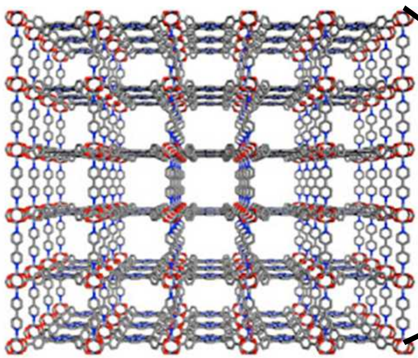
Conventional disordered BHJ

Highly ordered "Nano-HJ" using CNF platform

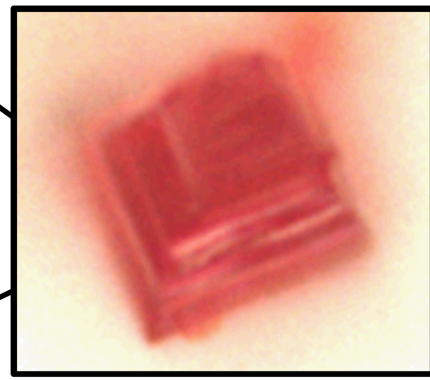


Integration of PPF-5 in DSSCs

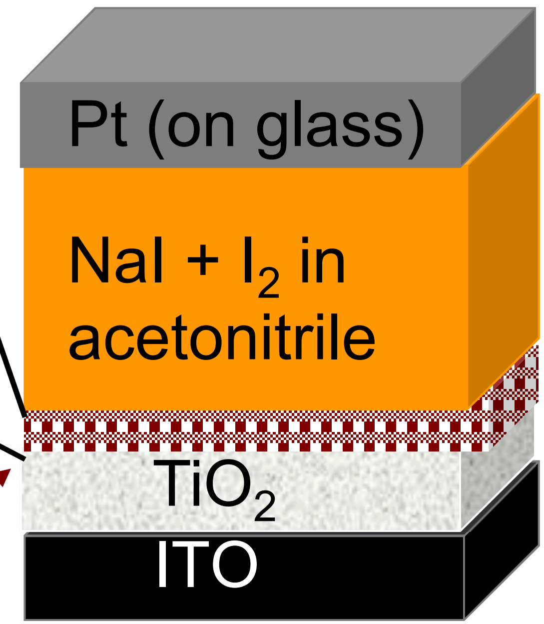
PPF-5 should be readily incorpoated into a DSSC device configuration…



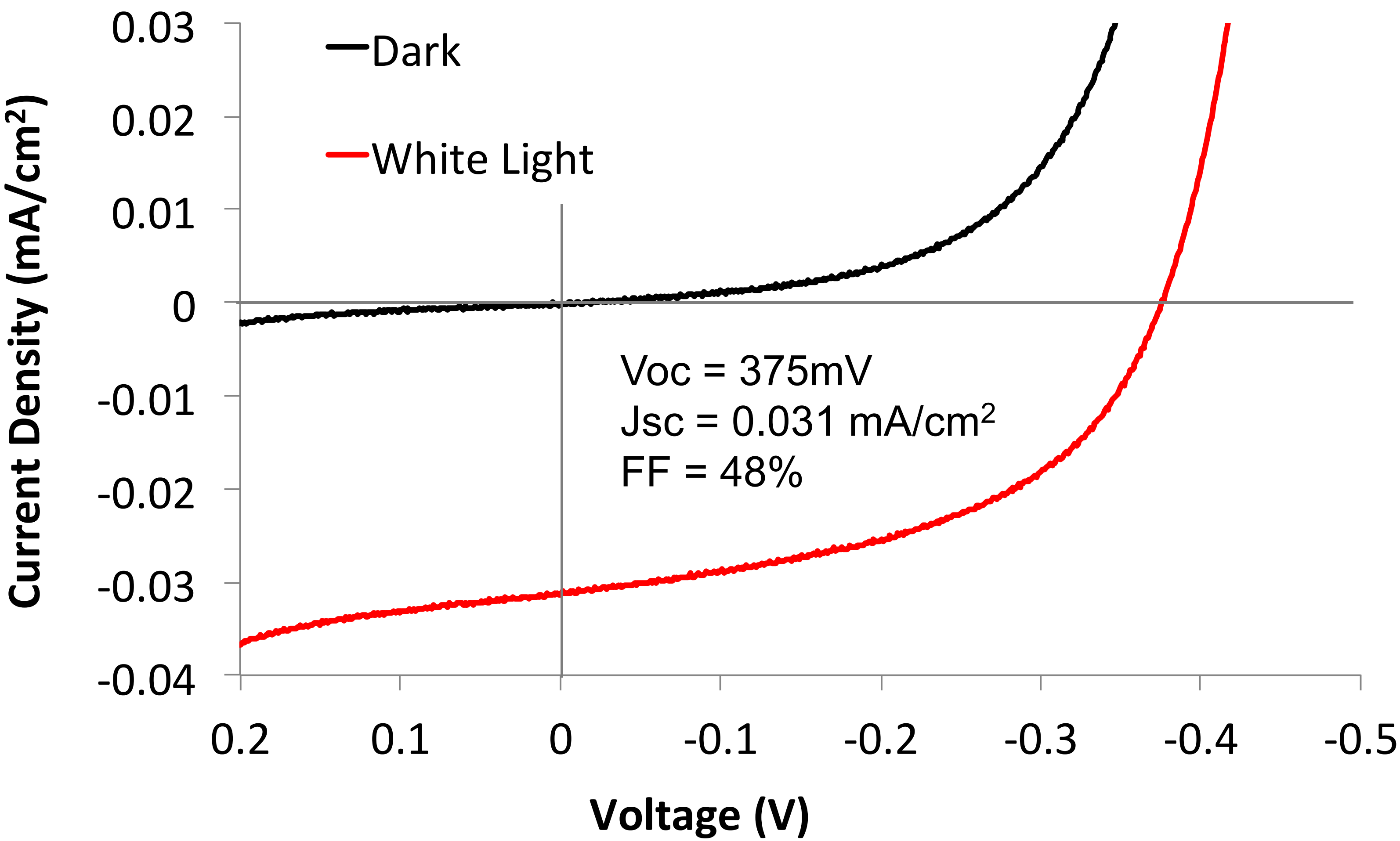
PPF-5 Porphyrin MOF structure



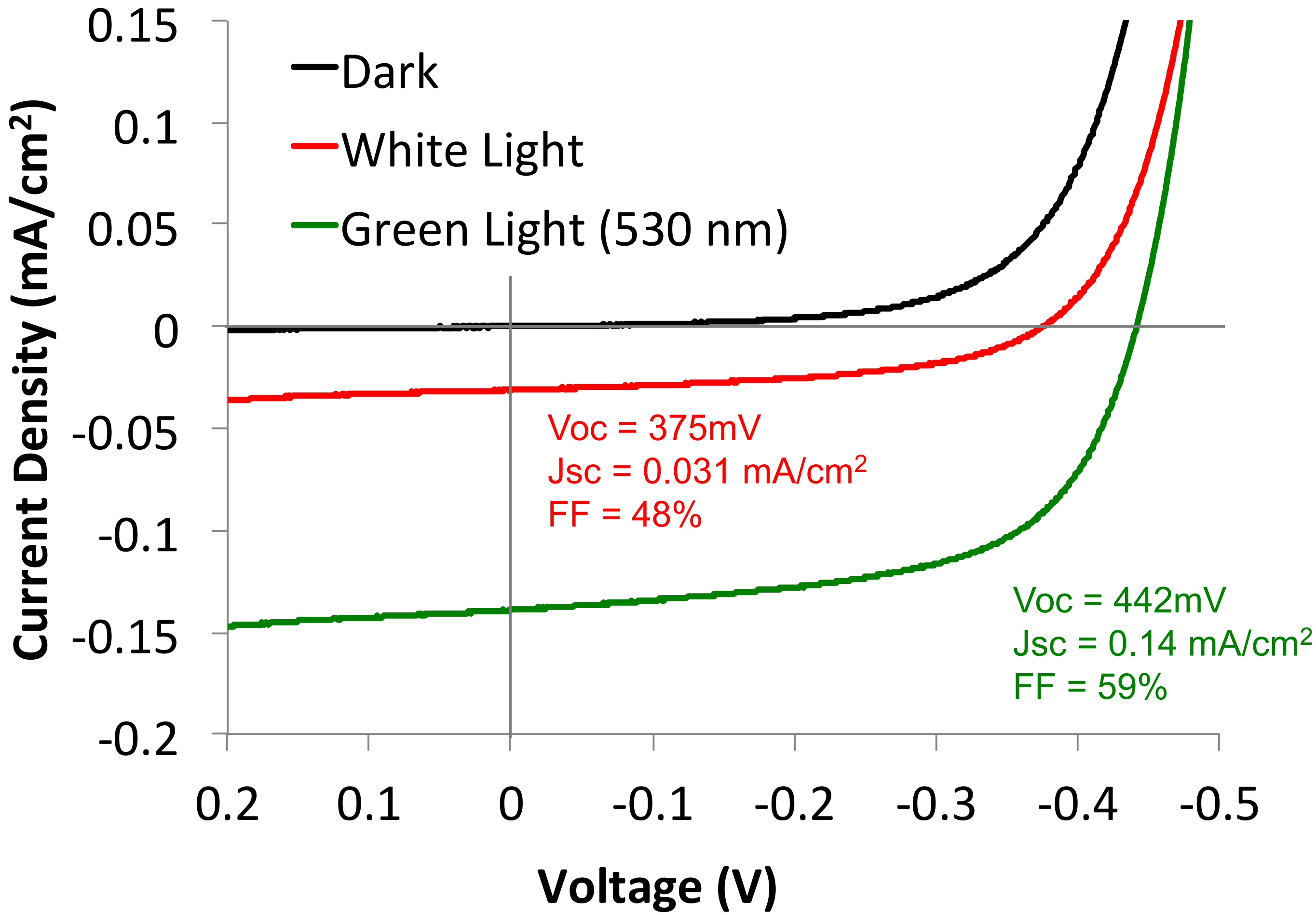
Charge injection dye: Porphyrin MOF nanostacks



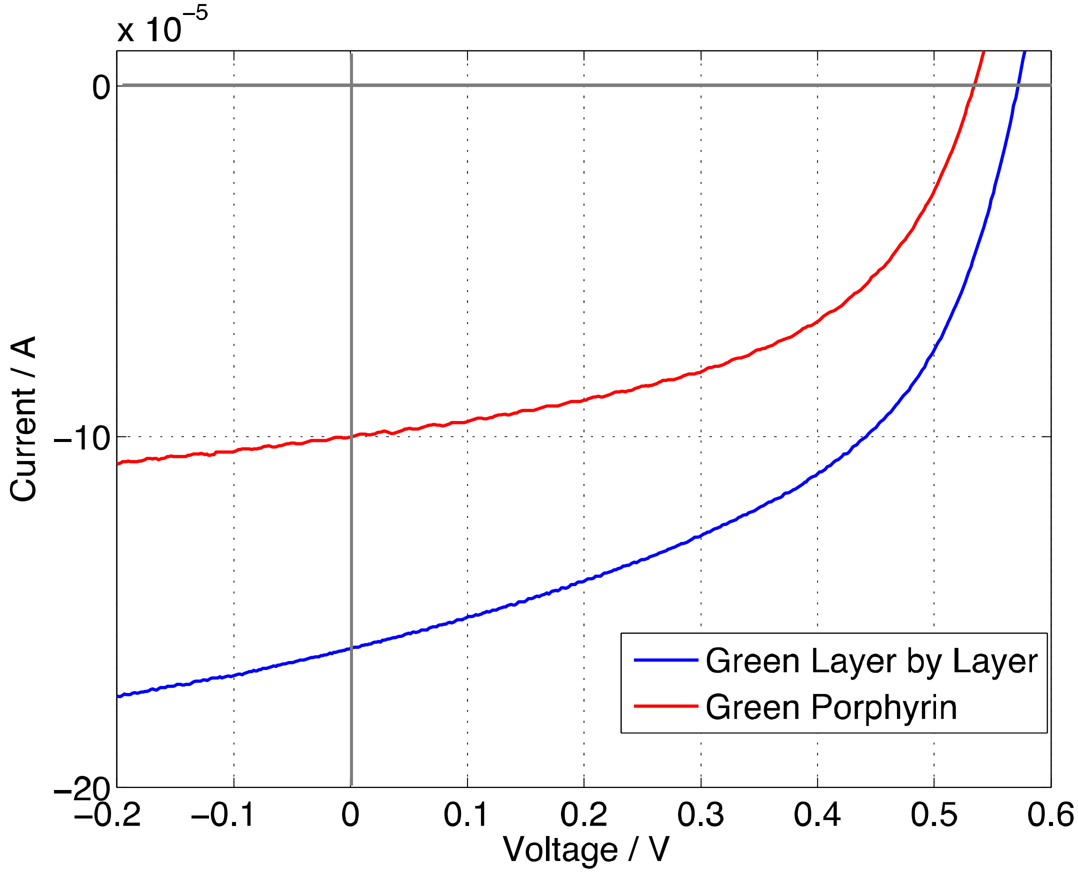
PPF-5 PV Performance in a DSSC



Optical “cheating”



Performance of PPF-5 in a DSSC



Voc = 0.57V
Jsc = 1.6E-4 A
FF = 0.49

Voc = 0.532V
Jsc = 1 E-4 A
FF = 0.506