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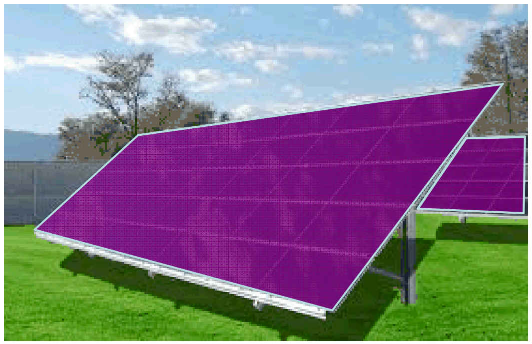

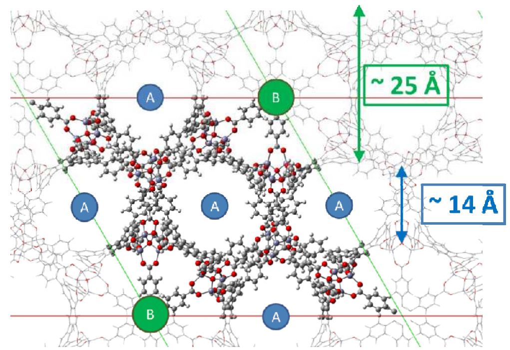

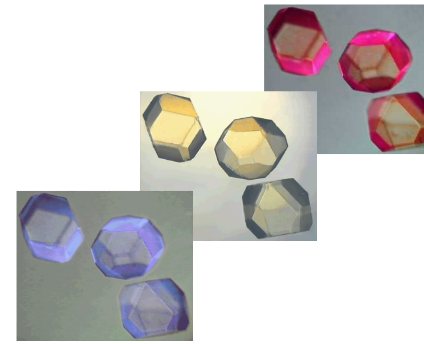

Optoelectronic "Tinker Toys":

Supramolecular Nanocomposite Frameworks for Next Generation Photovoltaics

Erik D. Spoerke

Dara Van Gough, Jill S. Wheeler, Steven Wolf, Michael Foster, Kirsty Leong, Vitalie Stavila, Alec Talin, and Mark D. Allendorf

Composites at Lake Louise
November 3-7, 2013
Alberta, Canada

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Outline

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- ✧ What are MOFs?
- ✧ A Basic Introduction to PV
- ✧ “Passive” MOF Scaffolds
- ✧ “Active” MOF Scaffolds

Outline

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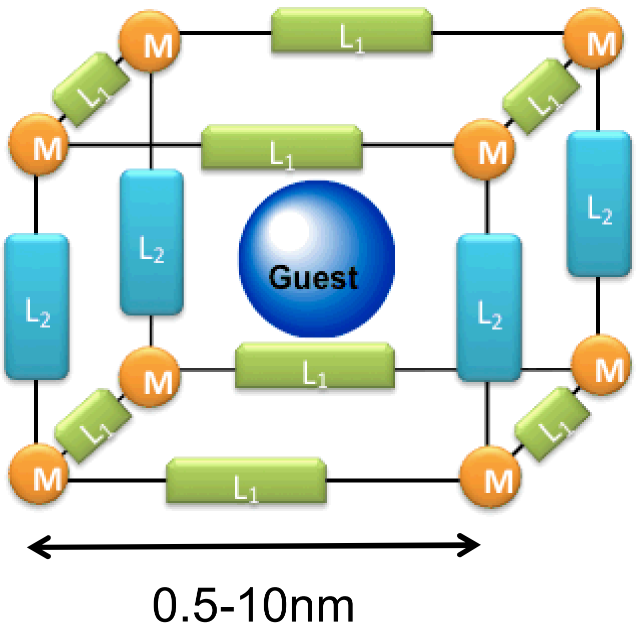
What are Metal Organic Frameworks?

Metal Organic Frameworks (MOFs)

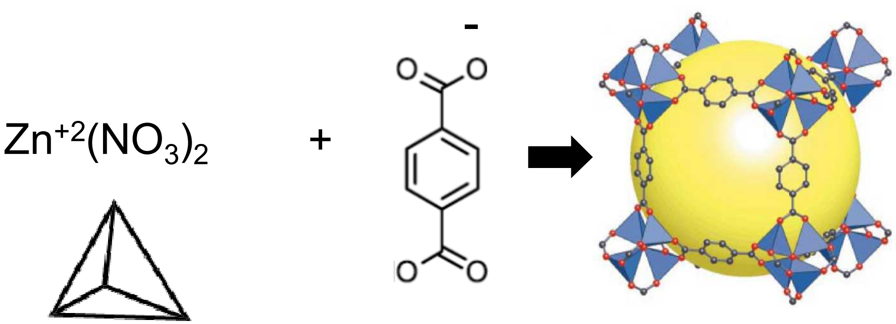
A subset of coordination polymers



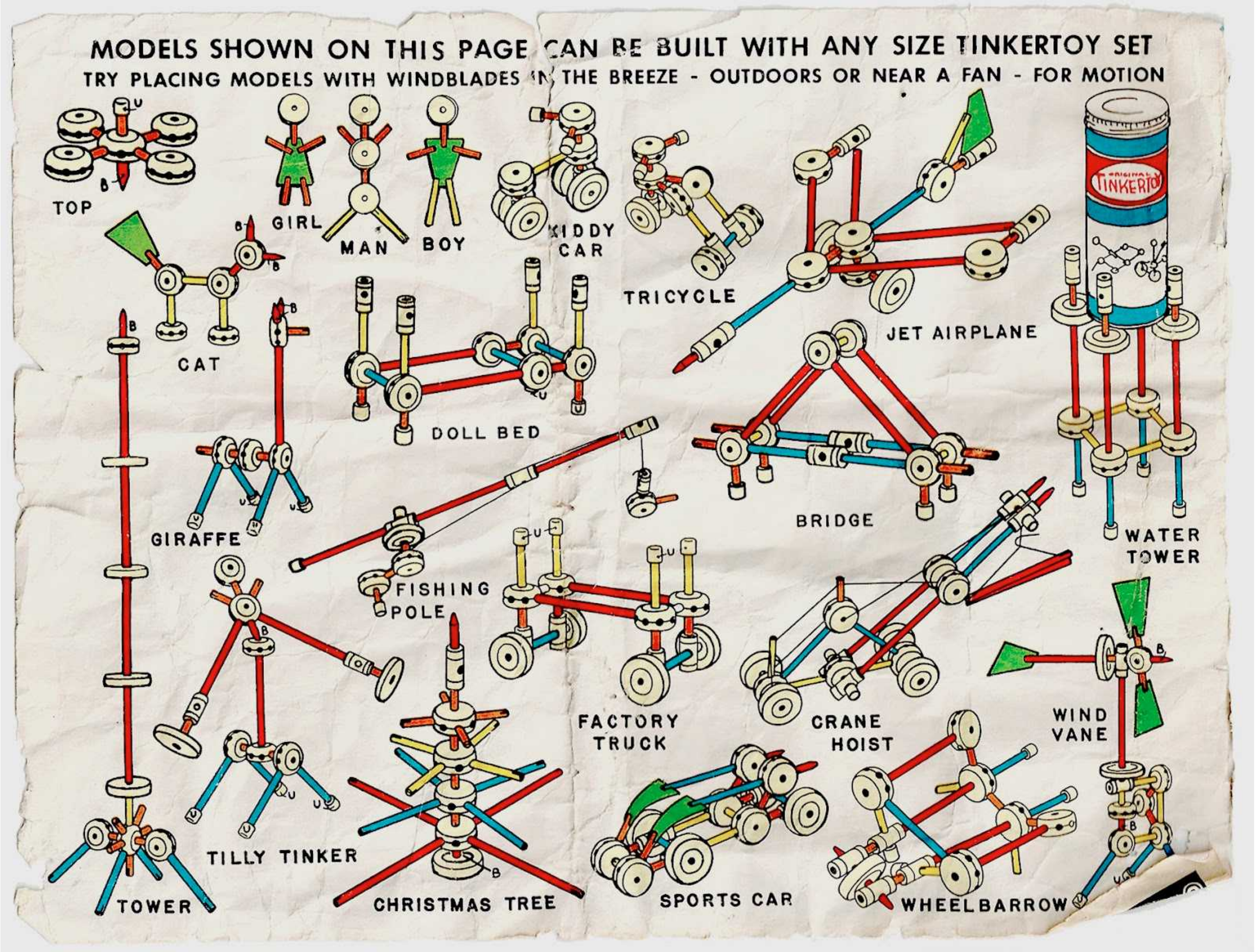
Crystalline MOF structures are composed of metal nodes (M), linkers (L_1) and pillars (L_2).

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

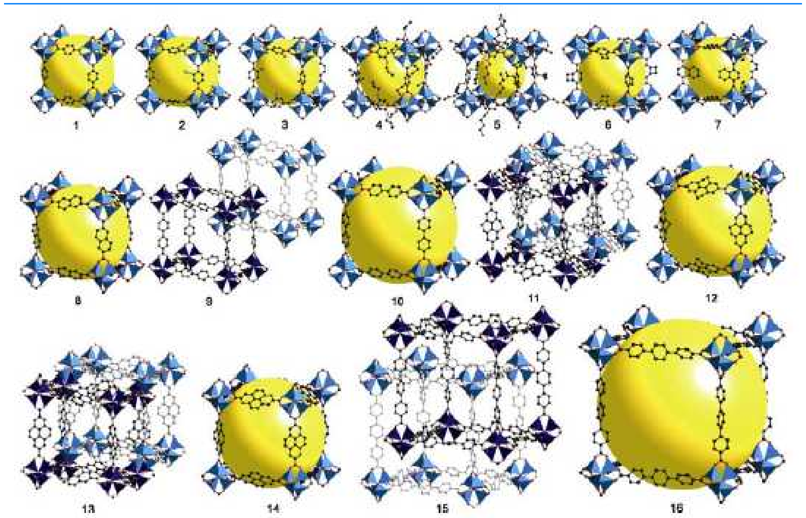
This chemically “modular” system allows for tuning of the structure, properties, and function of these materials.



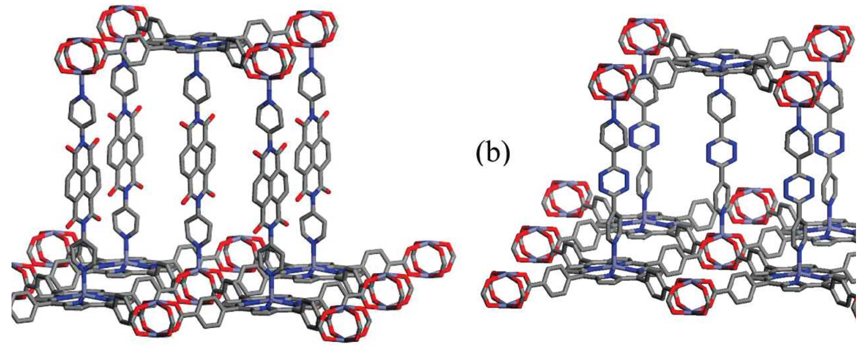
MOFs: Supramolecular "Tinker Toys"



MOF Building Block Chemistry Determines Crystal Structure

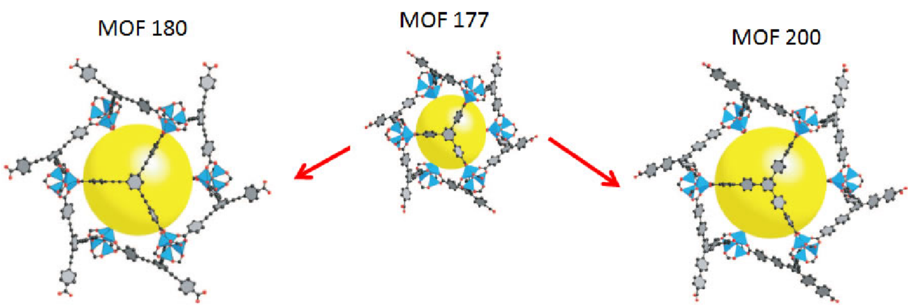


http://yaghi.berkeley.edu/research-MOF.html

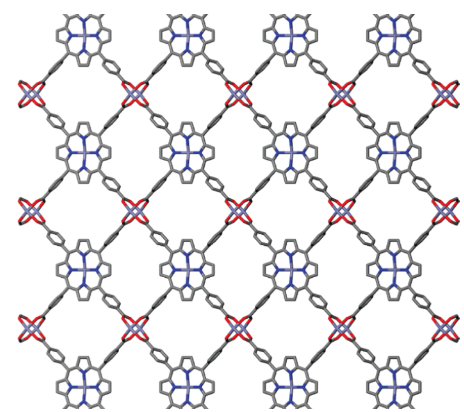


Side view of PPF-18

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

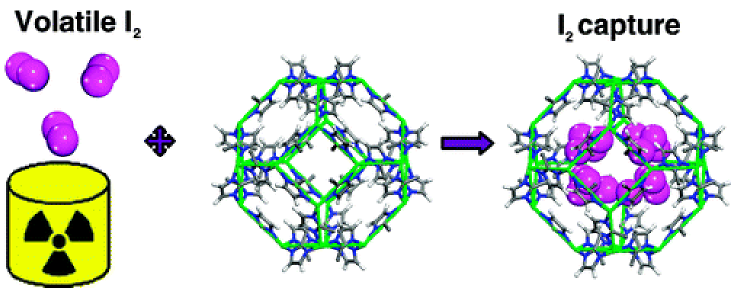


http://www.cchem.berkeley.edu/molsim/teaching/fall2011/CCS/Group7/structure.htm



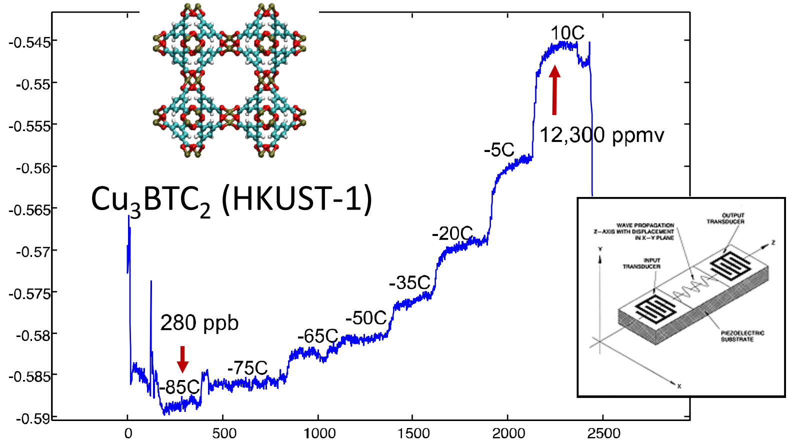
MOF Applications

Gas Sorption (I_2 capture)



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

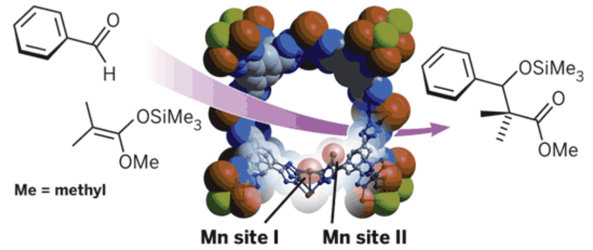
Sensing (H_2O sensing)



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

?

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- ✧ What are MOFs?
- ✧ A Basic Introduction to PV
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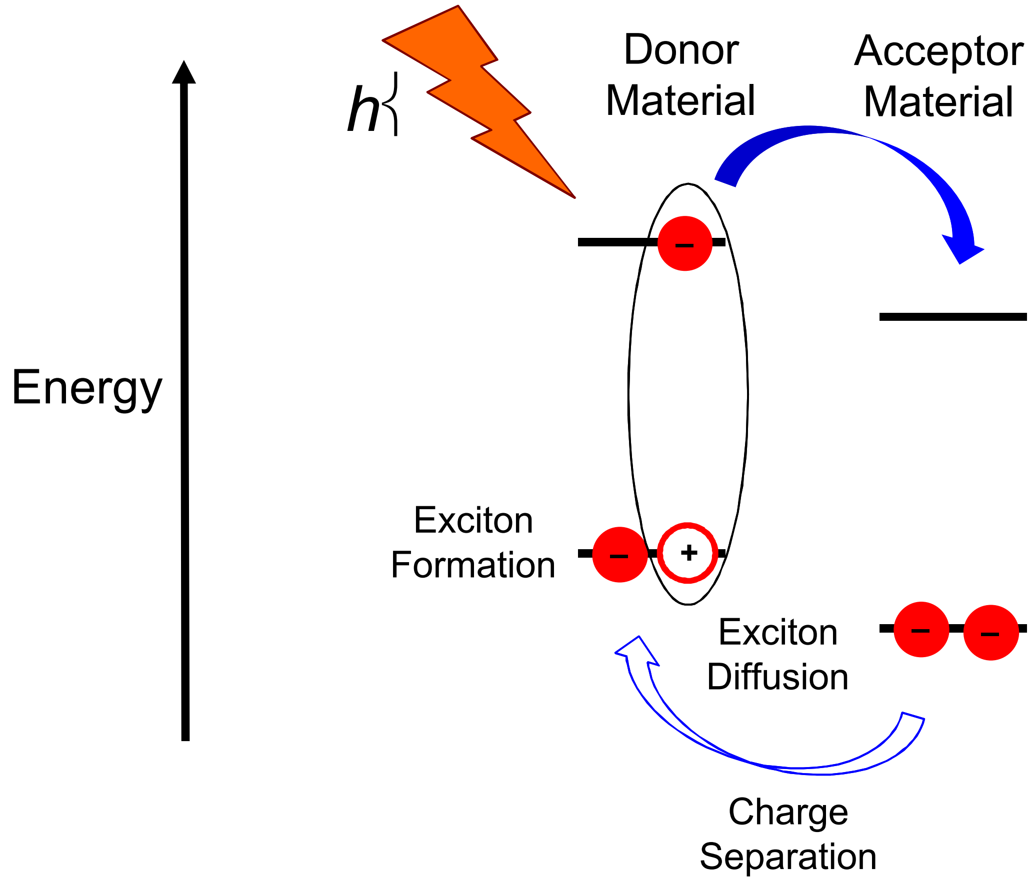
- ✧ “Active” MOF Scaffolds

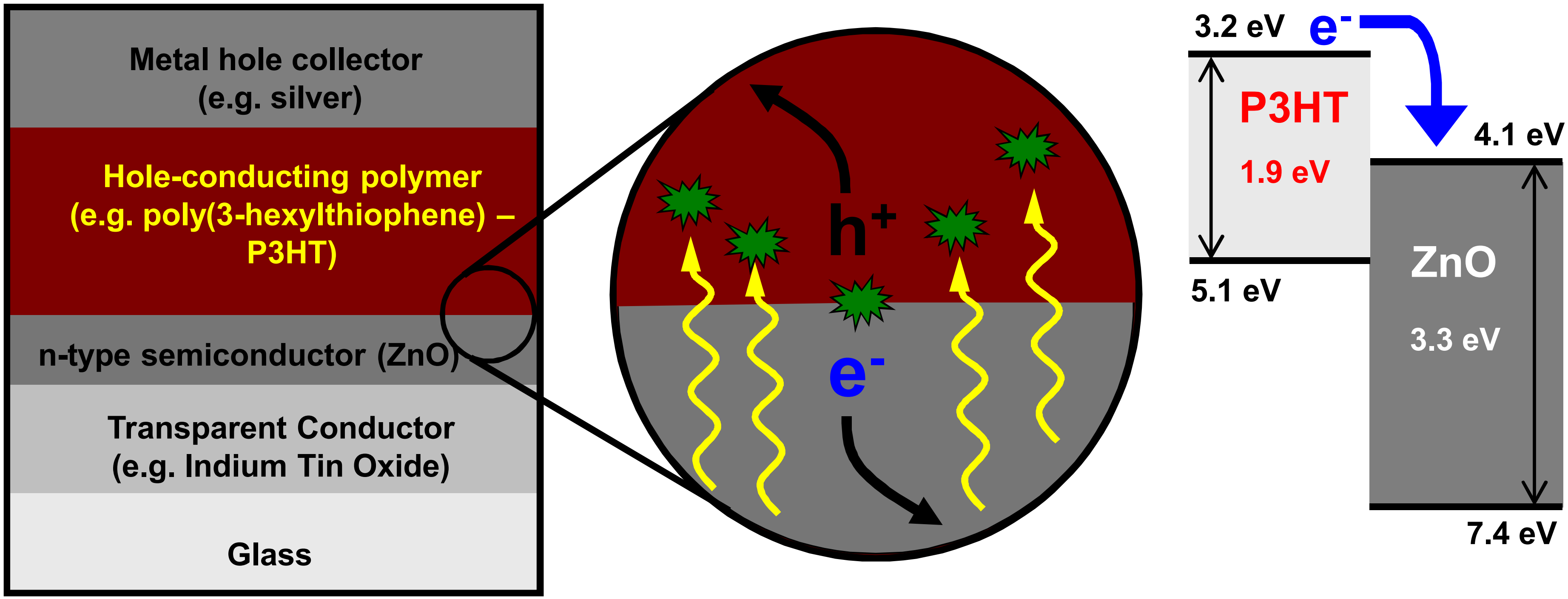
Organic photovoltaics: potential for low-cost renewable electricity

How does OPV work?



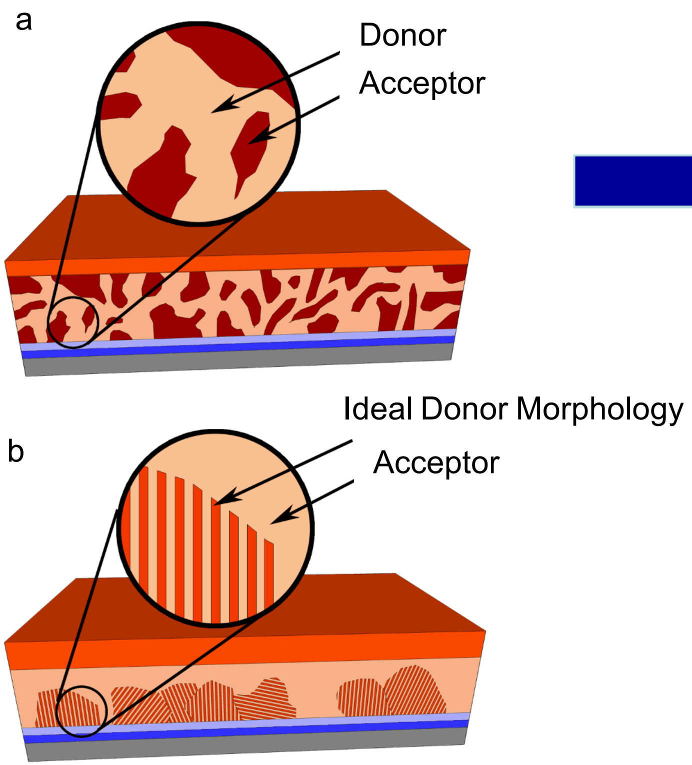
Realizing a Device Configuration

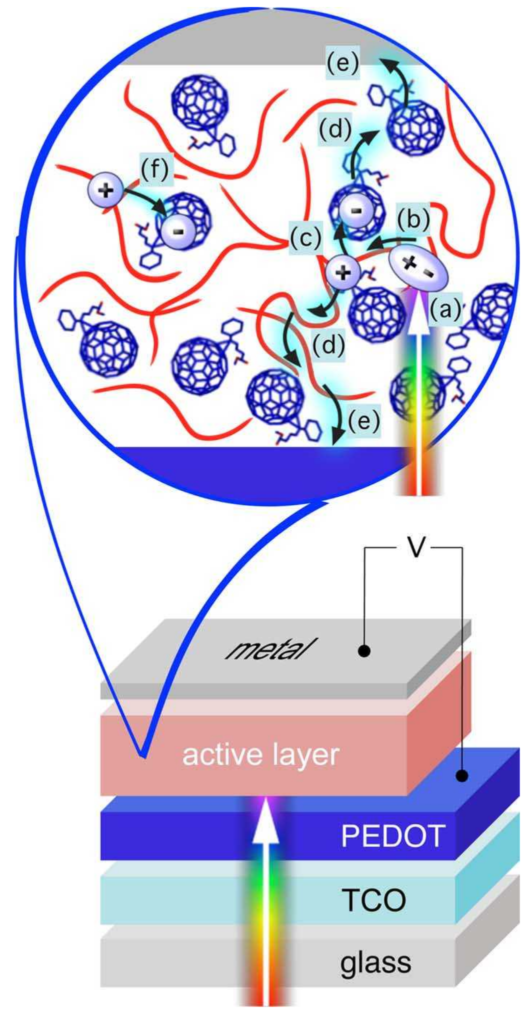
In a planar configuration, thin films of a conductive polymer (e.g., P3HT) and ZnO can form the charge separation interface.



Disorder is the enemy of efficiency

Bulk heterojunction





C. Deibel et al. IEEE Journal Of Selected Topics In Quantum Electronics, Vol. 16, No. 6, November/December 2010

Key Materials Considerations

Requirements for efficient OPV system:

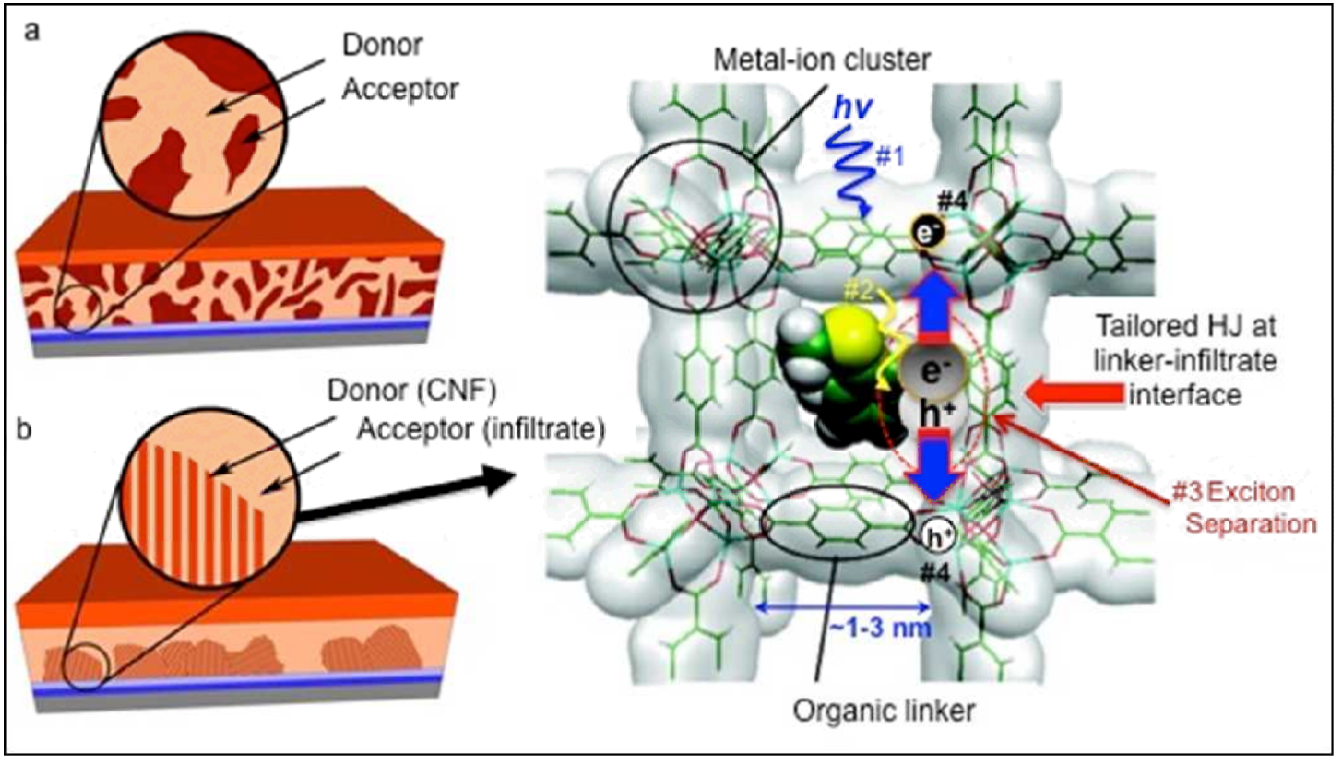
- Good p-type absorber
- Proper band alignments for charge separation/transfer
- Ordered molecular charge separation interfaces
- Short exciton diffusion distances

Introduction to MOFs

Order vs. disorder: creation of nano-heterojunctions

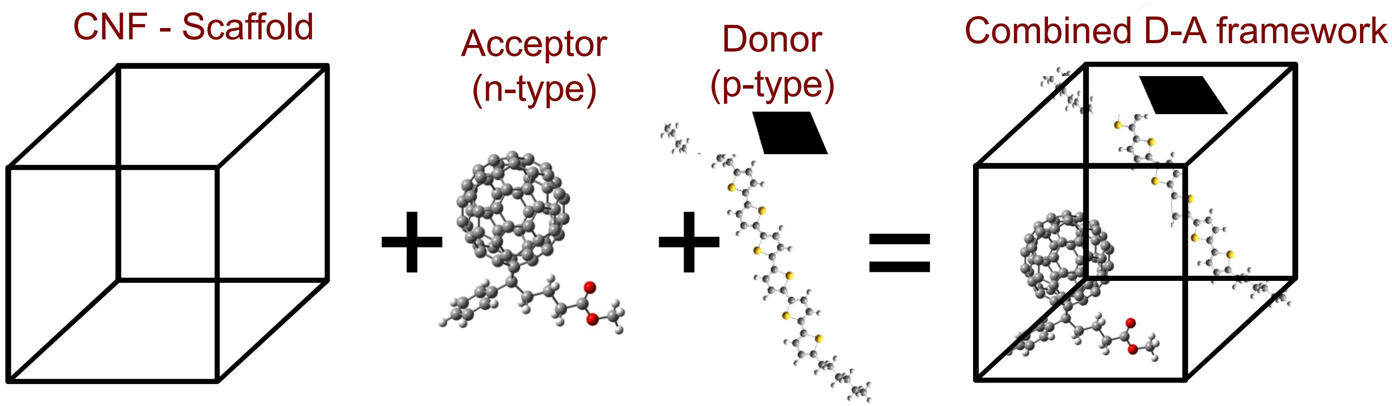
Conventional disordered BHJ

Highly ordered "Nano-HJ" using CNF platform

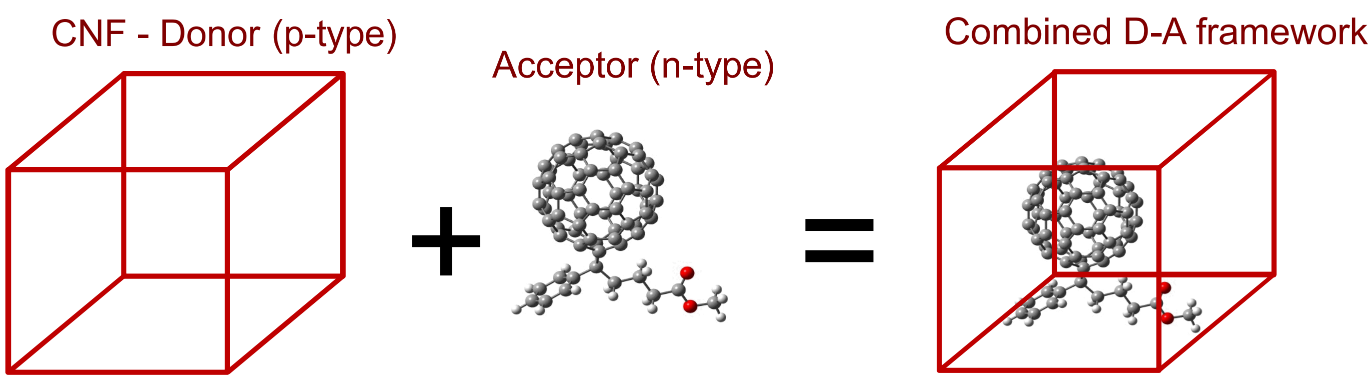


Composite MOF Scaffolds for OPV

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.



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MOF177: A Passive Scaffold for D-A Assembly

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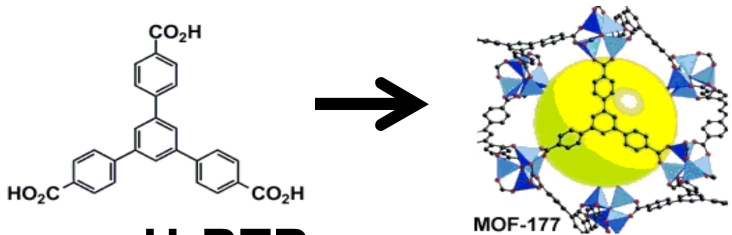
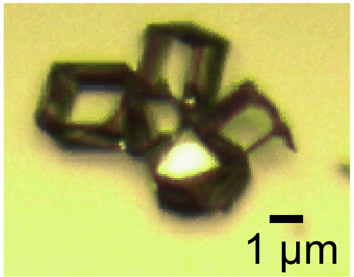
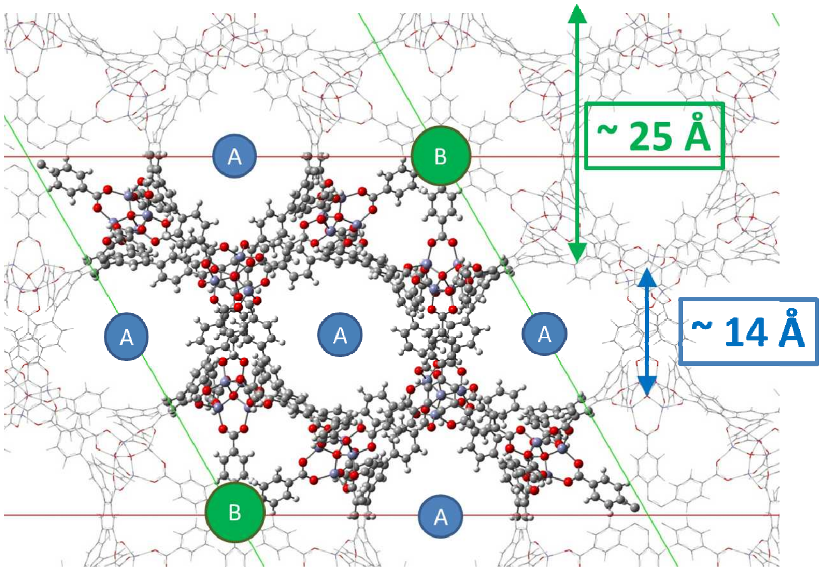
$Zn(NO_3)_2 \bullet 6H_2O + H_3BTB \longrightarrow$ MOF-177



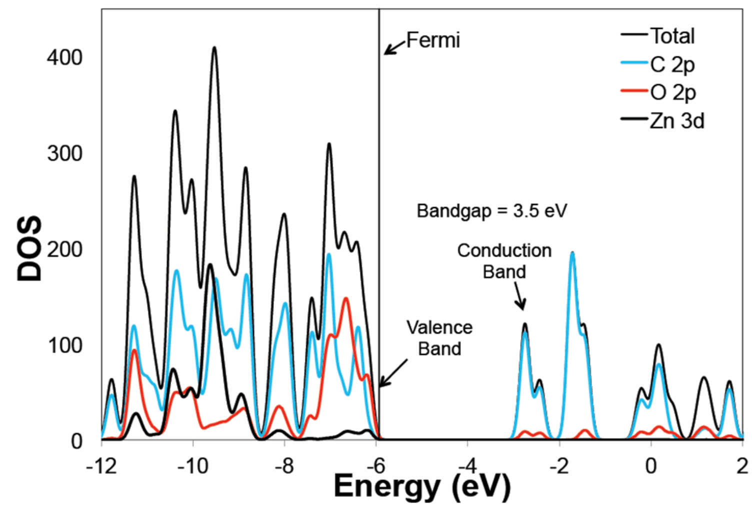
H_3BTB



Optical image of MOF-177 crystals.



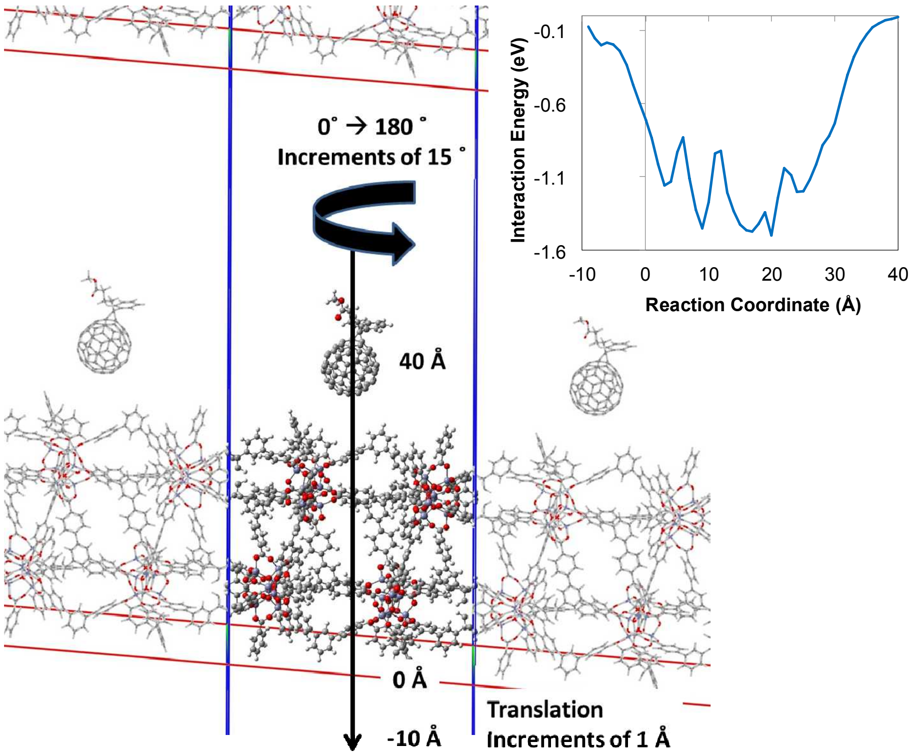
MOF-177 – sites “A” and “B” denote unique cavities; DFTB optimized structure.

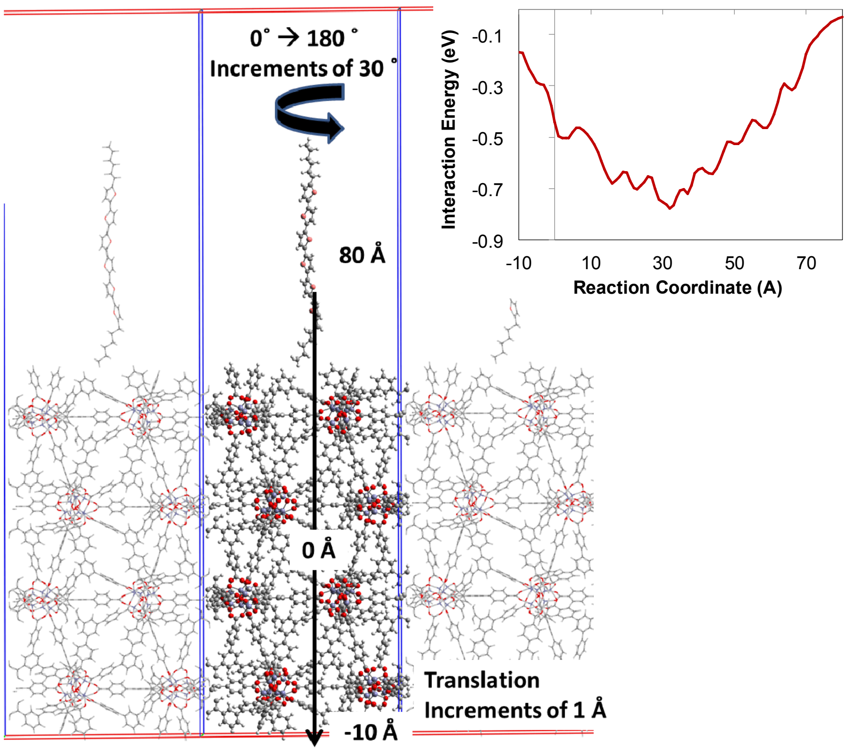


Partial Density of States (PDOS) - Density Functional Tight-Binding (DFTB) calculations of MOF-177.

Predicting Guest Infiltration

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

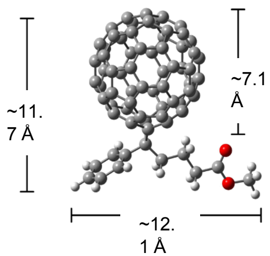


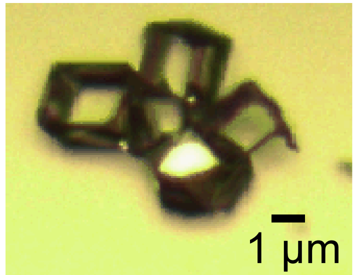


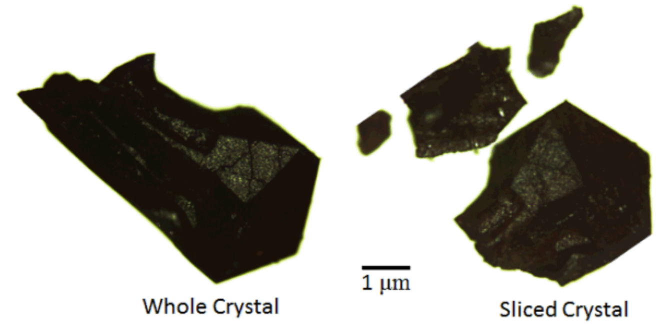
>600 structures generated for each case; 10 step geometry optimization performed to remove close contacts. Interaction energies determined using Density Functional based Tight Binding (DFTB) method.

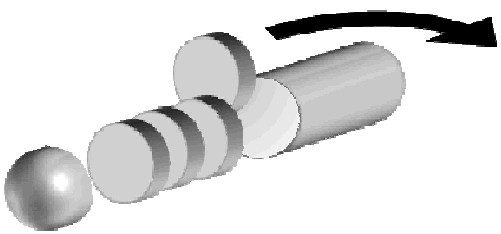
PCBM Integration into MOF177

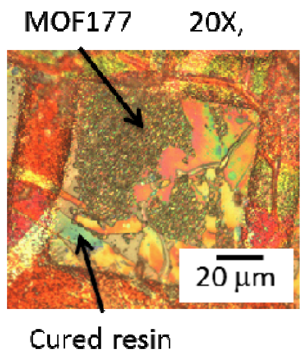
Incubation of MOF177 crystals in concentrated PCBM solutions leads to PCBM infiltration



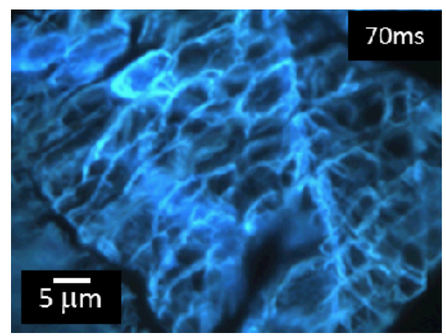




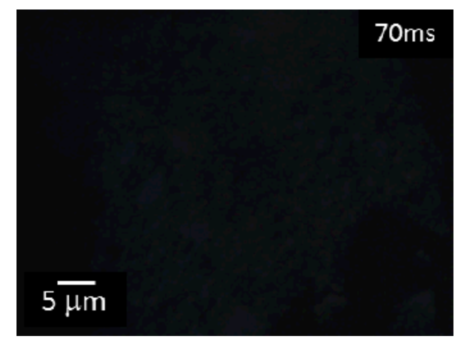




MOF177



MOF177/PCBM



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

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

Introduction to MOFs

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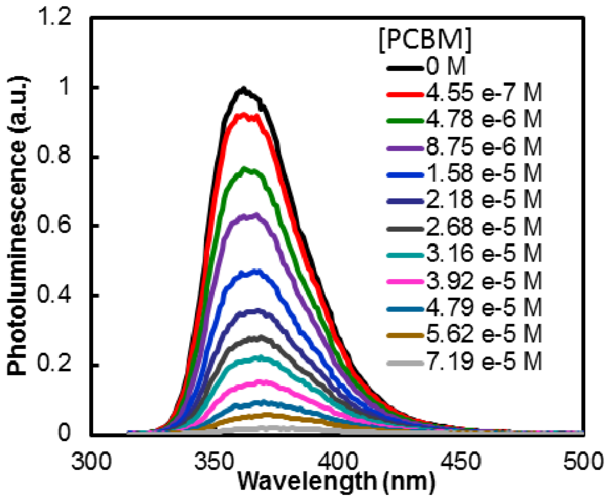
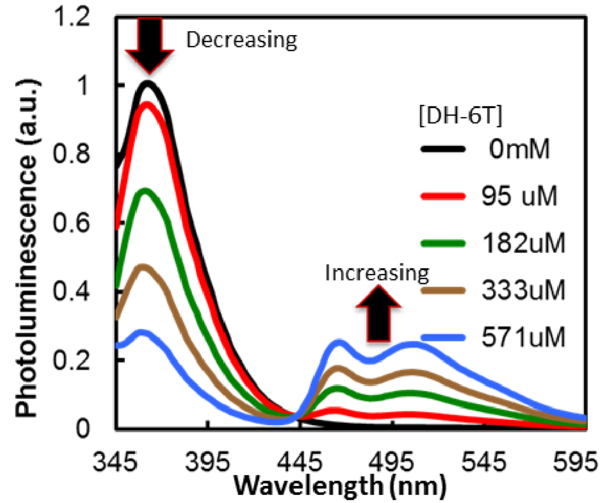
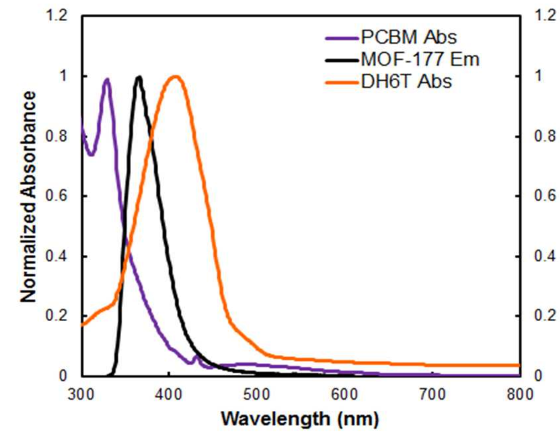
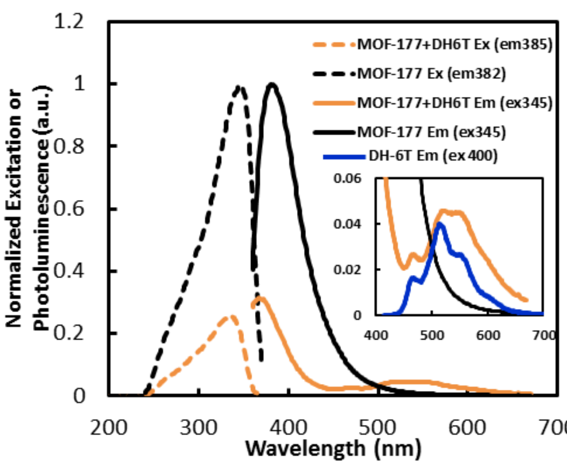
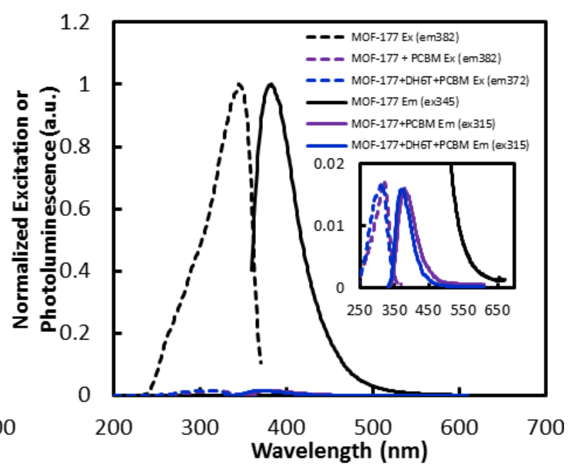
Spectral characterization reveals complex energy transfer between MOF177, PCBM, and DH6T

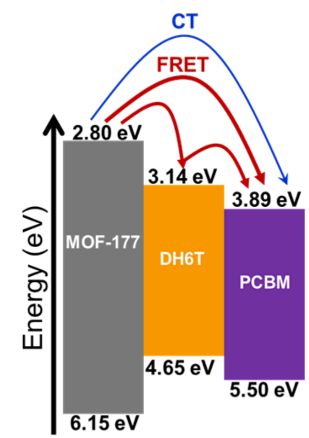








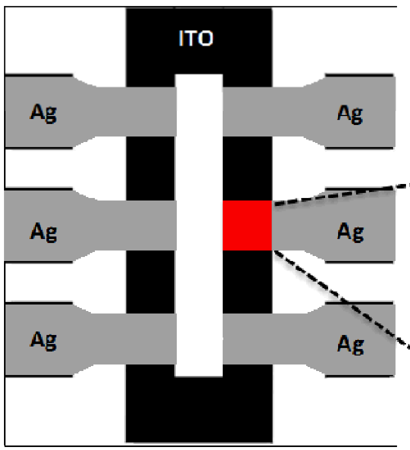


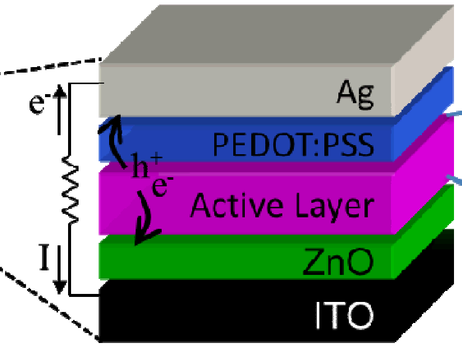


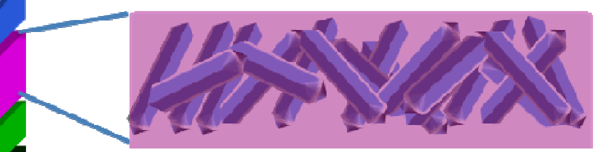
MOF177, DH6T, &PCBM band alignment predicted by SCC-DFTB

Device Integration

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





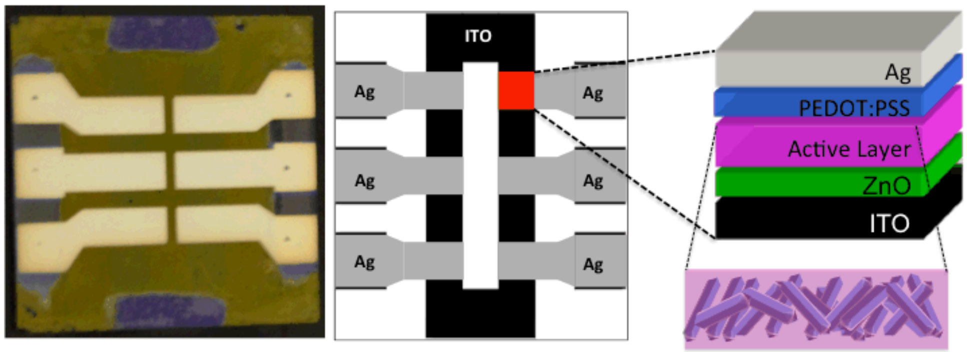


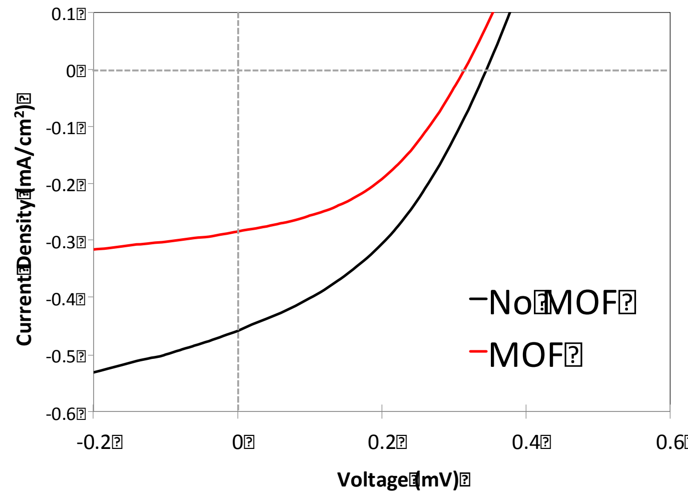
Patterned ITO and silver electrodes create controlled $0.1cm^2$ active areas.

Inverted device configuration

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

Device Testing





	V_{OC} (mV)	J_{SC} (mA/cm²)	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, ostensibly from reduced active area or charge trapping in suspended PCBM@MOF177 composites.

Key Materials Considerations

Requirements for efficient OPV system:

- Good p-type absorber
- Proper band alignments for charge separation/transfer
- Ordered molecular charge separation interfaces
- Short exciton diffusion distances
- Facile incorporation into device architectures!

Functional Host-Guest Interactions: Conducting MOFs

Guest molecules create multifunctional materials:

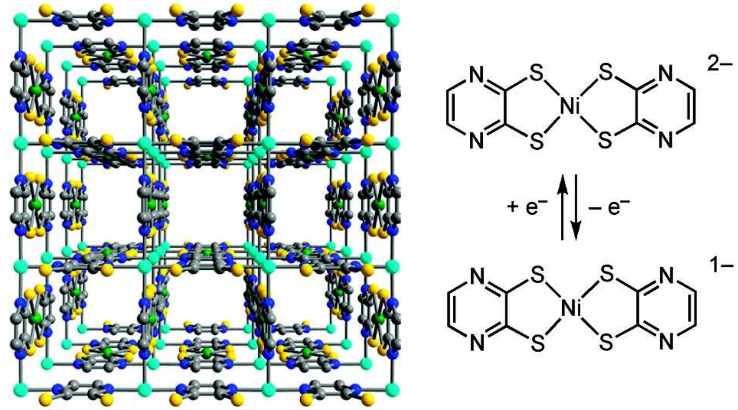
- ***Nanporous***
- ***Electrically conducting***

Electrically conducting porous MOFs are rare

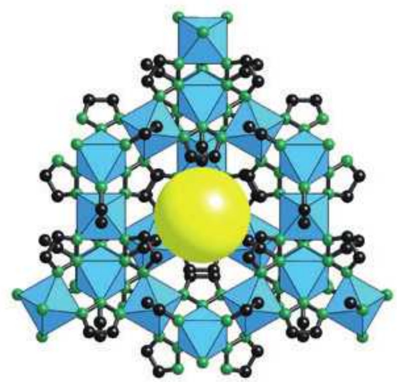
- **p-type Cu-Ni Dithiolene MOF**
  - First semiconducting, porous MOF
  - Conductivity increases with oxidative doping
  - Original Cu-Cu version is not porous (*Inorg. Chem.* 2009, 48, 9048)

- **Other examples**
  - MET-3 (Fe-triazolate MOF)
  - Mn(thiophenol) MOF: $(-Mn-S-)_\infty$ Chains

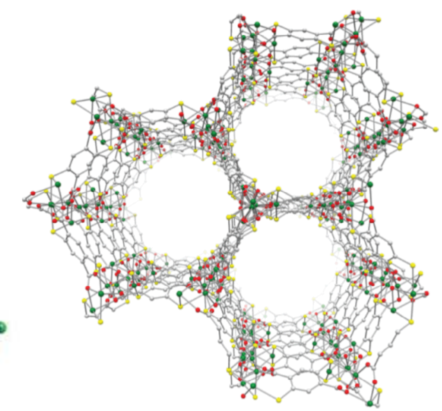
- **Strategies for conducting MOFs:**
  - Charge delocalization
  - 2^{nd}- and 3^{rd} row transition metals
  - Redox-active ligands (e.g., TCNQ)
  - Soft ligands (e.g. S-containing molecules)



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



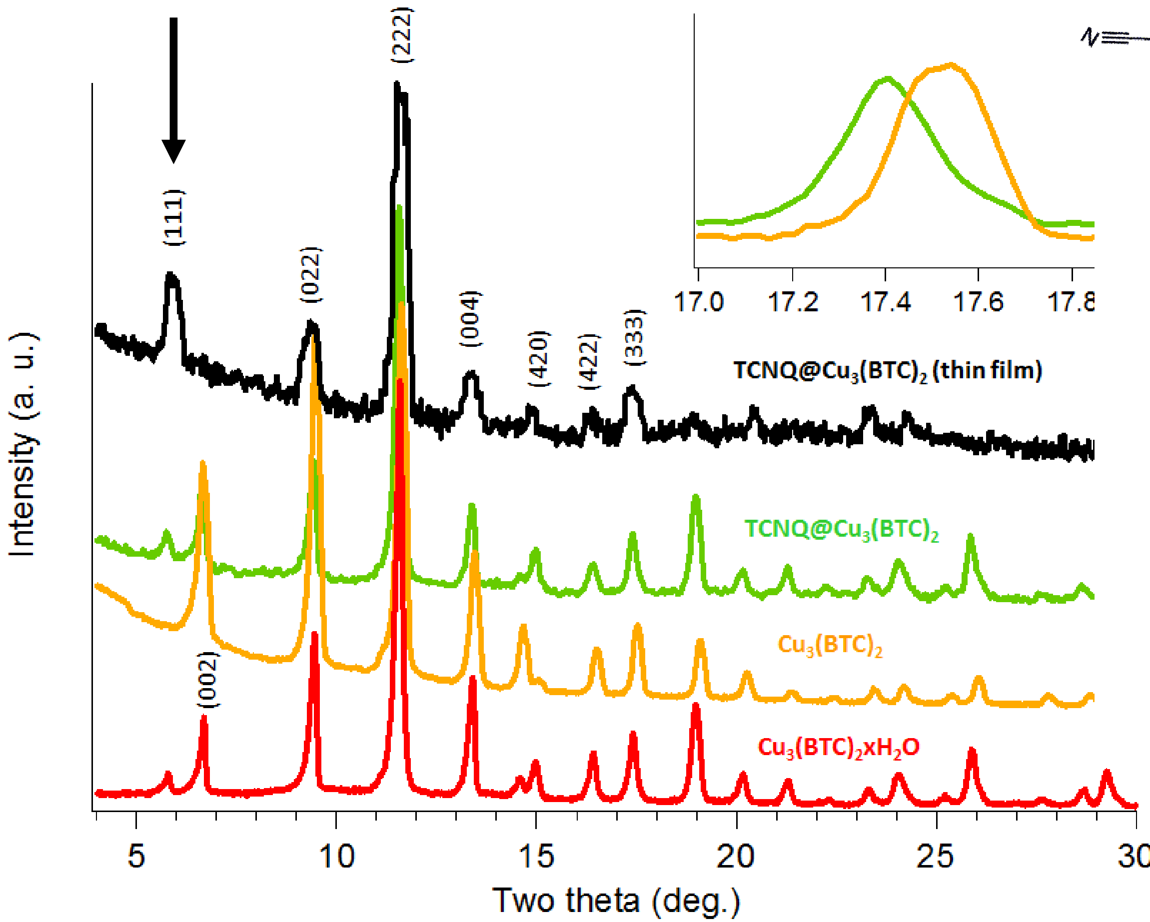
MET-3 (Fe)
Gándara et al.
Chem. Eur. J. 2012, 18, 10595

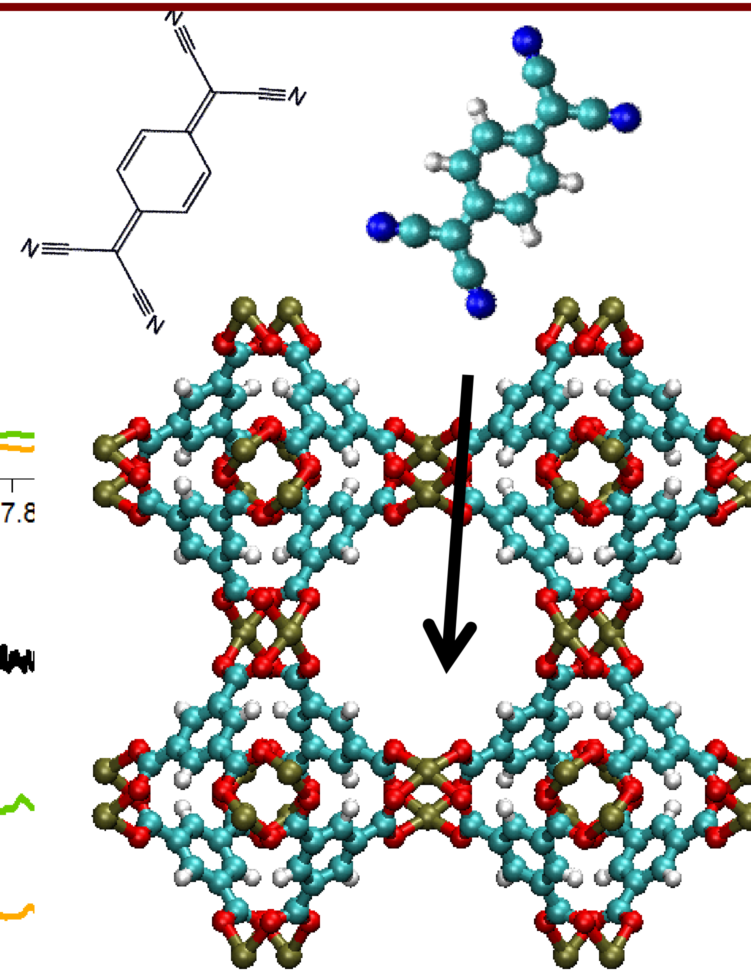


Mn(thiophenol) MOF
L. Sun et al.
J. Am. Chem. Soc. 2013, 135, 8185

Can guest molecules induce electrical conductivity in an insulating MOF?

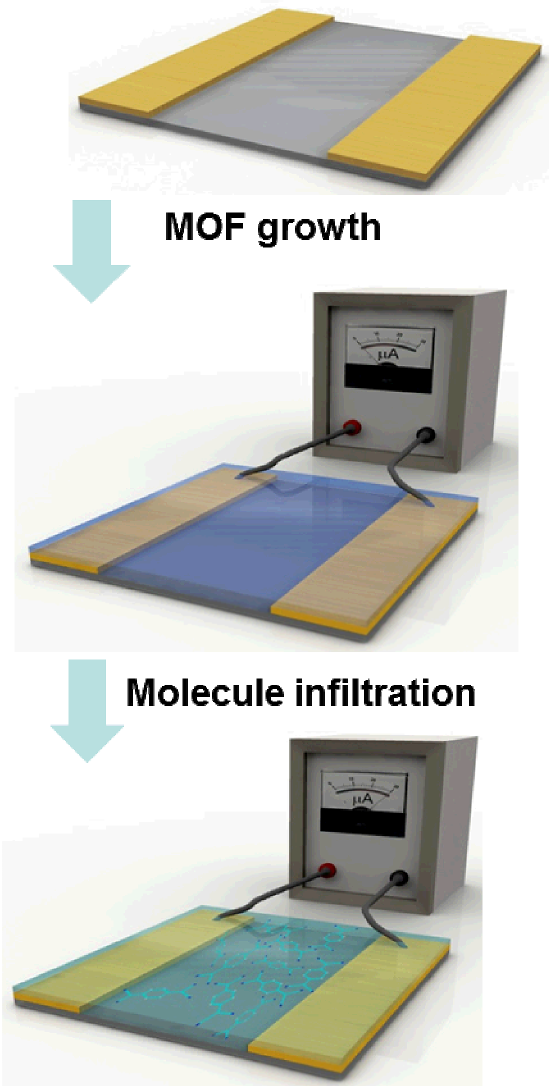
TCNQ: 1- or 2-e^- acceptor (π acid)

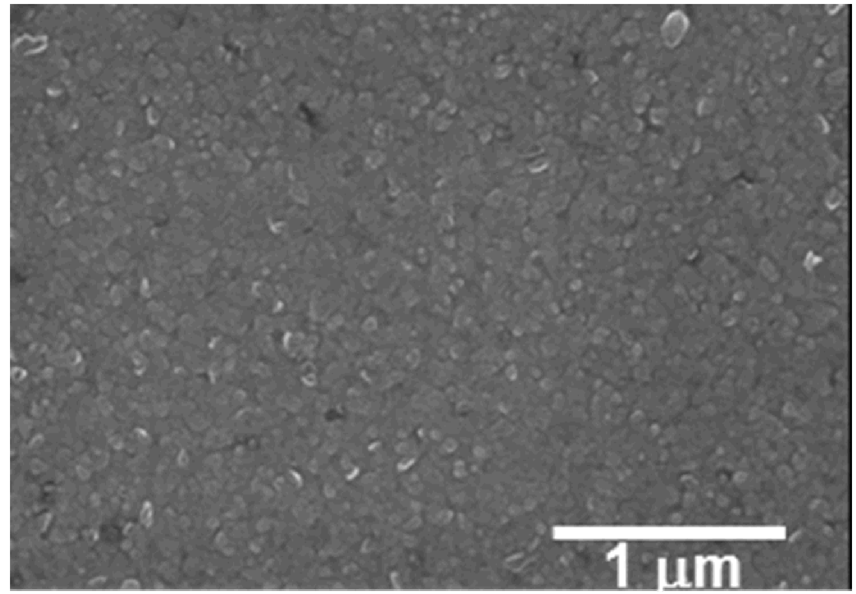


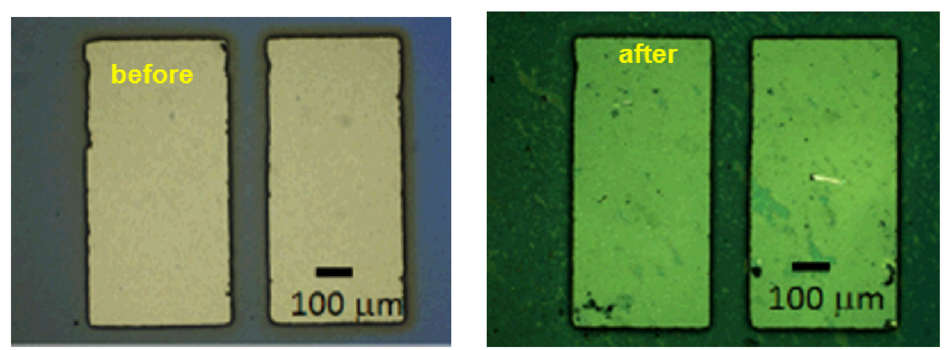


Cu_3BTC_2 (HKUST-1)

TCNQ→ $Cu_2(BTC)_3$ leads to color change…







… and >×10⁶ increase in conductivity

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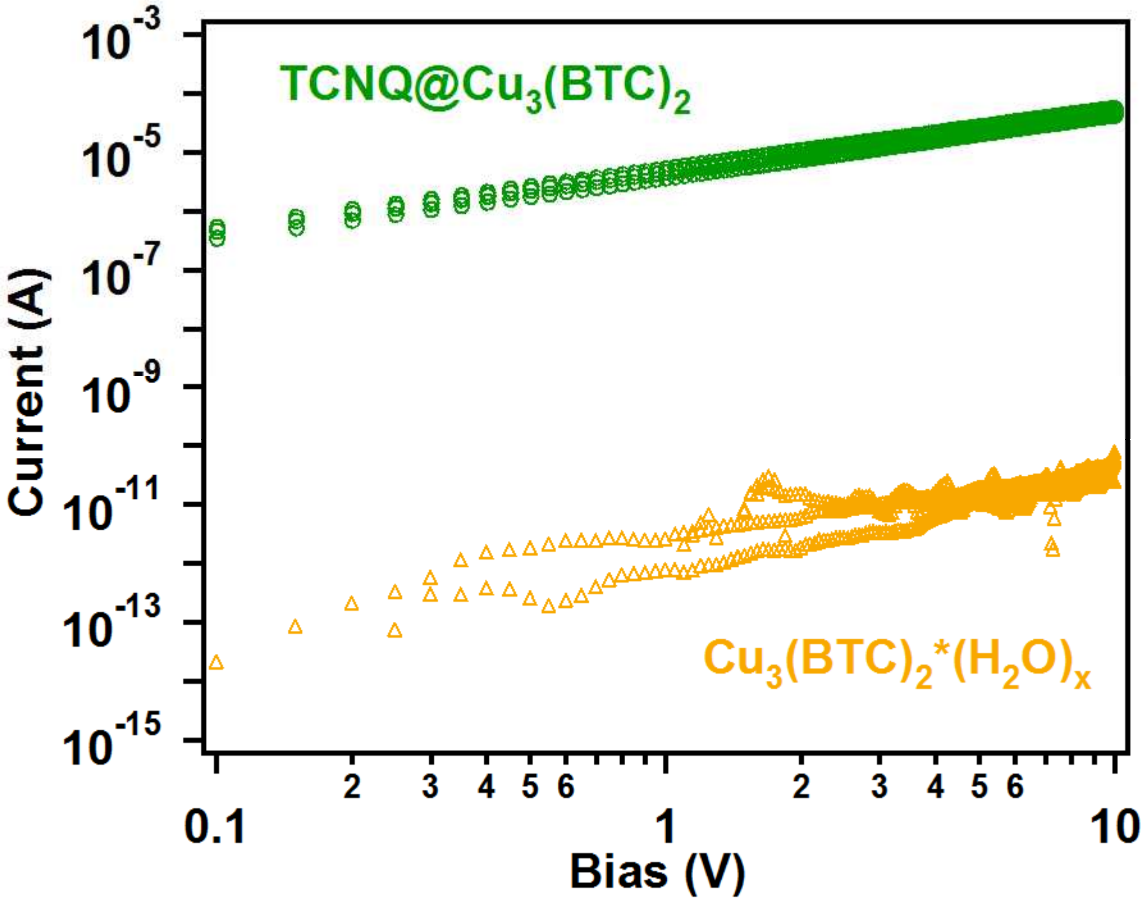
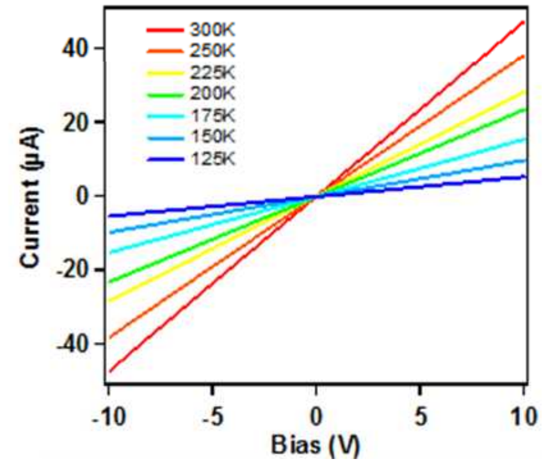
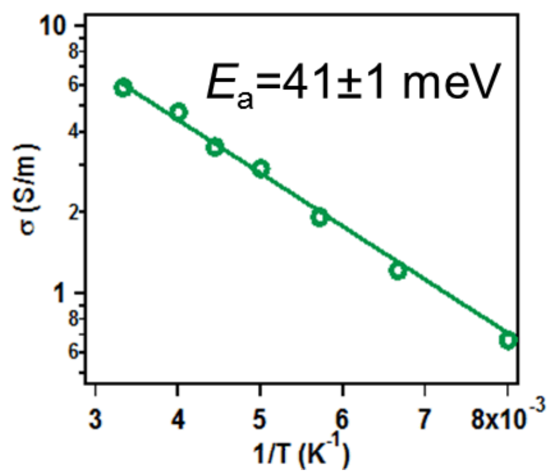
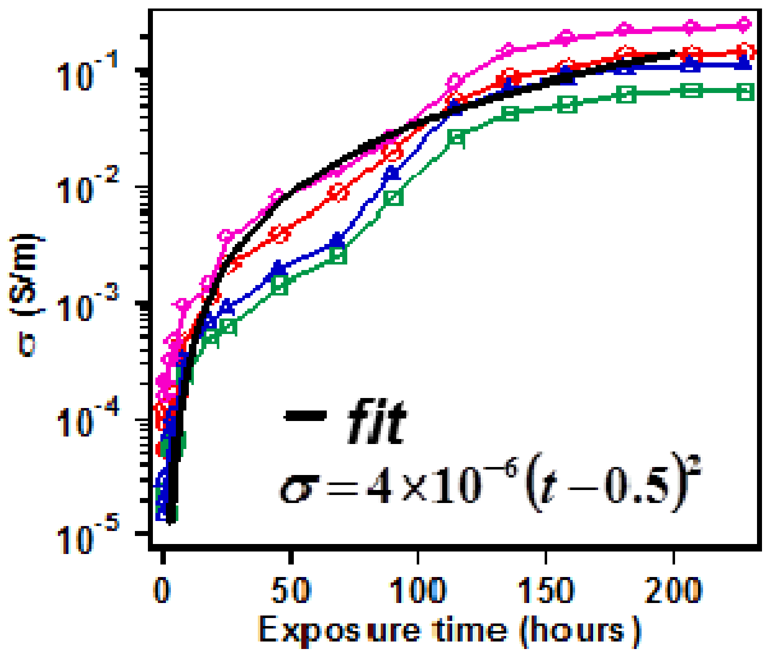
Conduction is Ohmic

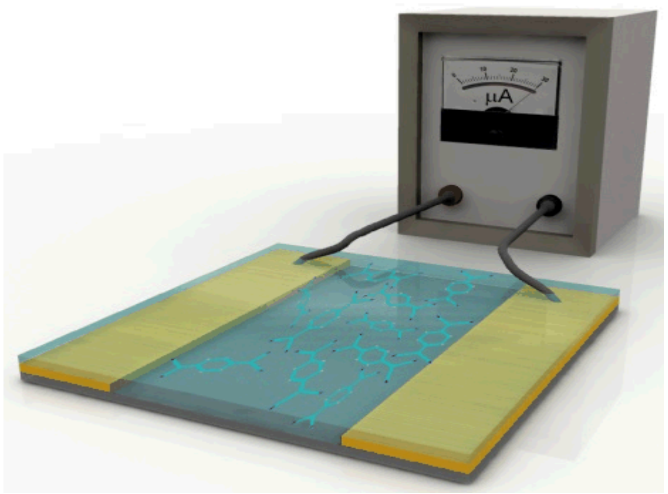






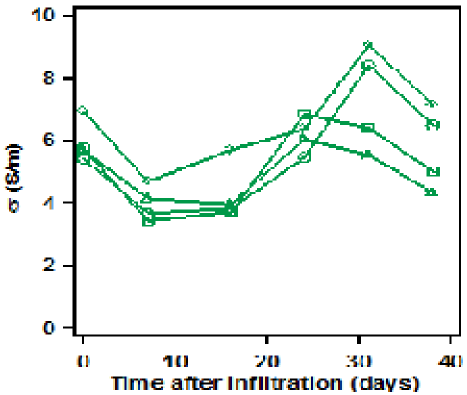
Conductivity follows classic percolation model



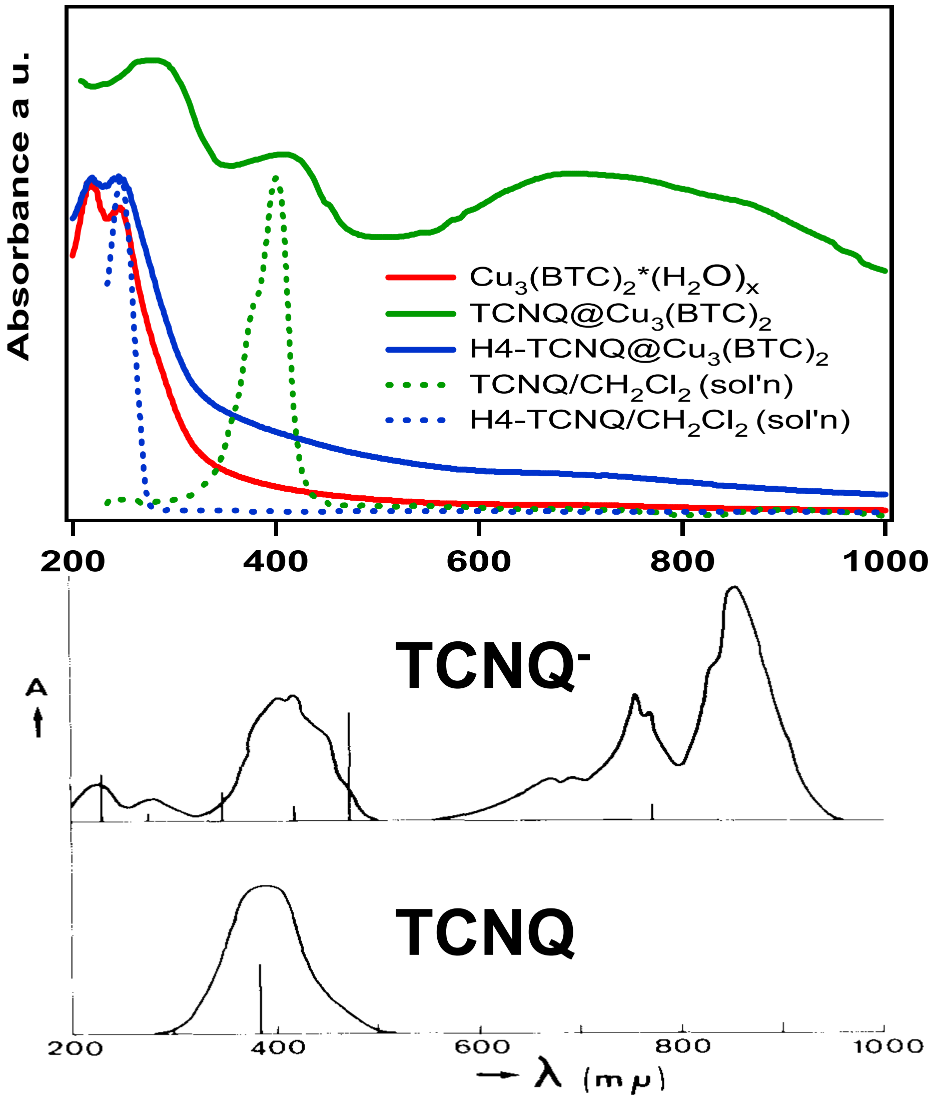


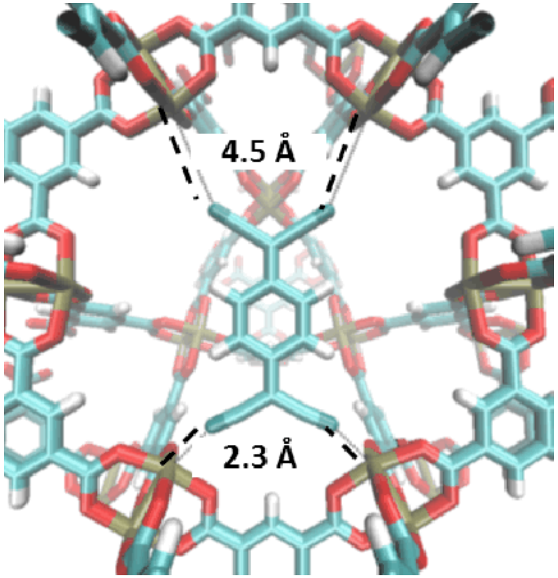
→ Tunable conductivity

Stable in air



UV-Vis suggests charge transfer between MOF and TCNQ

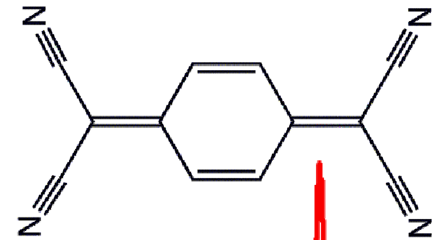


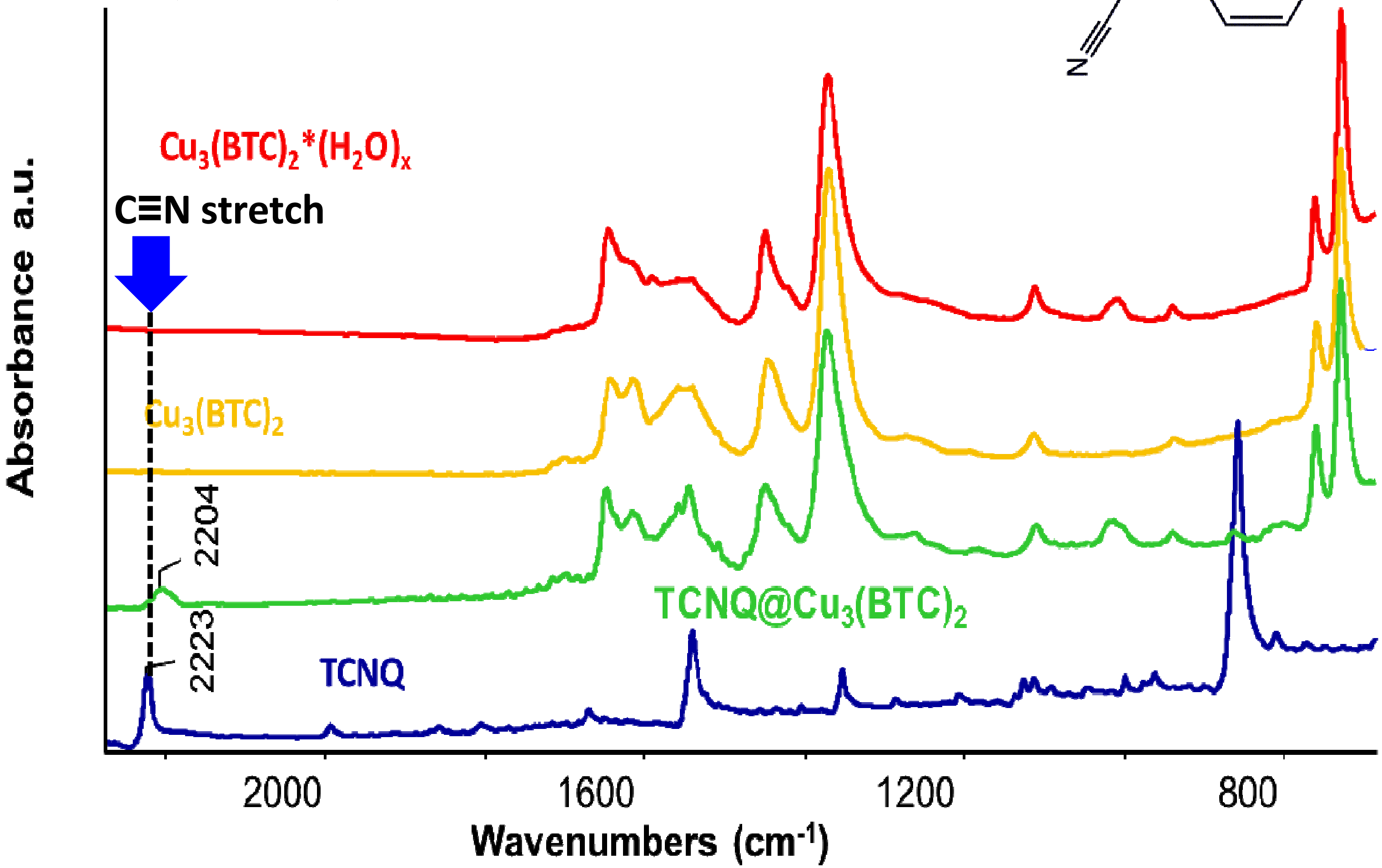


DFT-optimized structure

IR shift of -C≡N indicates charge transfer

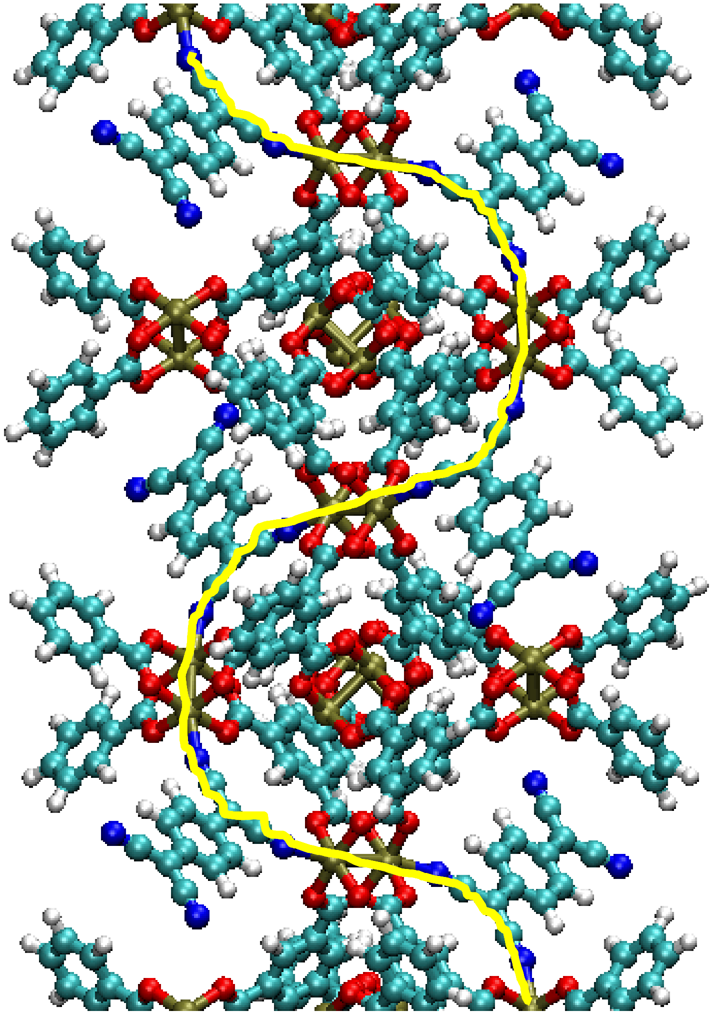
$$z = \left(\nu_o - \nu\right) / 44 cm^{-1} \;\; \approx \mathbf{0.43}\boldsymbol{e}$$

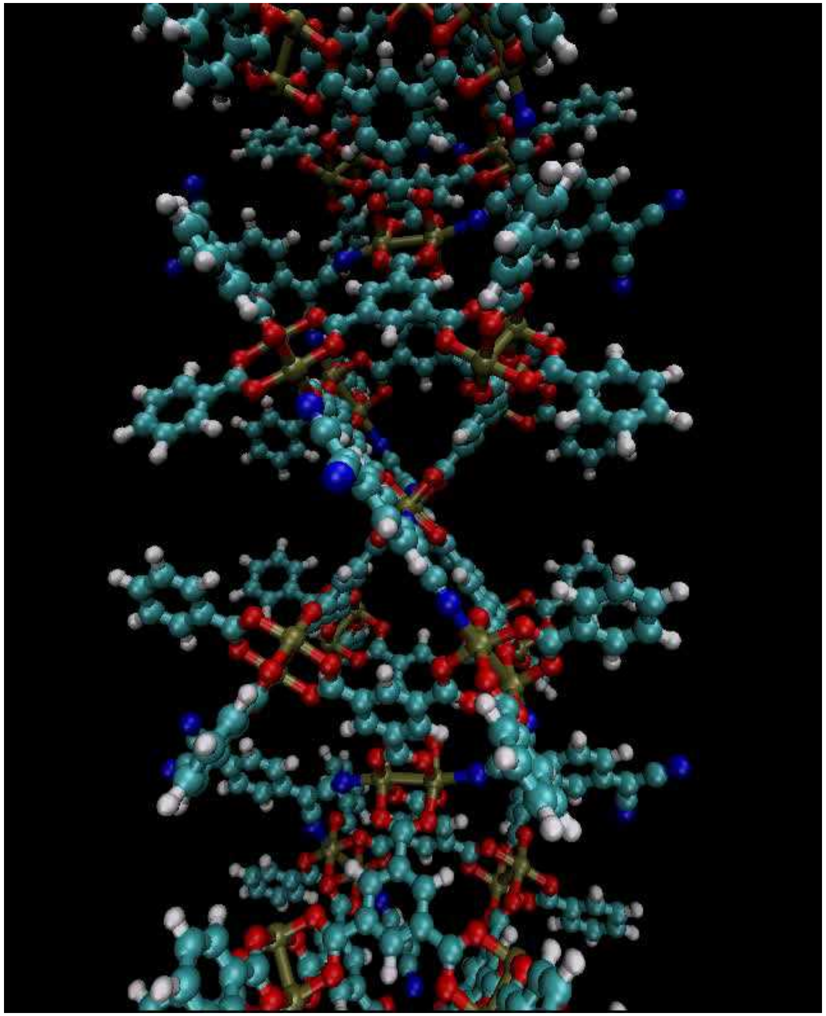




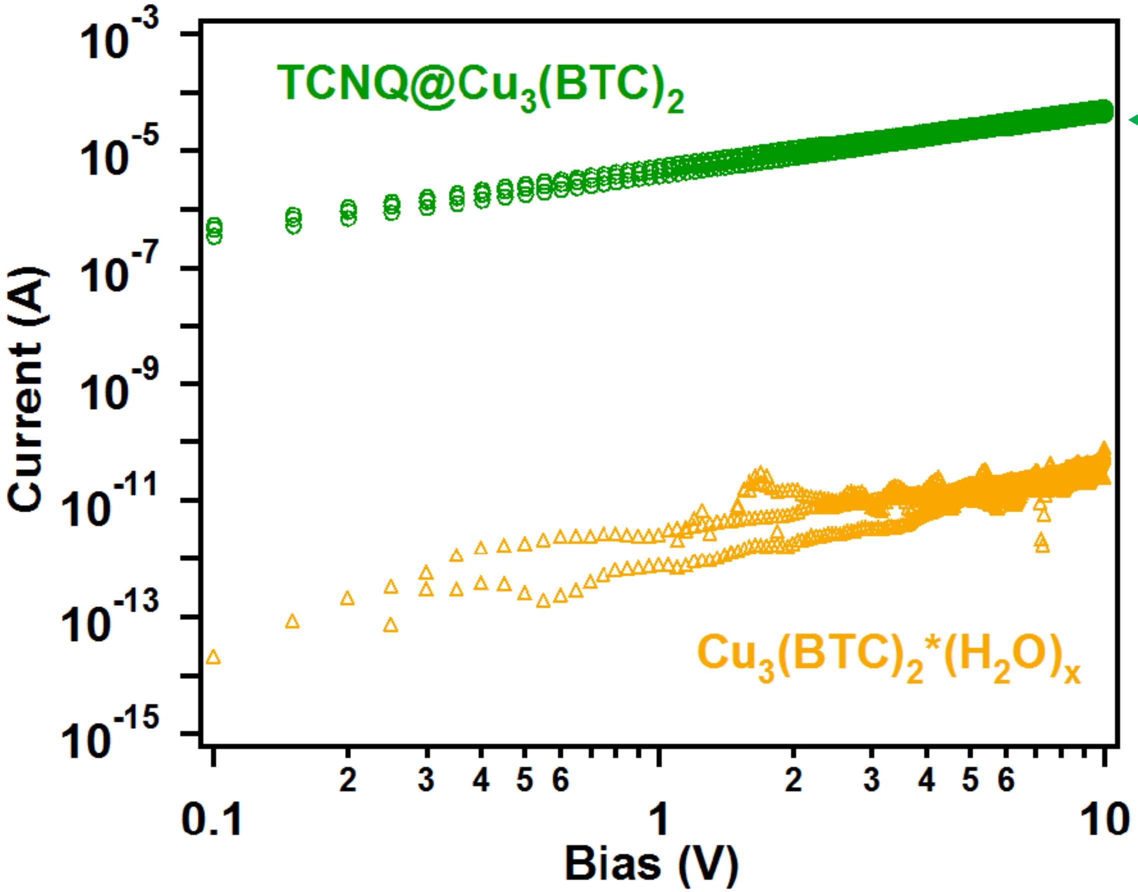
Proposed TCNQ@CuBTC Conduction Pathway

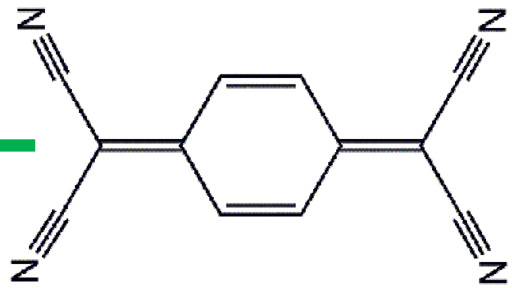
Plane-wave (periodic) DFT optimized structure



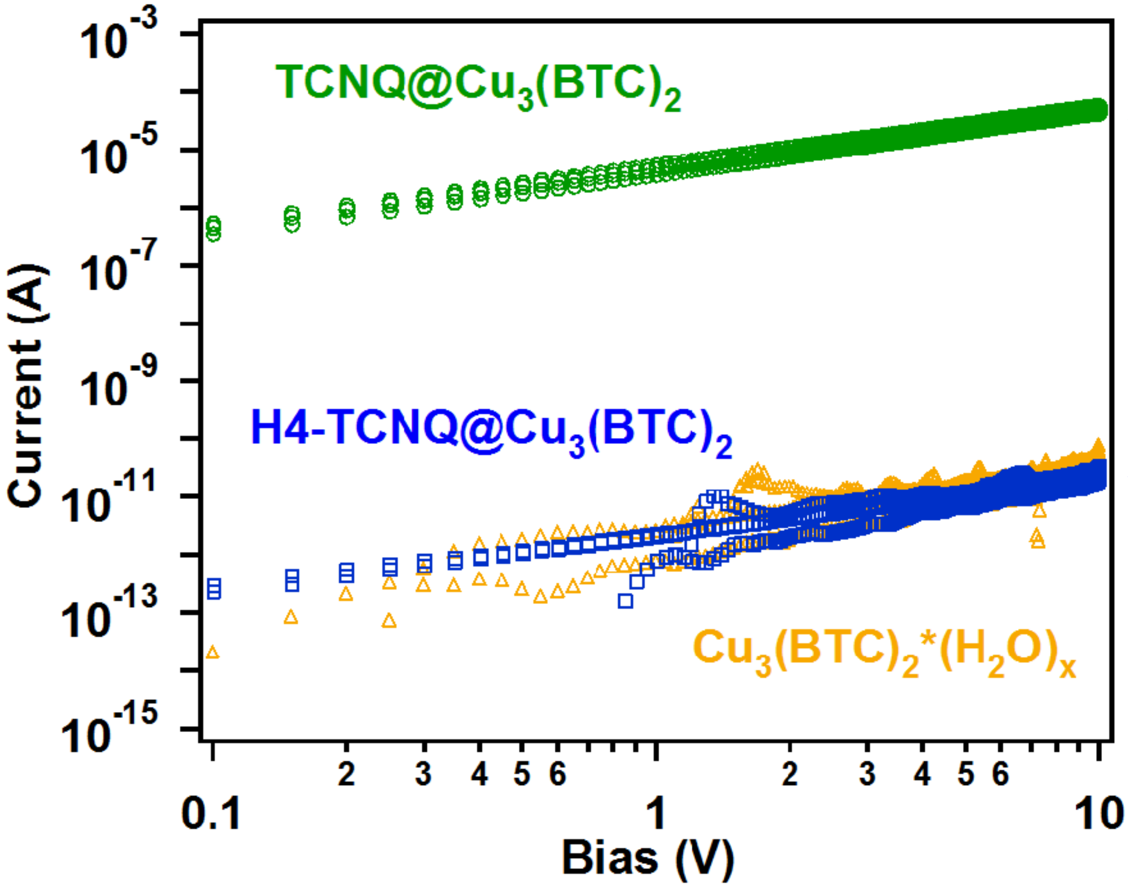


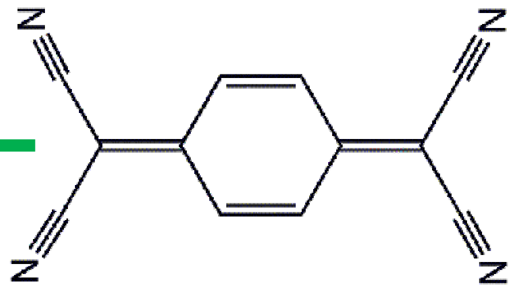
Extended π network essential for conductivity

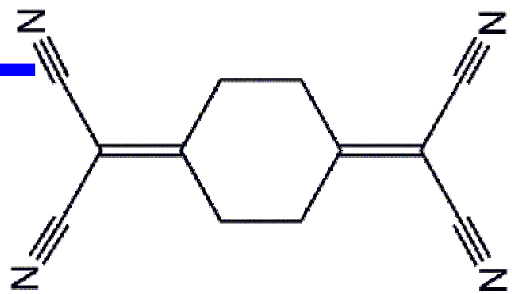




Extended π network essential for conductivity

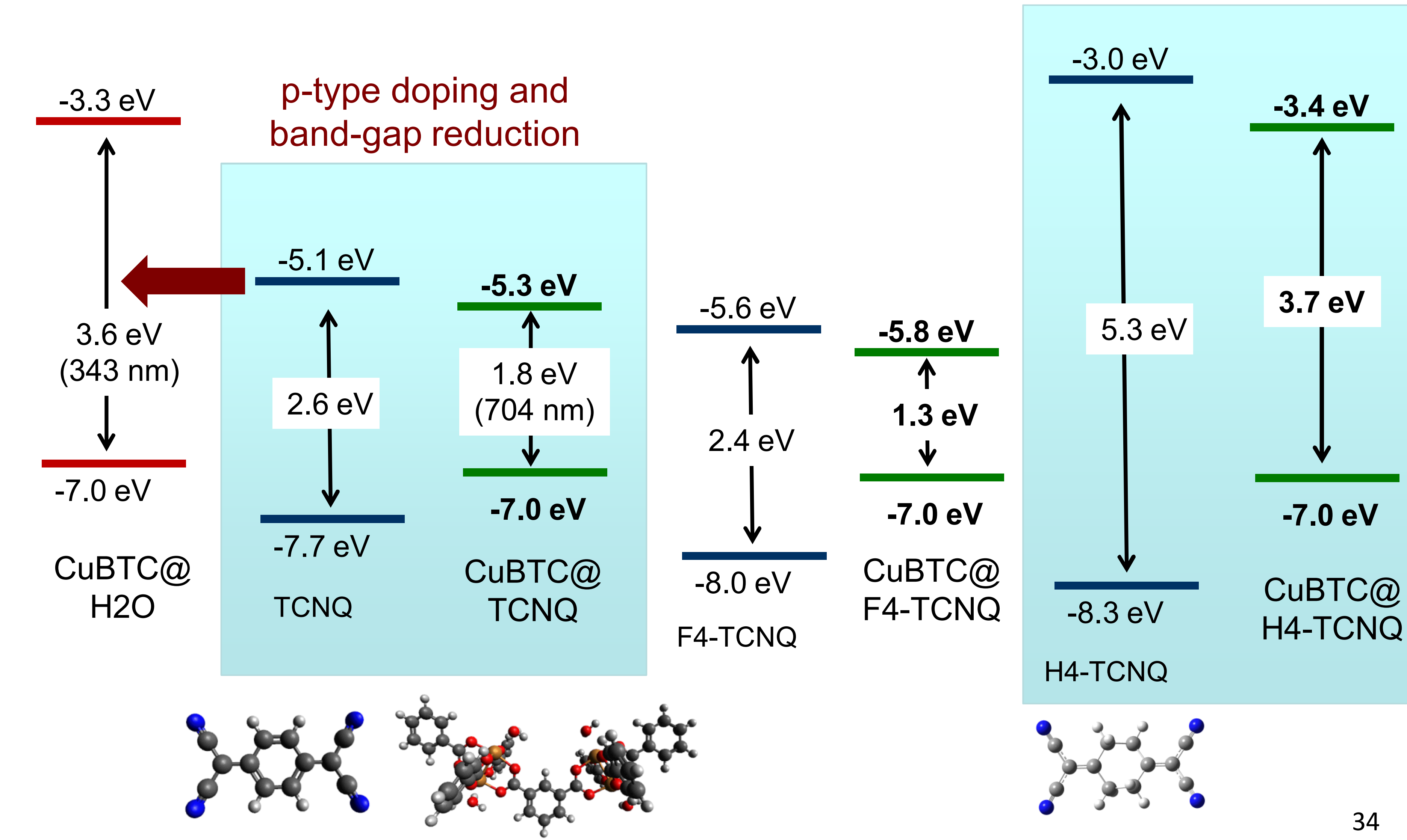






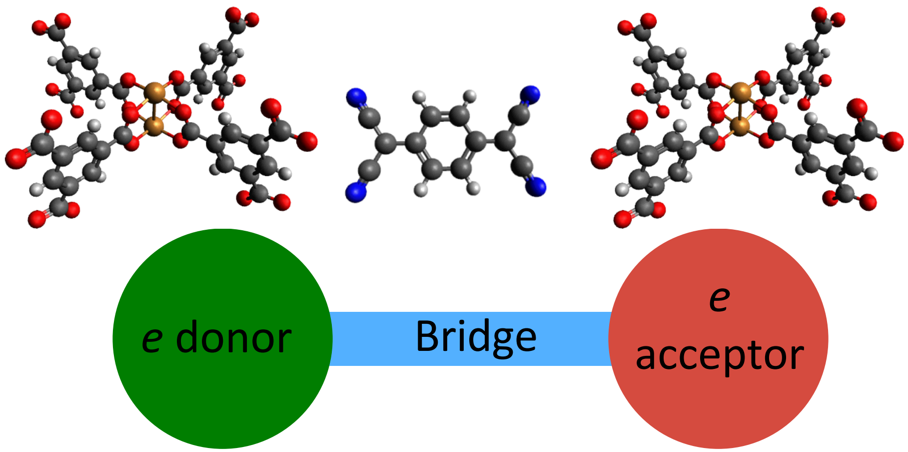
Cu-BTC band alignments: DFT/PBEsol calculations

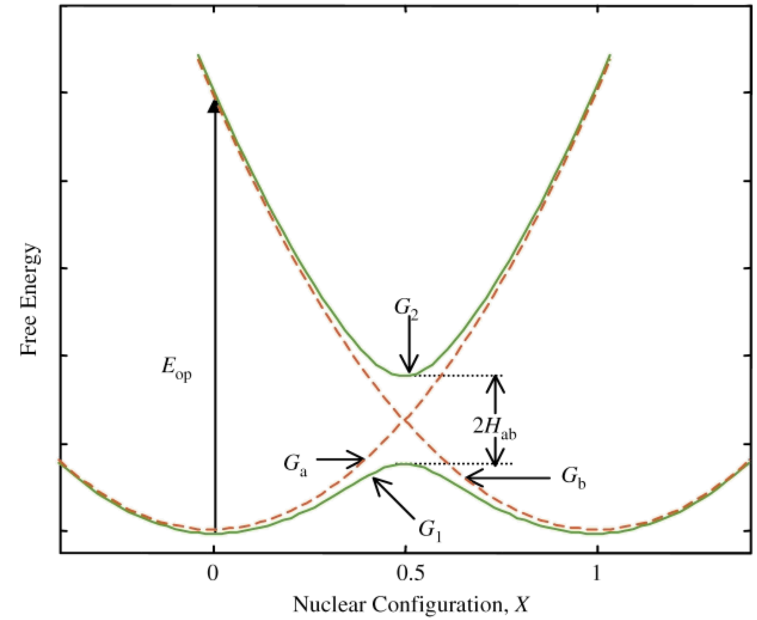
Effect of fluorination and hydrogenation of TCNQ



DFT predicts $TCNQ@Cu_3(BTC)_2$ is a delocalized system

Sandia National Laboratories





Robin-Day classification	Electronic coupling	$2H_{AB}/\lambda$	Optical/electronic Properties
Class I	very weak (isolated charge)	<< 1	no new features
Class II	intermediate (charge localized)	≤ 1	New Vis-near IR absorption
Class III	very strong (delocalized charge)	> 1	New Vis-near IR absorption

	H_{AB} (eV)	ΔG^* (eV)	λ (eV)	H_{AB}/λ	
TCNQ	2.32	0.041	3.84	1.21	➡ Class III
F_4-TCNQ	1.04	0.104	3.23	0.64	➡ Class II-III

Outline

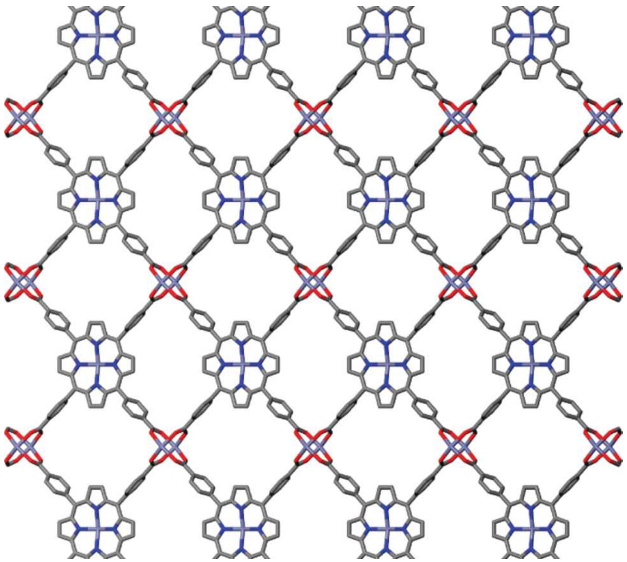
Sandia National Laboratories

- ✧ What are MOFs?
- ✧ A Basic Introduction to PV
- ✧ “Passive” MOF Scaffolds
- ✧ “Active” MOF Scaffolds

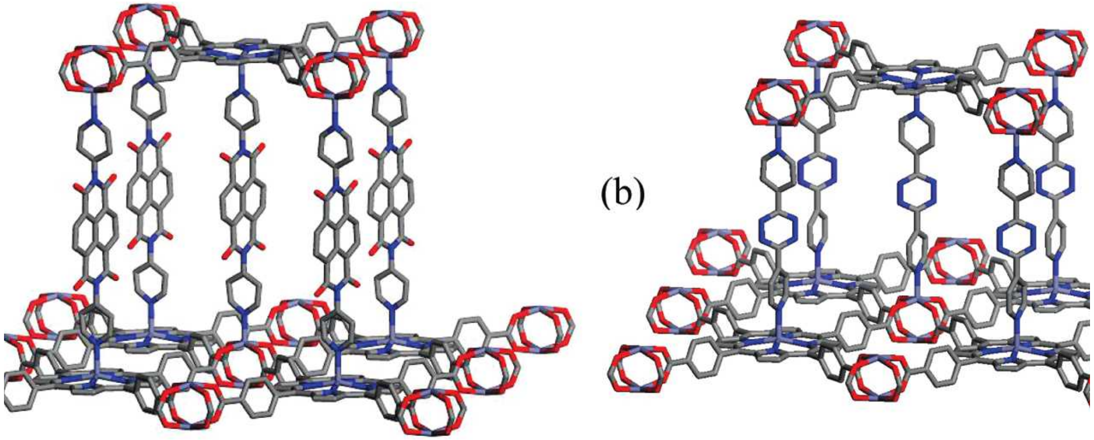
Building Photoactive MOFs

Consider Pillared Porphyrin Frameworks (PPFs)

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



2D porphyrin sheet commonly found in PPF series



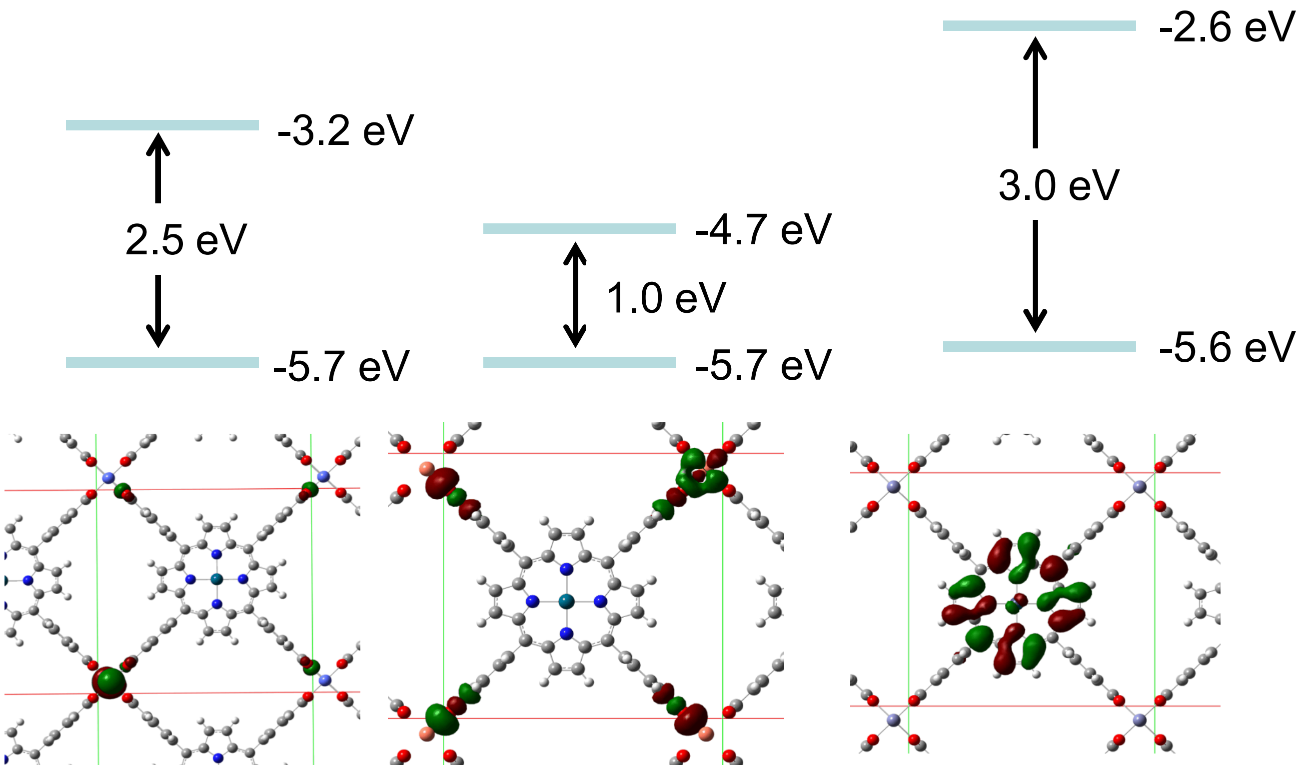
Side view of PPF-18

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

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

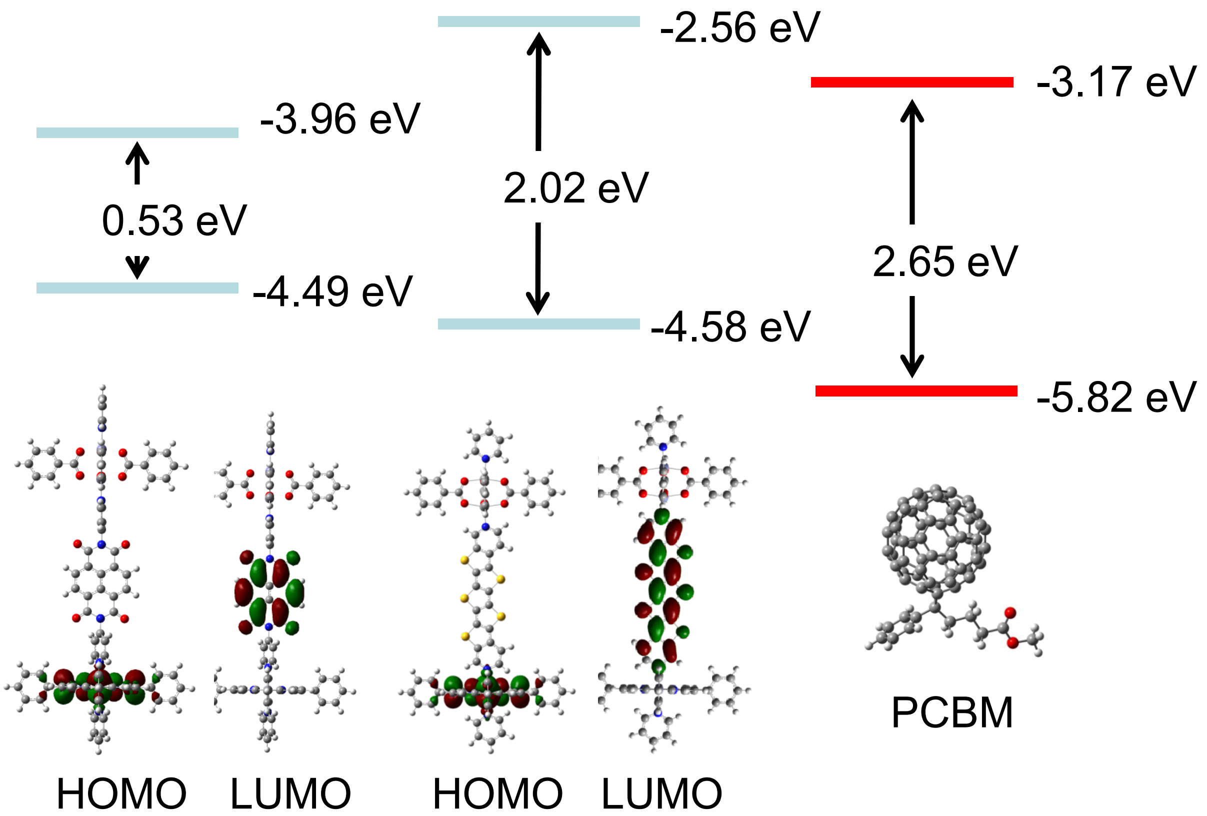
LUMO
Pd porphyrin - Zn layer

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.

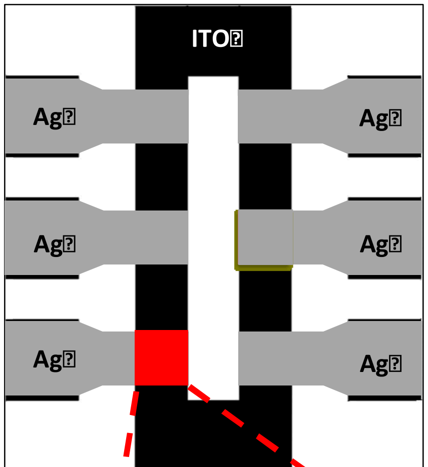
<u>Varying organic pillars</u>



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

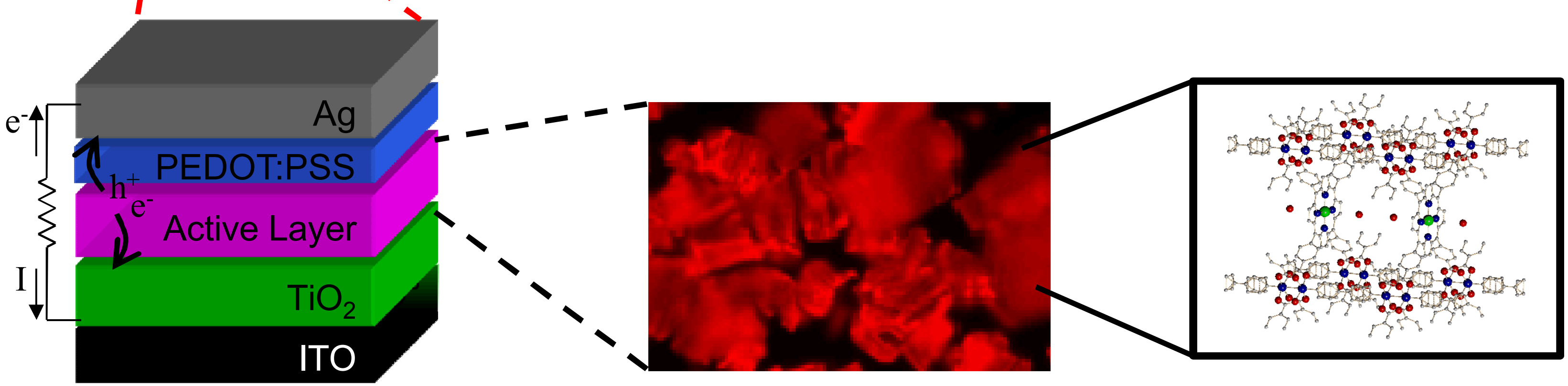
Integration of PPF-5 into Devices

Challenge: *Can we develop the chemistry to integrate these versatile materials into HOPV devices?*



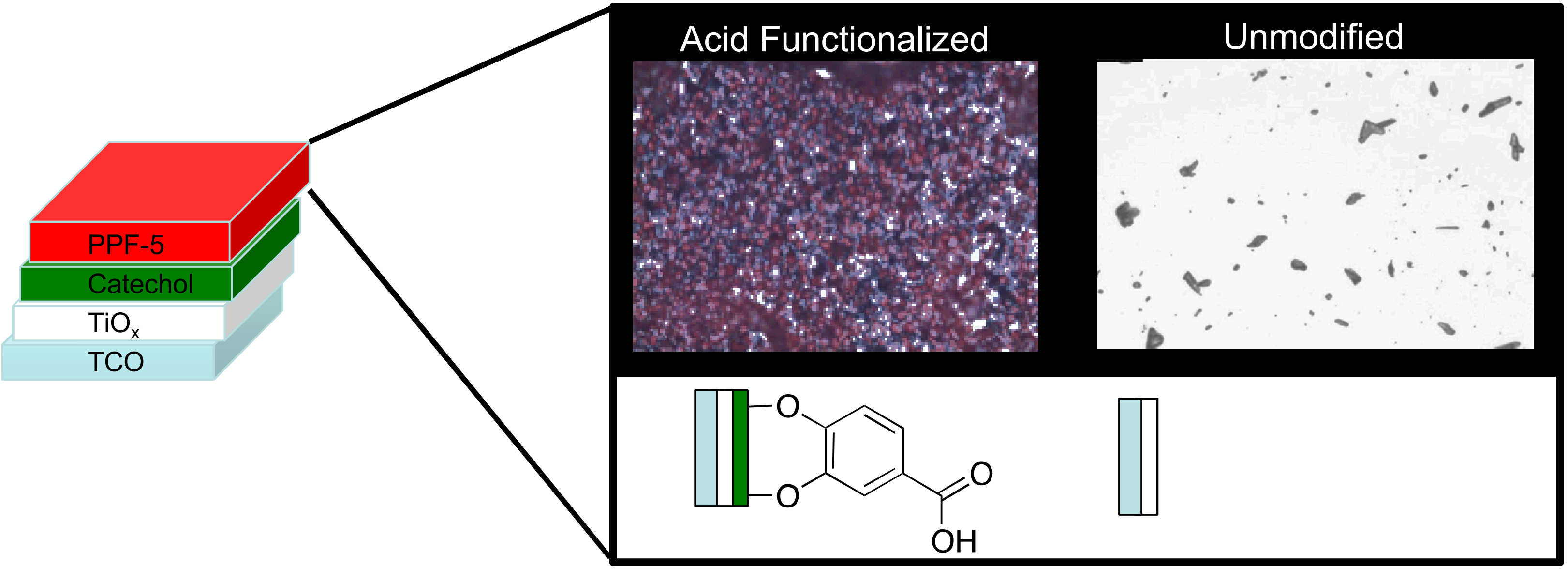
Patterned ITO and Ag define 0.1 cm2 device areas.

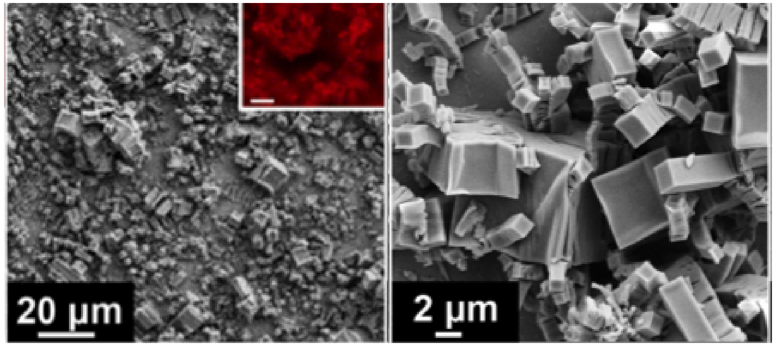
Photoactive PPF-5 MOF incorporated into active layer of "inverted" HOPV device.

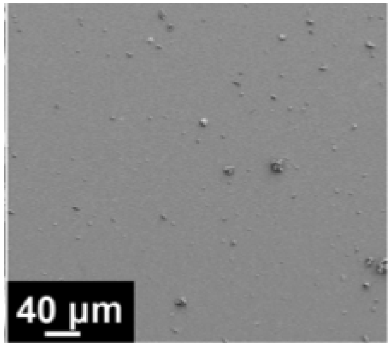


Introduction to MOFs

Solvothermal PPF-5 growth on acid-functionalized surfaces promotes surface-nucleated PPF-5 crystal growth.

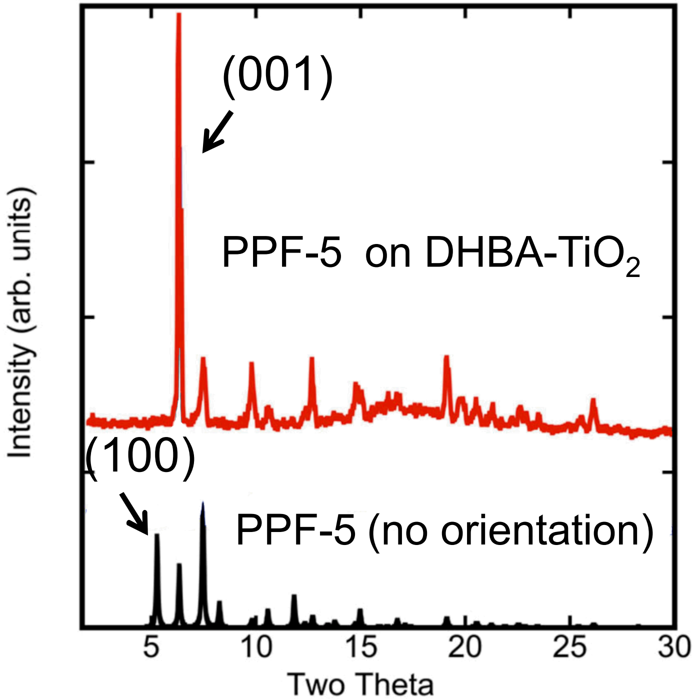




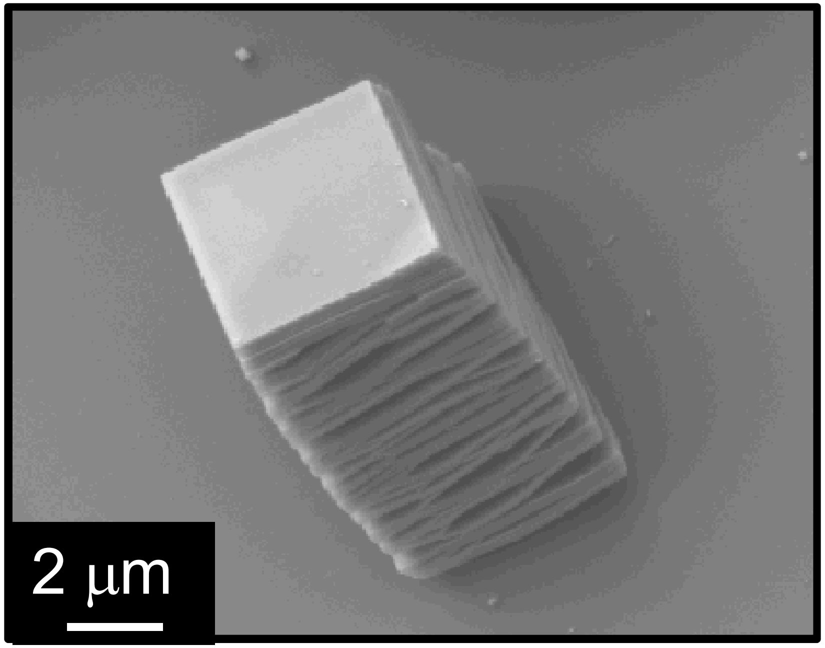


Oriented Solvothermal PPF-5

Solvothermal PPF-5 is oriented, appearing as stacks of MOF-sheets.



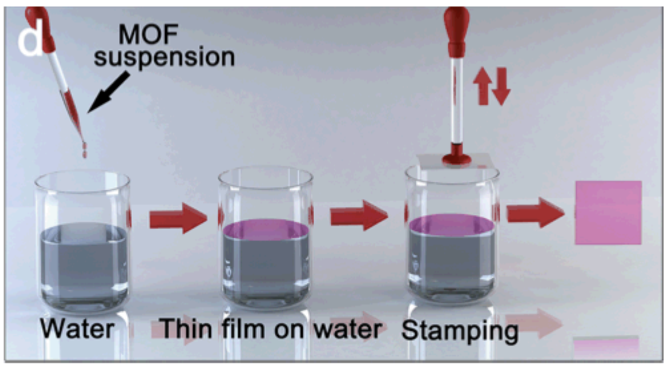
Grazing Incidence XRD shows growth of PPF-5 with preferential (001) orientation (red).



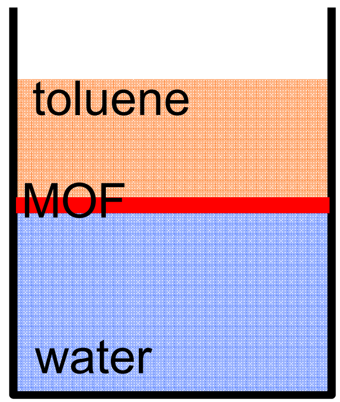
Scanning electron micrograph of PPF-5 stacks

An Alternative Approach to PPF5 Thin Film Formation

Assembling MOF thin films at solvent interfaces allows for formation of dense, robust porphyrin-MOF thin films

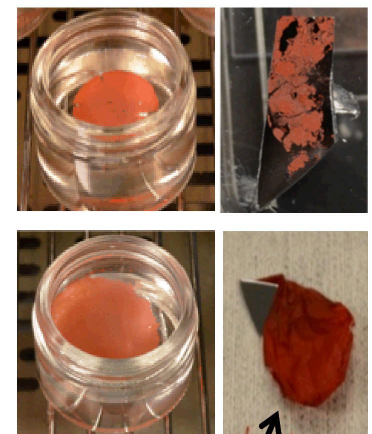


G. Xu, et al., *JACS* 2012, 134, 16524



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

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



Self-supporting film!

Robust films are too thick for OPV!

Starting point for device applications: thin films

In-situ methods

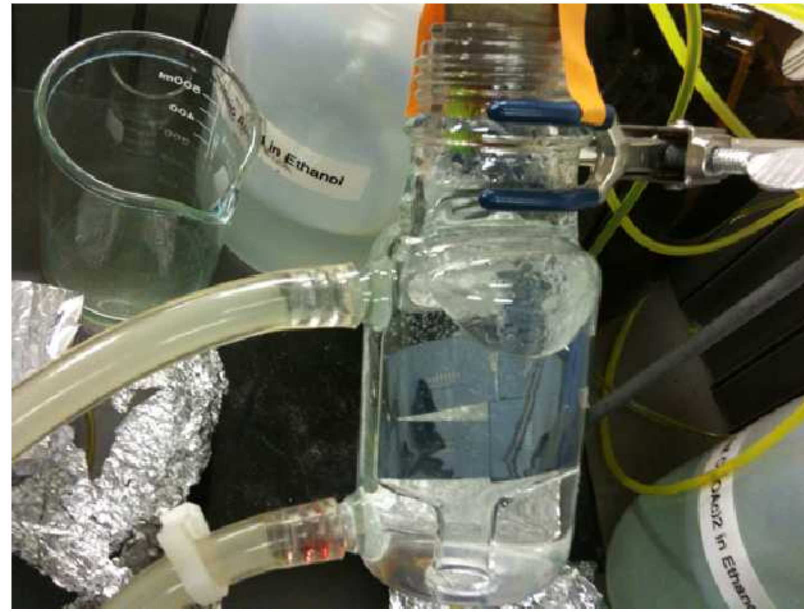
- Layer-by-layer (Fischer, Woell)
- Gel-layer (Bein et al. *Angew. Chem.* 2010)
- Electrochemical/redox (DeVoos *Chem.Mat.* 2009)

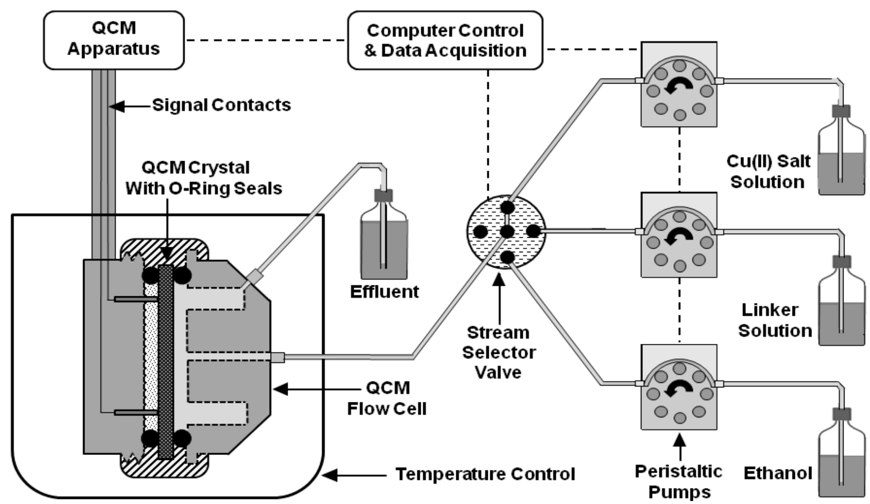
Seeding methods

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

Ex-situ methods

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

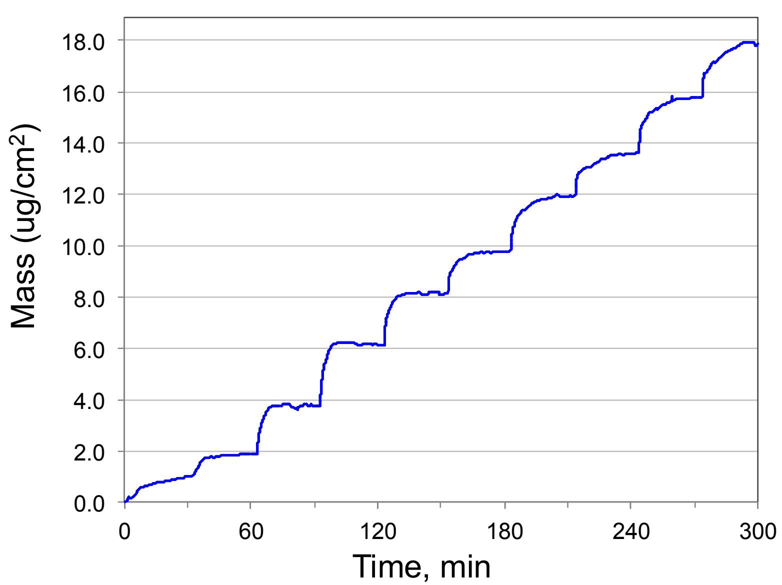


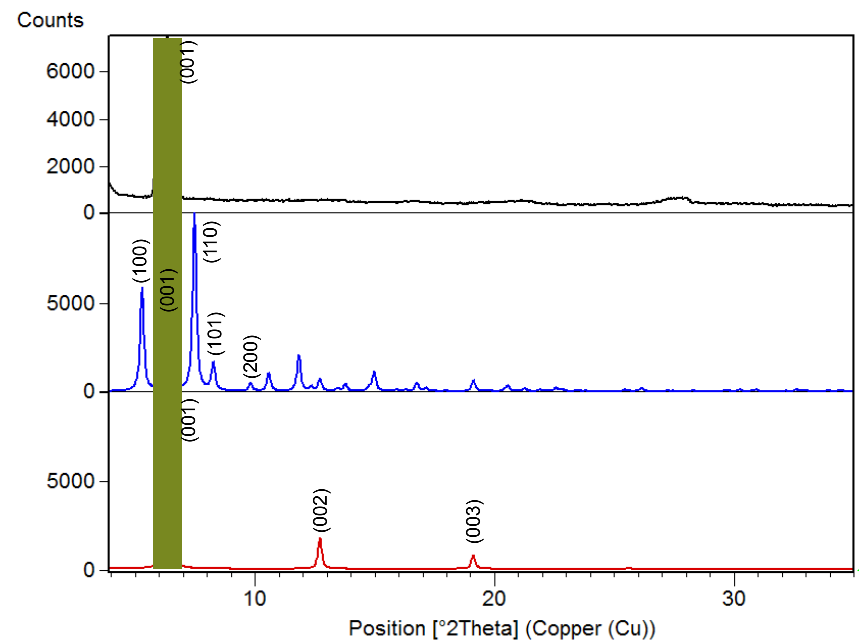


Schematic representation of automated MOF film growth/QCM capability

Layer by Layer Growth of PPF-5

Layer-by-layer growth of PPF-5 is monitored by QCM and shows step-wise growth of an oriented PPF-5 film.

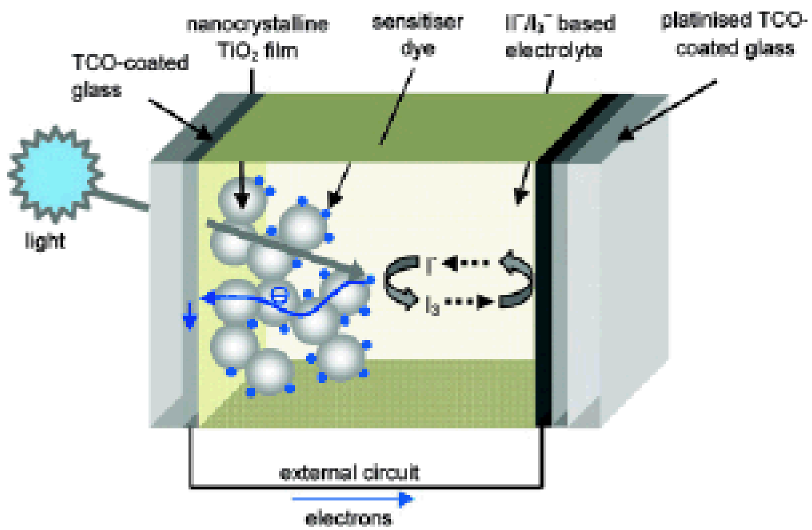


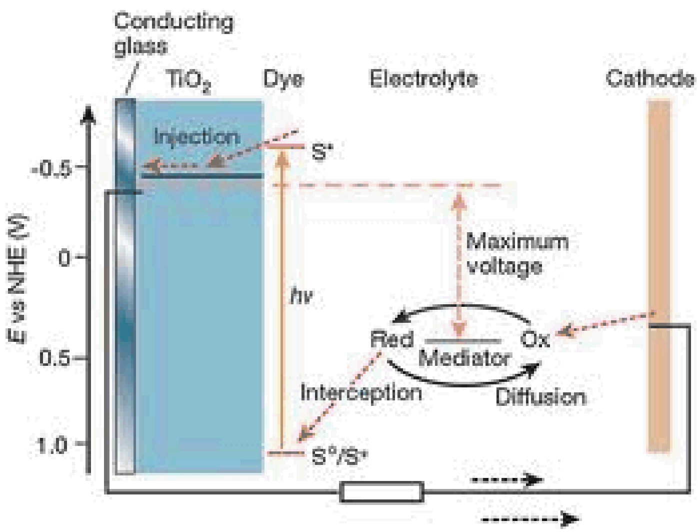


The grazing incidence XRD pattern indicates a strong preferred orientation along the (001) axis.

Resolving the “Wiring” Issue

An alternative approach to the solid-state PV systems involves incorporating MOFs into DSSCs.

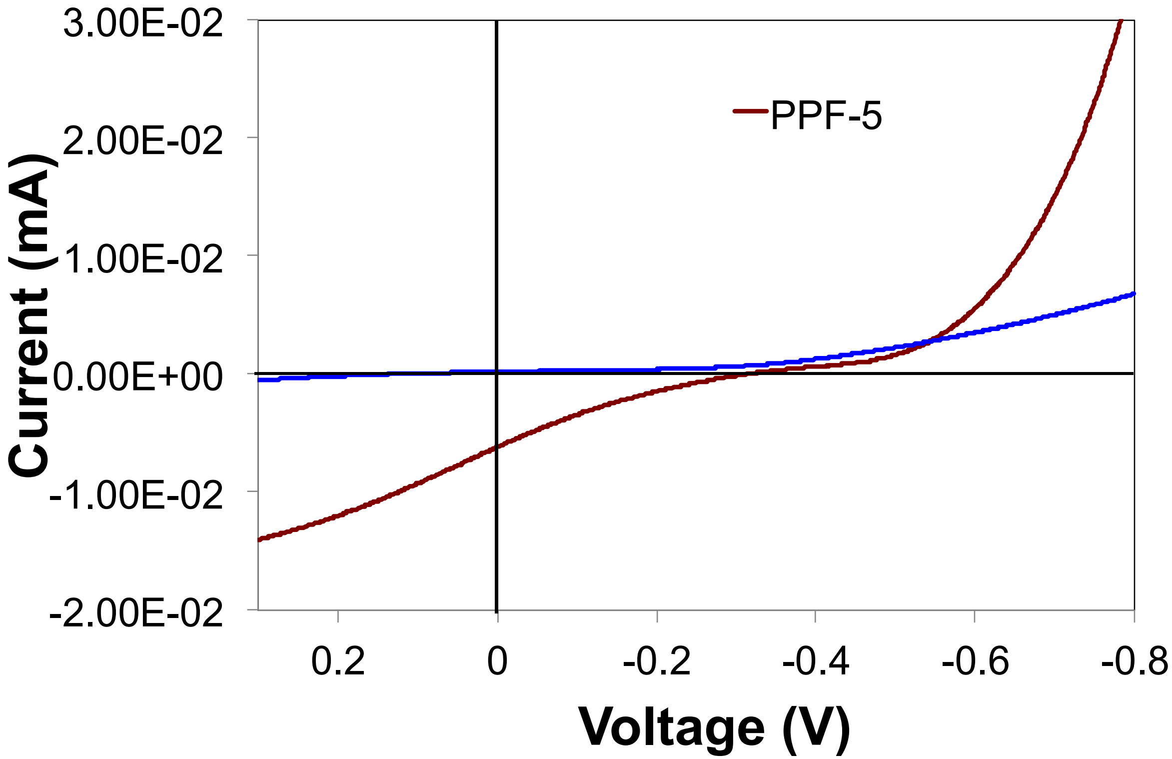




www2.warwick.ak.uk

Chem. Soc. Rev., 2012,41, 4909-4927

PPF-5 in a DSSC



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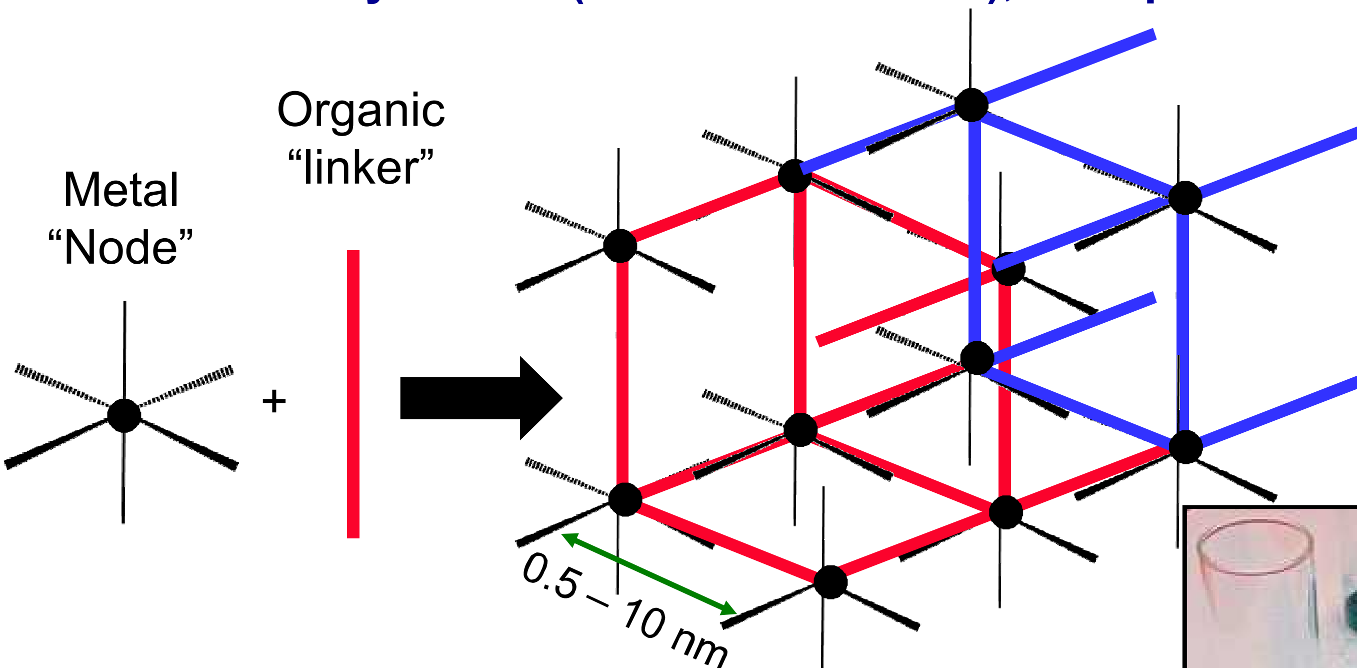
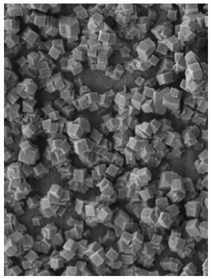
Backup Slides

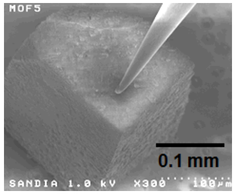
What are Metal-Organic-Frameworks (MOFs)?

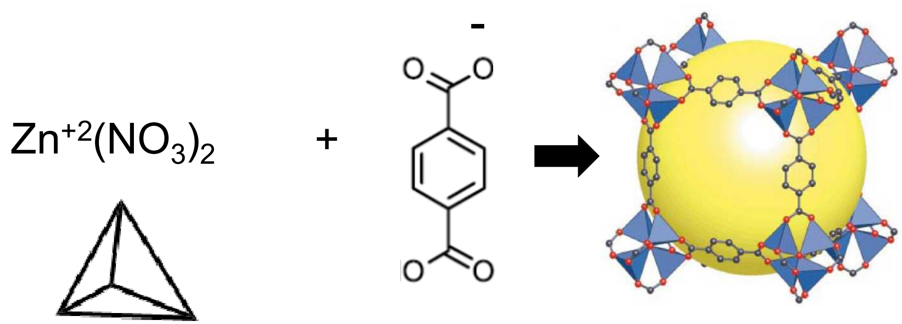
A subset of "Coordination Polymers"

Crystalline (therefore ordered), nanoporous structure



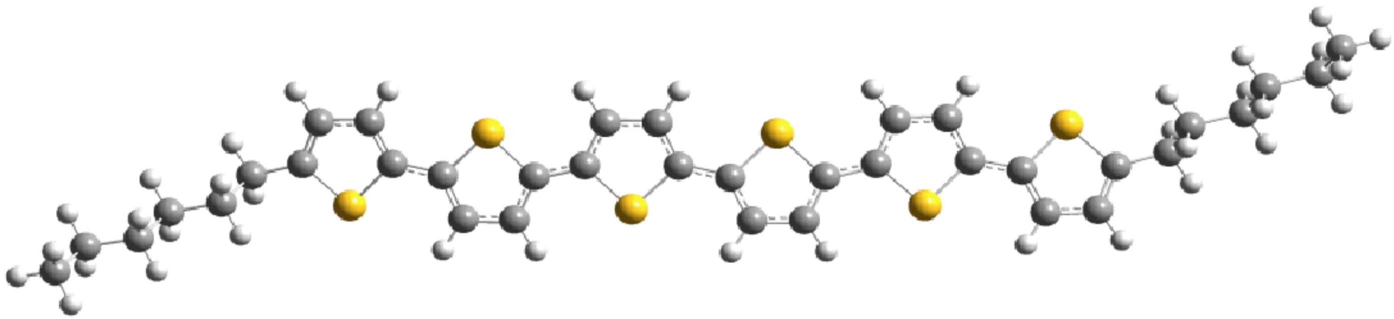






Ultrahigh surface areas (record ~ 7000 m^2/g)

DH6T



Step-by-step synthesis of PPF-5