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Nanoporosity and the Welcome Guest: Metal-Organic Frameworks as Active Components of Electronic Devices

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U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

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Remember these?

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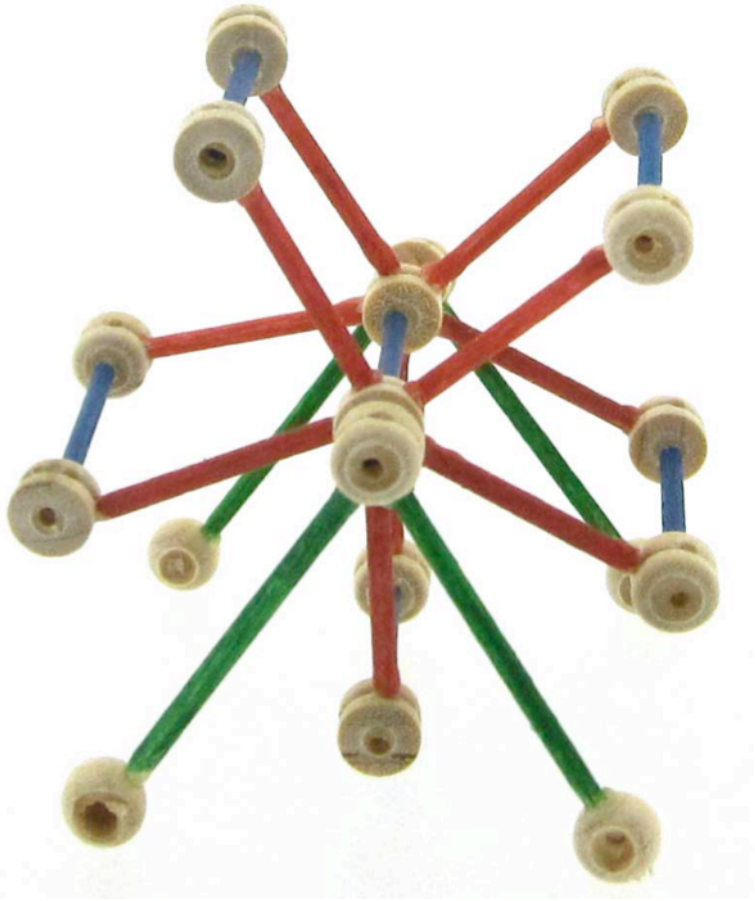

Knowing structure is POWER…because you can relate it to function!

What is a Metal-Organic Framework?

Crystalline (therefore ordered), nanoporous structure

Metal "Node"

Organic "linker"

+

0.5 – 10 nm

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

MOFs are a subset of a growing category of self-assembled, nanoporous materials

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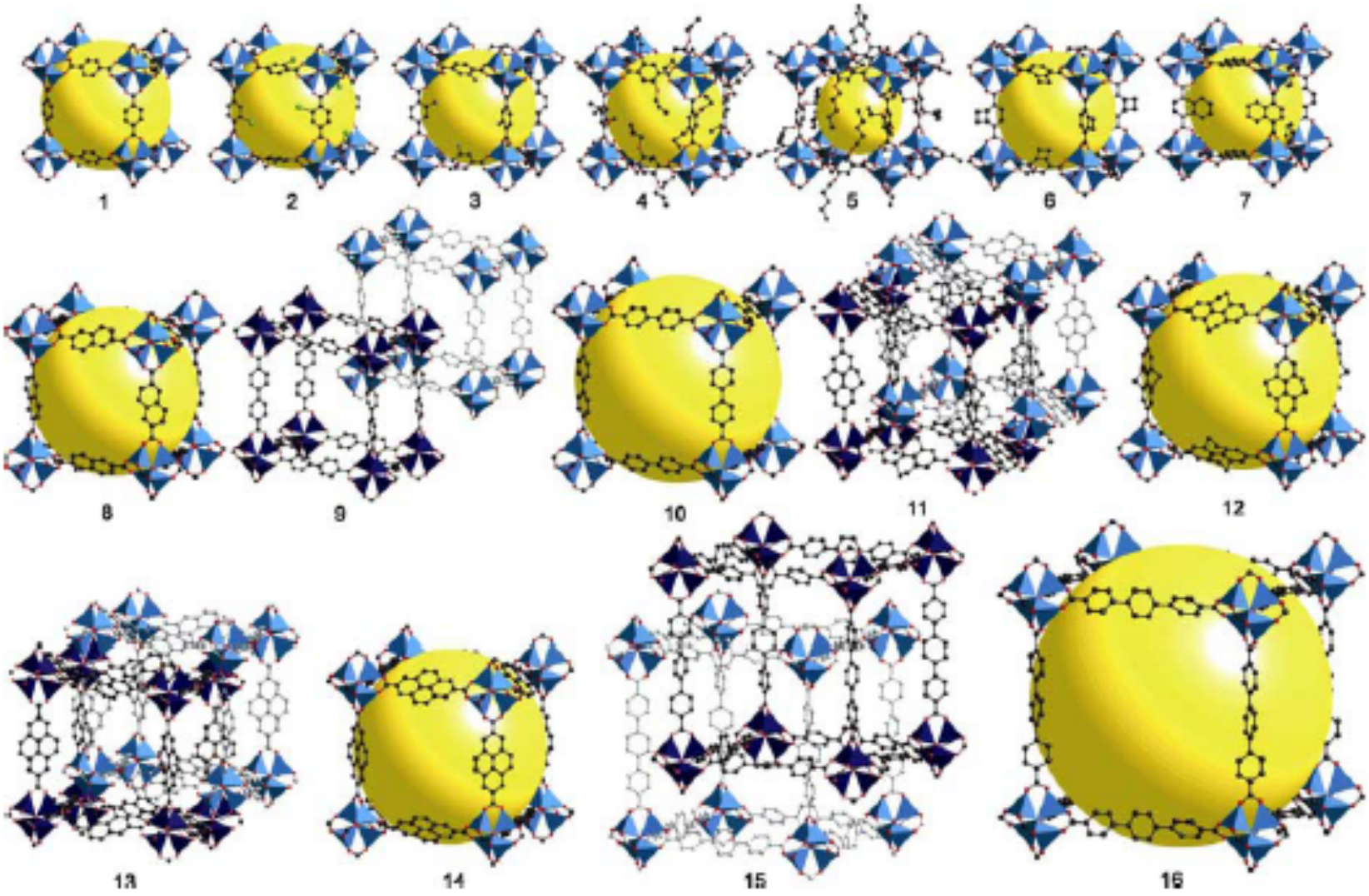

MOFs can serve as a highly ordered, tailorable platform for controlling interactions at the nanoscale

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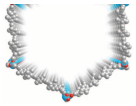
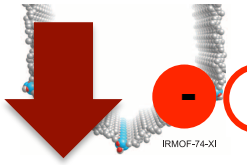
Amino acids

MOF-74-XI

Exciton Diffusion Distance



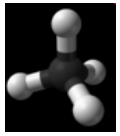
50 Å



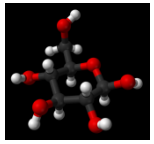
Hemoglobin
~ 10 nm

all viruses
~ 50 nm

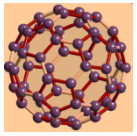
C_3H_8
4.3 Å



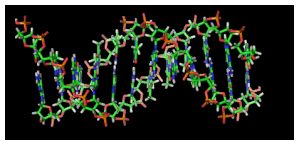
Glucose
(~ 9 Å)



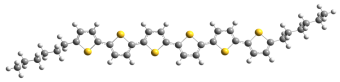
C_{60} (~ 10 Å)



DNA (~ 20 Å)

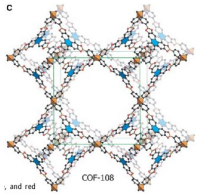


Thiophene oligomers (up to 37 Å)

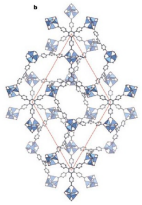


10.0 nm

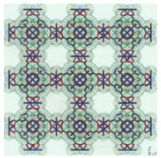
COF-108



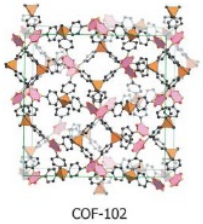
MOF-177



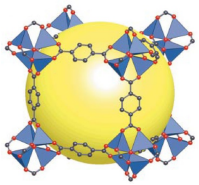
HKUST-1



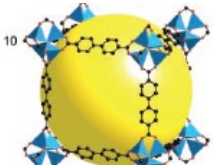
COF-102



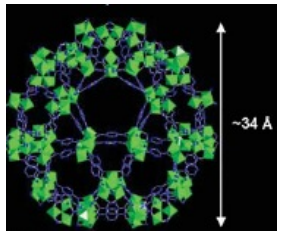
IRMOF-1



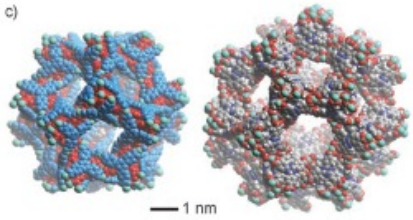
IRMOF-10



MIL-101



$\{Tb_{16}(TATB)_{16}\}$



1.0 n | 2.0 | 3.0 nm | 4.0 nm | 5.0 nm

Interior pore diameter

Presentation topics

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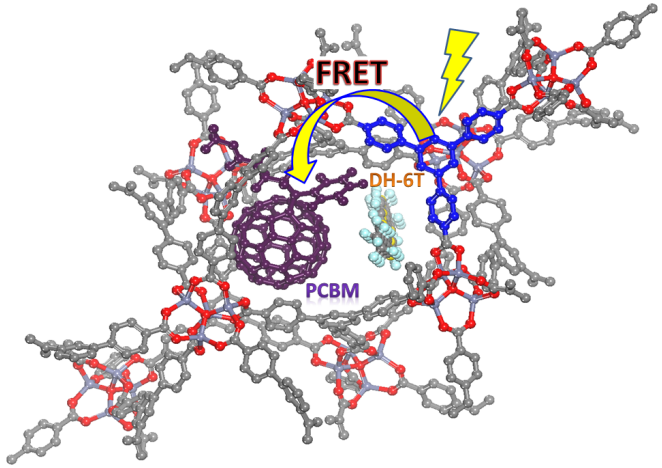
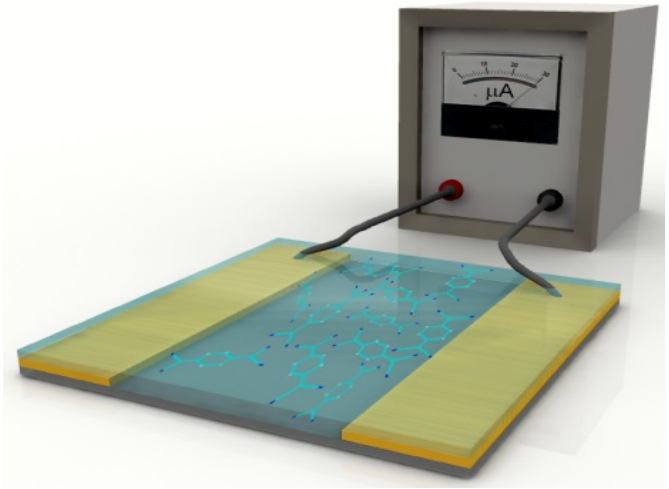
Energy transfer in MOFs via FRET



Electrically conducting MOFs



Organic photovoltaics: potential for low-cost renewable electricity

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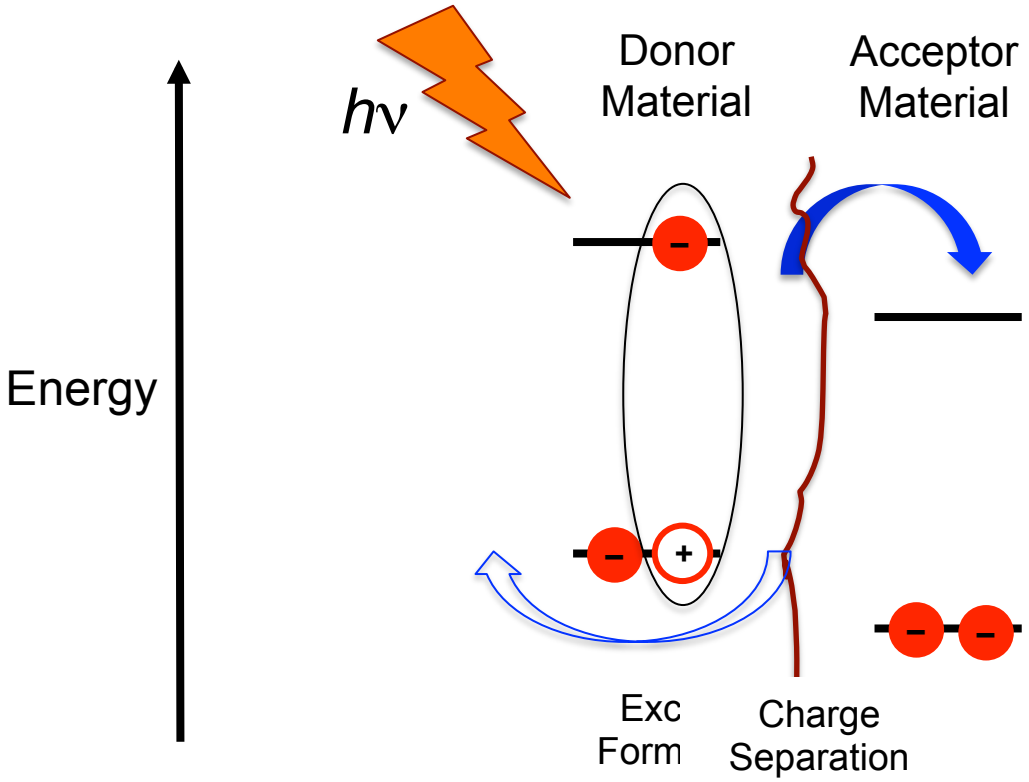
How does OPV work?



Disorder is the enemy of efficiency

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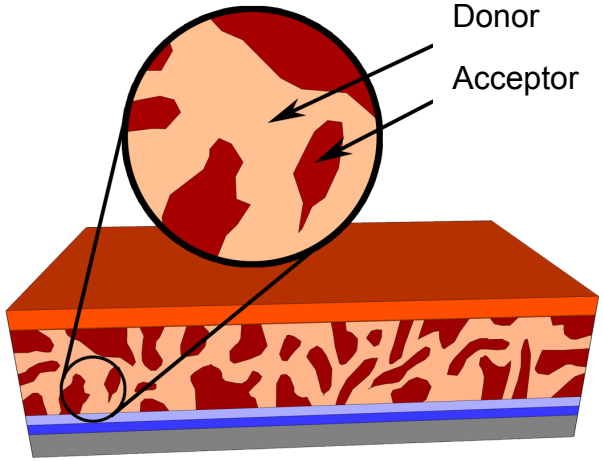
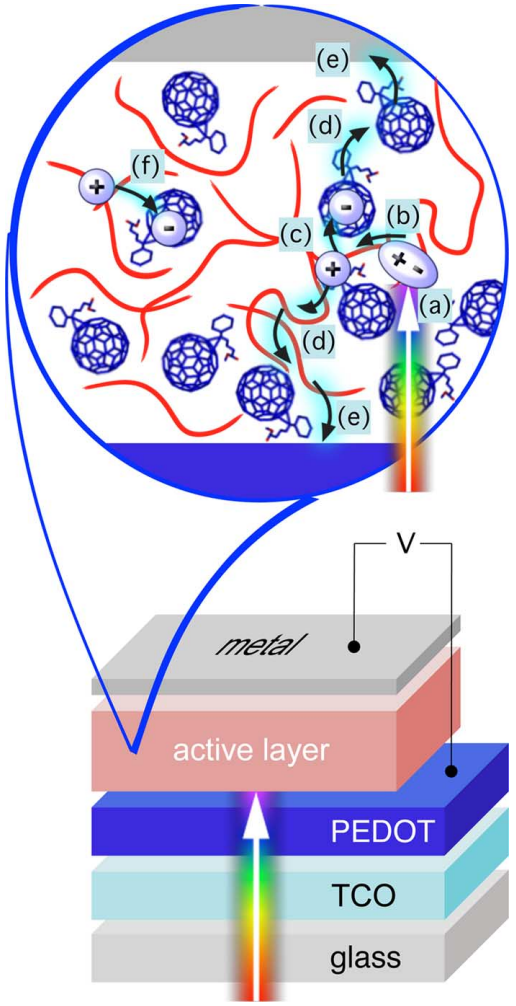
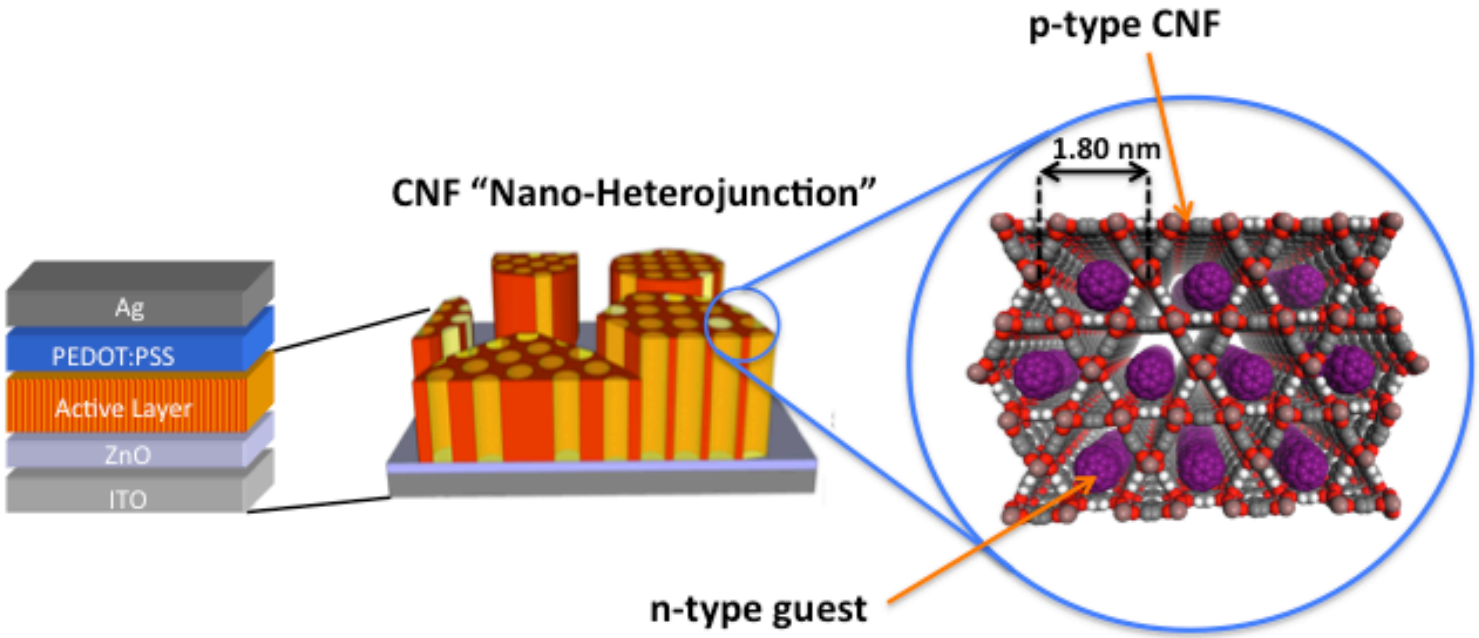
Bulk heterojunction





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


p-type CNF
1.80 nm
CNF "Nano-Heterojunction"
Ag
PEDOT:PSS
Active Layer
ZnO
ITO
n-type guest

MOF-177: A passive (?) host for donor and acceptor molecules

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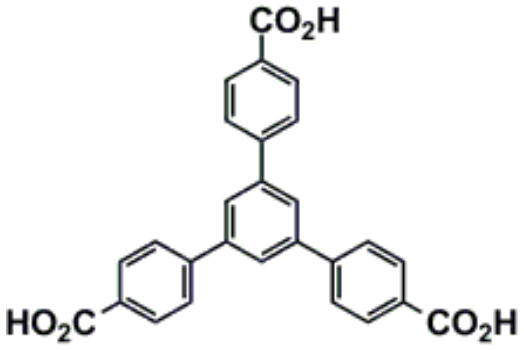
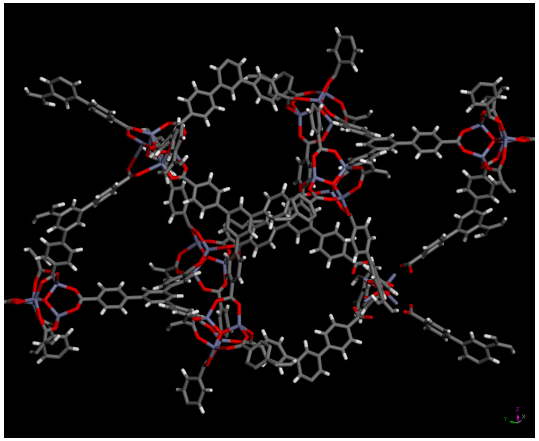
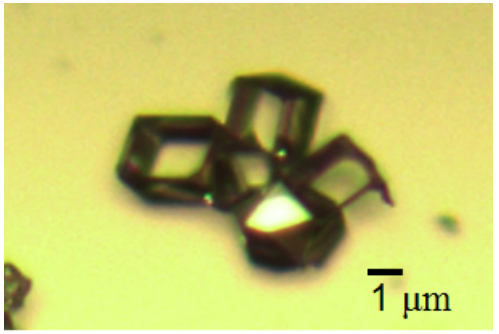
$$Zn(NO_3)_2 \cdot 6H_2O \quad + \quad H_3BTB \longrightarrow \text{MOF-177}$$

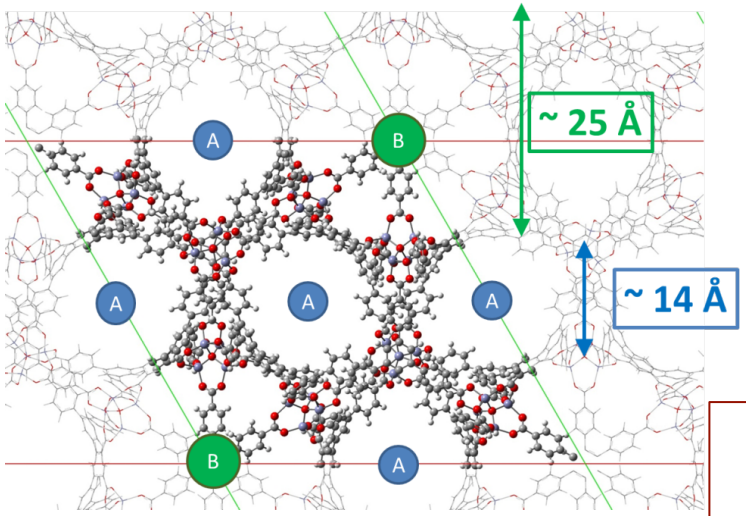


H_3BTB





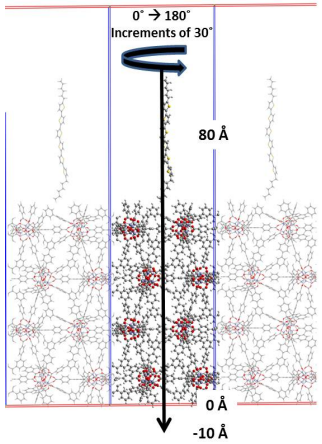
Optical image of MOF-177 crystals

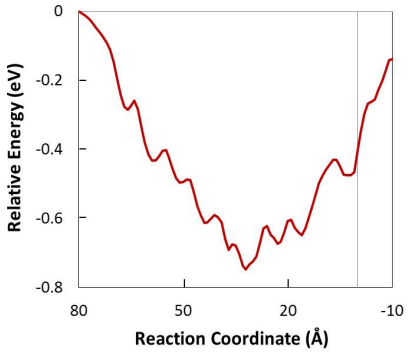


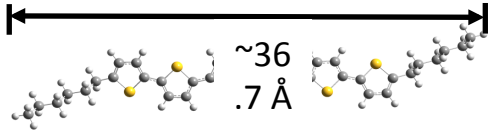
- 808 atoms in the primitive unit cell
- Transparent colorless block shaped crystals
- Open three-dimensional and ordered structure with extra large pores.
- Two unique cavities denoted by “A” and “B”

Optimized structure: computed using Tight-Binding Density Functional Theory (DFT-TB)

Infiltrating MOF-177 pores with thiophenes and PCBM proceeds without an energy barrier

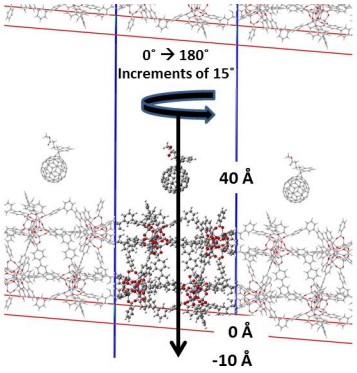


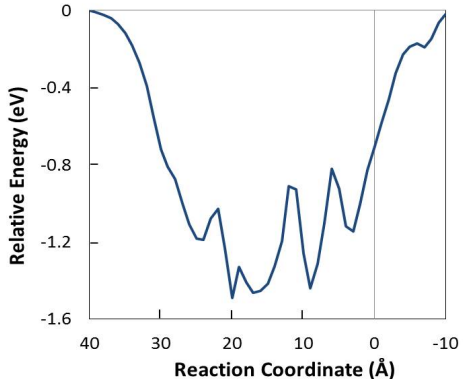


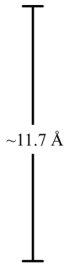


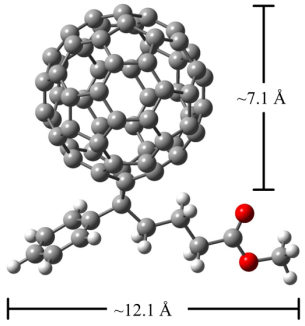
Sexithiophene -
Electron Donor

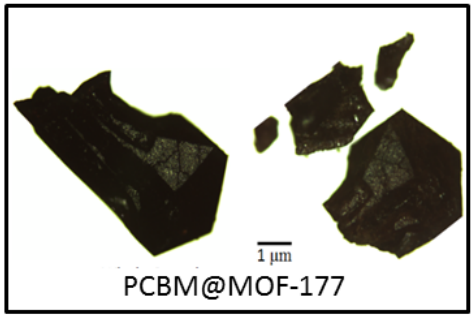
≤ 1 DH6T/unit cell
(~ 125 Å apart)











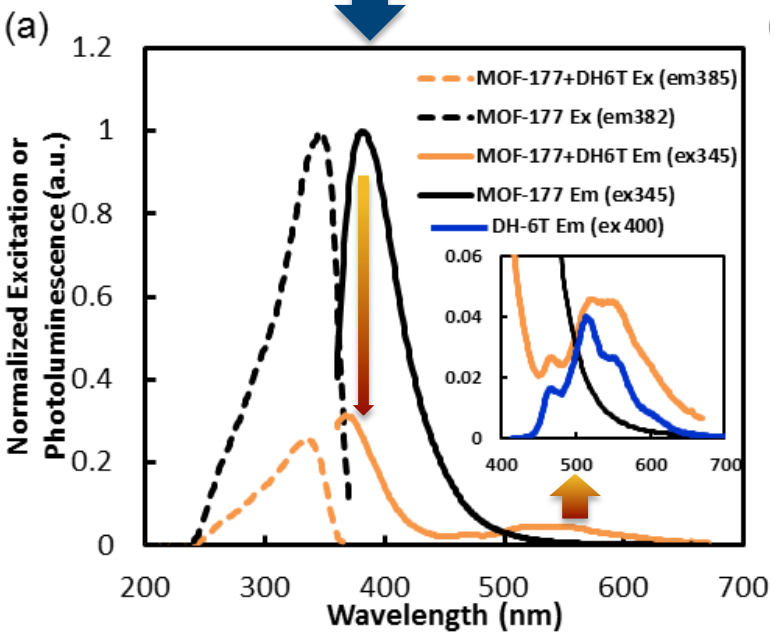
2 – 3 PCBM/unit cell
Up to 22 wt%
(≤ 60 Å apart)

No phase segregation is observed upon infiltration

Guest infiltration quenches MOF luminescence

Donor@MOF
DH6T@MOF-177

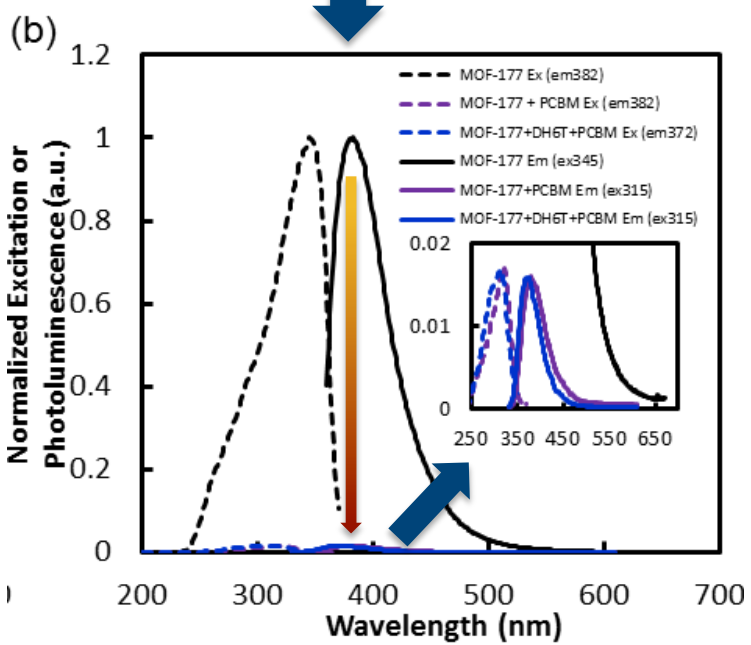
Quenching



Energy transfer

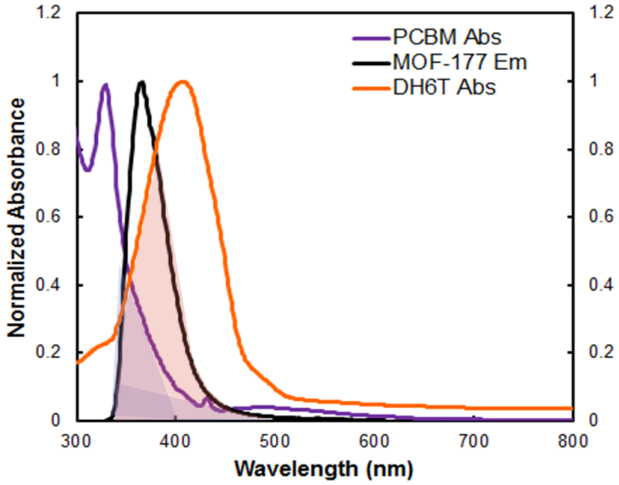
Acceptor@MOF
PCBM@MOF-177

Quenching

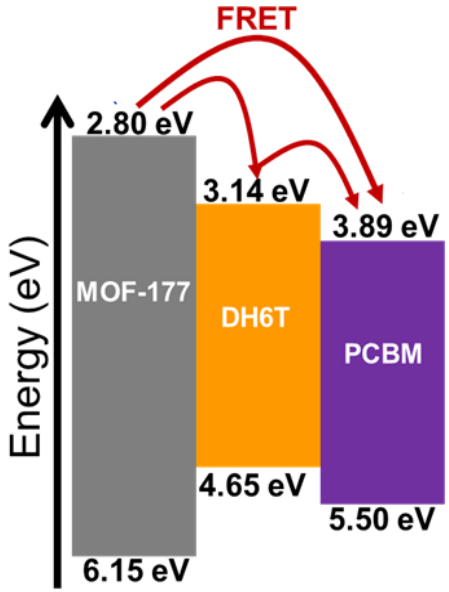


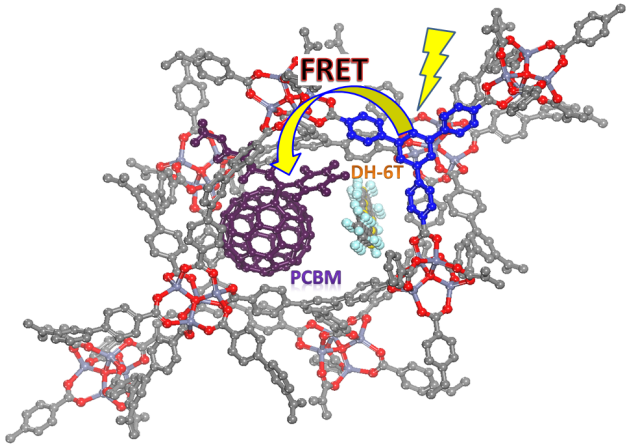
Energy transfer ?

MOF-guest spectral overlap leads to efficient energy transfer via FRET



A "FRET cascade" is feasible





The MOF has three functions:

- Confines/stabilizes donor and acceptor
- Prevents phase segregation
- Serve as a photon antenna

Presentation topics

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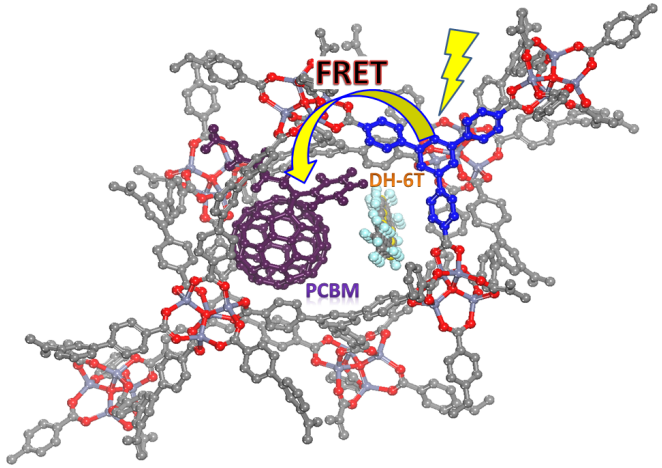
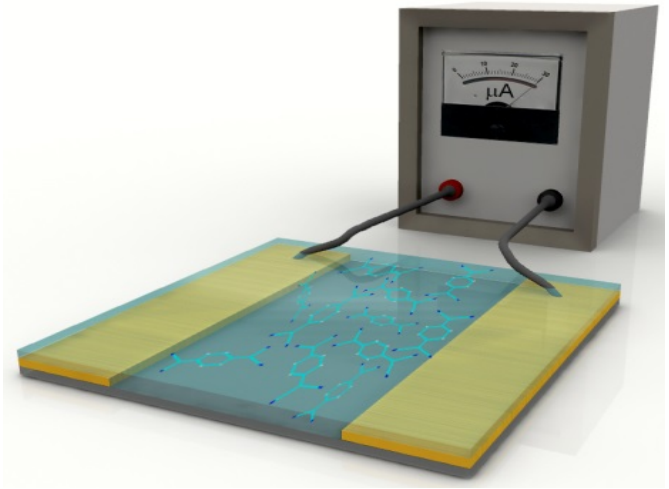
Energy transfer in MOFs via FRET



Electrically conducting MOFs



No class of conducting materials combines the high performance of inorganic semiconductors with the tailorability of organic materials

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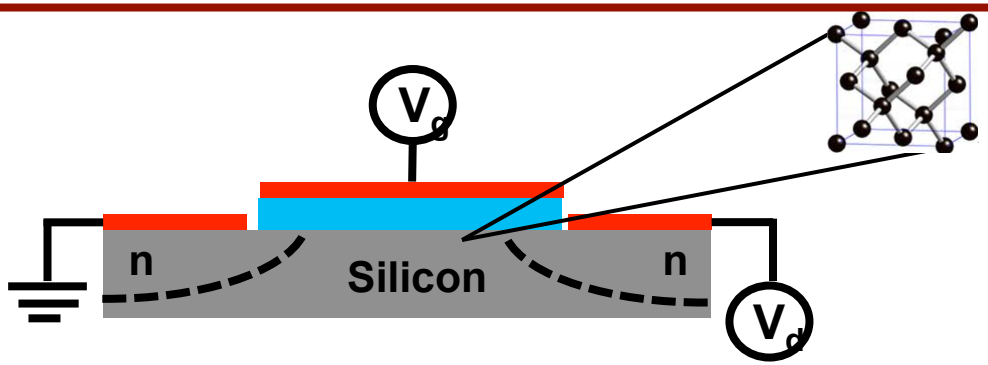
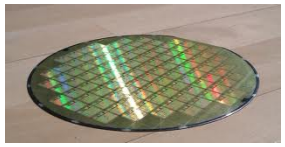
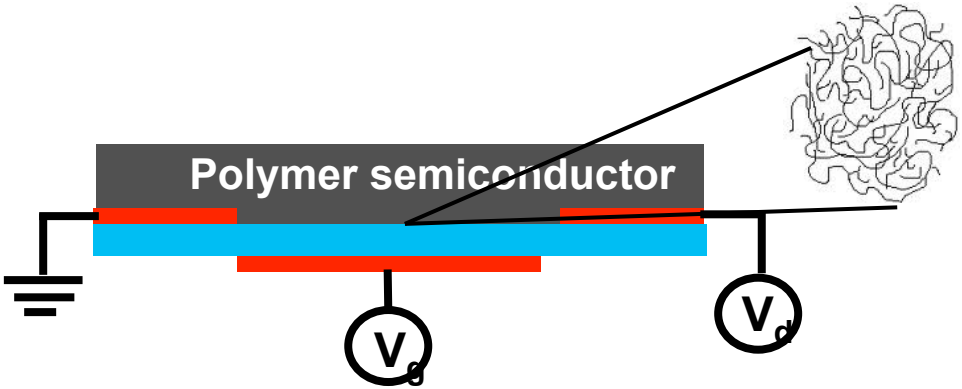


Crystalline inorganic semiconductor

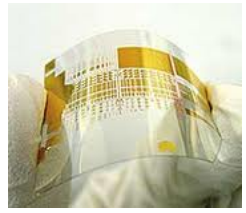
- High mobility
- Stability
- High cost
- Non-flexible
- Radiation damage

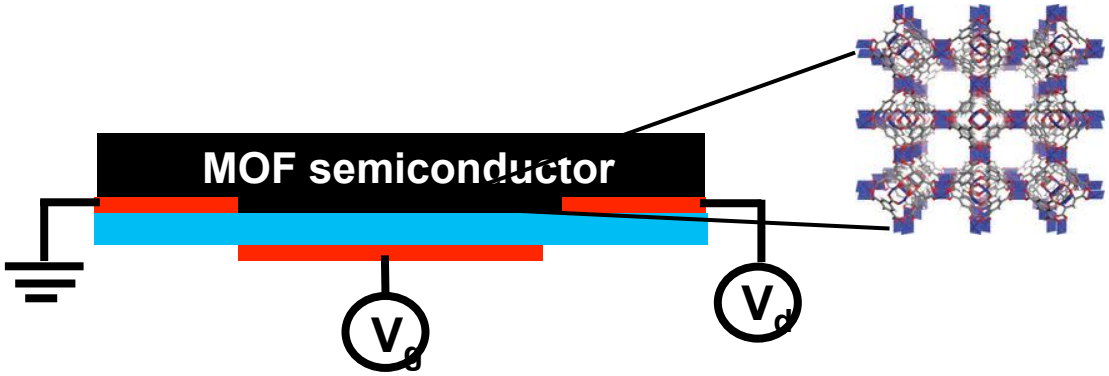




Disordered organic semiconductor

- Flexible
- Tunable w/ chemistry
- Low cost fabrication
- Poor mobility
- Instability
- Low free carrier densities





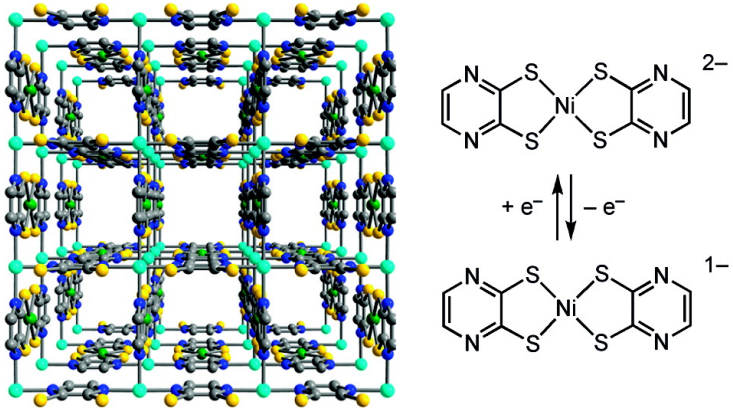
Crystalline MOF semiconductor

- Structurally flexible
- Tunable w/ chemistry
- Scalable to nanometers
- Low cost fabrication
- Reconfigurable electronics
- Rad-hard
- Novel electronic material

MOFs combine features of inorganic and organic materials

Electrically conducting porous MOFs are rare

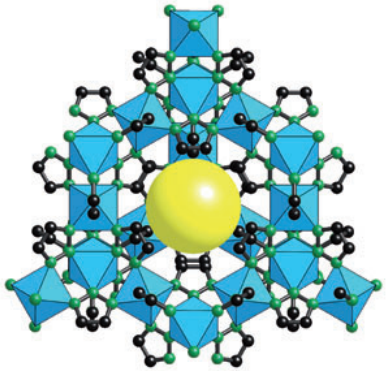
- **p-type Cu-Ni Dithiolene MOF**
  - First semiconducting, porous MOF
  - Conductivity increases with oxidative doping
  - Original Cu-Cu version is not porous (*Inorg. Chem.* 2009, 48, 9048)



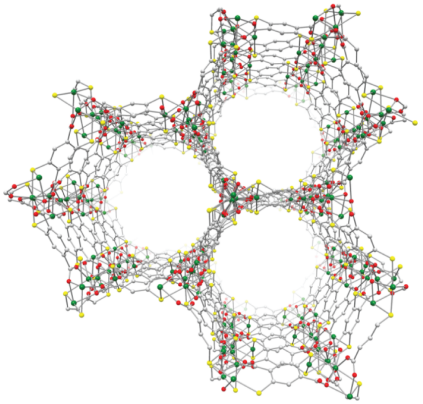
Y. Kobayashi et al. *Chem. Mater.* 2010, 22, 4120

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

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



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?

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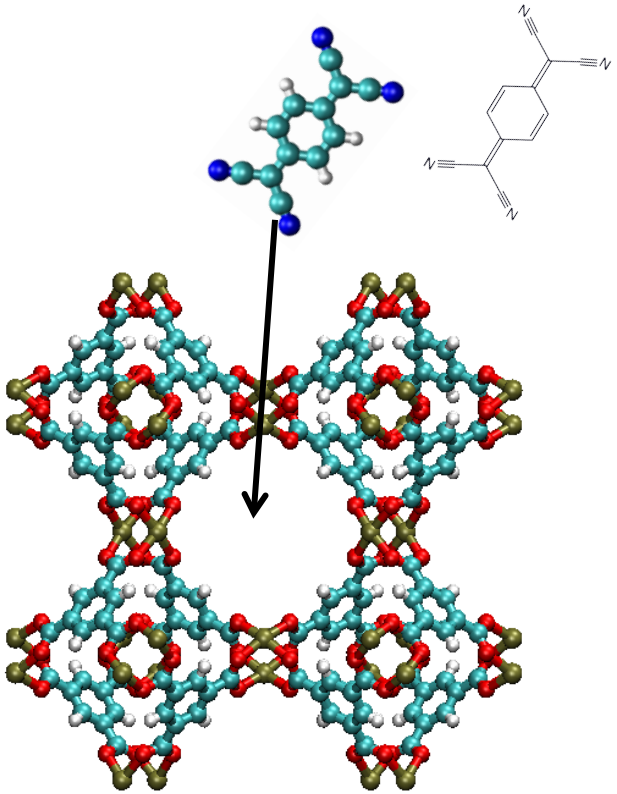

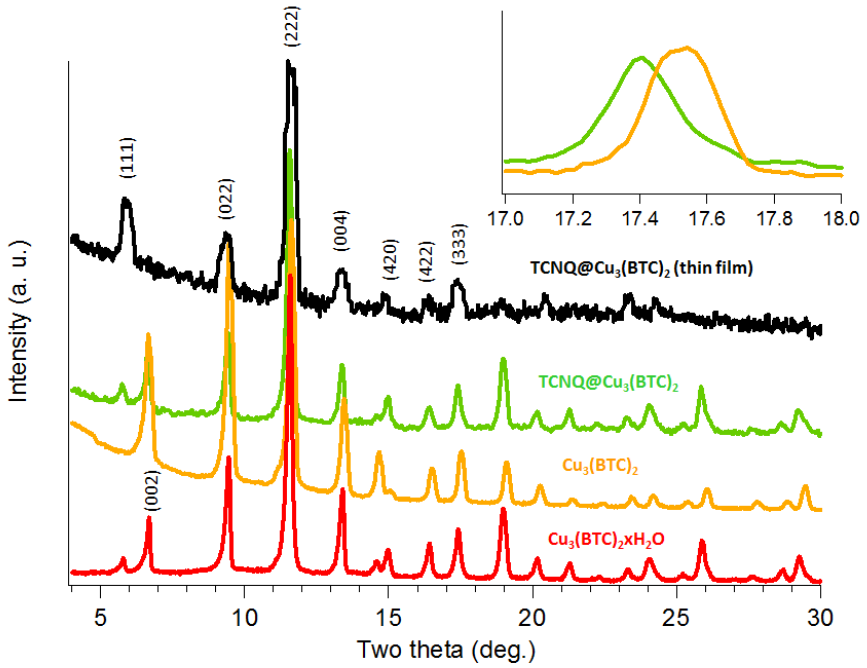

Cu-TCNQ is a well-known conducting CP

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144 *Inorg. Chem.* **1999,** *38,* 144−156

New Insight into the Nature of Cu(TCNQ): Solution Routes to Two Distinct Polymorphs and Their Relationship to Crystalline Films That Display Bistable Switching Behavior

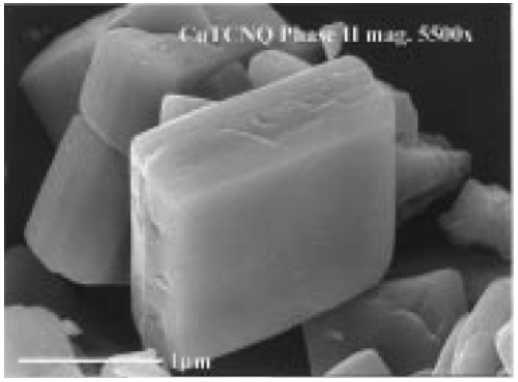
Robert A. Heintz,† Hanhua Zhao,† Xiang Ouyang,† Giulio Grandinetti,† Jerry Cowen,‡ and Kim R. Dunbar*†

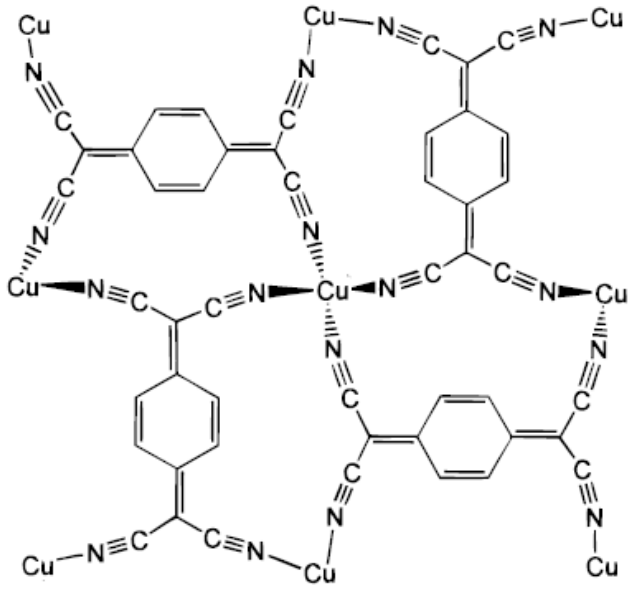
$$[Cu^{+}(TCNQ^{-})]_n \leftrightarrow$$

"OFF" state

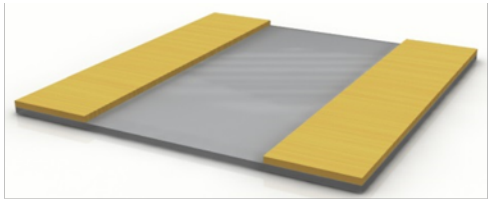
$$[Cu^{0}]_x + [TCNQ^{0}]_x + [Cu^{+}(TCNQ^{-})]_{n-x} \quad (1)$$

"ON" state

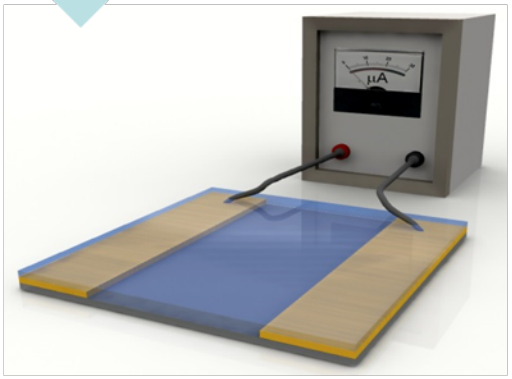




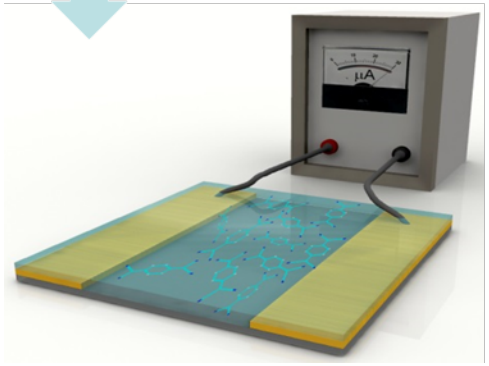
TCNQ→ $Cu_2(BTC)_3$ leads to color change…

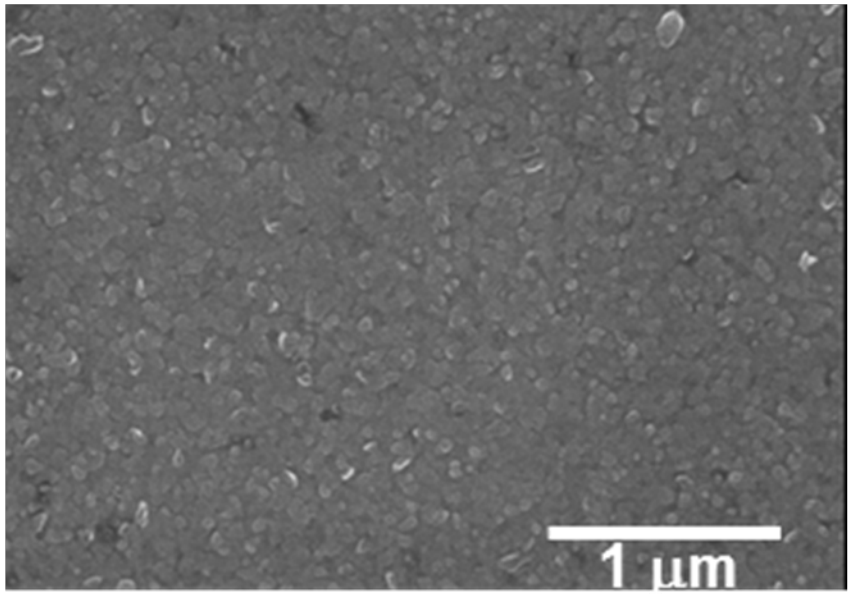


MOF growth

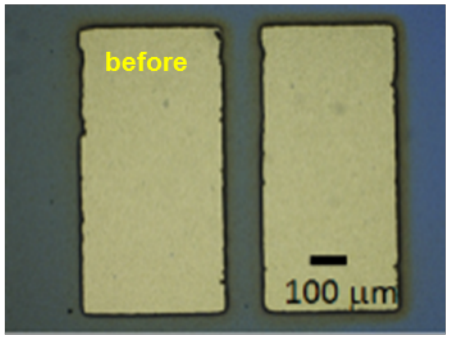


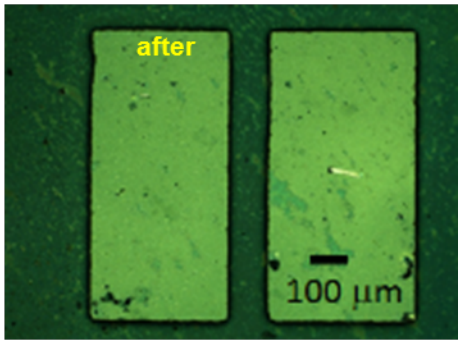
Molecule infiltration



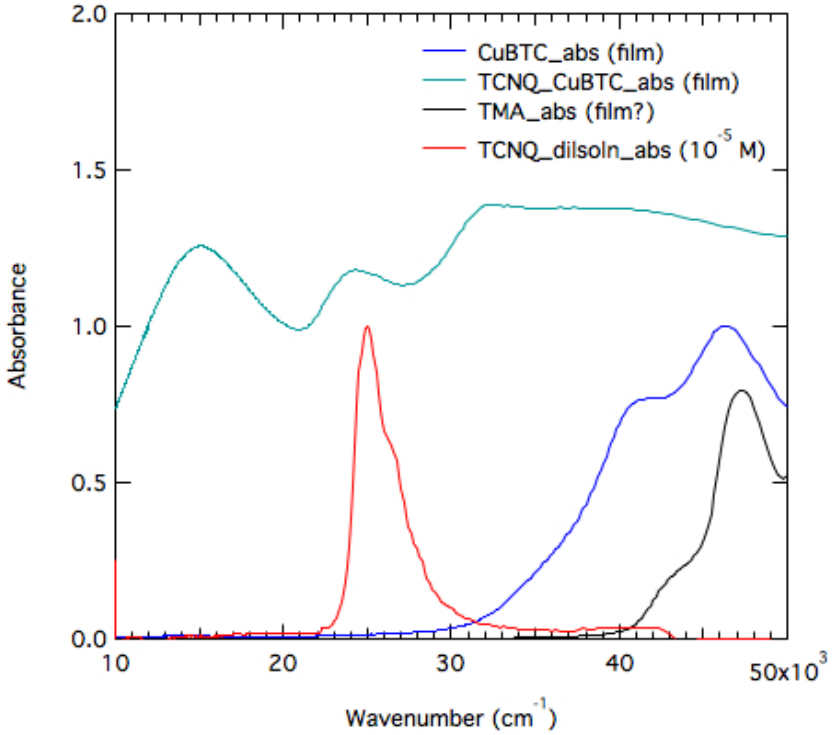


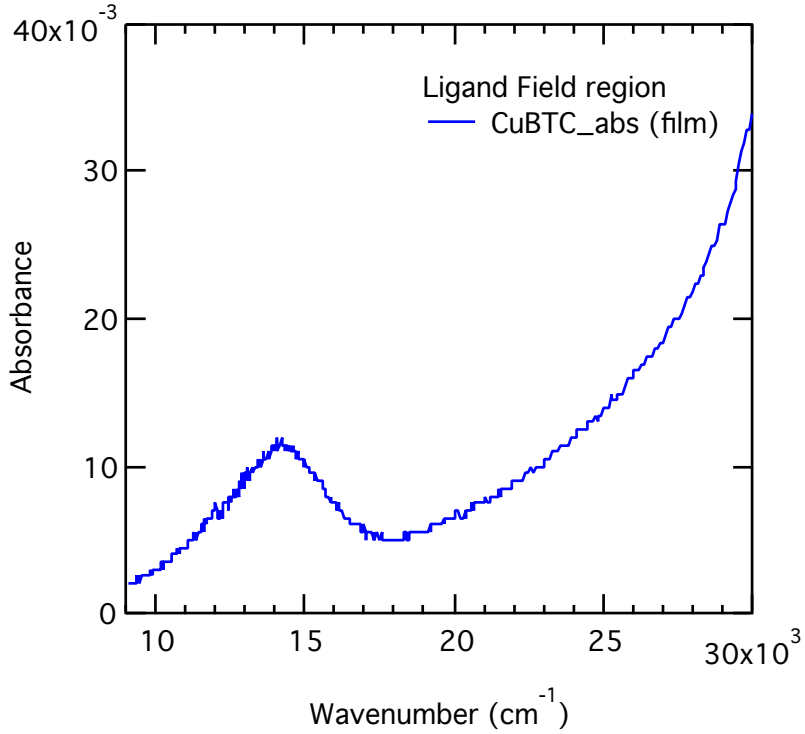
MOF film grown by layer-by-layer method



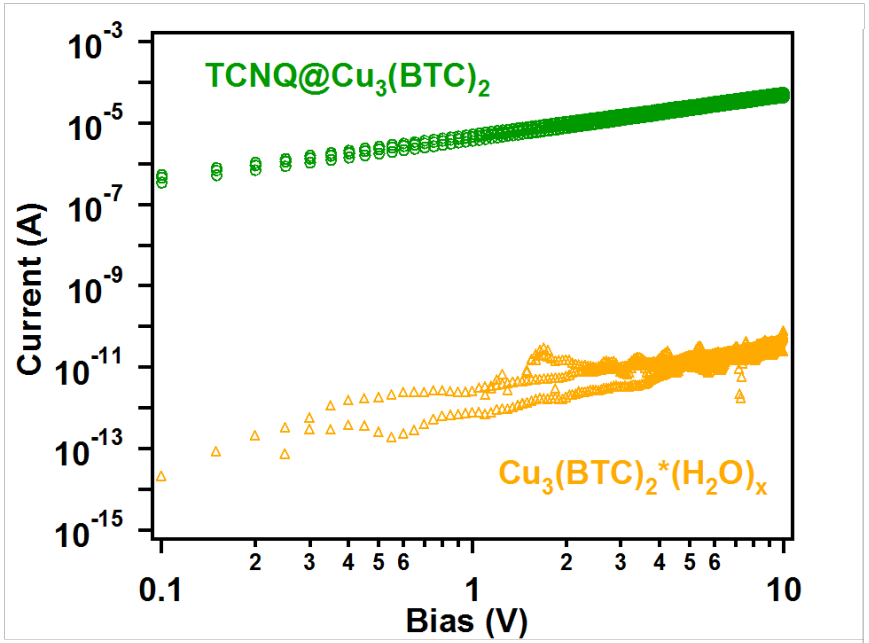


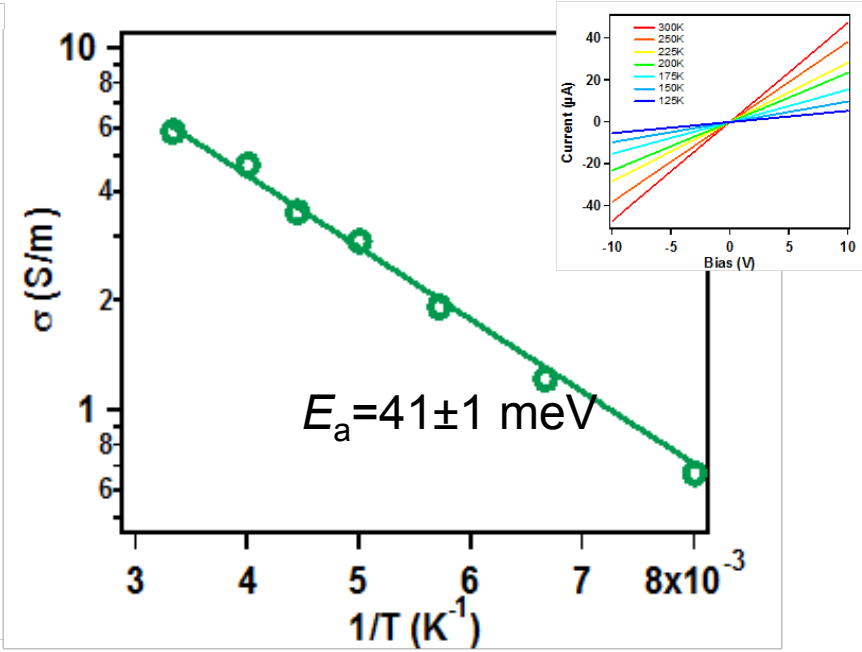
TCNQ@$Cu_2(BTC)_3$ produces new absorption band

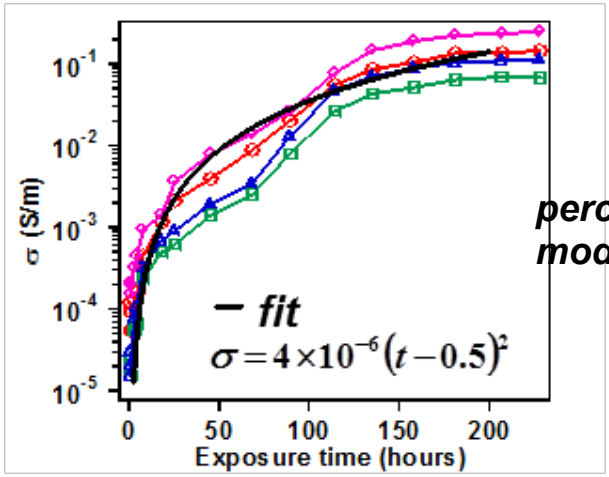




… and >10^7 increase in conductivity, air stable > 1 year

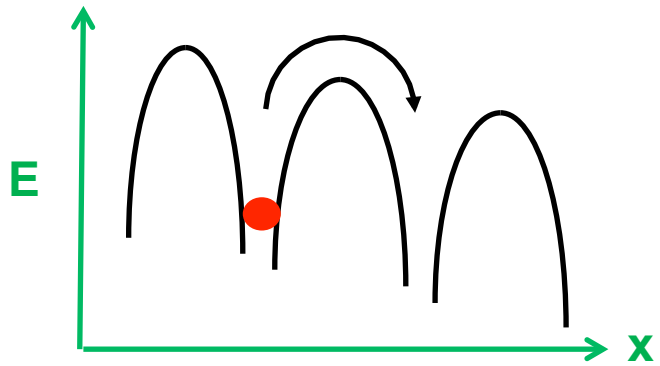






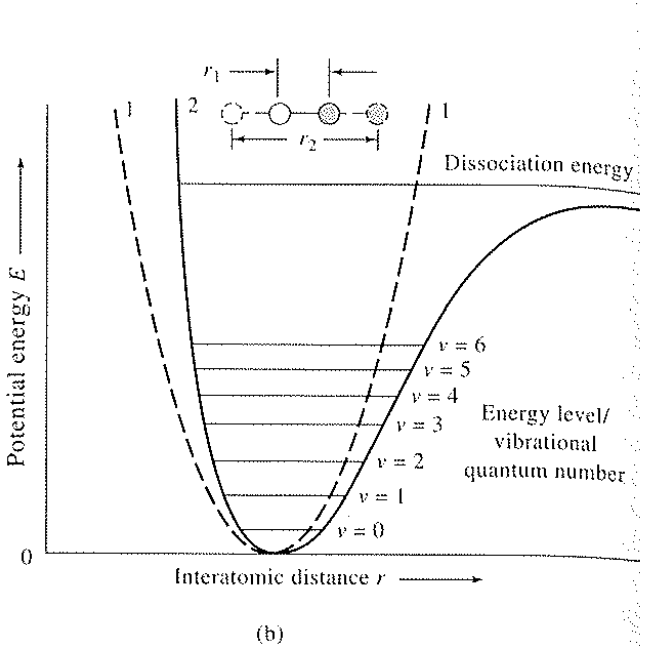
percolation model

Hopping conduction

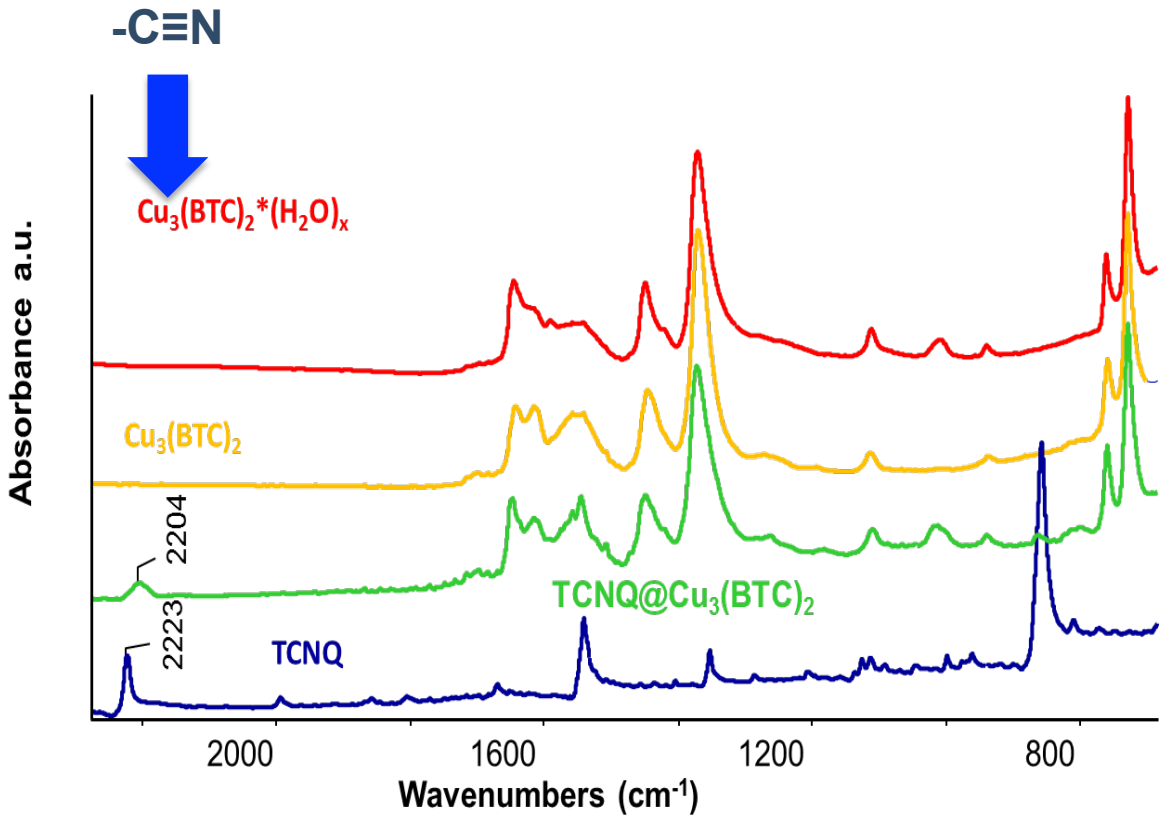


IR shift of -C≡N indicates charge transfer

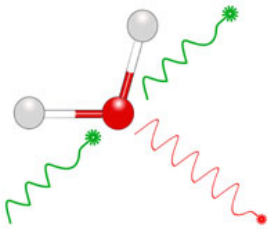
$$z = (\nu_o - \nu)/44 cm^{-1} \approx \mathbf{0.43}e$$

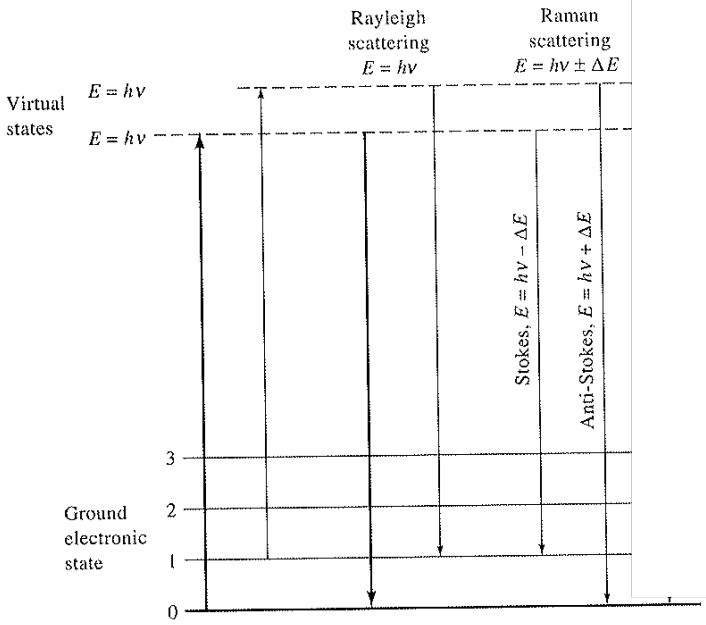


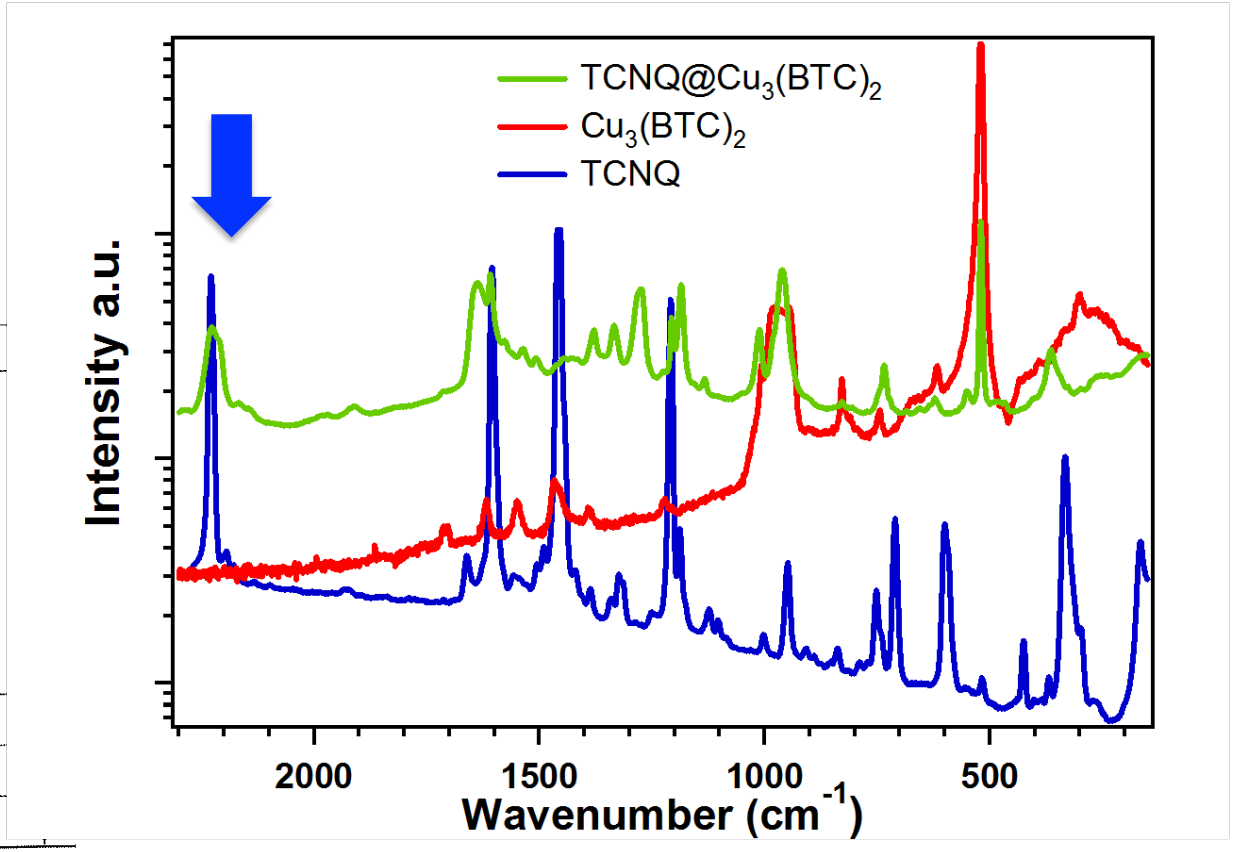
Skoog, Holler, Nieman,
Instrumental Analysis



Raman also shows shift of -C≡N







C≡N stretch splitting observed only inside dark colored, conducting region

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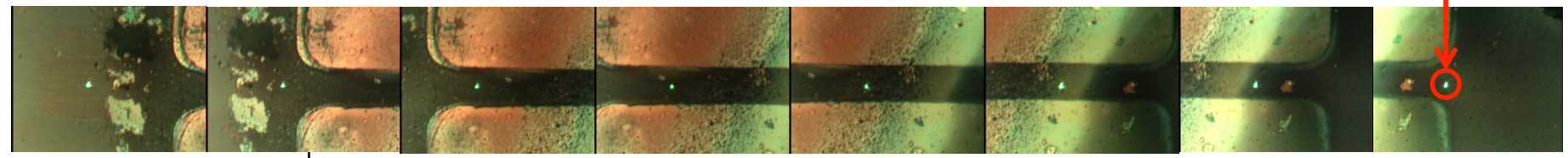

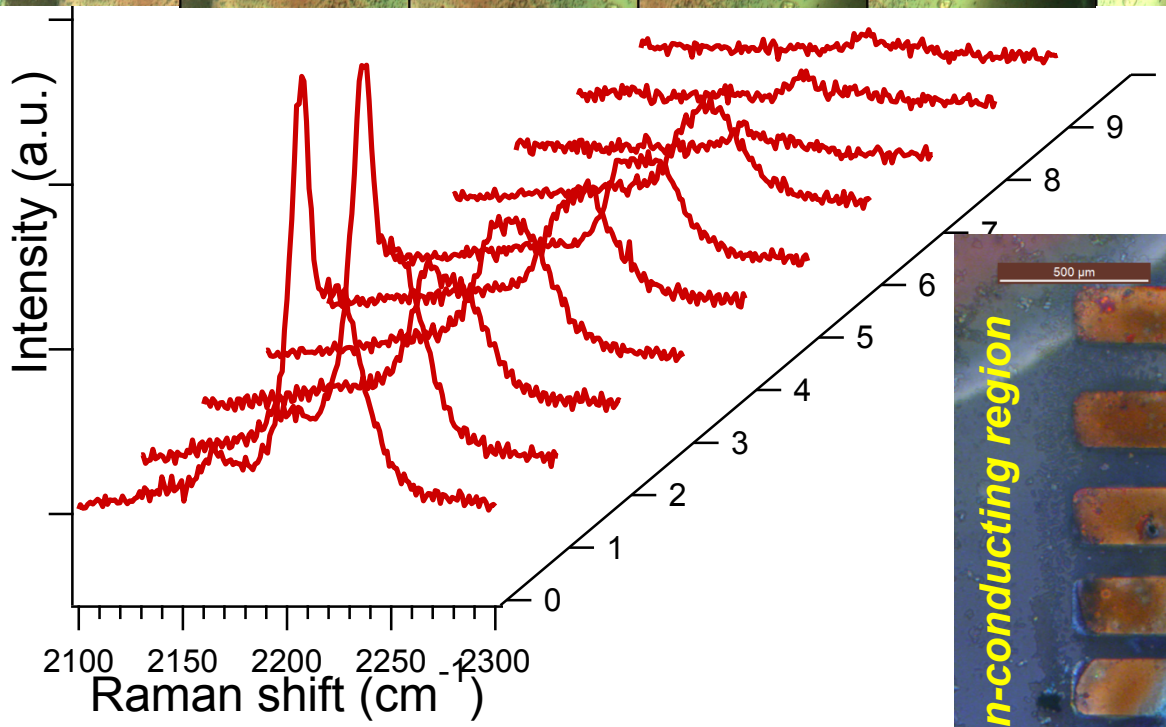

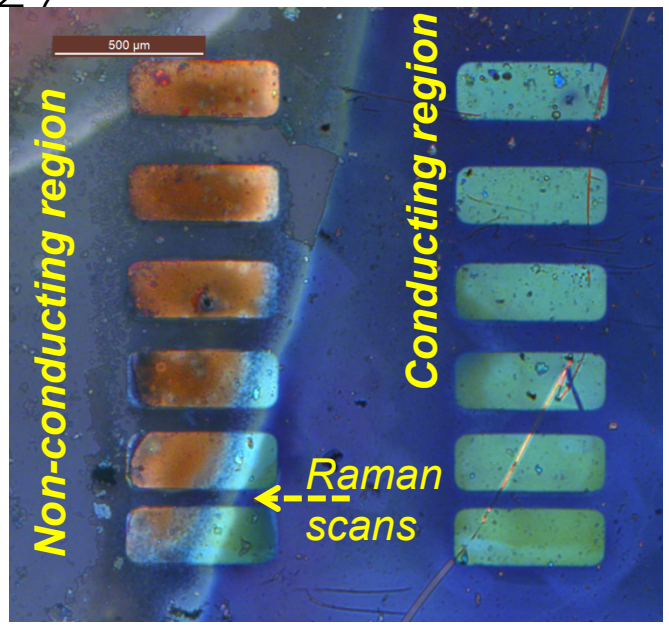

Peak splitting indicates 2 inequivalent -C≡N groups

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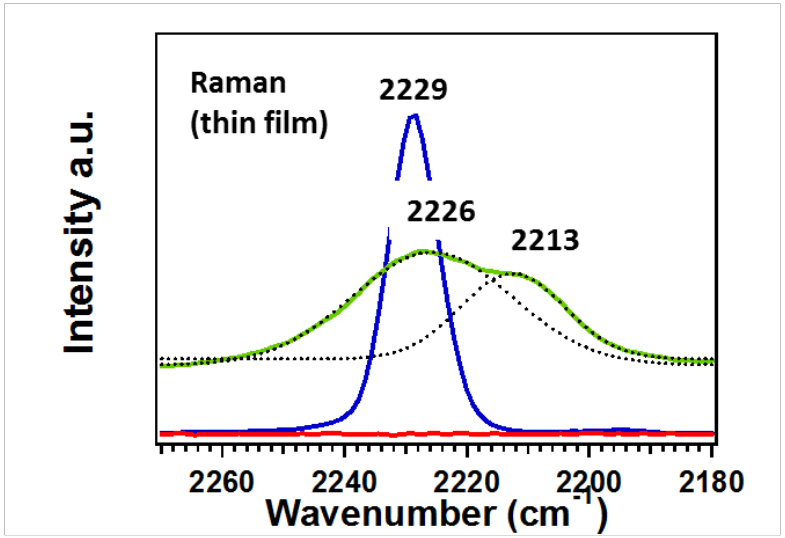
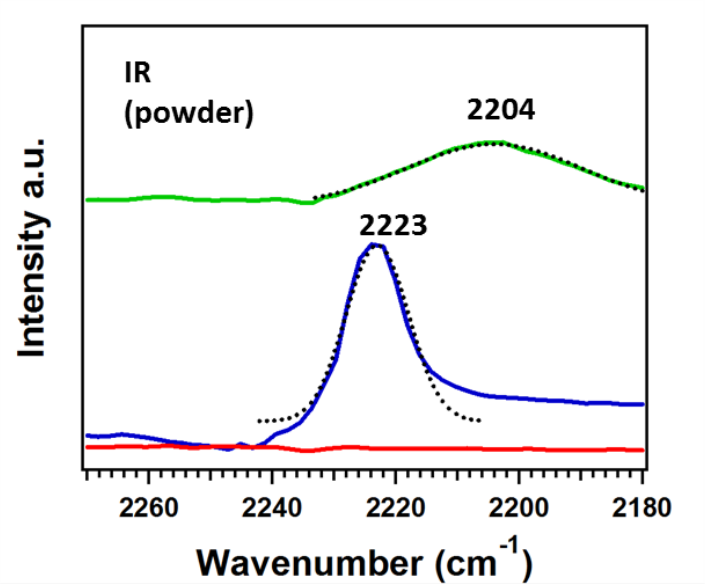
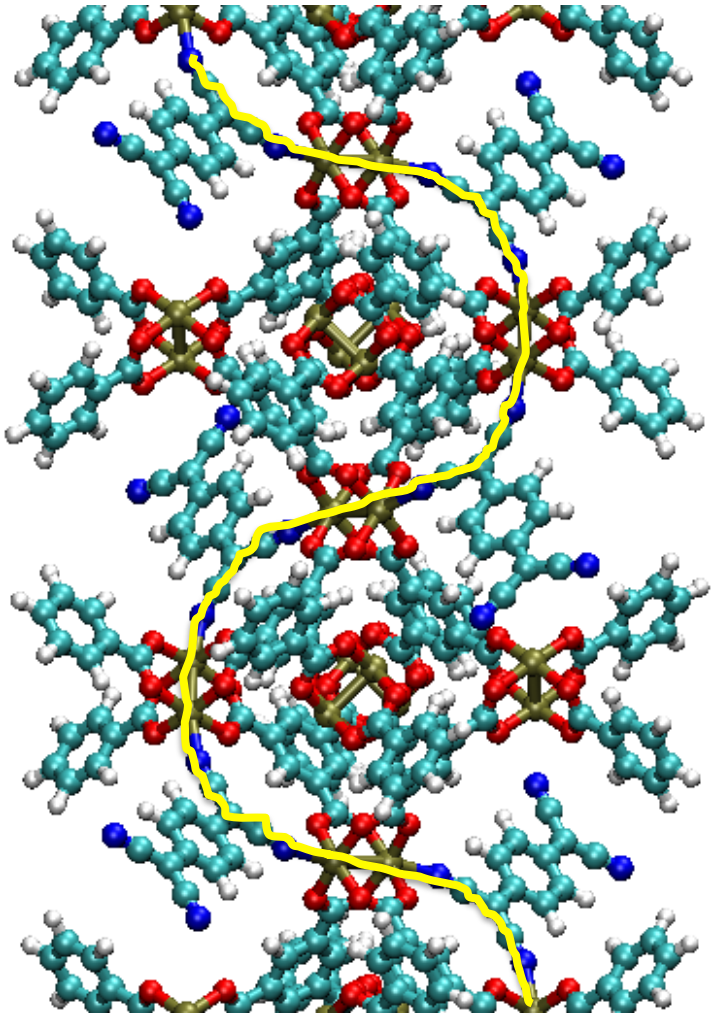


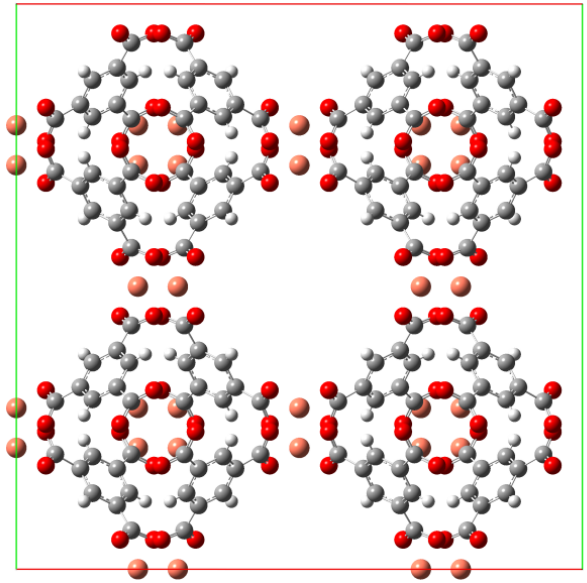


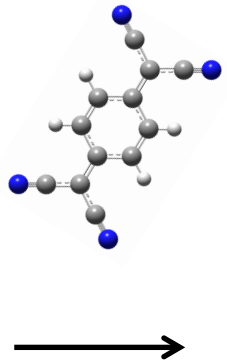


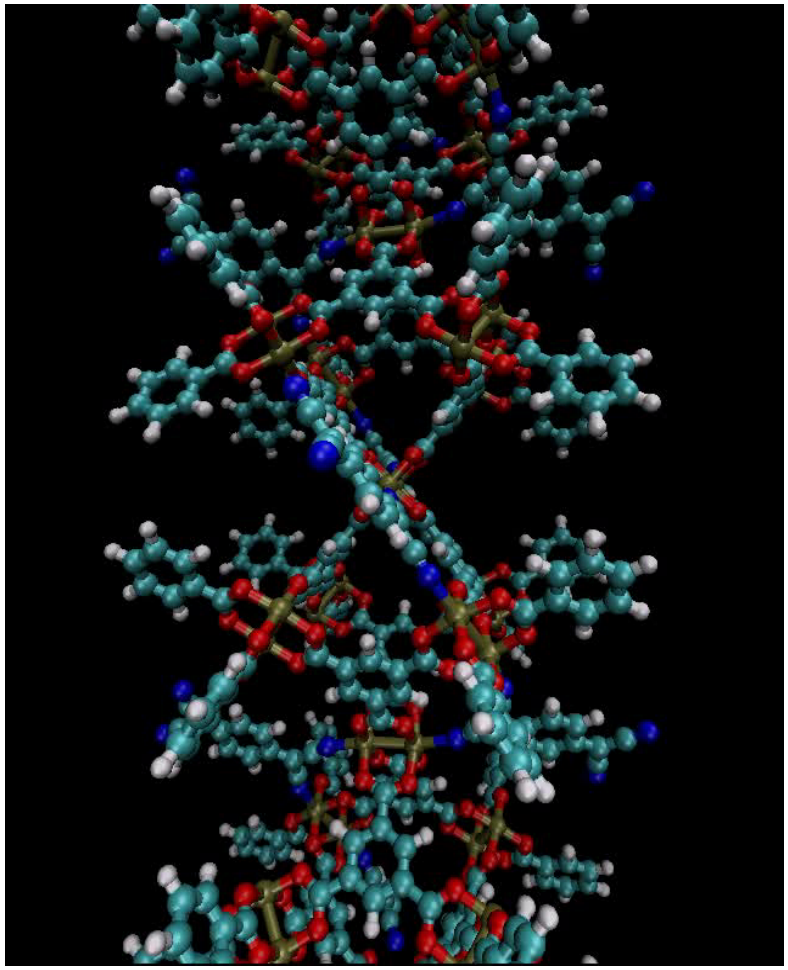
DFT: Cu dimers linked by TCNQ

$$BE = E\downarrow total - (E\downarrow TCNQ + E\downarrow MOF) = 84 \text{ kJ/mol}$$

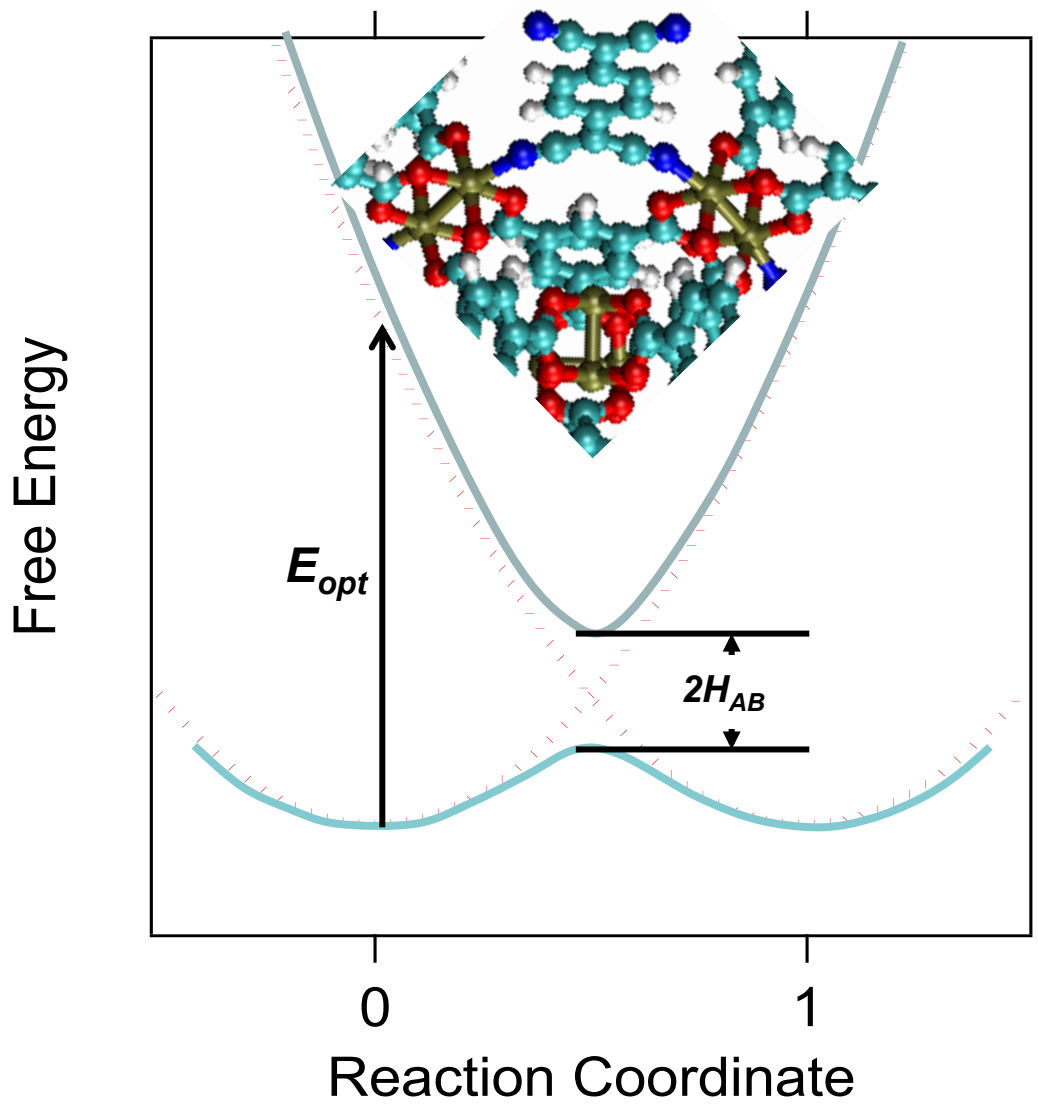
A continuous TCNQ@CuBTC pathway through the unit cell can be achieved with 4 TCNQs. Based on the experimental loading of 8 TCNQs per unit cell two continuous pathways are possible.







Increased coupling between neighboring Cu dimers lowers barrier to charge transfer



$$\Delta G^* = \frac{(\lambda - 2H_{AB})^2}{4\lambda}$$

H4-TCNQ < F4-TCNQ < TCNQ 0.19 eV < 1.03 eV < 2.32 eV

Guest aromaticity, electronegativity affect conductivity

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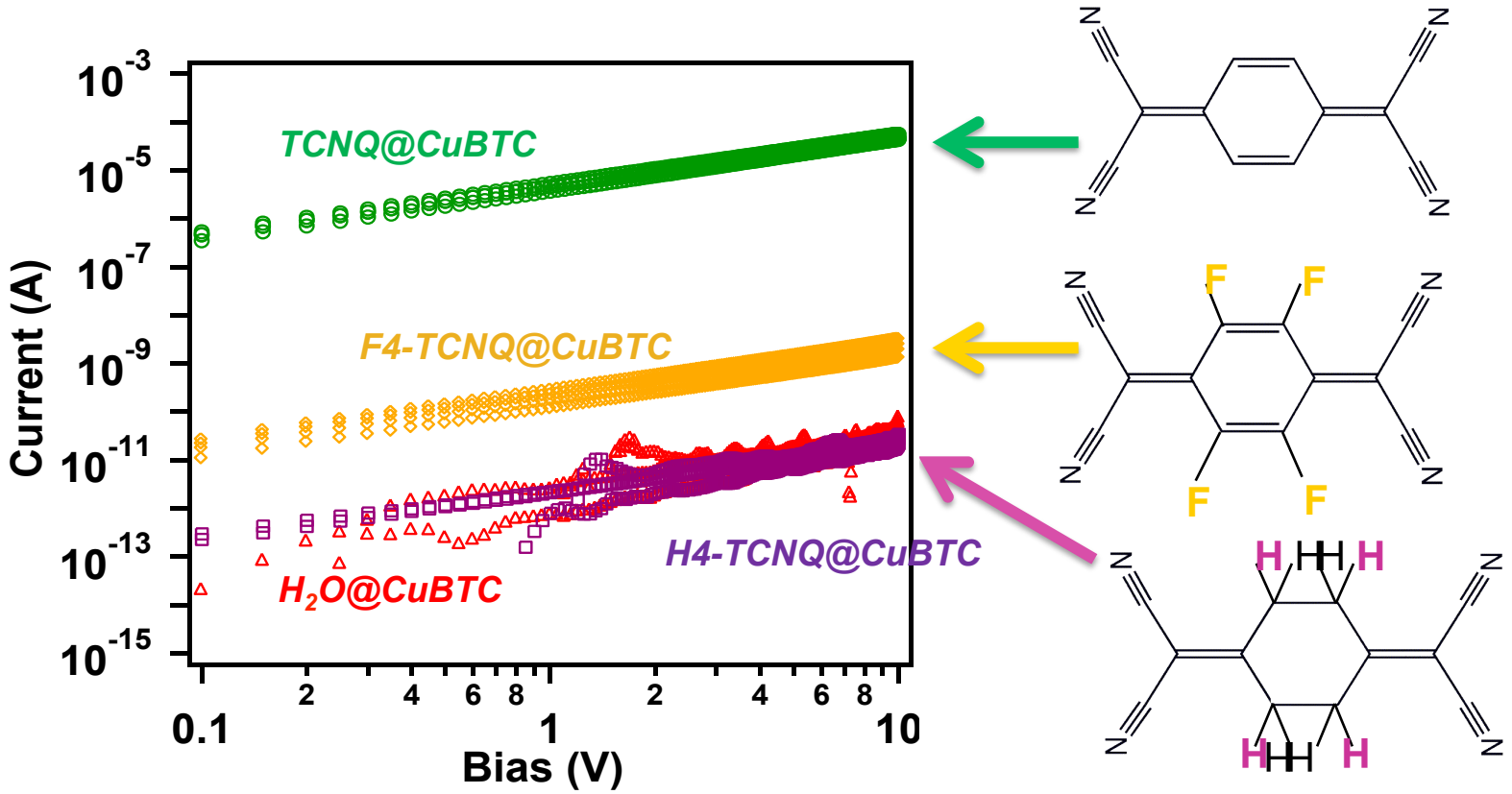
Extended π network essential for conductivity



Cu-BTC band alignments: DFT/PBEsol calculations

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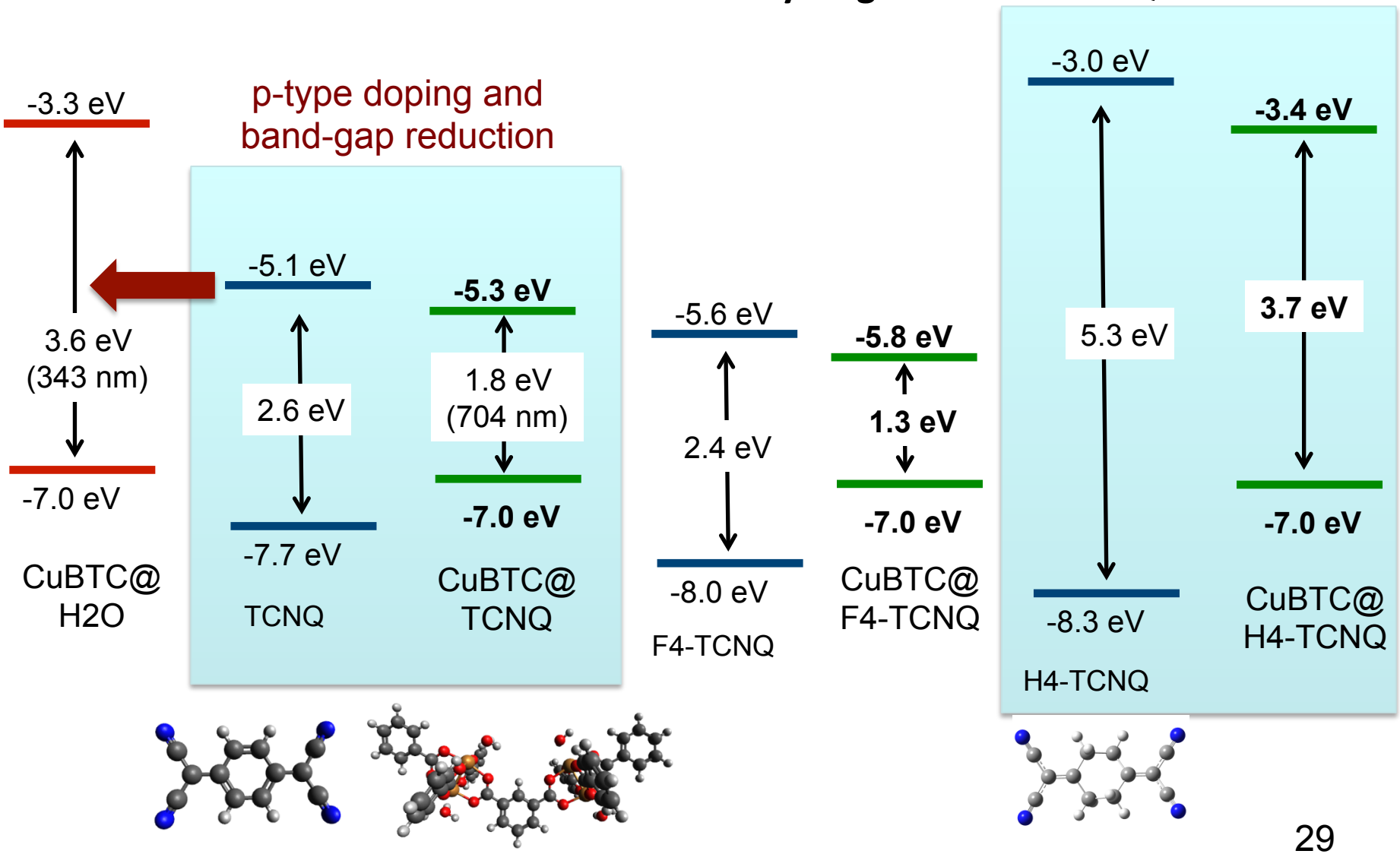
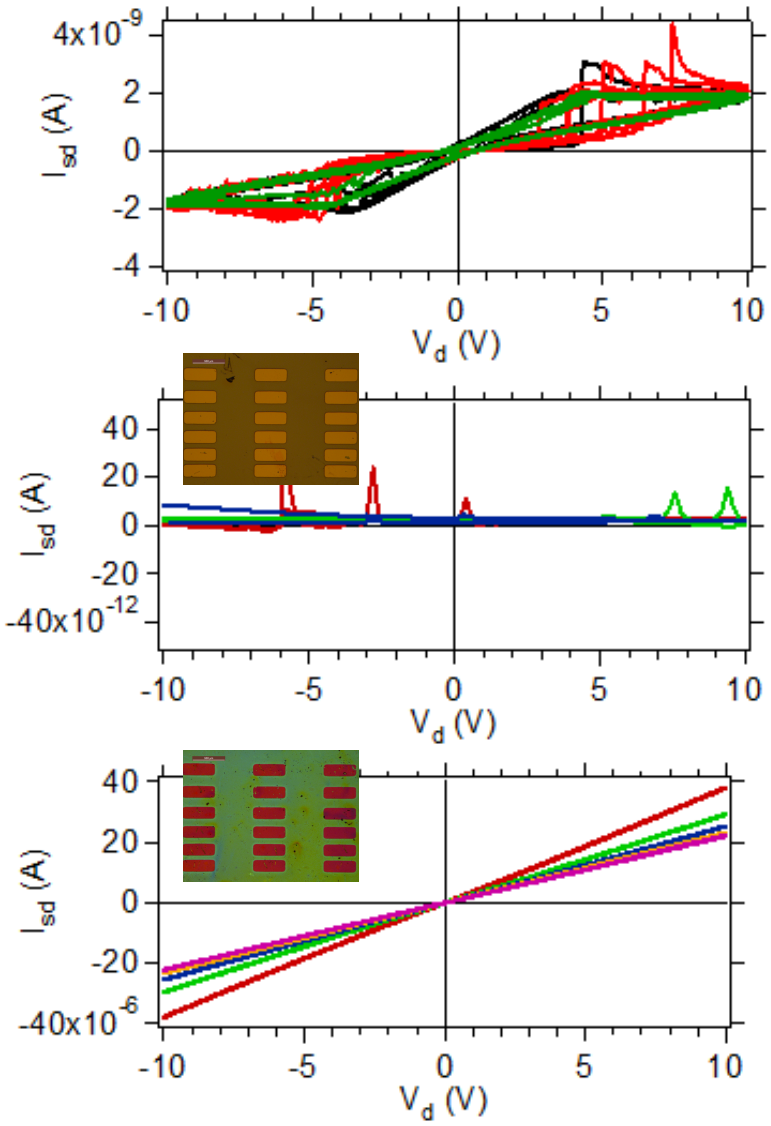
Effect of fluorination and hydrogenation of TCNQ



Solvent, precursor likely responsible for conductivity in as deposited $Cu_3(BTC)_2$.

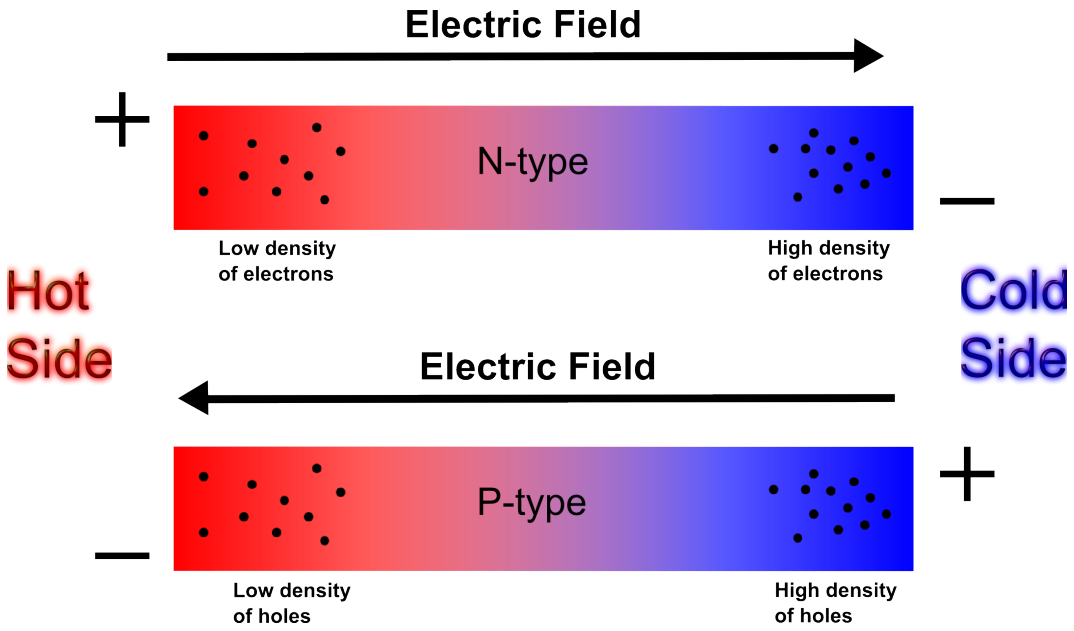


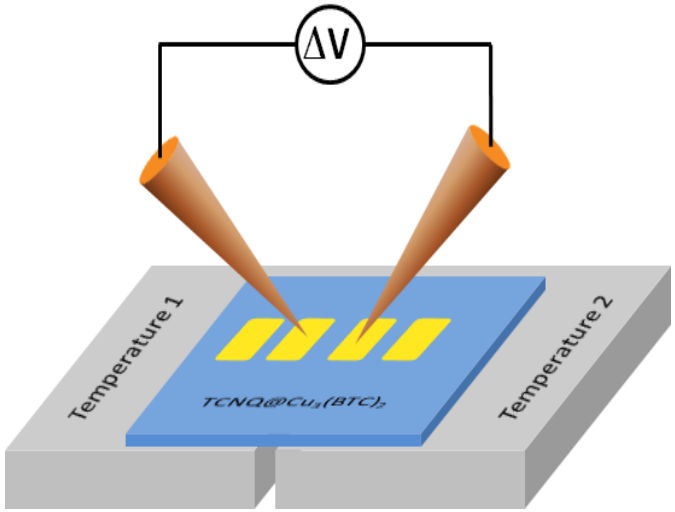
As deposited: Low but measurable conductivity, ionic/electronic?

Activated, exposed to ambient: No measurable conductivity at 10V ($<10^{-12}$ A)

Infiltrated MOF: s~0.1S/cm, ~10^8 increase

What about the carrier type (electron or hole?) Seebeck effect is one way to find out…

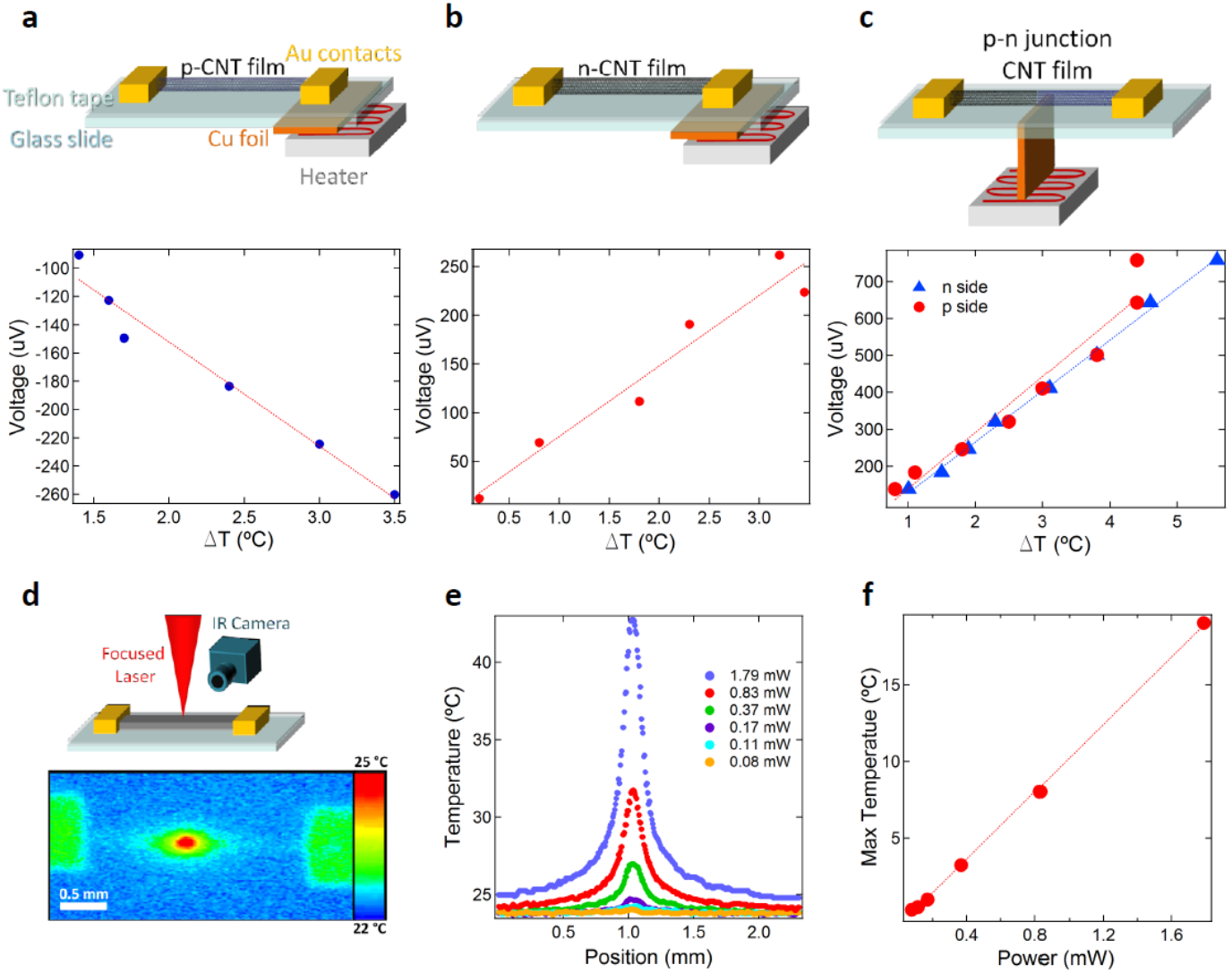




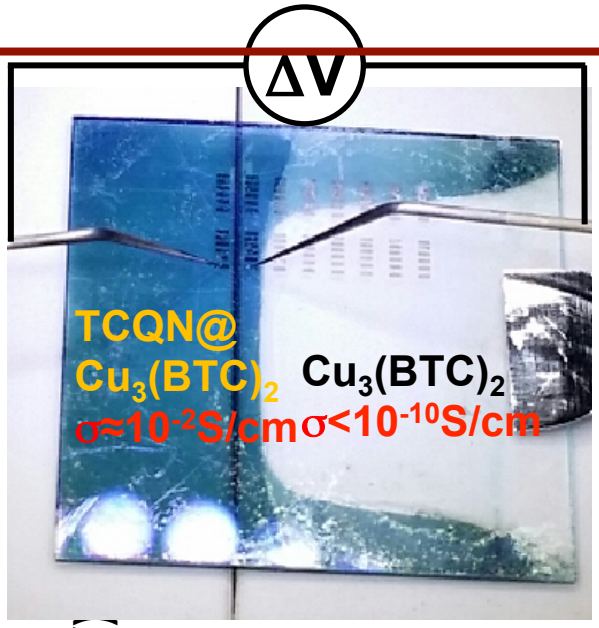
http://www.mn.uio.no/fysikk/english/research/projects/bate/thermoelectricity/

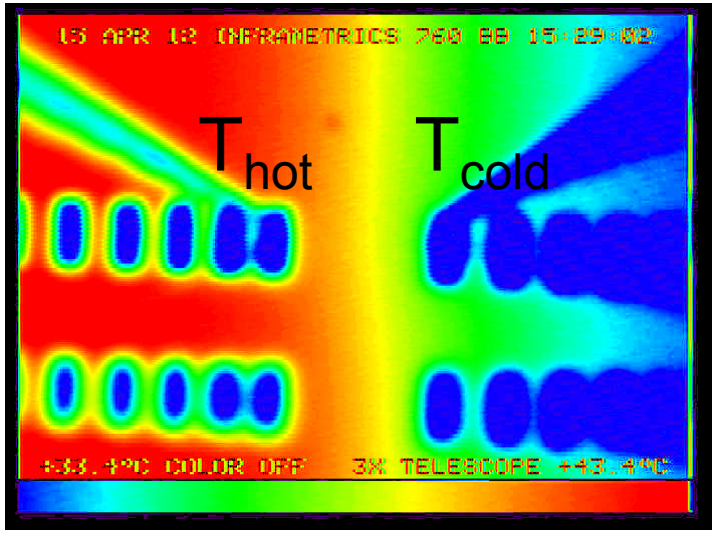
Example from recent work with CNT films

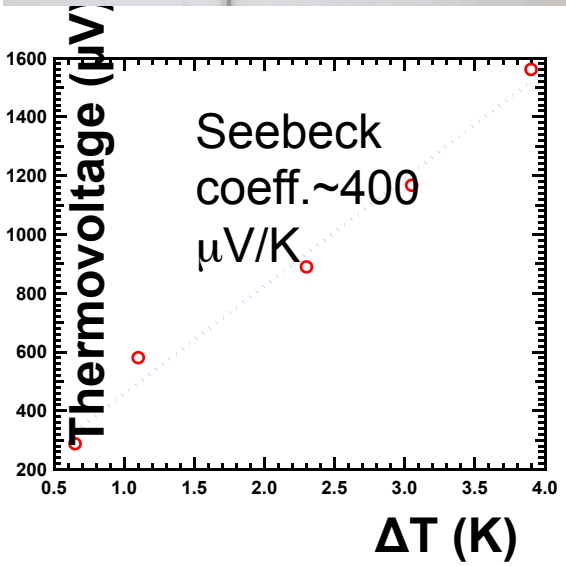
X. He, N. Fujimura, J. M. Lloyd, K. J. Erickson, A. A. Talin, Q. Zhang, W. Gao, Q.Jiang, Y. Kawano,R. H. Hauge, F.Léonard, J. Kono, CNT THz detectors, Nano Lett., just accepted

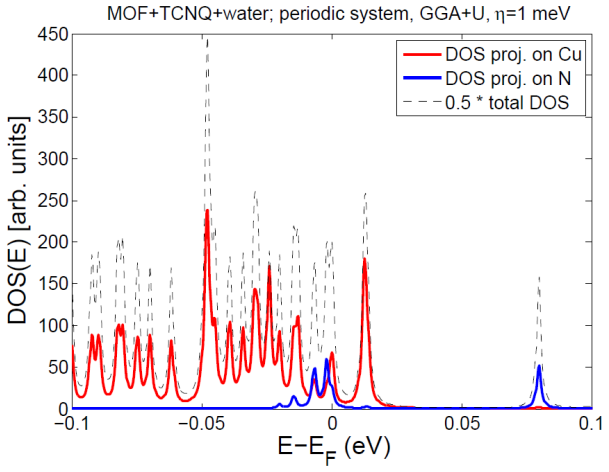


High, positive Seebeck coeff. (i.e Fermi level in VB)

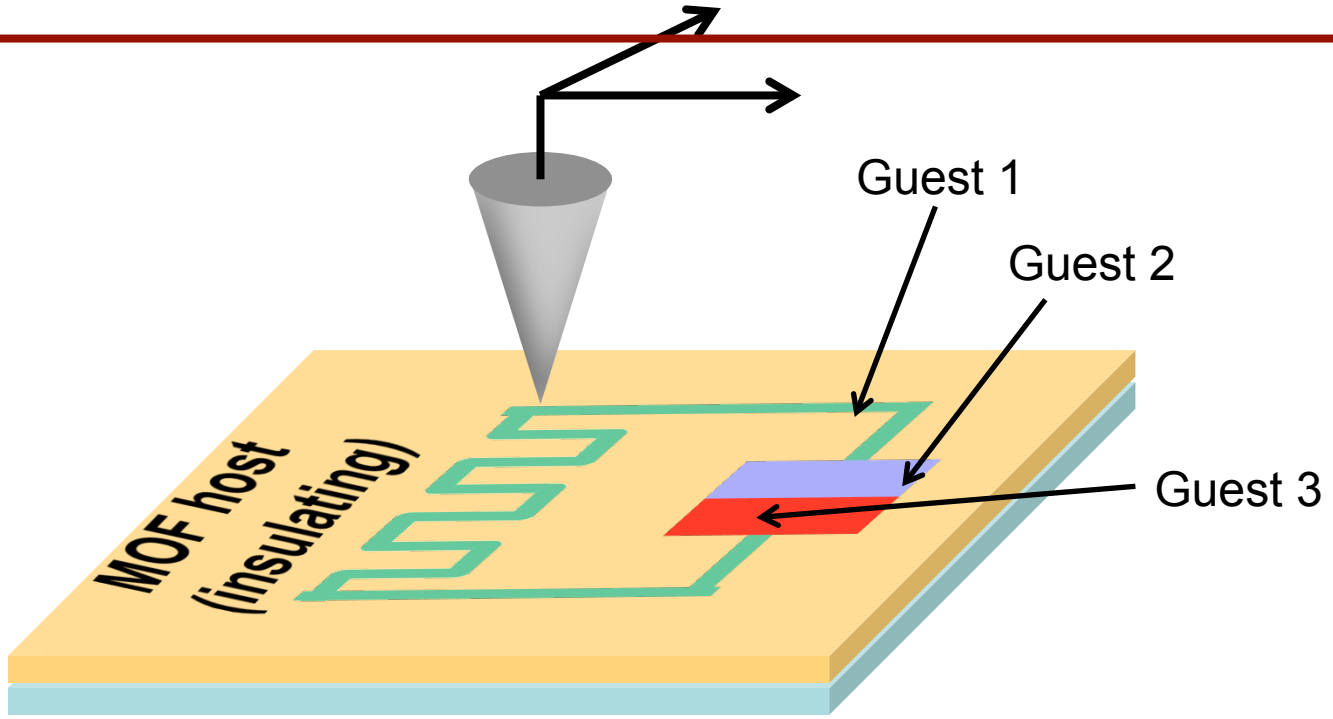


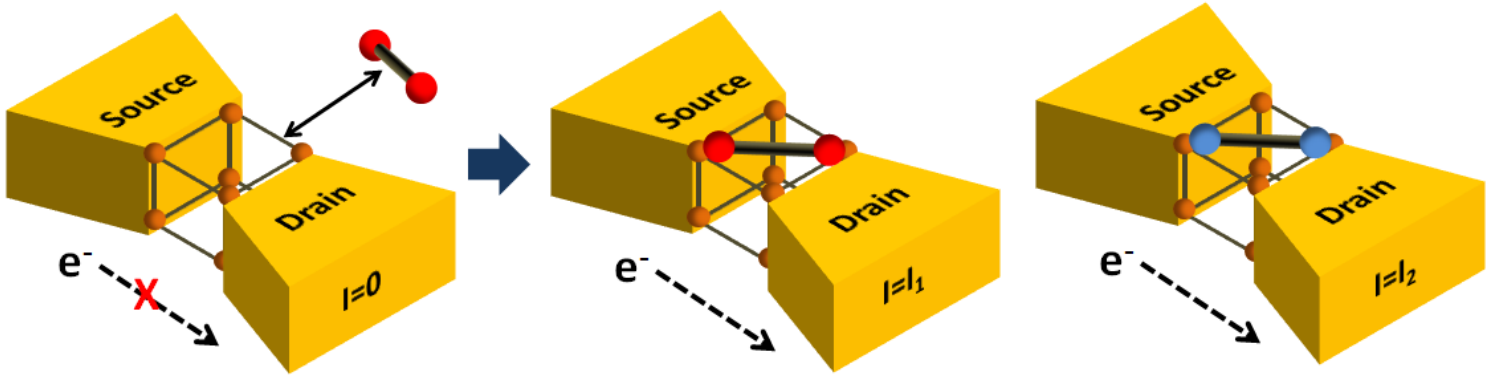






Visions for Molecule@MOF ICs, nanodevices





Conclusions

- MOFs are hybrid materials with ordered, chemically tunable porosity
- Ideal for gas storage, separations, catalysis, sensors, templates for nanomaterial synthesis
- MOF thin films can be grown LBL in solution
- Conductivity of $Cu_3(BTC)_2$ tunable $10^{-8} \rightarrow 10^{-1}$ S/cm with TCNQ
- UV-Vis, IR indicate partial charge transfer
- Extended π network essential for conductivity
- Opportunities for tuning properties w/ molecule@MOF expanding

A. A. Talin, A. Centrone, M. E. Foster, V. Stavila, P. Haney, R. A. Kinney, V. Szalai, F. El Gabaly, H. P. Yoon, F. Léonard, M. D. Allendorf, *Science* **343**, 66 (2014);

V. Stavila, A. A. Talin, M. D. Allendorf, Chem. Soc. Rev. 10.1039/c4cs00096j (ASAP)

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