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Guest-Induced Electrical Conductivity in Metal-Organic Frameworks

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Inorganic vs. organic conducting materials: the best and the worst of two worlds

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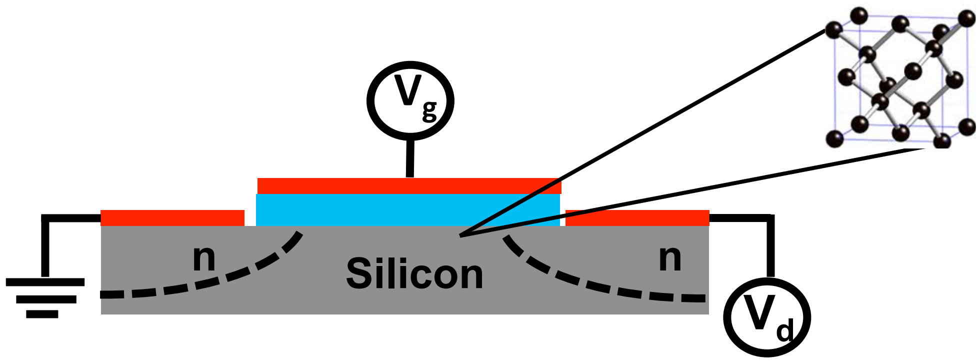
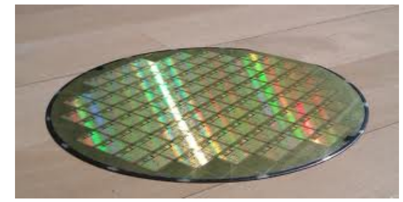
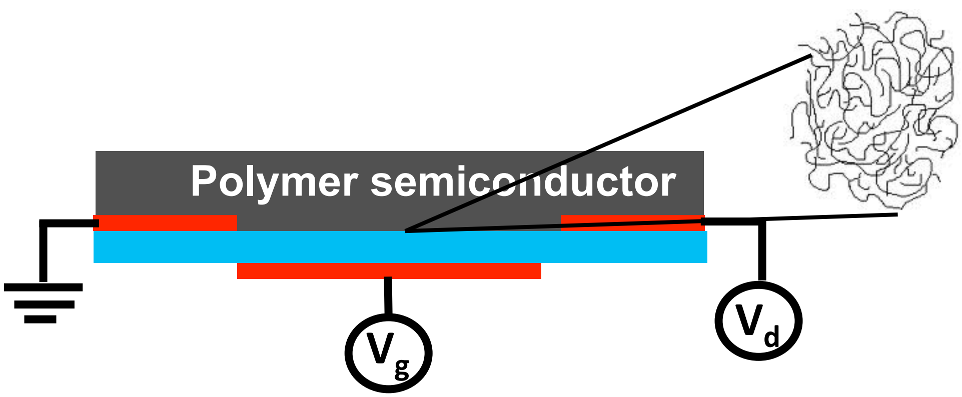


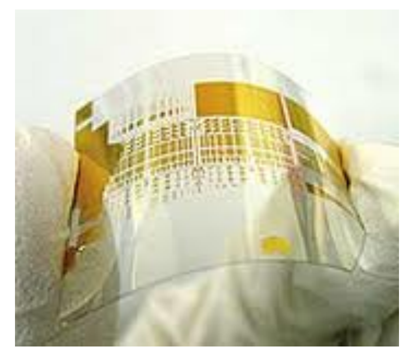
Crystalline inorganic semiconductors



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



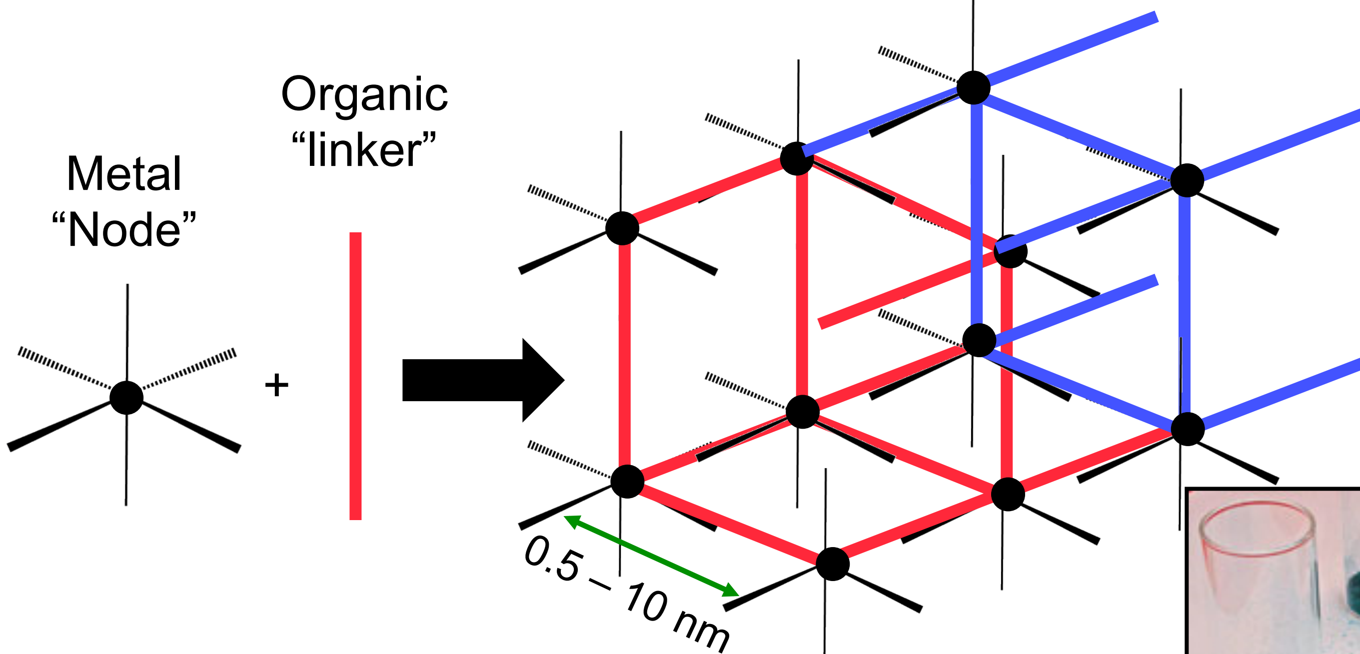
Disordered organic semiconductors

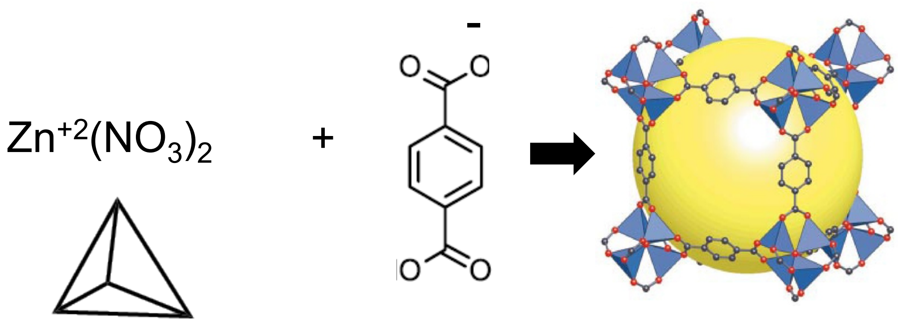


- Flexible
- Tunable w/ chemistry
- Low cost fabrication
- Poor mobility
- Instability
- Low free carrier densities

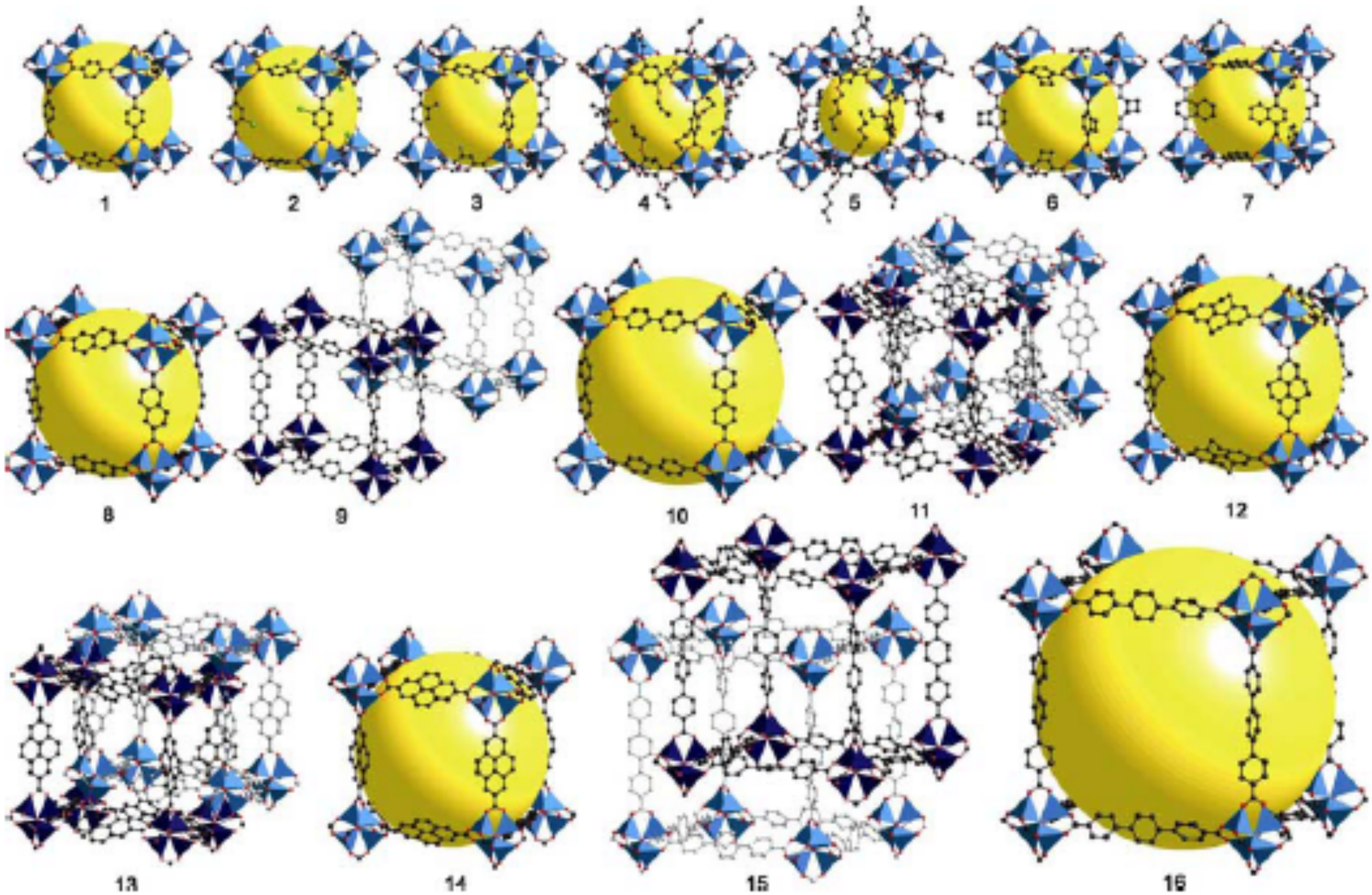
What is a Metal-Organic Framework?

Crystalline (therefore ordered), nanoporous structure



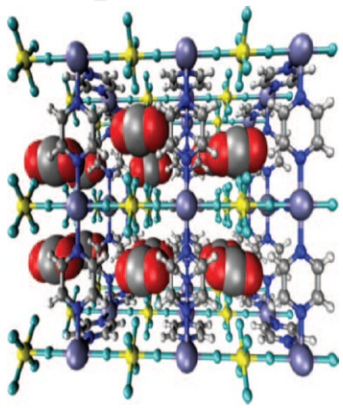


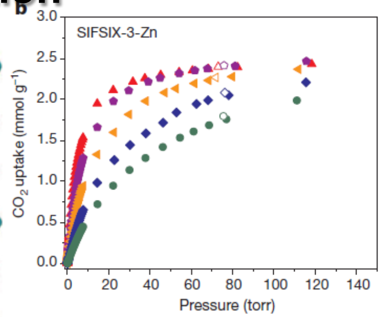
MOFs are a subset of a growing category of self-assembled, nanoporous materials



MOFs are attractive for gas storage, catalysis, separations, ionic conductors

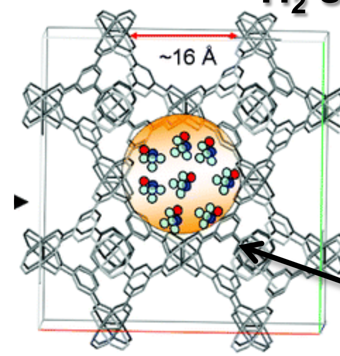
CO_2 sequestration





Nugent et al., Nature 495, 83 2013

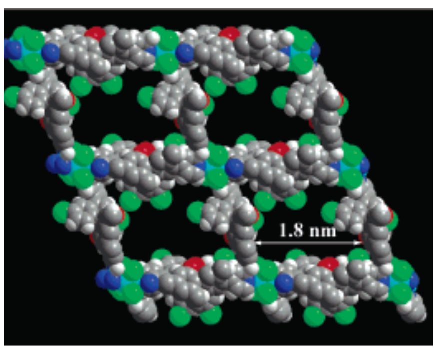
H_2 storage

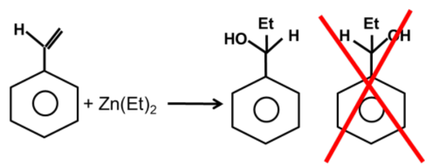


$NaAlH_4$

Bhakta, Allendorf et al., JACS 131, 13198, 2009

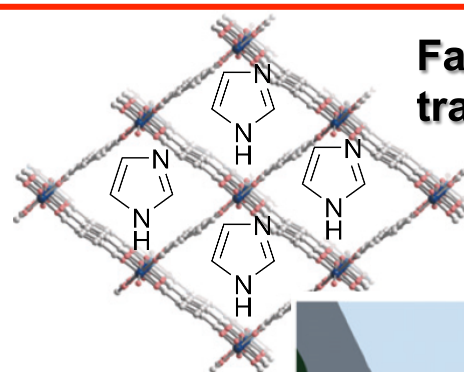
Catalysis

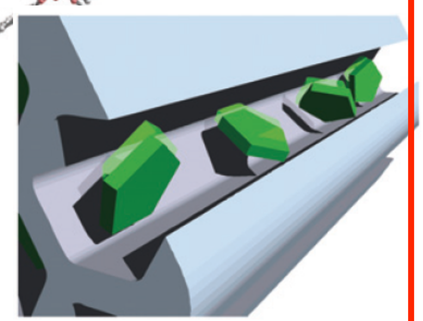




Wu, Hu, Zhang, Lin JACS 127, 8940, 2005

Fast H^+ transport





Bureekaew et al., Nat. Mat. 8, 831, 2009

Can the high performance of inorganic semiconductors with the tailorability of organic materials be achieved using MOFs?

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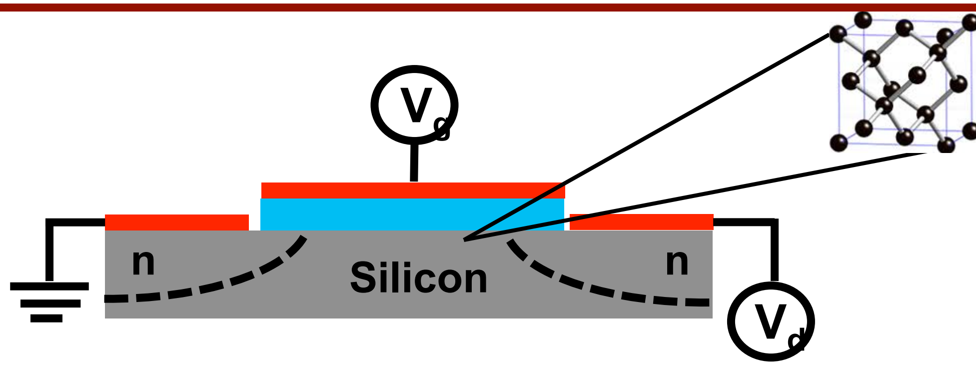
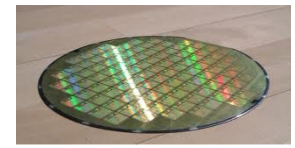
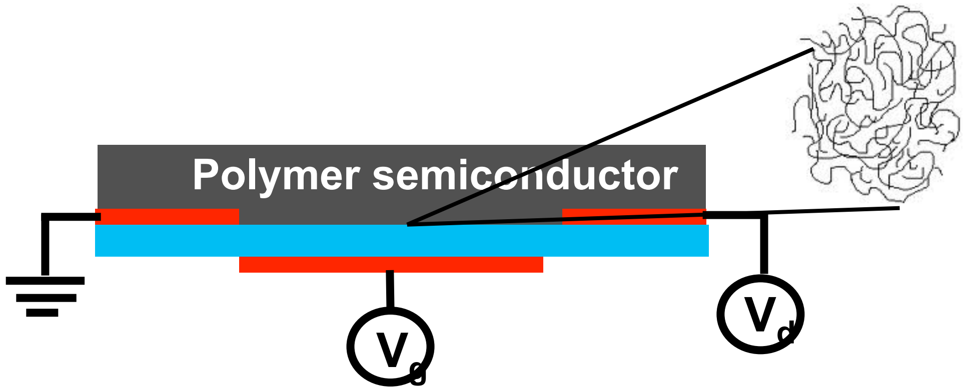


Crystalline inorganic semiconductor

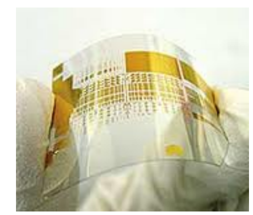
- High mobility
- Stability
- High cost
- Non-flexible
- Radiation damage

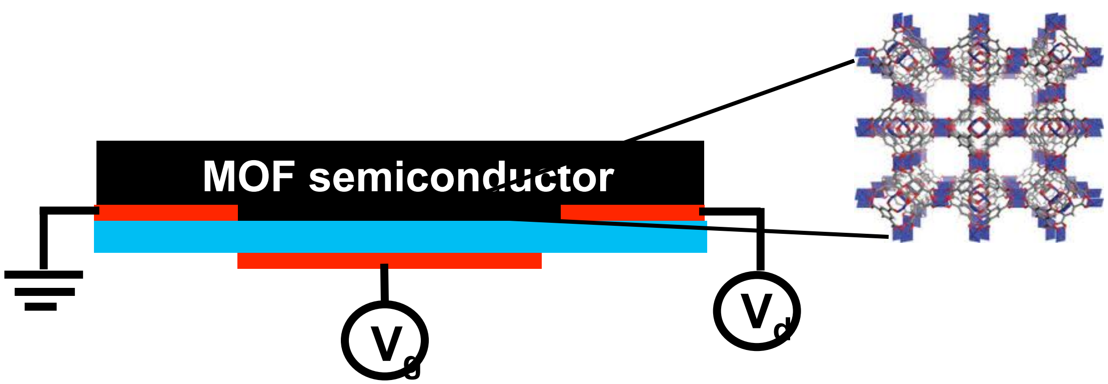




Disordered organic semiconductor

- 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

Thin film growth for MOF device applications

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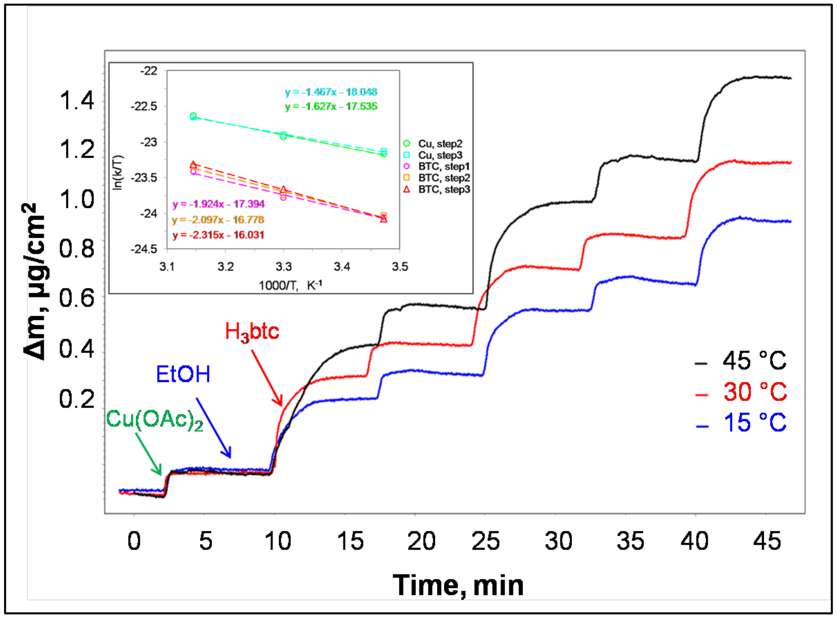
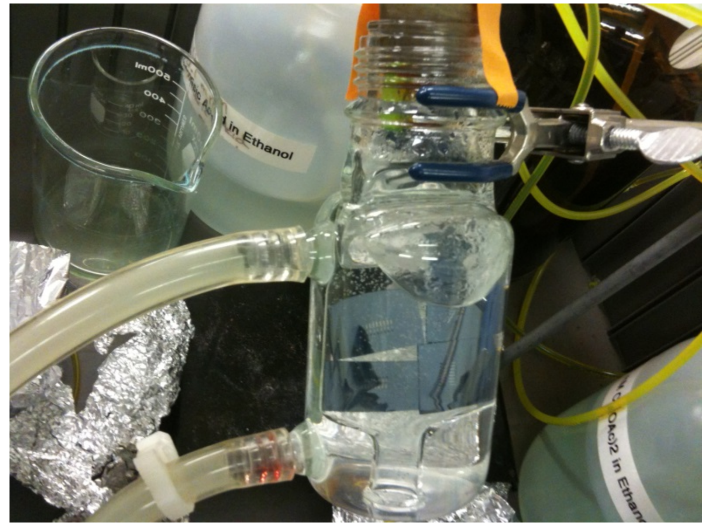
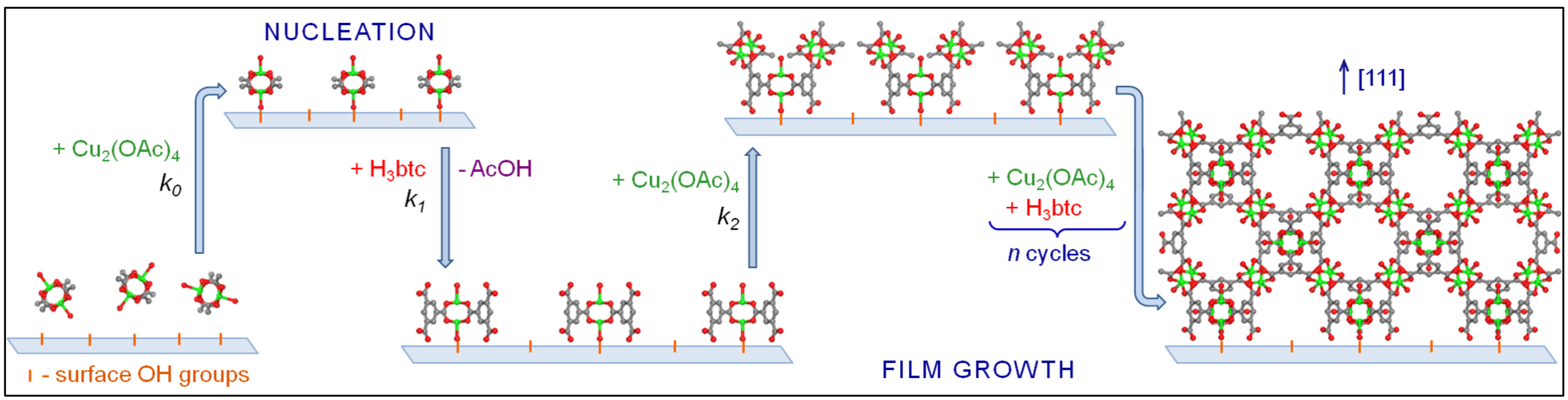
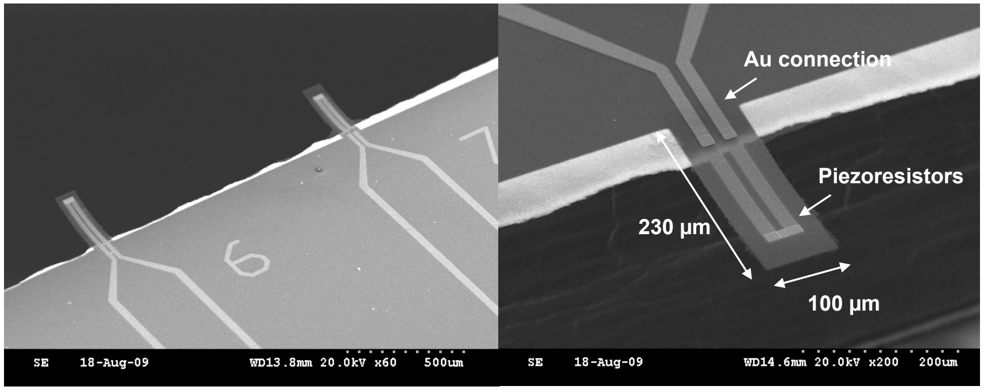


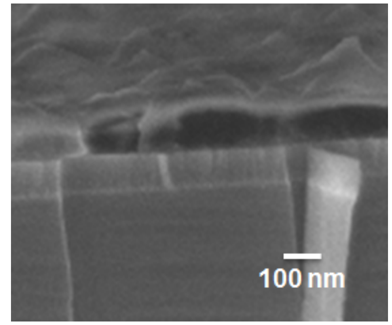




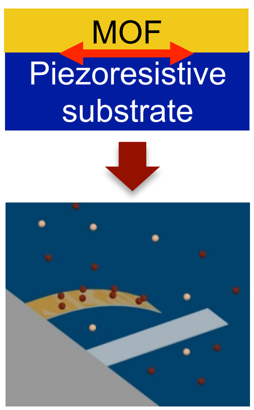
V. Stavlia et al. *Chem. Sci.* **3** (2012), 1531–1540

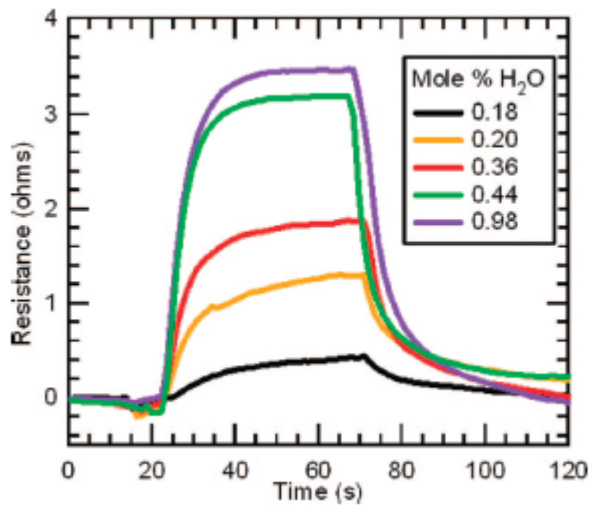
MOF films make sensitive, selective gas sensors

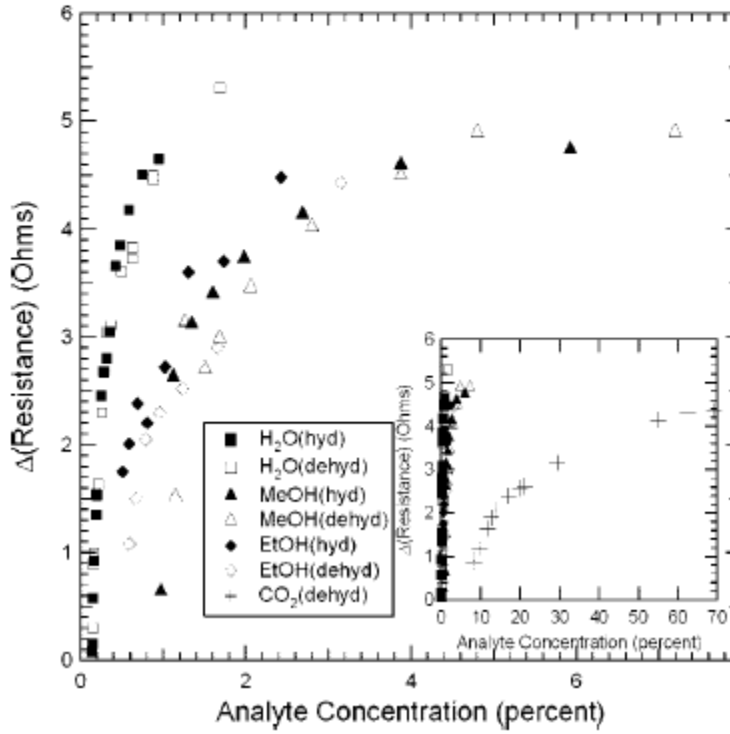




Microcantilevers (fg sensitivity)



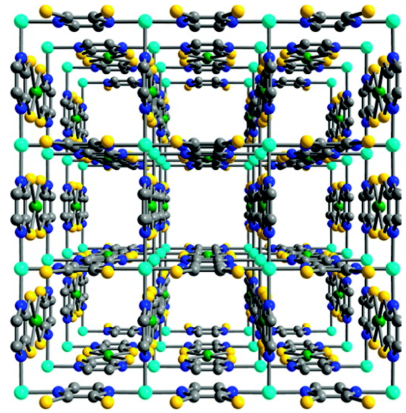




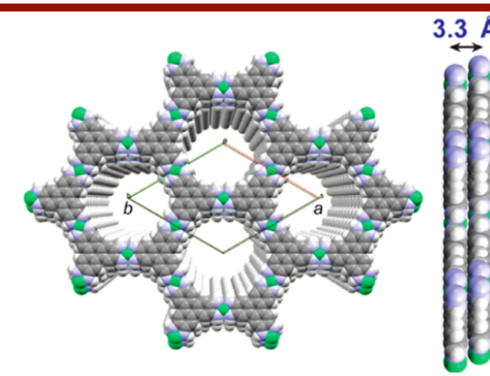
Allendorf, Talin, Hesketh, et al., *J. Amer. Chem. Soc.* 130, 14404 (2008)

Electrically conducting porous MOFs are rare

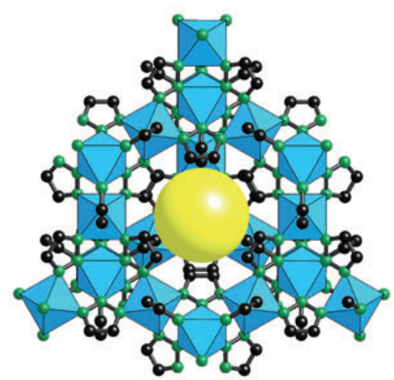
- p-type Cu-Ni Dithiolene MOF
- MET-3 (Fe-triazolate MOF)
- Mn(thiophenol) MOF: (−Mn−S−)∞ chains
- Metal-Organic Graphene analogues (MOGs)



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

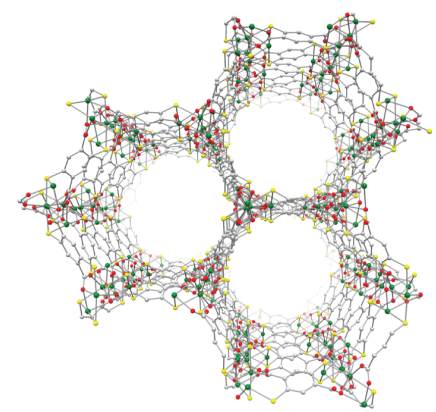


$Ni_3(HITP)_2$ MOG
D. Sheberla et al.
JACS 2014 ASAP



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

Guest molecule + MOF → ordered, tunable platform for controlling interactions at the nanoscale

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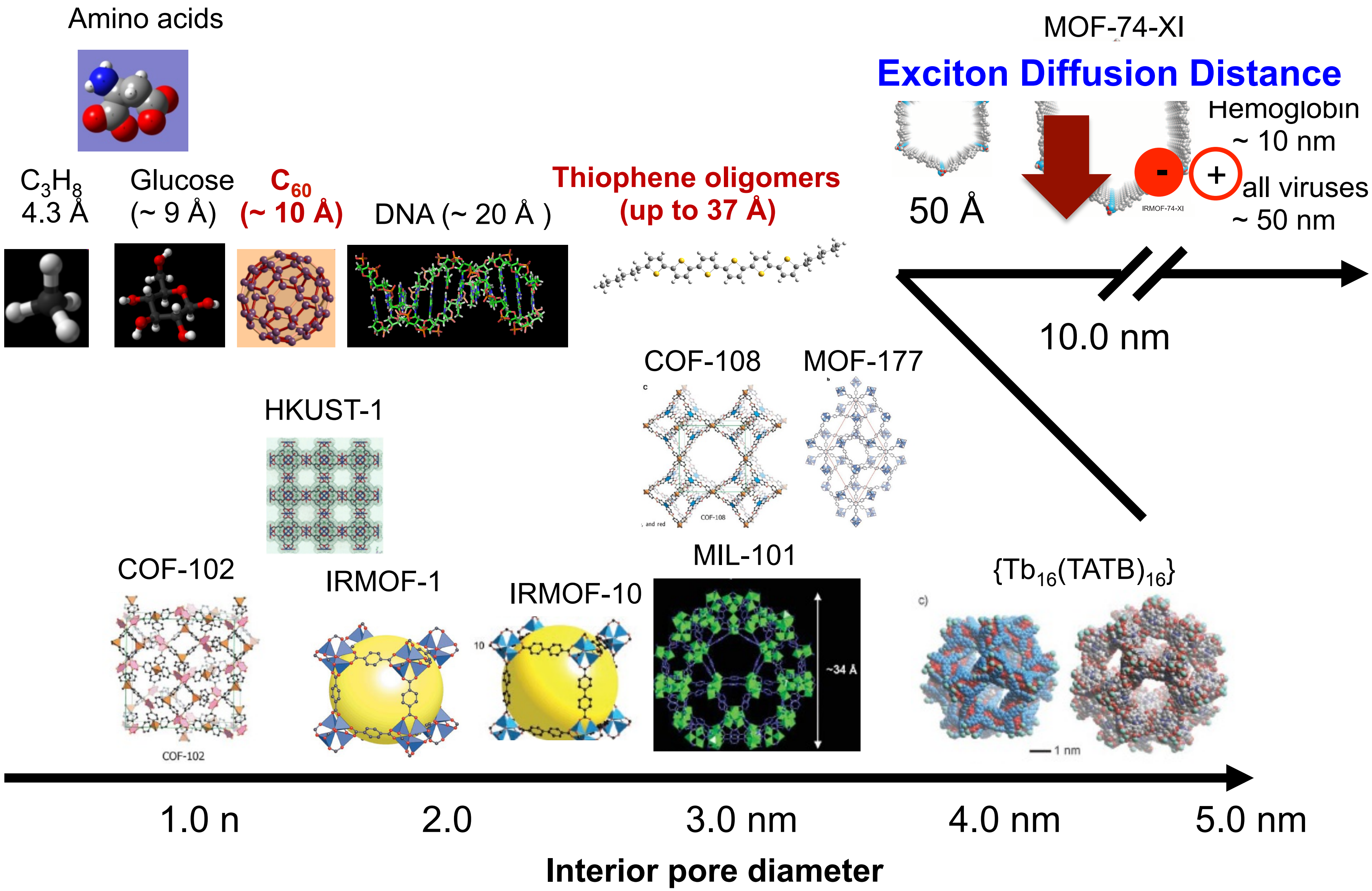

Cu-TCNQ is a well-known conducting coordination polymer

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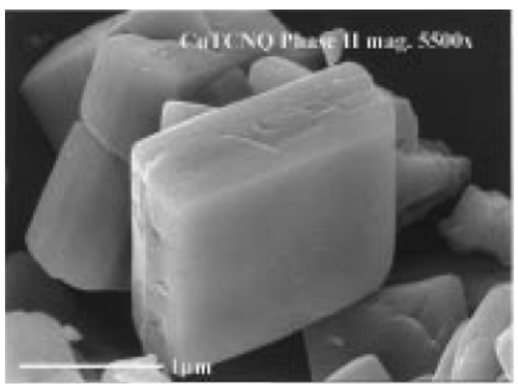
144 *Inorg. Chem.* **1999**, *38*, 144−156

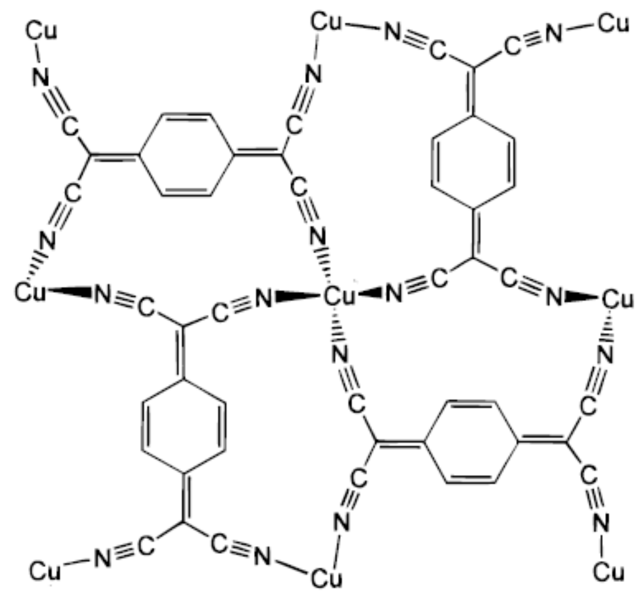
New Insight into the Nature of Cu(TCNQ): Solution Routes to Two Distinct Polymorphs and Their Relationship to Crystalline Films That Display Bistable Switching Behavior

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

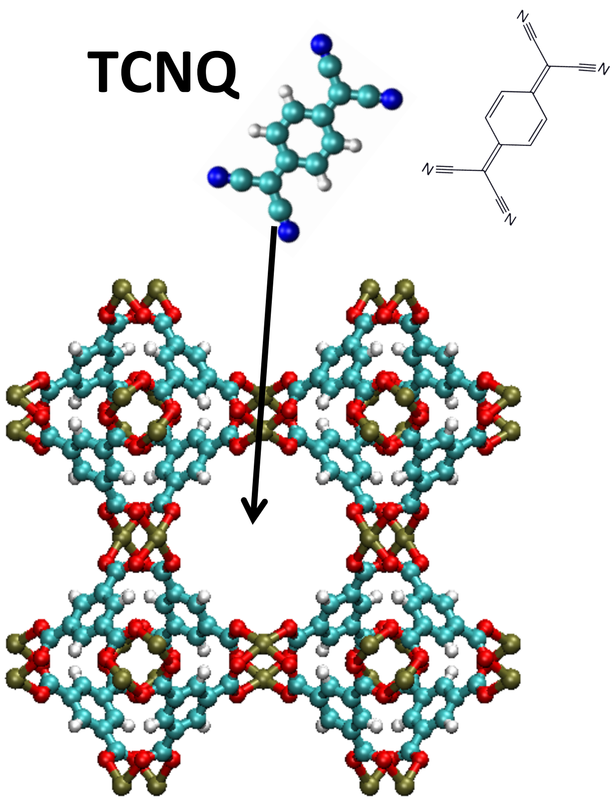
$$[Cu^{+}(TCNQ^{-})]_n \leftrightarrow$$
"OFF" state

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

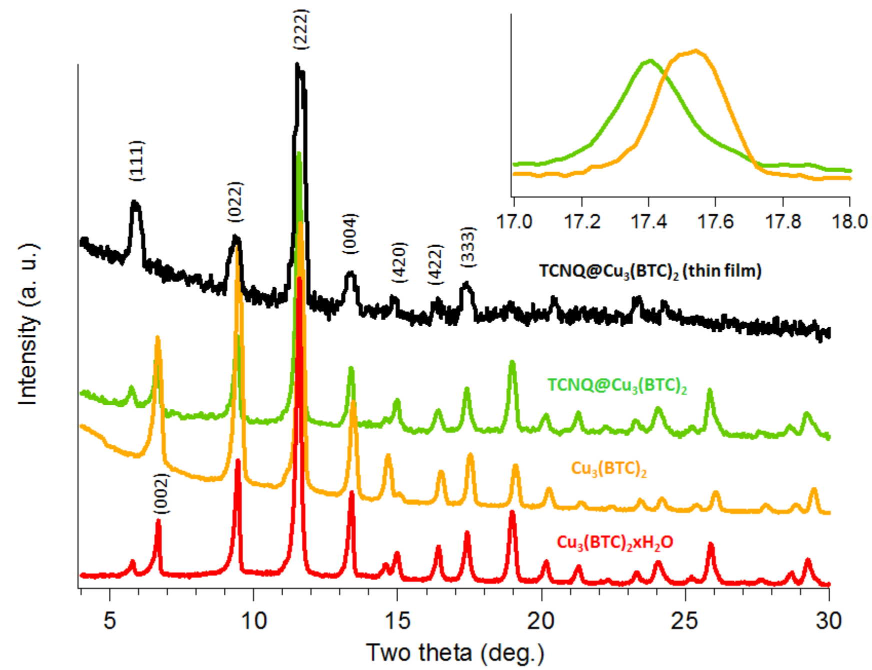




Guest@MOF: Emergent properties by infiltrating with guest molecules?

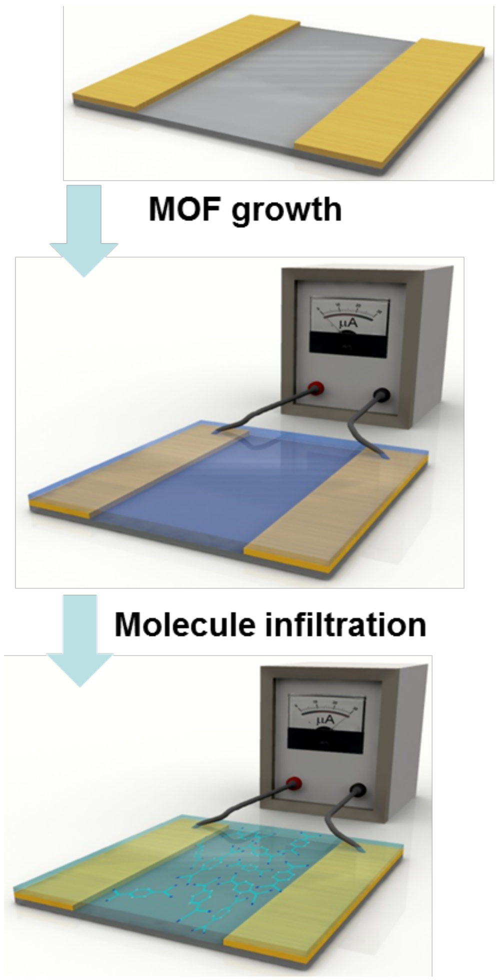


$Cu_2(BTC)_3$
(HKUST-1)

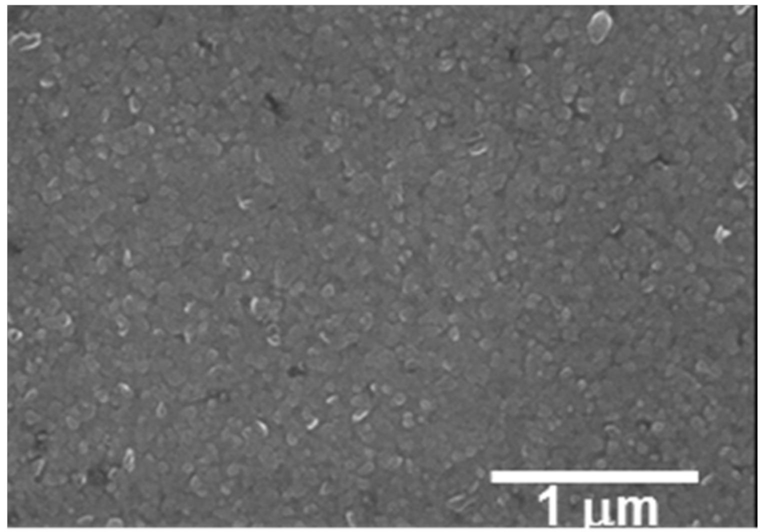


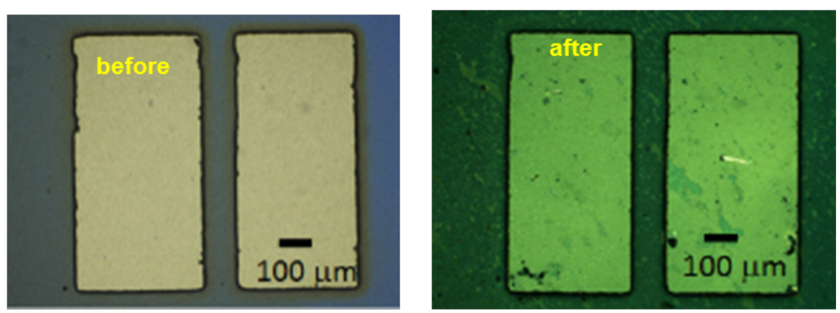
TCNQ loading: ~ 1 molecule/large pore

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

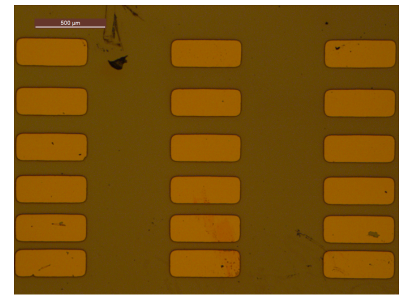


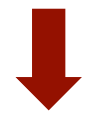
MOF film grown by layer-by-layer method



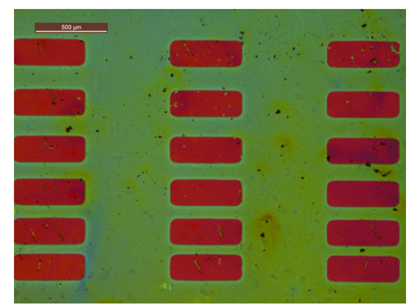


MOF film on SiO_x with Pt electrodes

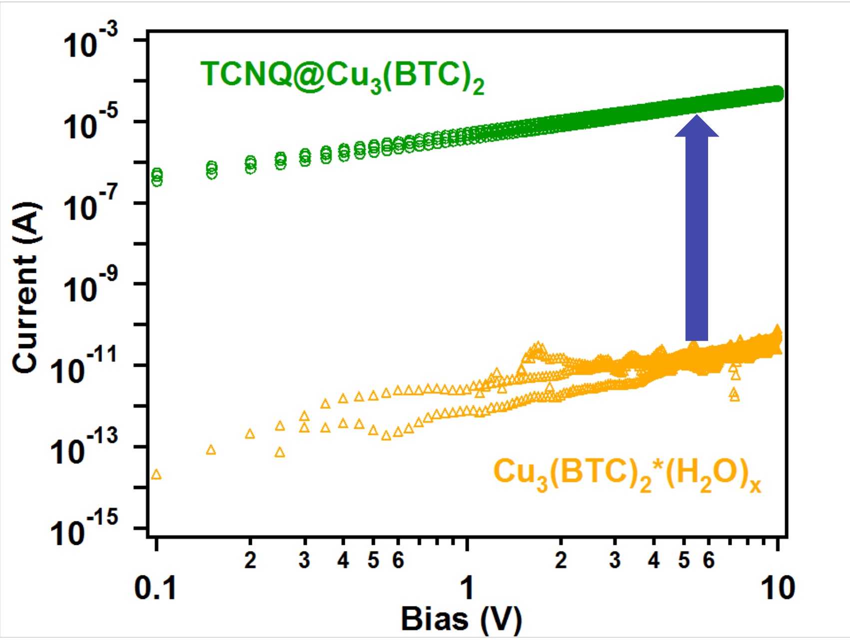


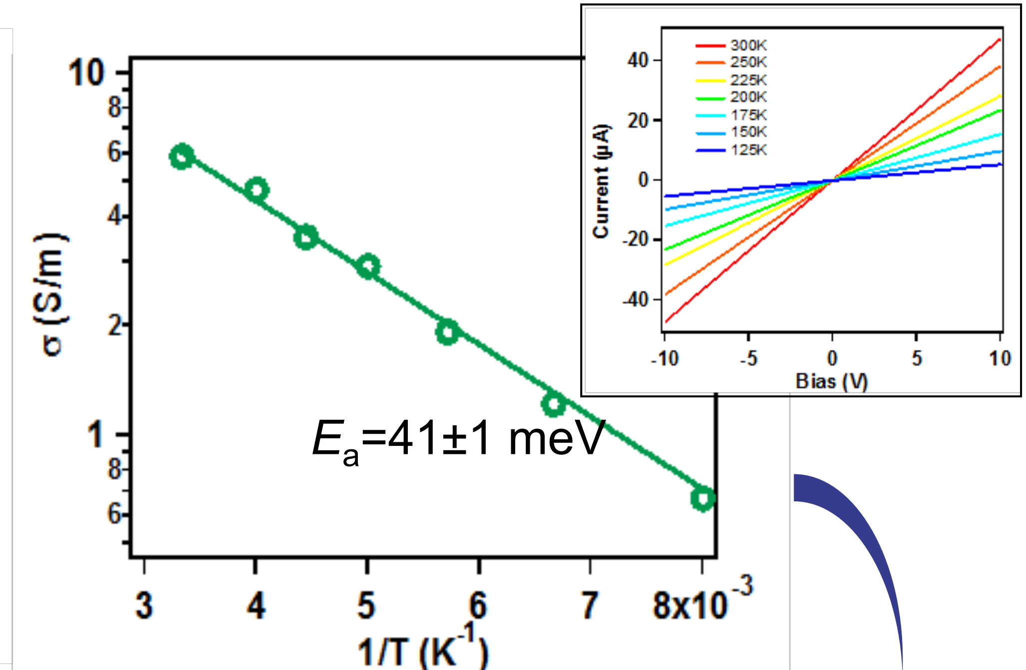


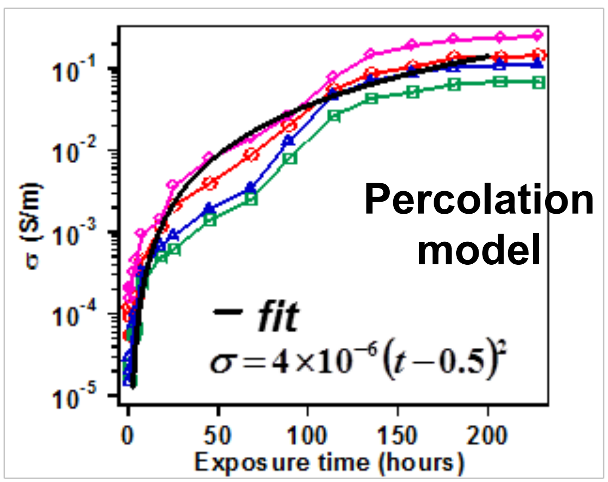
MOF film + TCNQ



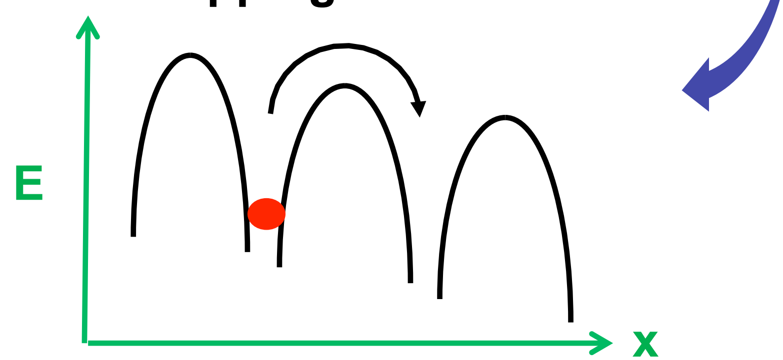
… and >10^7 increase in conductivity, air stable > 1 year



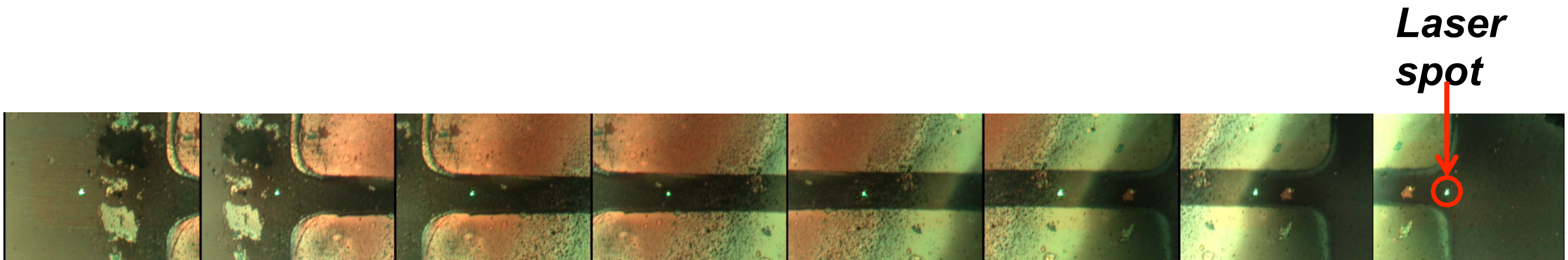


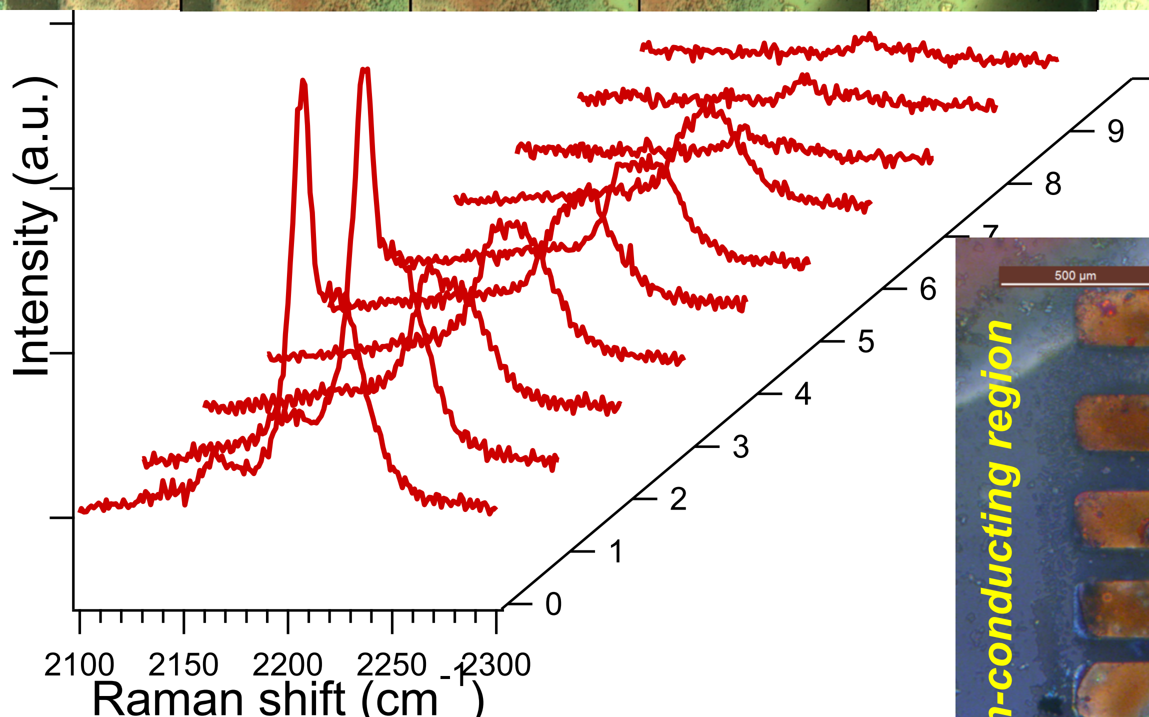


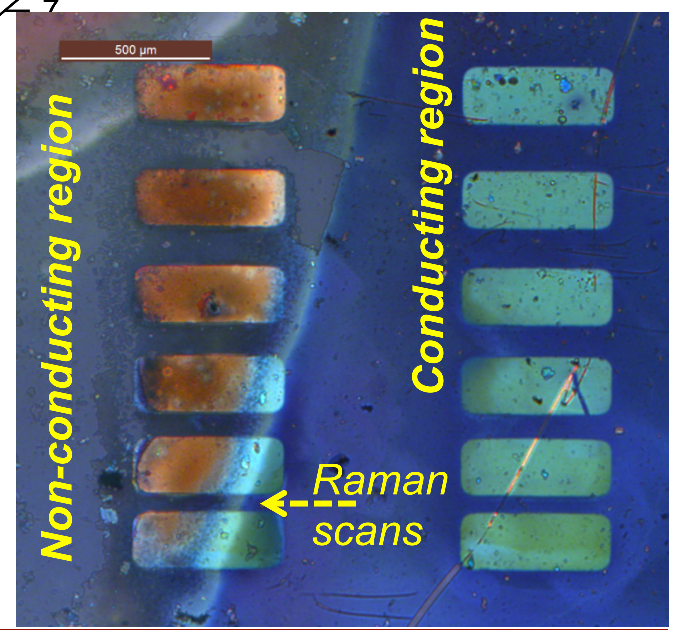
Hopping conduction



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







$TCNQ@Cu_2(BTC)_3$ exhibits strong new absorption bands

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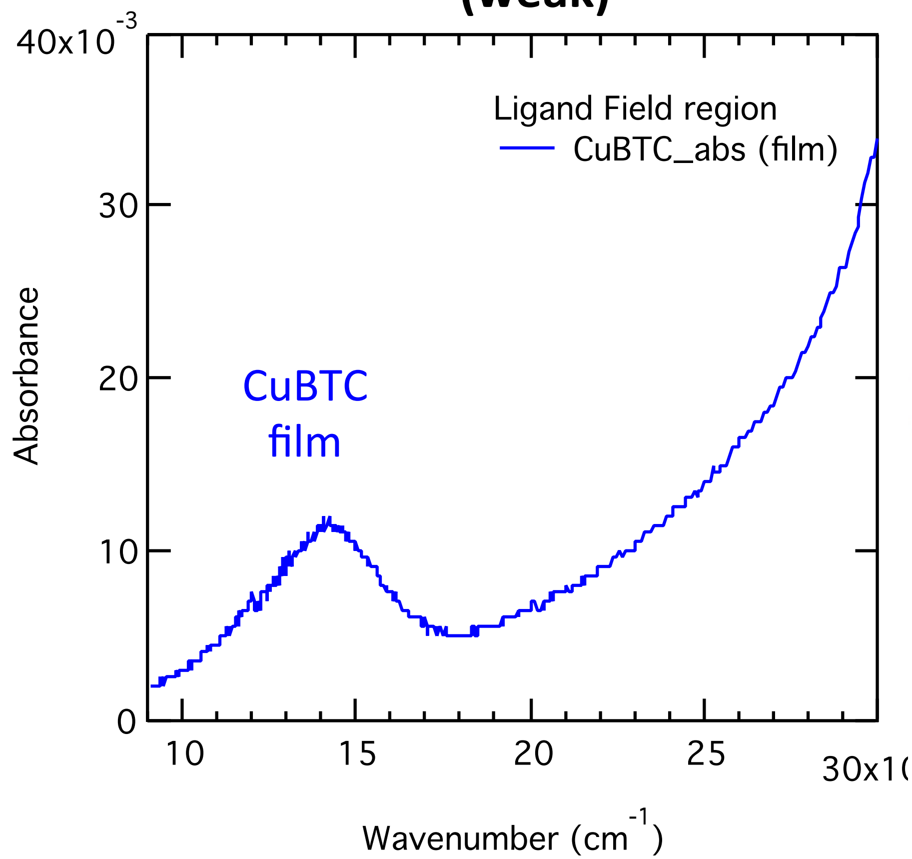
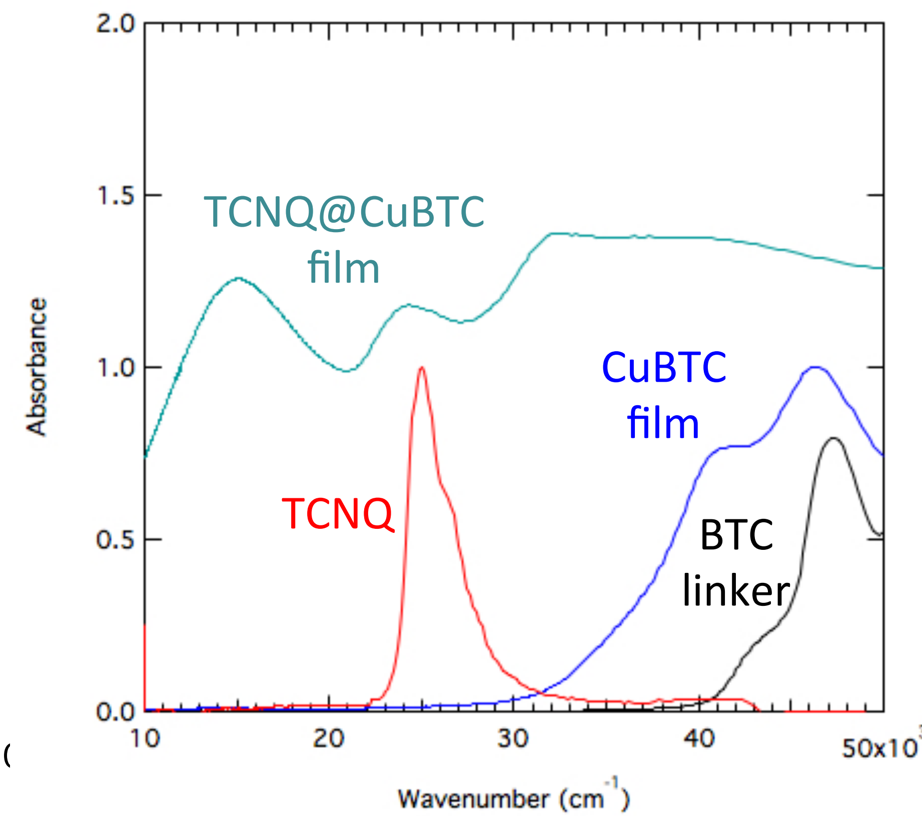
$H_2O@Cu_2(BTC)_3$

Cu(II) d-d transitions (weak)

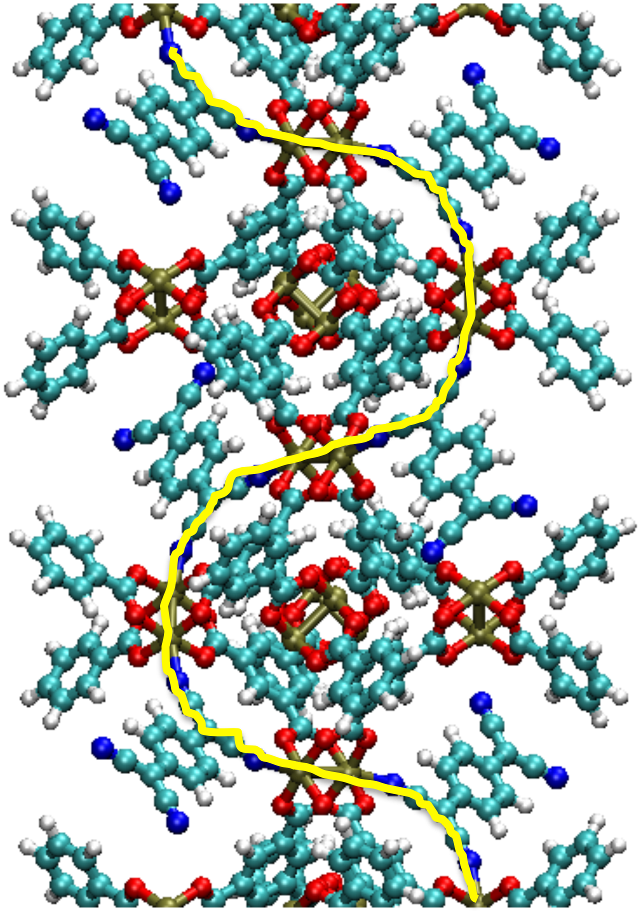
$TCNQ@Cu_2(BTC)_3$

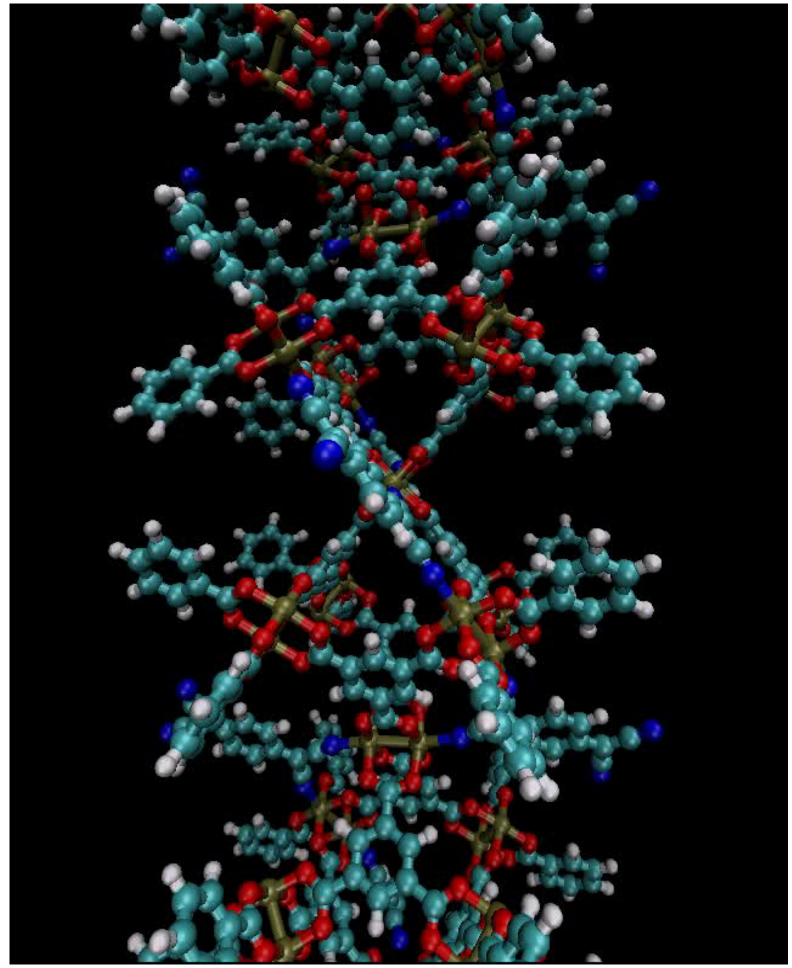
Charge transfer transitions





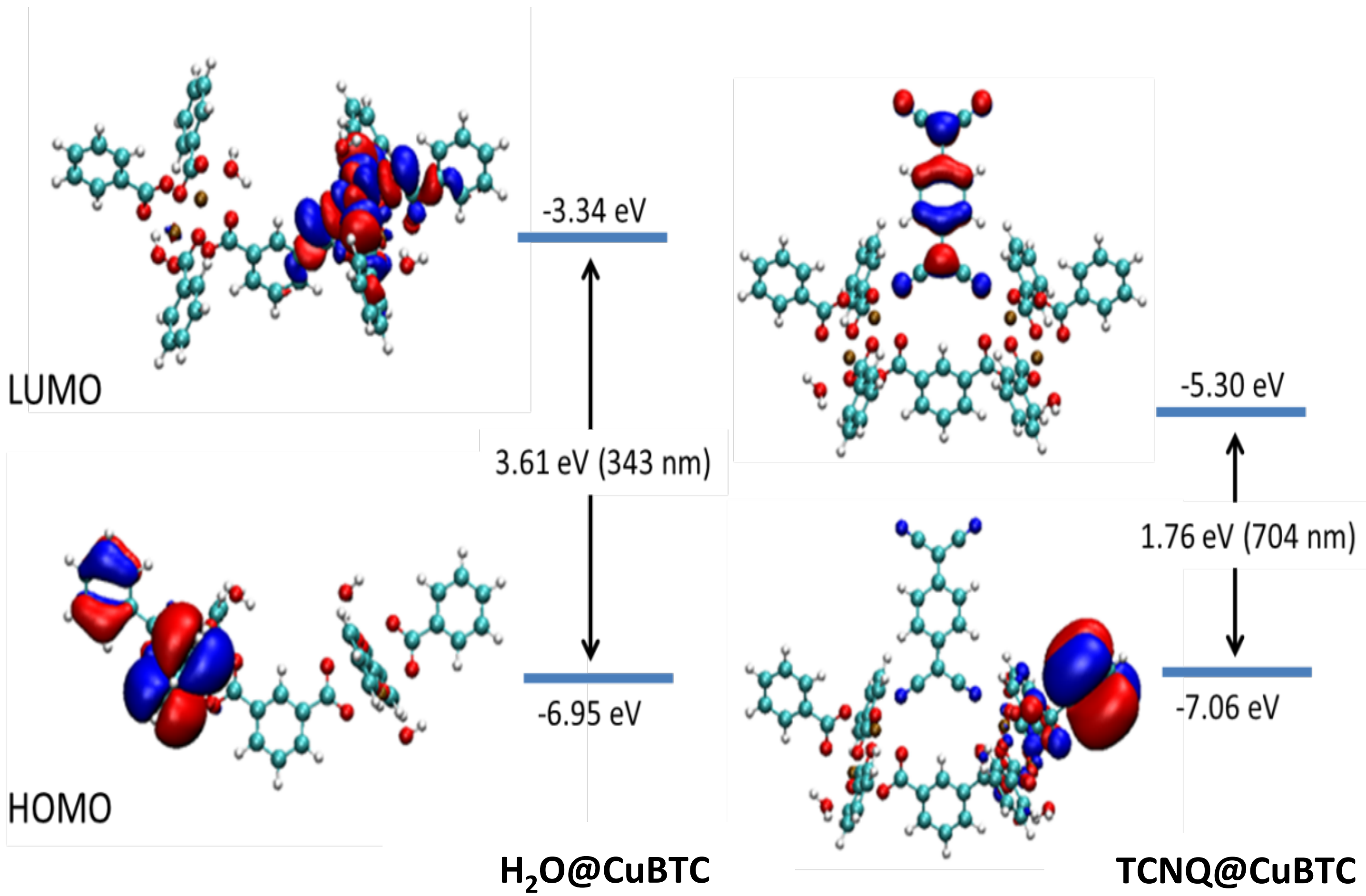
DFT: Cu(II) dimers linked by TCNQ





Continuous TCNQ@CuBTC pathway is achievable with 4 TCNQs
Experimental loading = 8 TCNQs/unit cell → two continuous pathways are possible

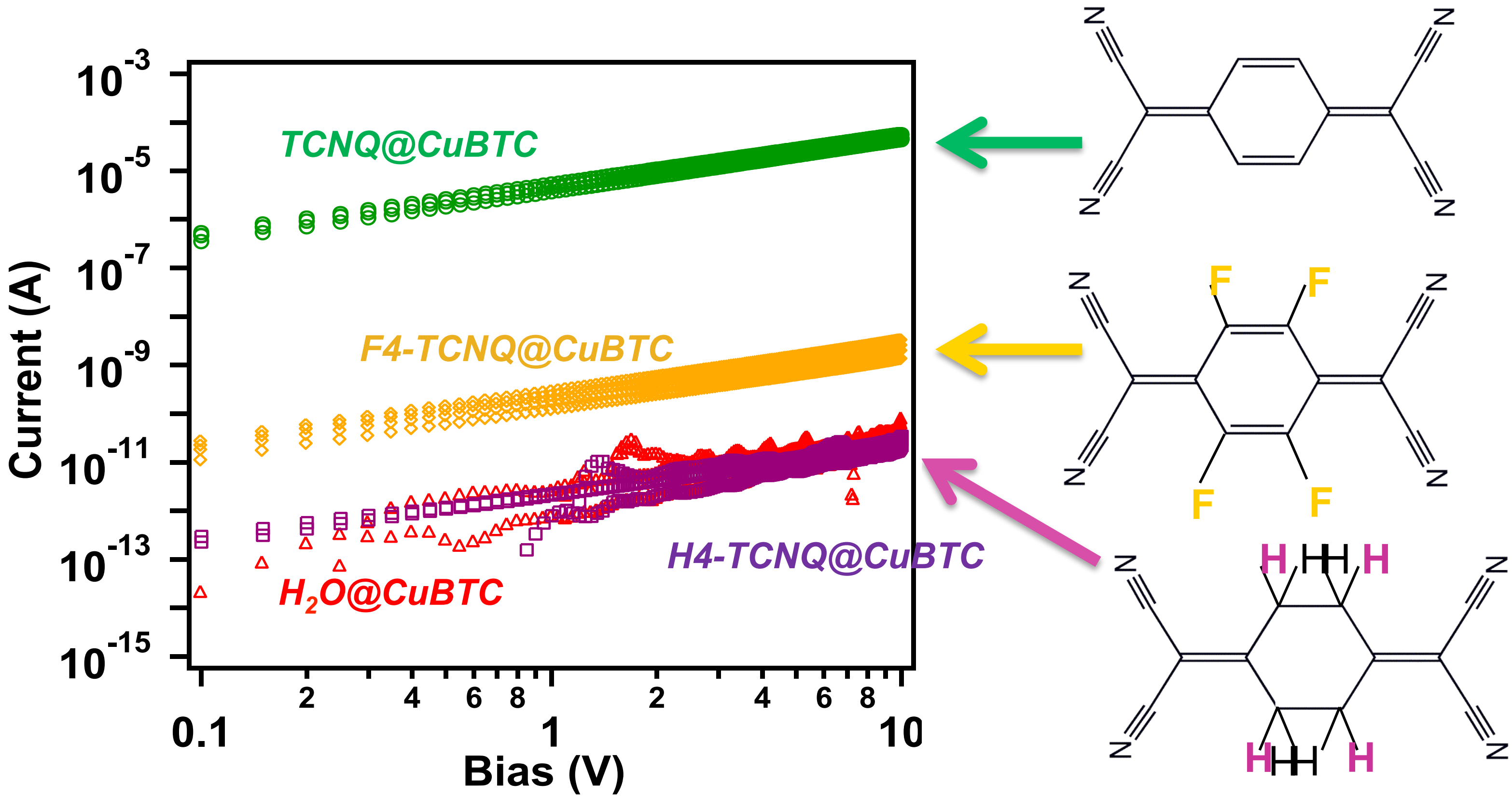
Bridging TCNQ molecules create new charge transfer states



DFT/PBEsol calculations

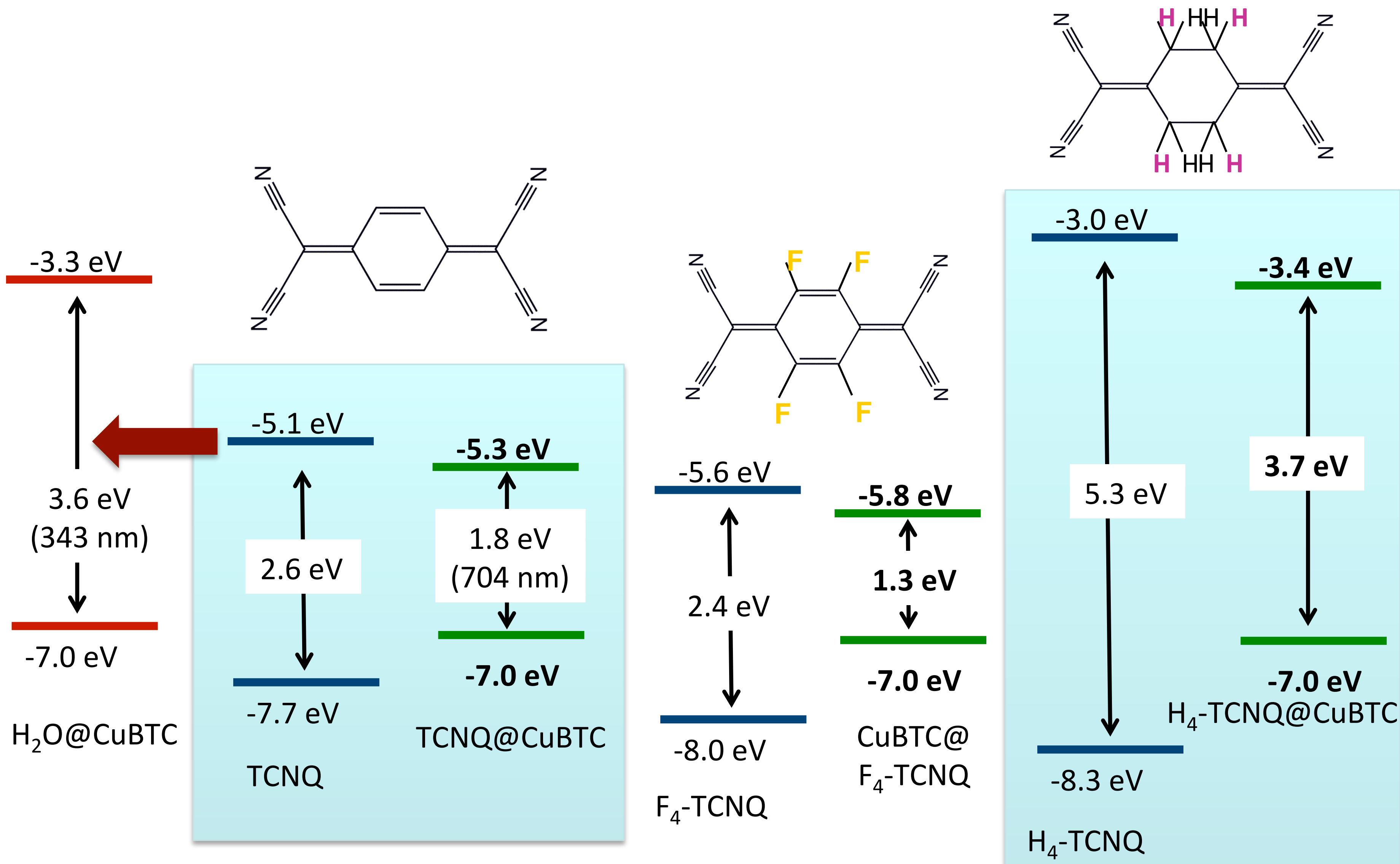
Guest aromaticity, electronegativity affect conductivity

Extended π network essential for conductivity

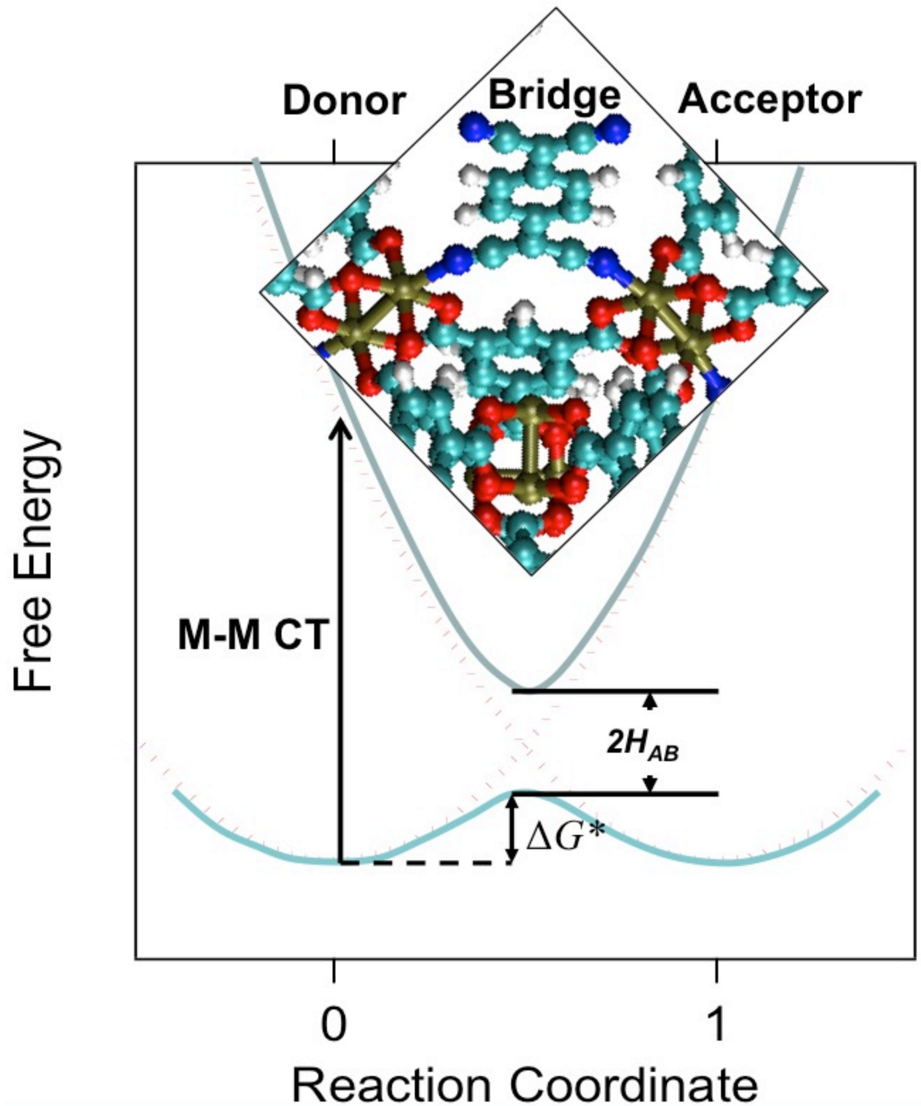


Cu-BTC band alignments: DFT/PBEsol calculations

Effect of fluorination and hydrogenation of TCNQ



TBCNQ increases coupling between neighboring Cu dimers → lowers barrier to charge transfer



Two-site model:
Donor-Bridge Acceptor

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

H_{AB}-Electronic coupling matrix element

$$H_{AB} = \langle \Psi_A | H | \Psi_B \rangle$$

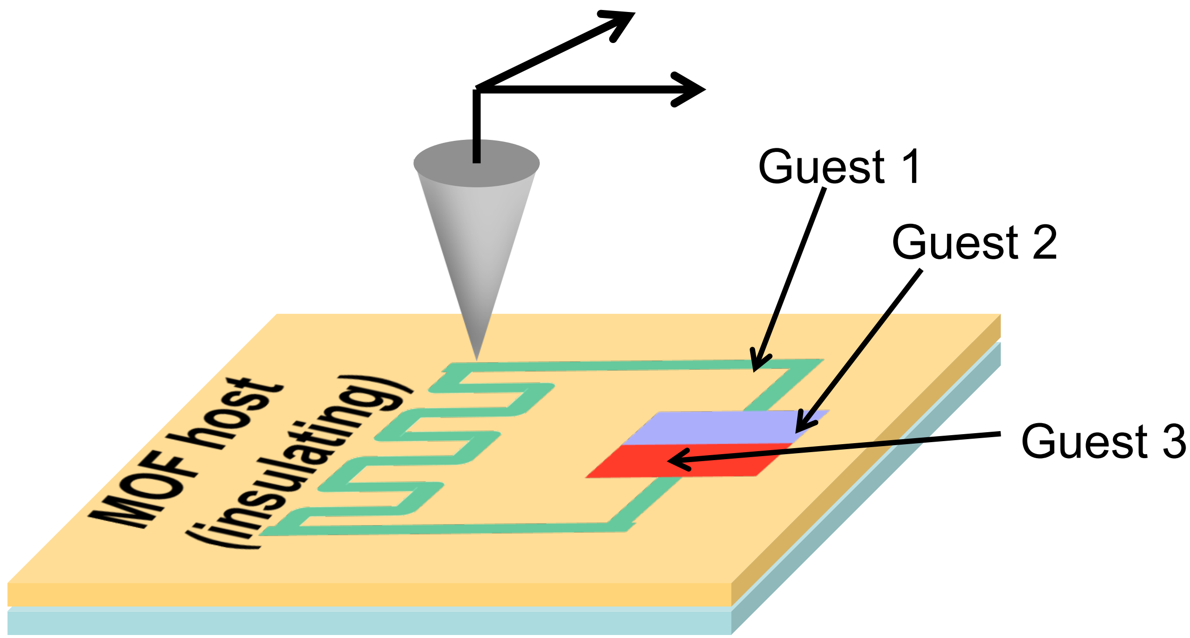
λ-Reorganization energy

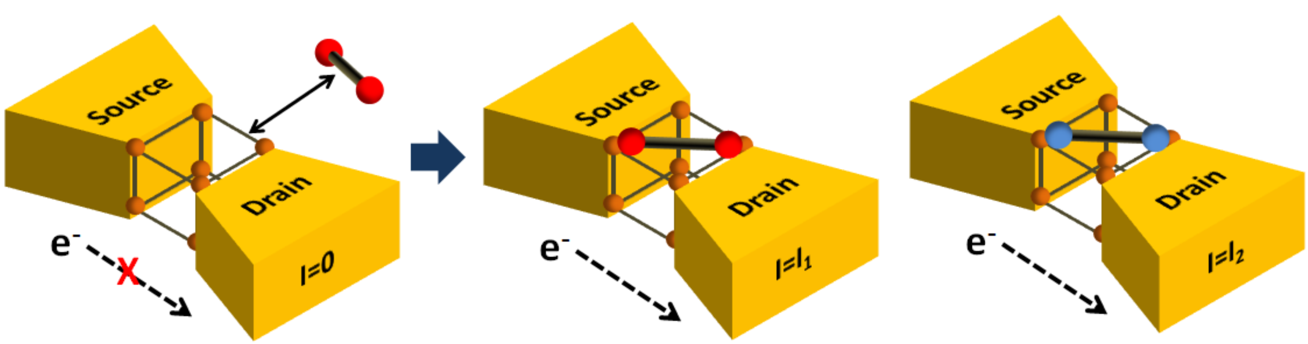
Computed by Constrained DFT:

H_4-TCNQ < F_4-TCNQ < TCNQ

H_{AB} = 0.19 eV < 1.03 eV < 2.32 eV

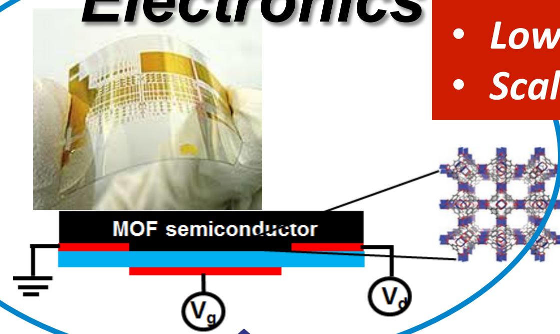
Vision for Molecule@MOF ICs, nanodevices



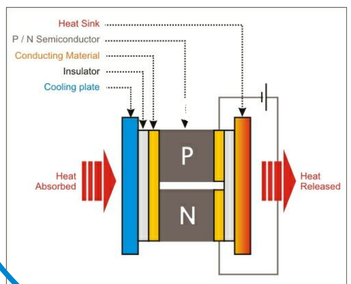


Electronics

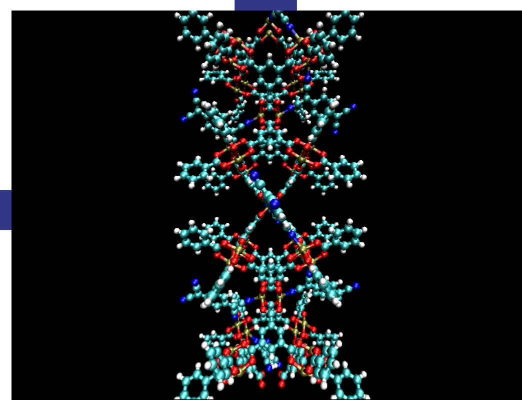
- *Chemically tunable*
- *Low cost, low-T deposition*
- *Scalable down to ~1nm (?)*



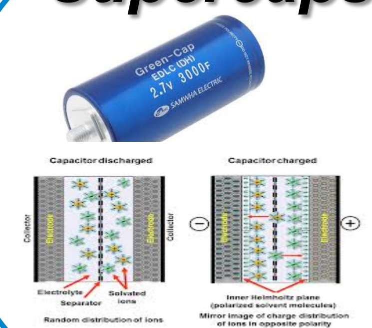
Thermoelectrics



- *Ultrahigh surface area*
- *Redox active centers*

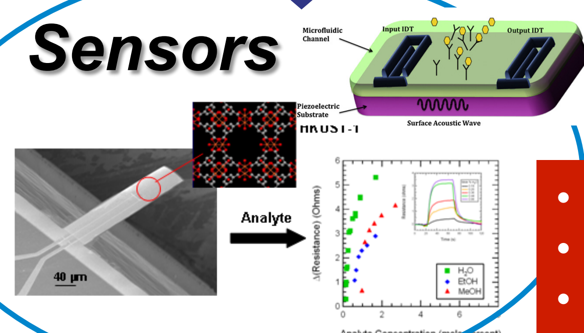


Supercaps



- *Ultrahigh surface area*
- *Redox active centers*

Sensors



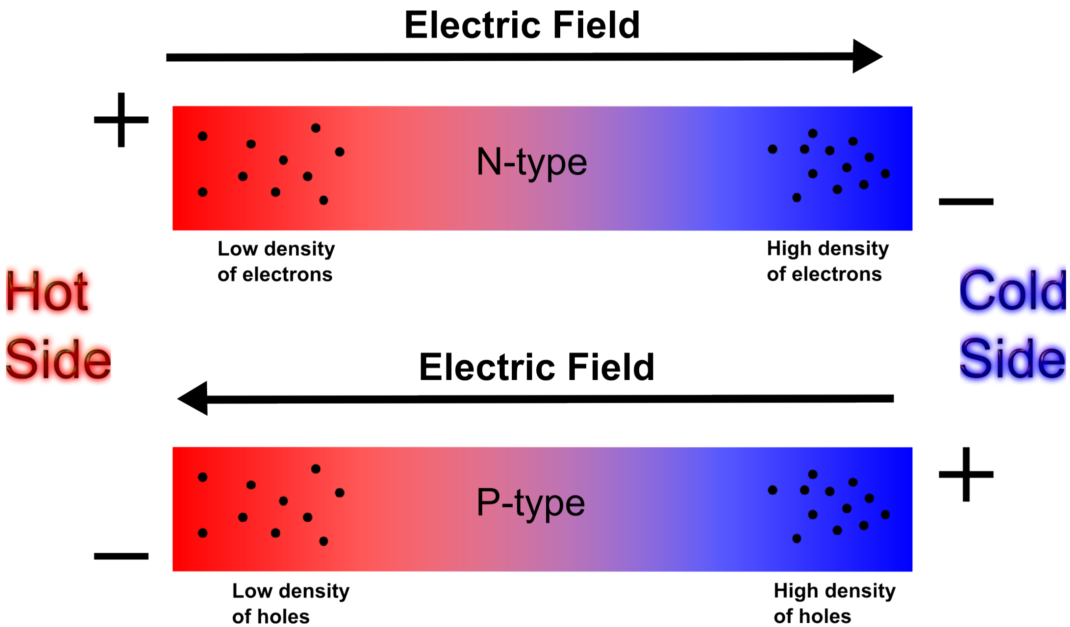
- *Multi-axis response*
- *Chemical specificity*
- *High surface area*

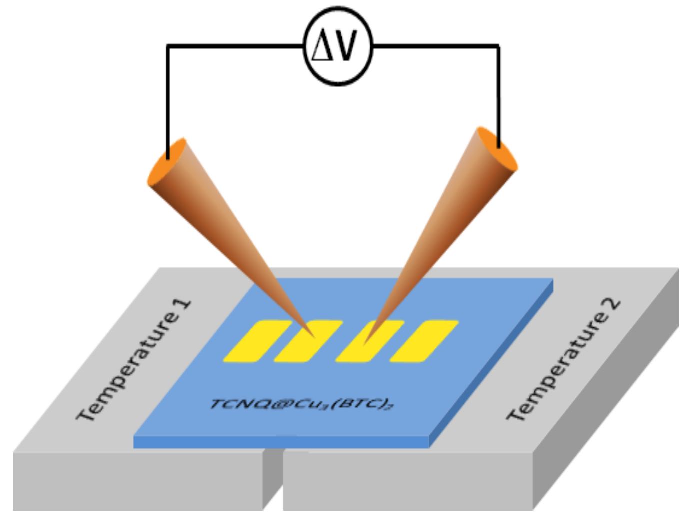
Conclusions

- MOFs are hybrid materials with ordered, chemically tunable porosity
- MOF thin films can be grown layer-by-layer from solution
- Conductivity of $Cu_3(BTC)_2$ tunable $10^{-8} \rightarrow 10^{-1}$ S/cm with TCNQ
- UV-Vis, IR indicate partial charge transfer
- Opportunities for tuning properties w/ molecule@MOF expanding

Backup Slides

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





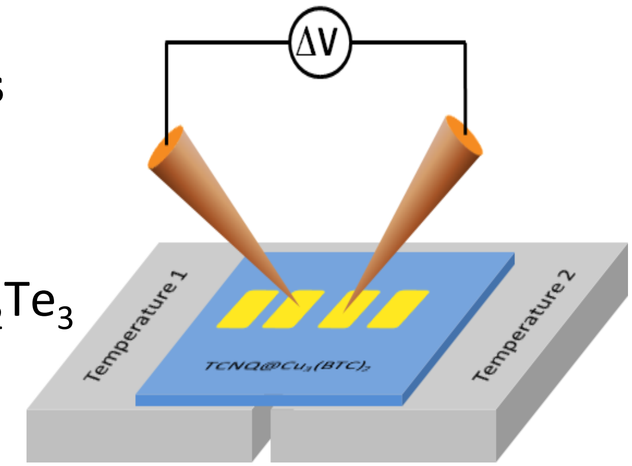
http://www.mn.uio.no/fysikk/english/research/projects/bate/thermoelectricity/

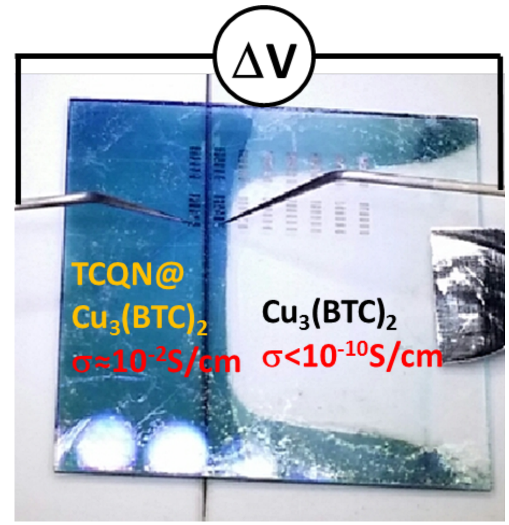
Thermoelectric measurements of TCNQ@$Cu_3(BTC)_2$

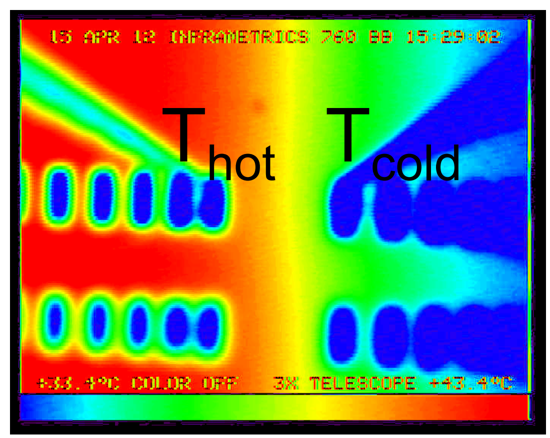
- **Majority carriers are holes**
- **<u>High Seebeck coefficient</u>**

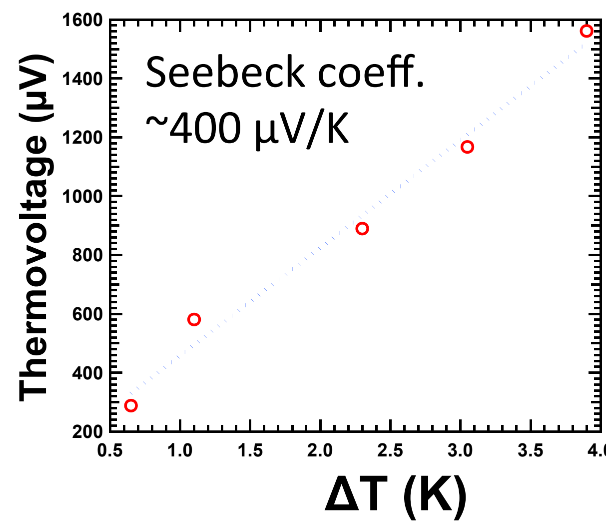
~400 µV/K vs 170 µV/K for Bi_2Te_3

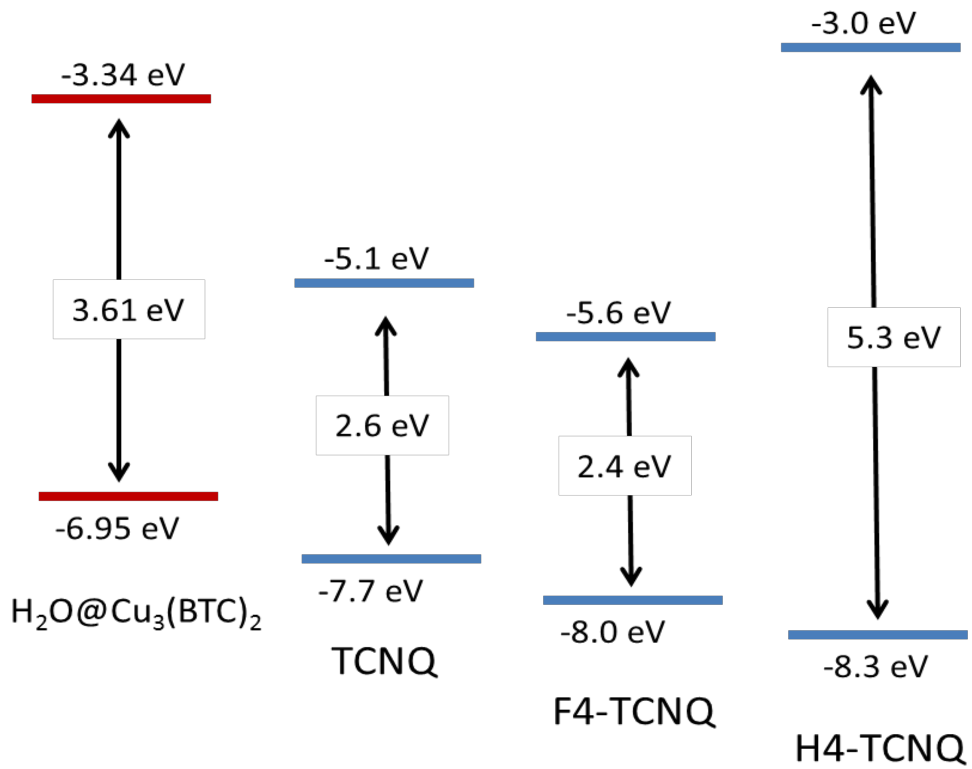
→ promising material for thermoelectrics







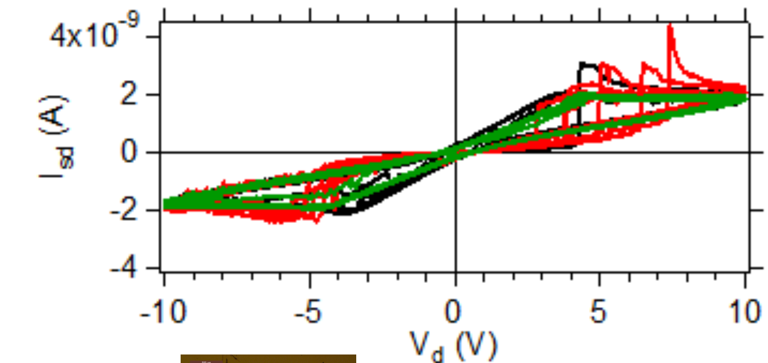




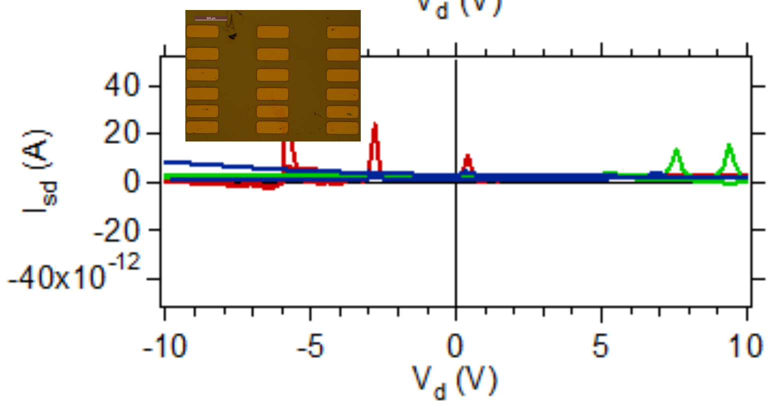
A schematic representation of the alignment of the HOMO/LUMO orbitals and bandgaps of H_2O@CuBTC, TCNQ, F4-TCNQ, and H4-TCNQ determined at the UB3LYP/VTZP level of theory.

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

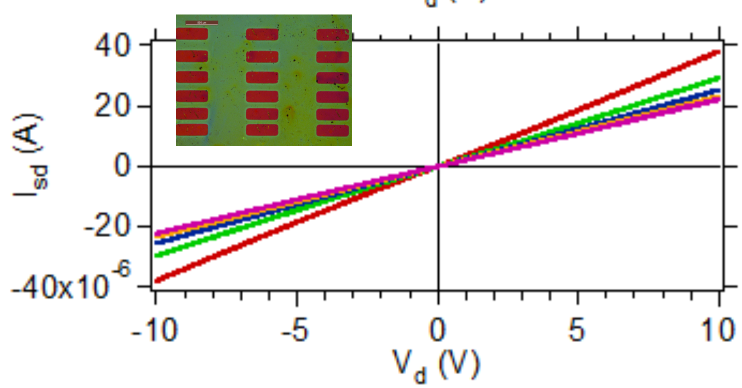
Sandia National Laboratories



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



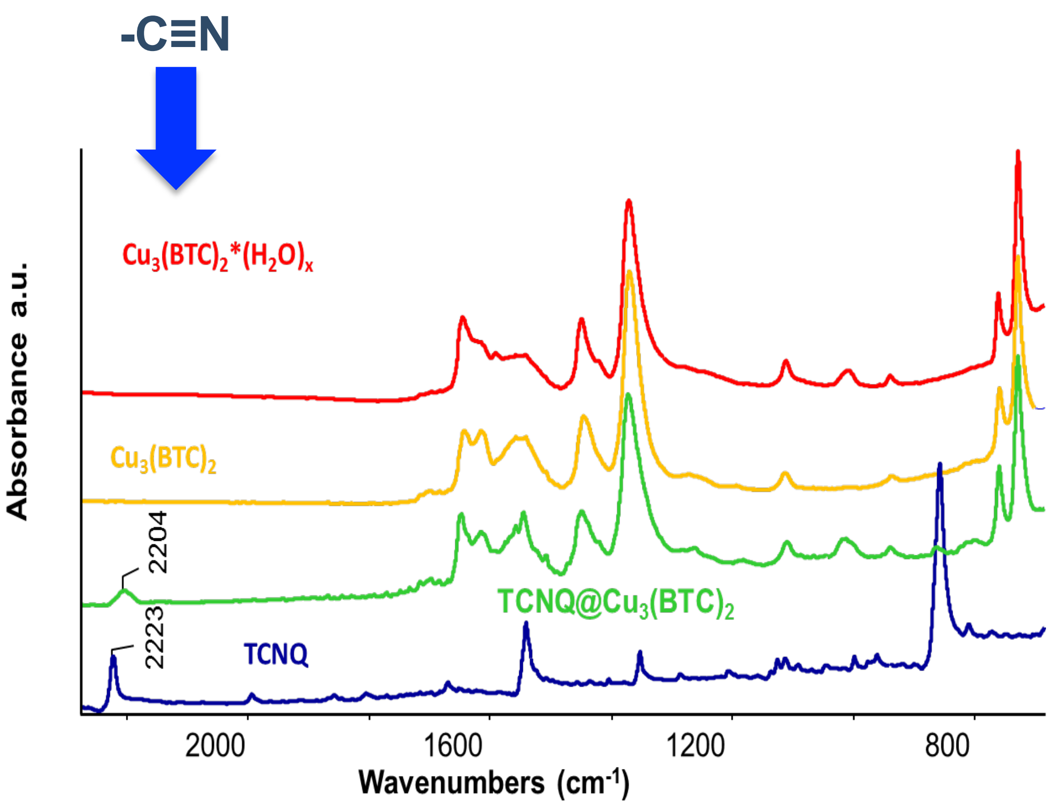
Activated, exposed to ambient: No measurable conductivity at 10 V (<10^{-12} A)

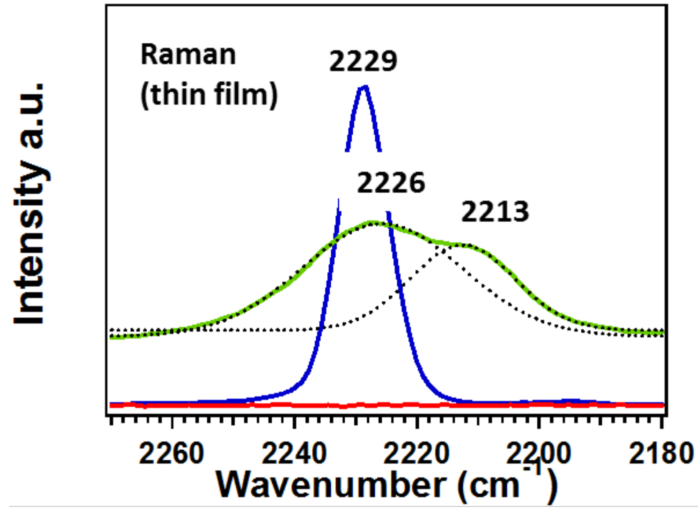


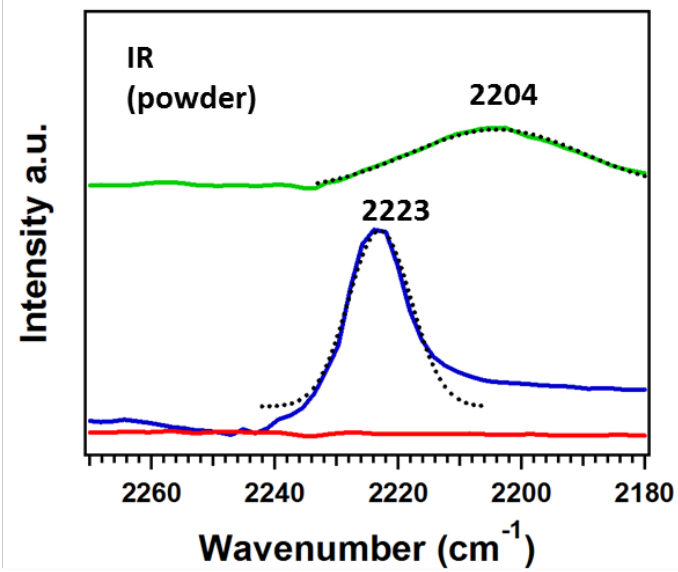
Infiltrated MOF (trace water): s~0.1 S/cm, ~10^8 increase

Vibrational spectra show shift of -C≡N indicates charge transfer

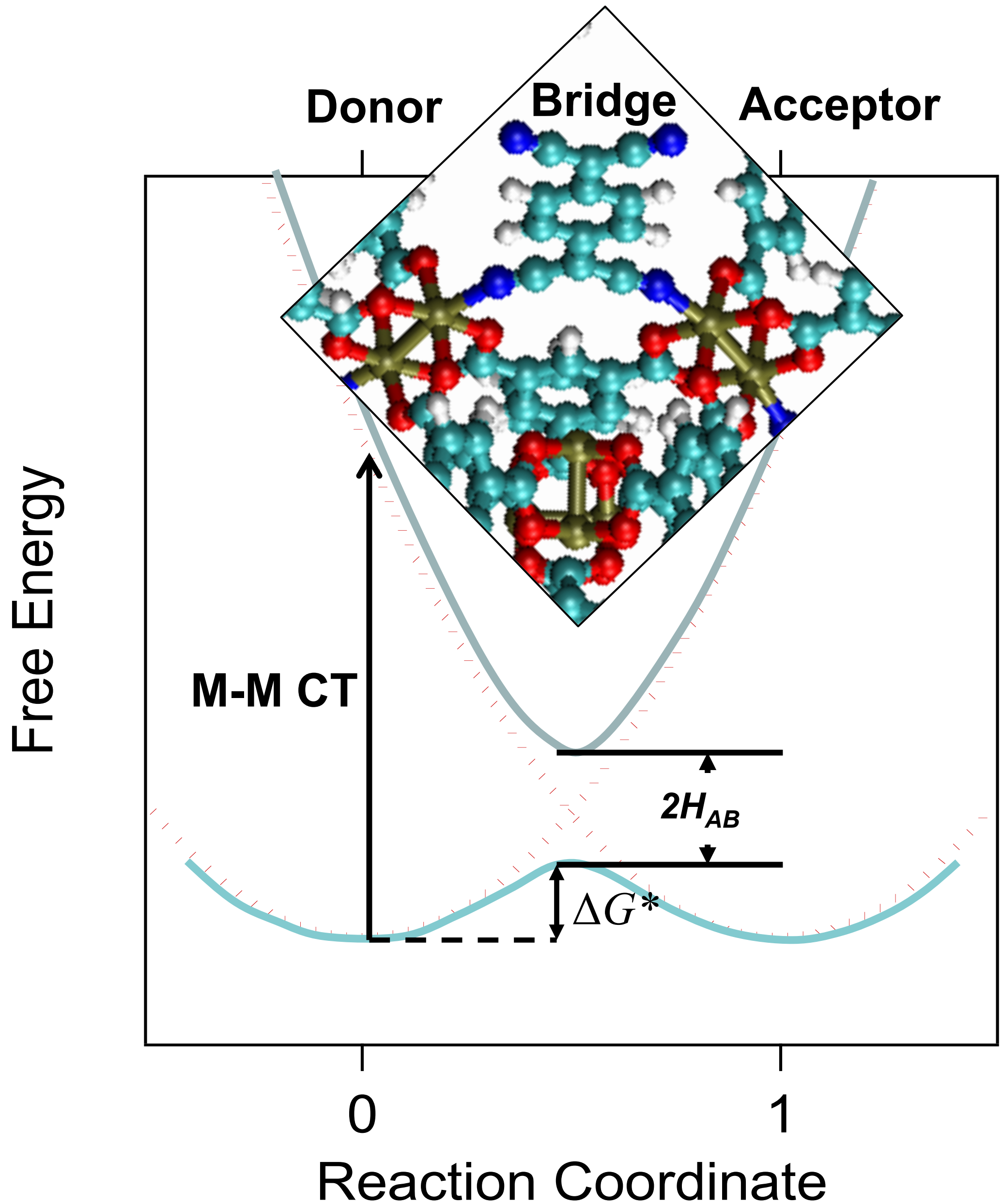
$$z = (\nu_o - \nu)/44cm^{-1} \approx \mathbf{0.43e}$$







Raman peak splitting indicates 2 inequivalent CN groups



Donor
Bridge
Acceptor
Free Energy
M-M CT
2H_{AB}
ΔG^*
0
1
Reaction Coordinate