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Molecule meets MOF: bridging the gap between organic and inorganic electronic materials

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SPIE Optics and Photonics 2014 Meeting
August 20, 2014

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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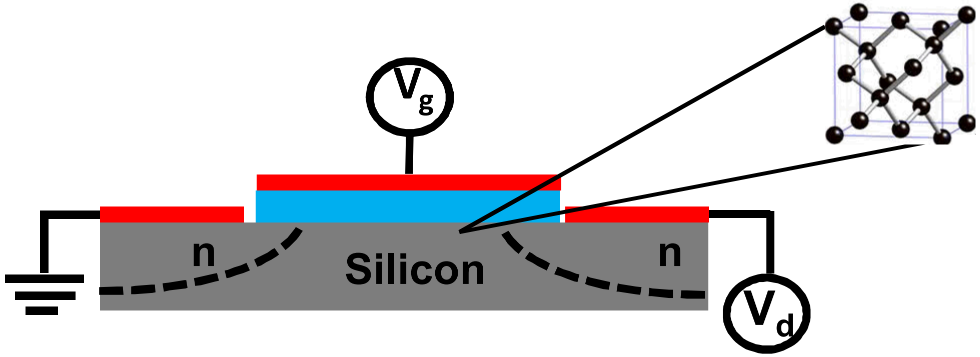
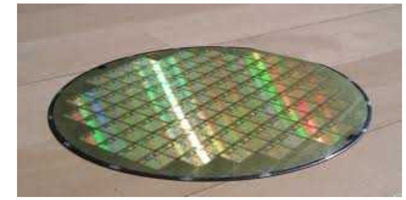
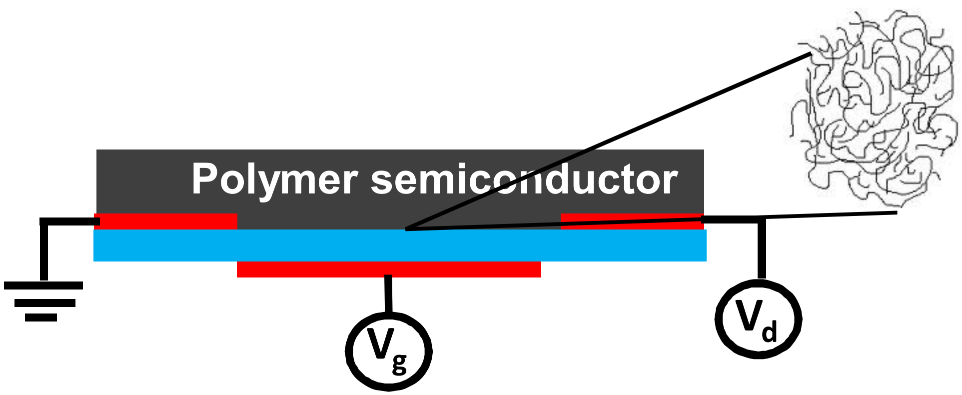


Crystalline inorganic semiconductors

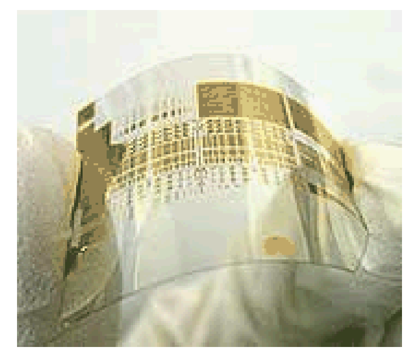
- High mobility
- Stability
- High cost
- Non-flexible
- Limited tailorability
- Radiation damage



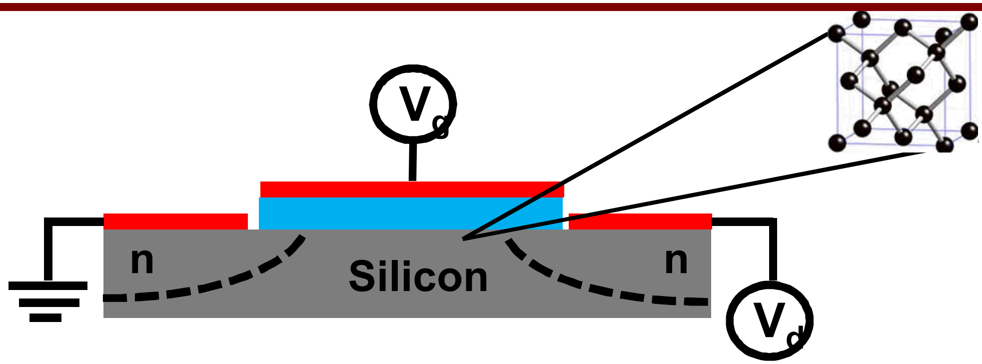


Disordered organic semiconductors

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



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



Crystalline inorganic semiconductor

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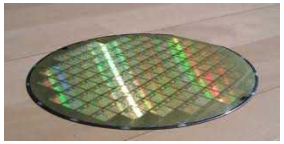

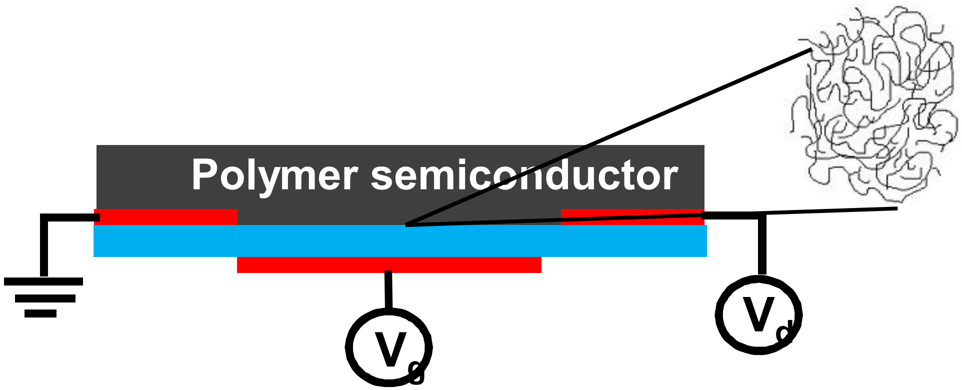

Disordered organic semiconductor

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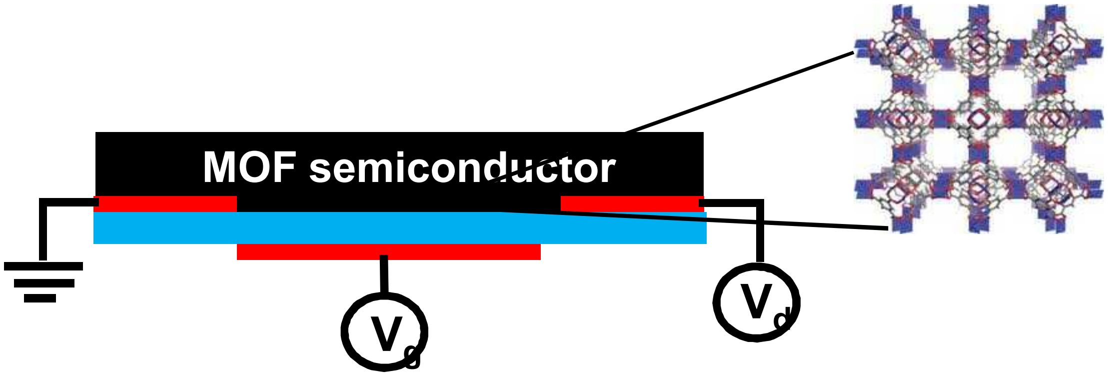


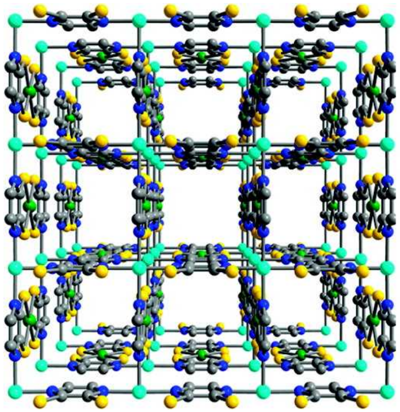
Crystalline MOF semiconductor

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

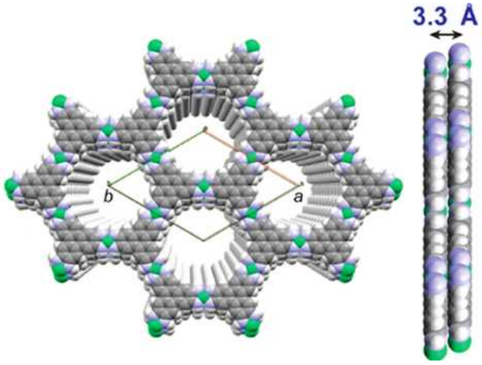
MOFs combine features of inorganic and organic materials

Electrically conducting porous MOFs are rare

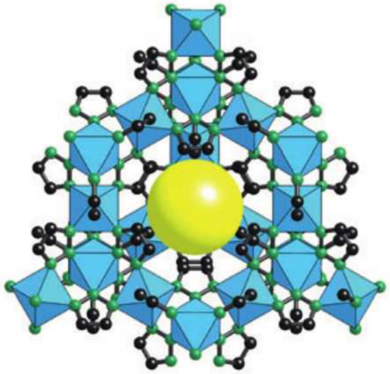
- p-type Cu-Ni Dithiolene MOF
- MET-3 (Fe-triazolate MOF)
- Mn(thiophenol) MOF: (−Mn−S−)∞ chains
- Metal-Organic Graphene analogues (MOGs)



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

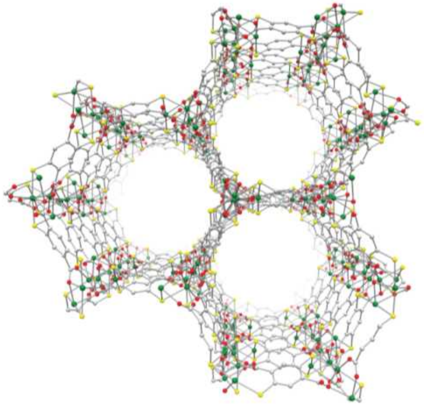


$Ni_3(HITP)_2$ MOG
D. Sheberla et al.
JACS 2014 ASAP



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

Cu-TCNQ is a well-known conducting coordination polymer

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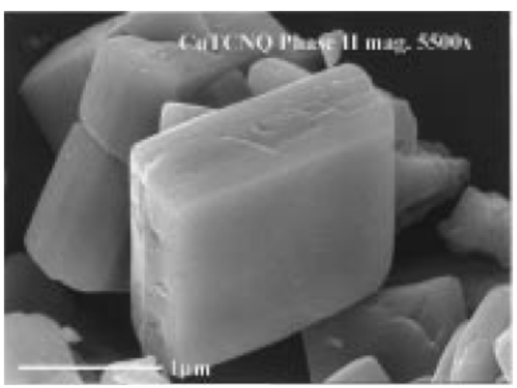
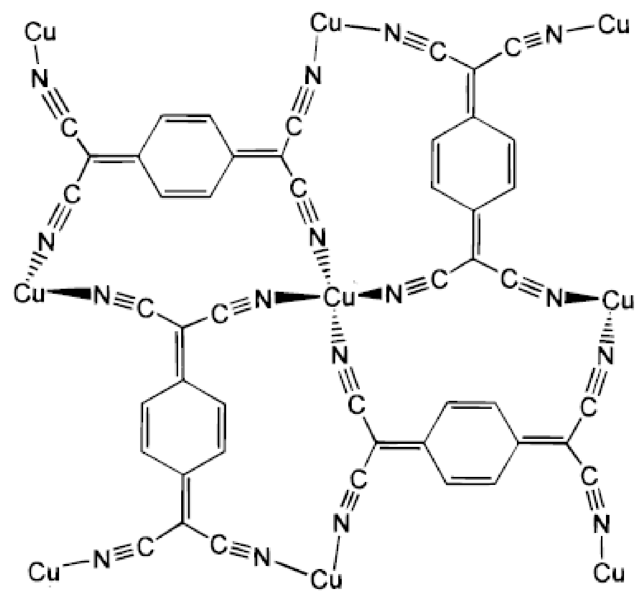
144 *Inorg. Chem.* **1999**, *38,* 144−156

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

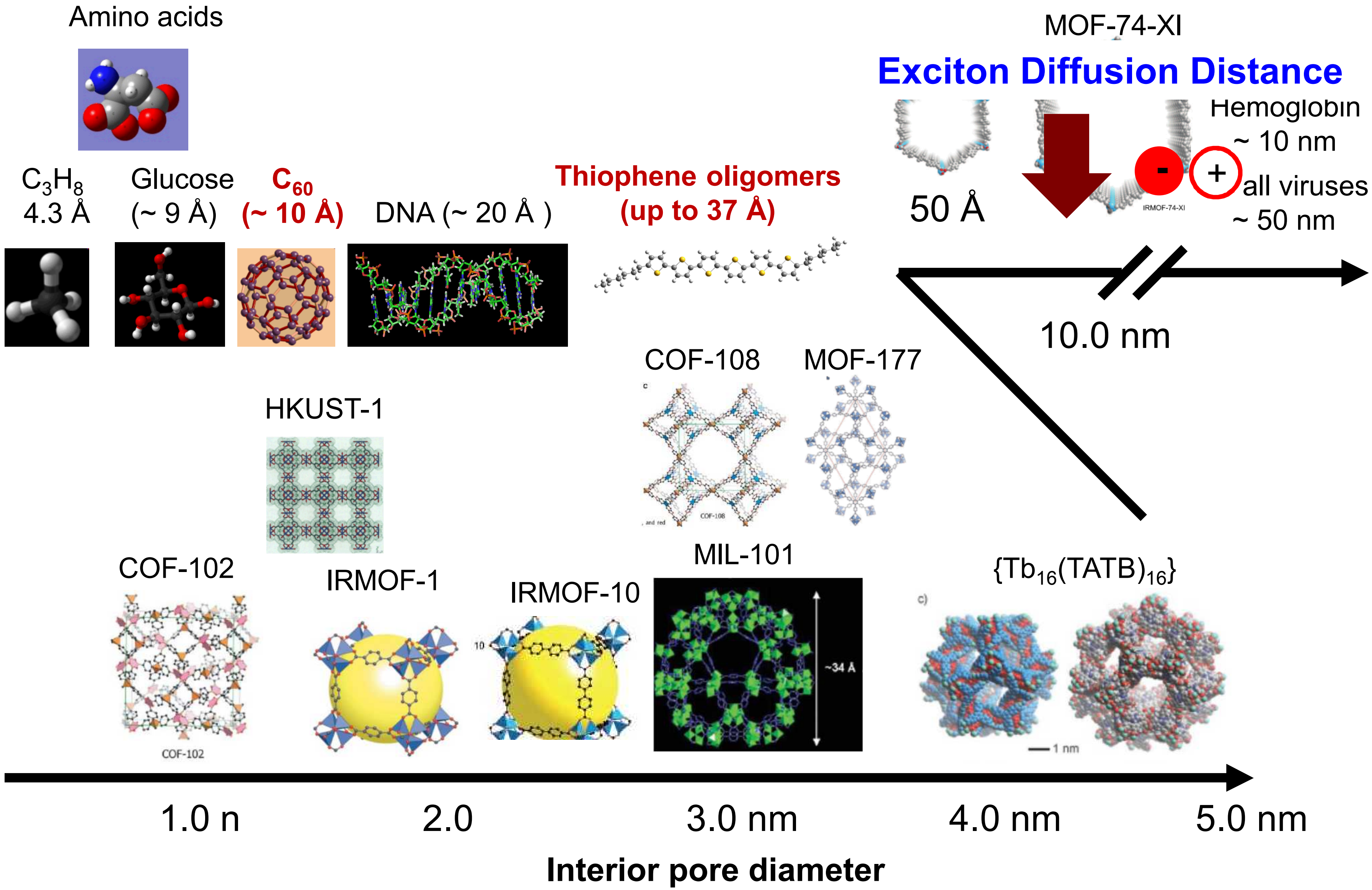
Robert A. Heintz,† Hanhua Zhao,† Xiang Ouyang,† Giulio Grandinetti,† Jerry Cowen,‡ and Kim R. Dunbar*†

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

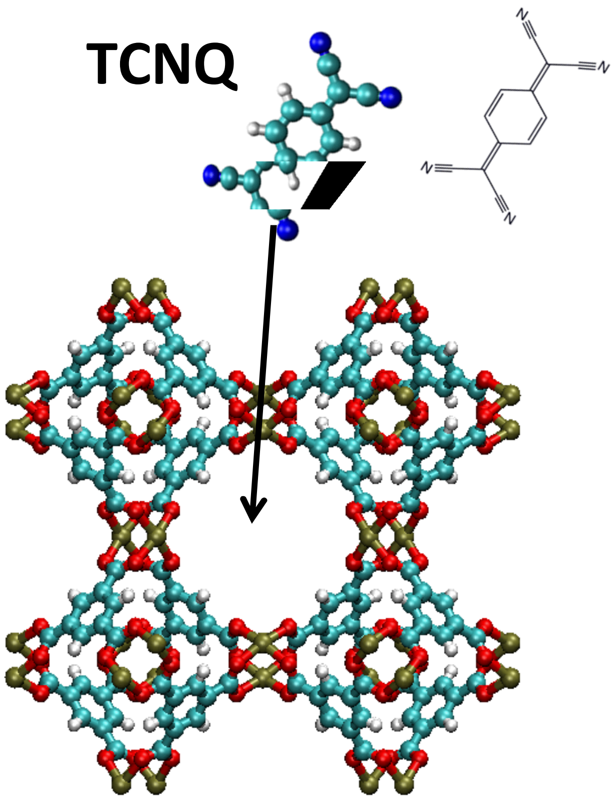


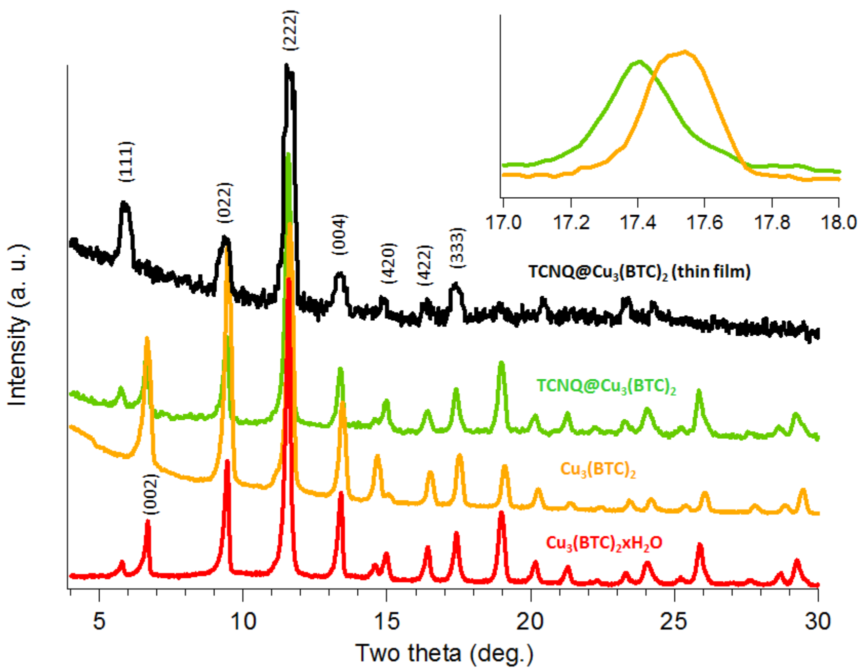


Guest molecule + MOF → ordered, tunable platform for controlling interactions at the nanoscale



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





TCNQ loading: ~ 1 molecule/large pore

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

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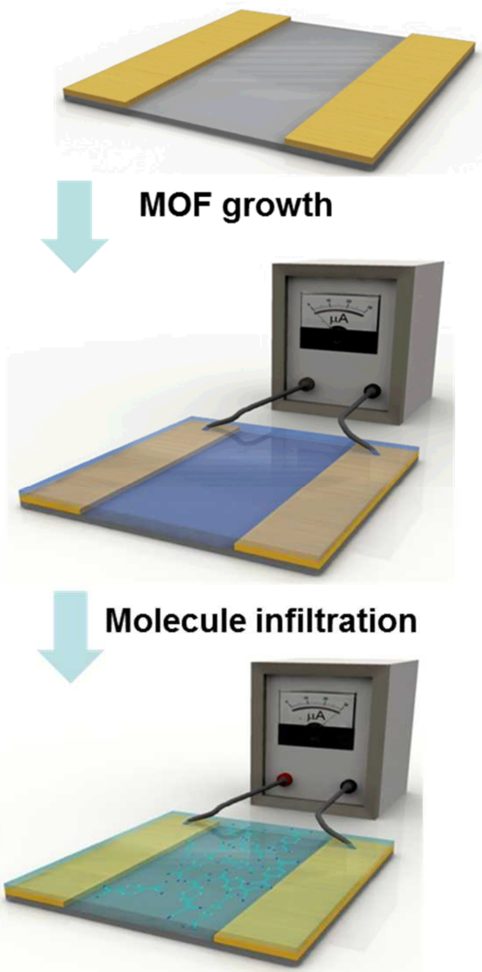
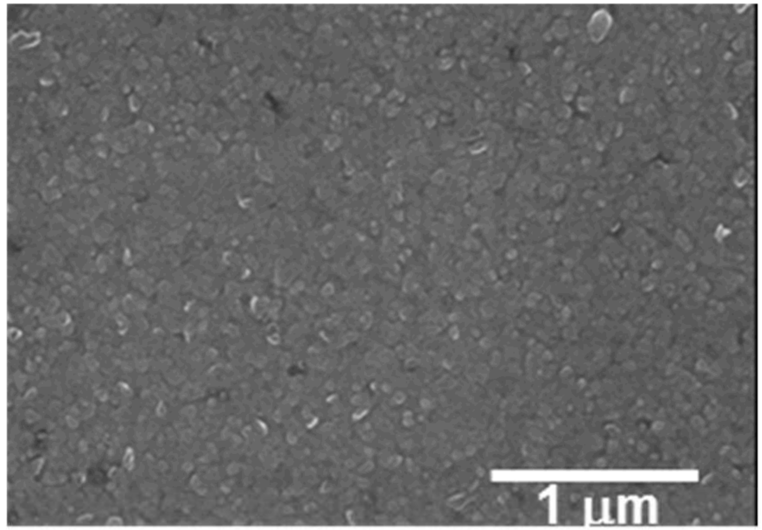
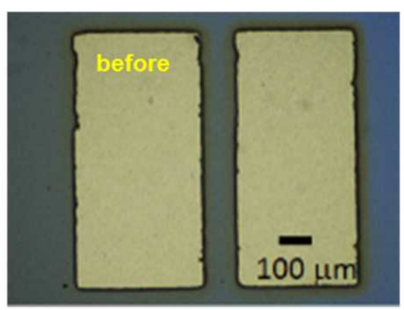
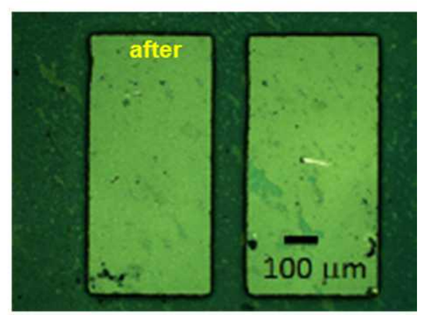


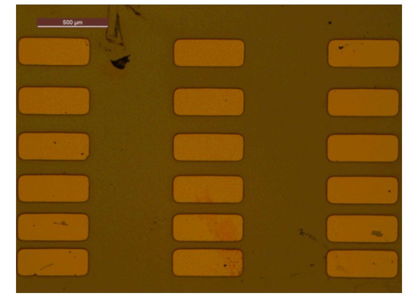
MOF film grown by layer-by-layer method



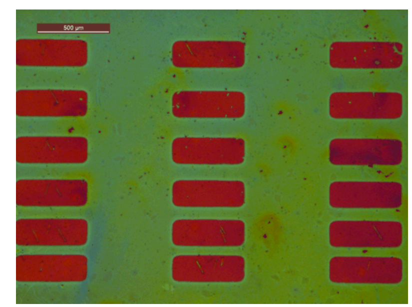




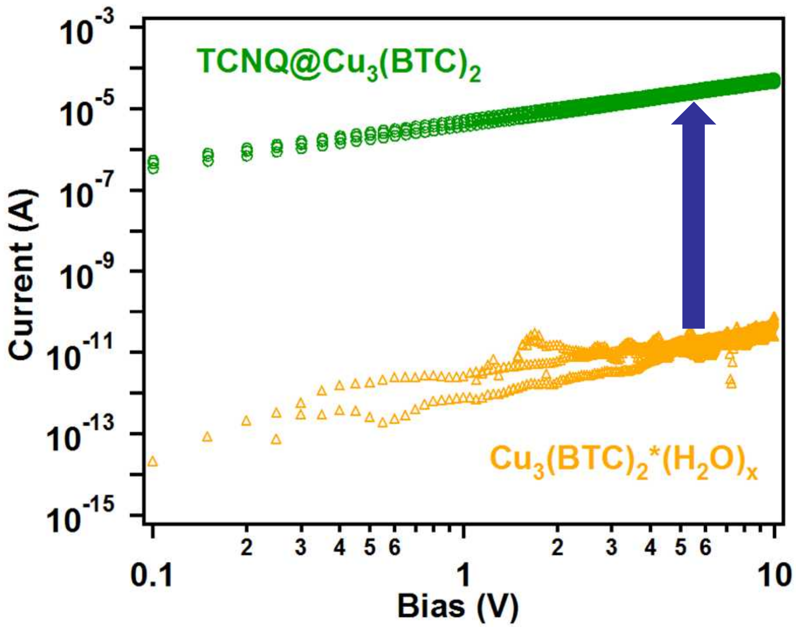
MOF film on SiO_x with Pt electrodes

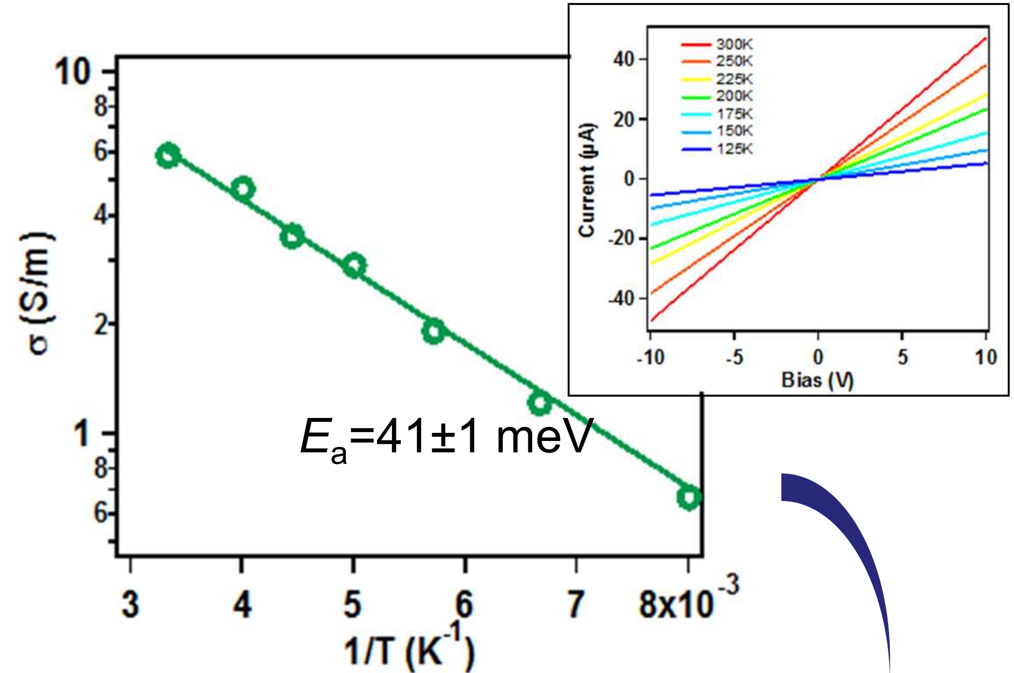


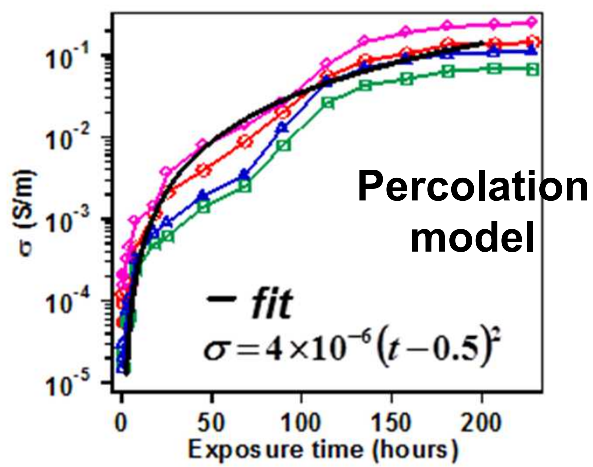
MOF film + TCNQ

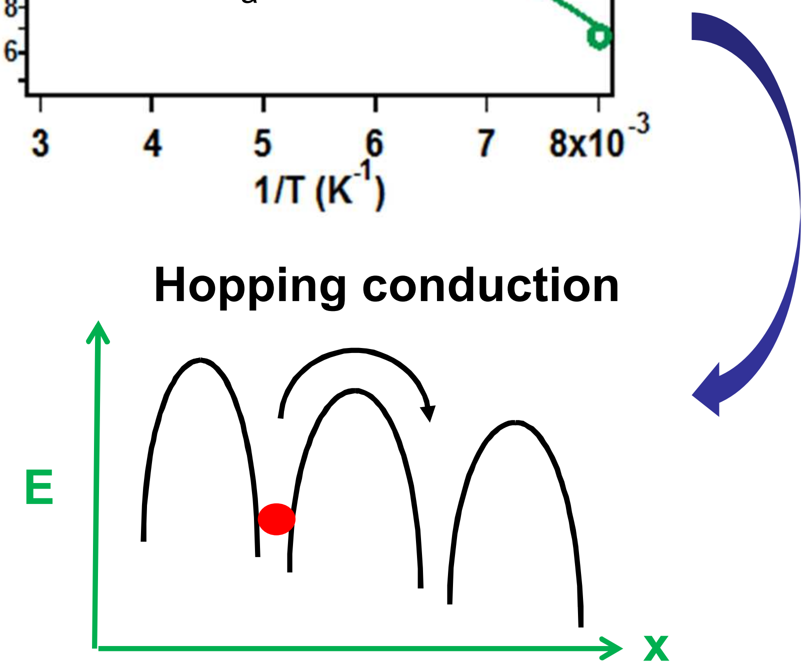


… and >10^7 increase in conductivity, air stable > 1 year









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

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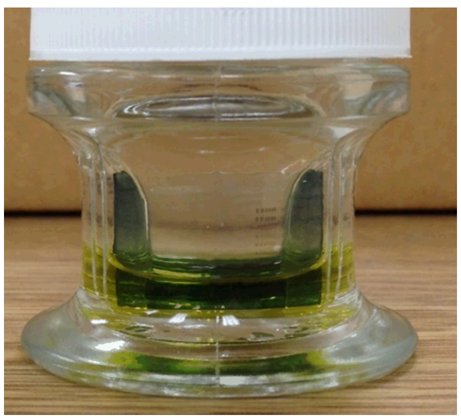
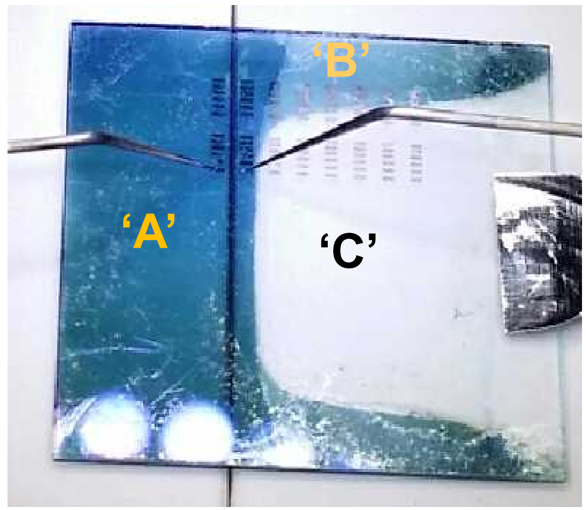
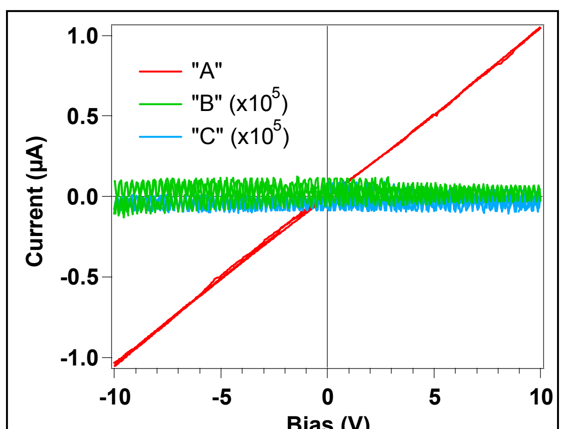
Patterned substrate immersed in TCNQ solution

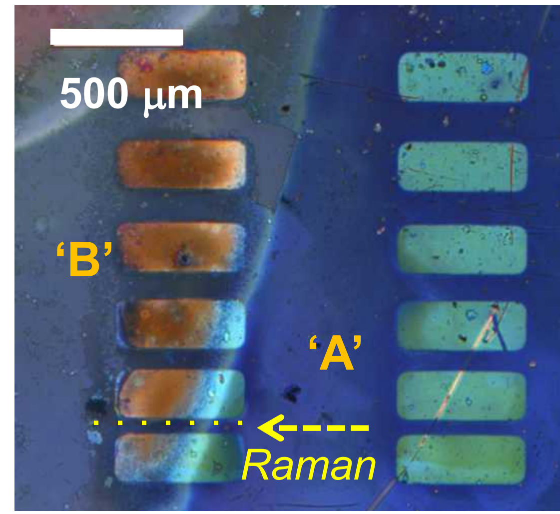


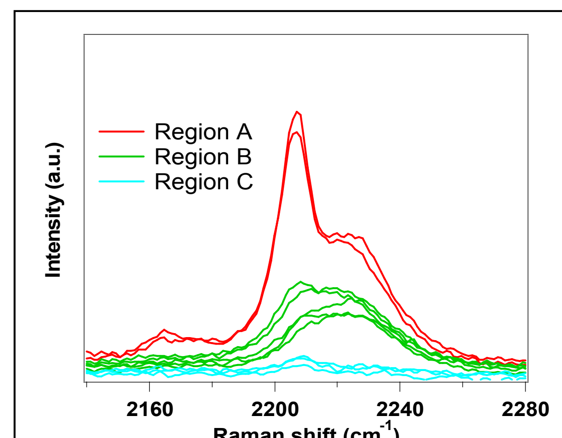
Conductivity





Raman spectrum





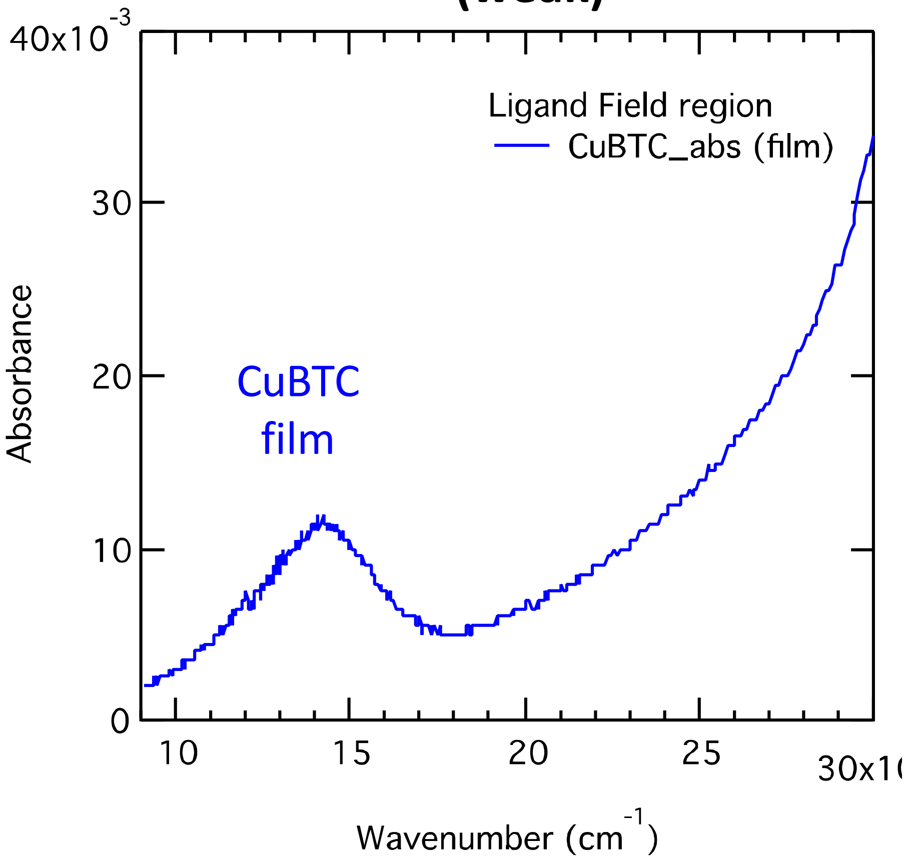
$TCNQ@Cu_2(BTC)_3$ exhibits strong new absorption bands

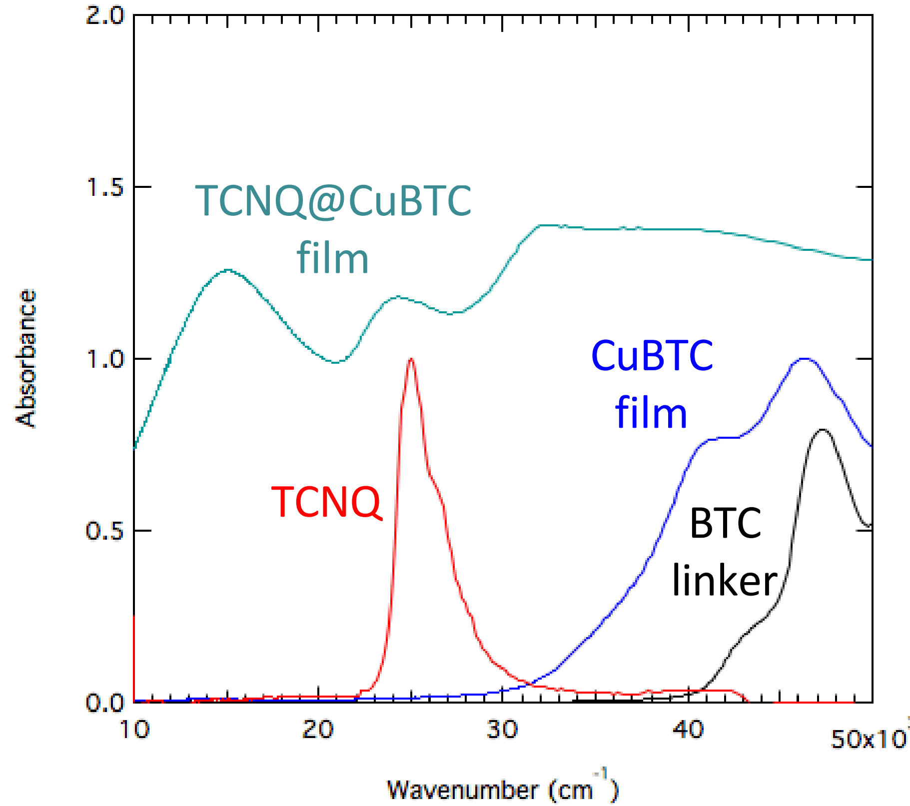
$H_2O@Cu_2(BTC)_3$

Cu(II) d-d transitions (weak)

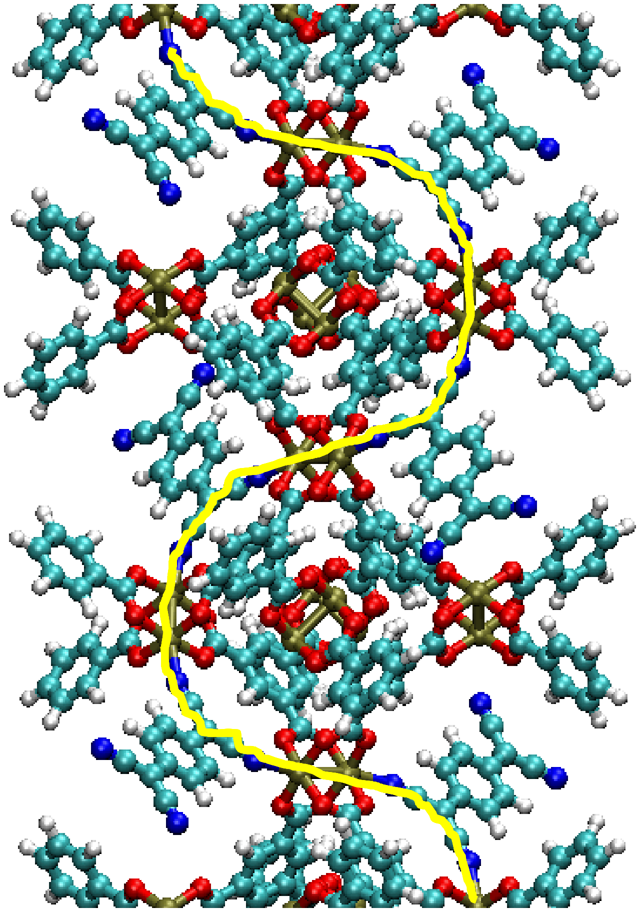
$TCNQ@Cu_2(BTC)_3$

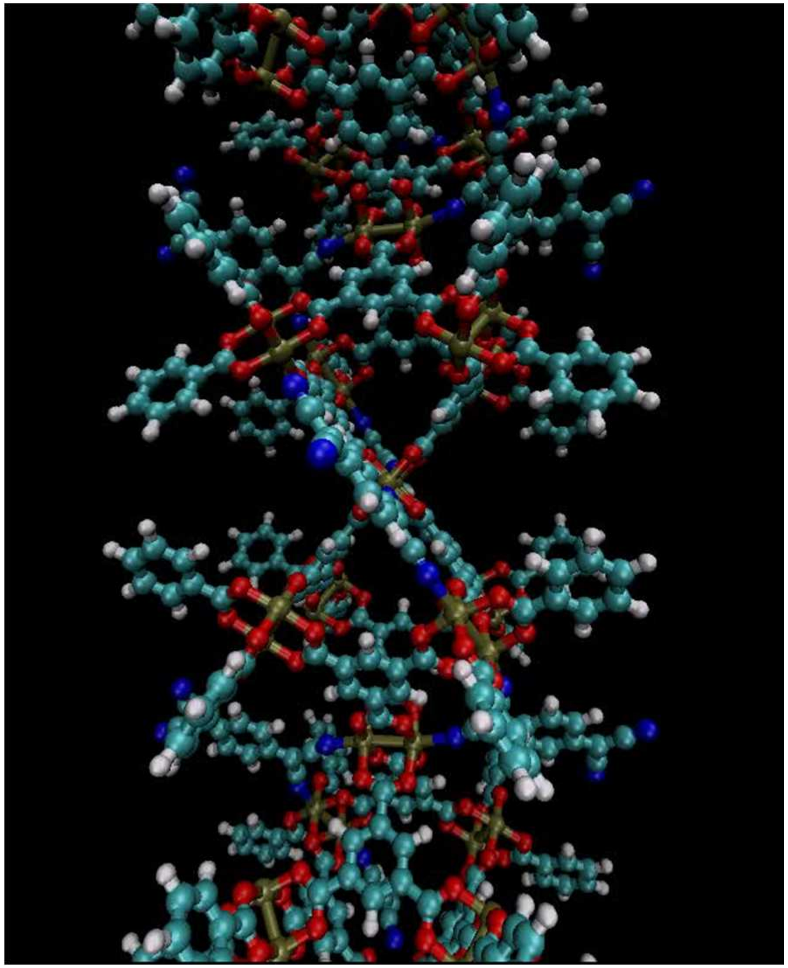
Charge transfer transitions





DFT: Cu(II) dimers linked by TCNQ

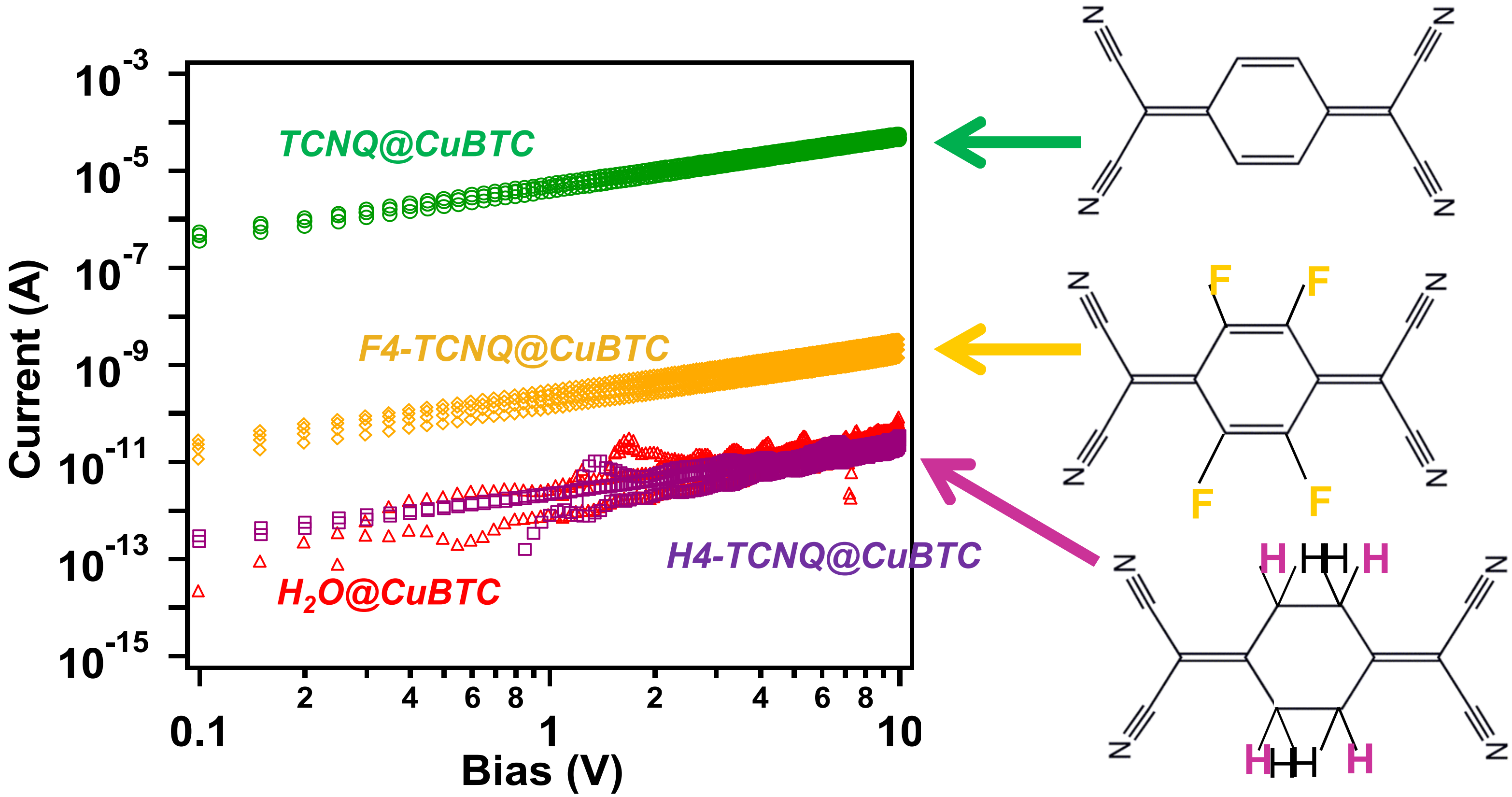




Continuous TCNQ@CuBTC pathway is achievable with 4 TCNQs
Experimental loading = 8 TCNQs/unit cell → two continuous pathways are possible

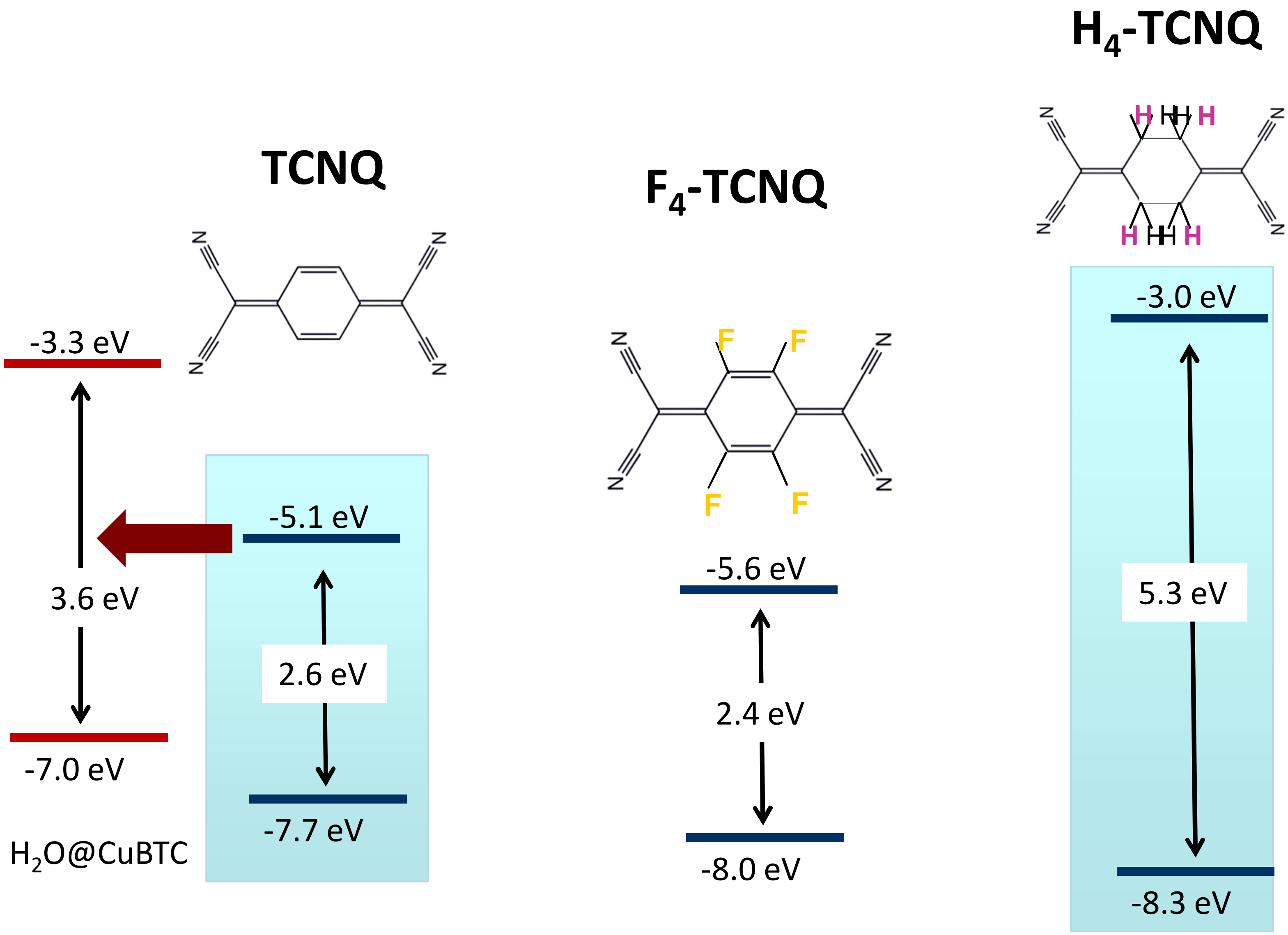
Guest aromaticity, electronegativity affect conductivity

Extended π network essential for conductivity

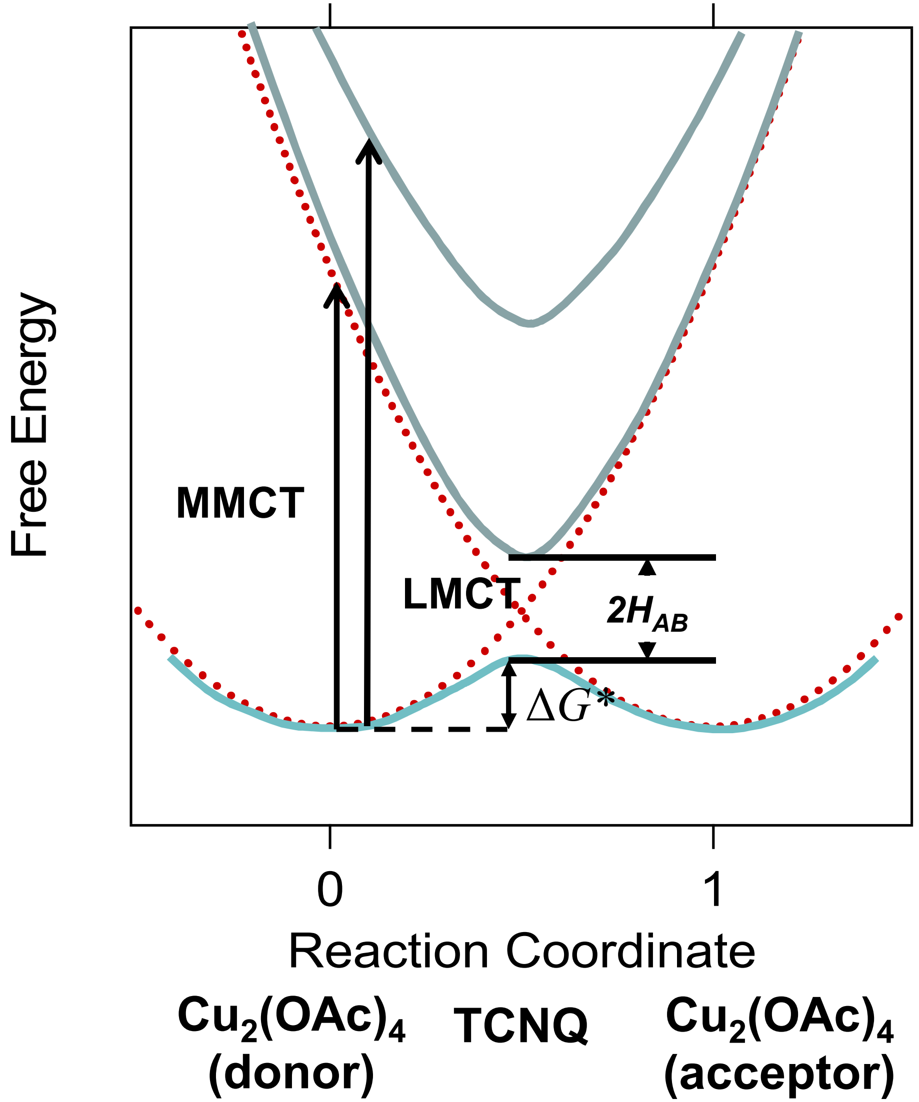


Cu-BTC band alignments: DFT/PBEsol calculations

Effect of fluorination and hydrogenation of TCNQ



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



Three-site model:
Donor-Bridge Acceptor

H_{AB}-Electronic coupling matrix element

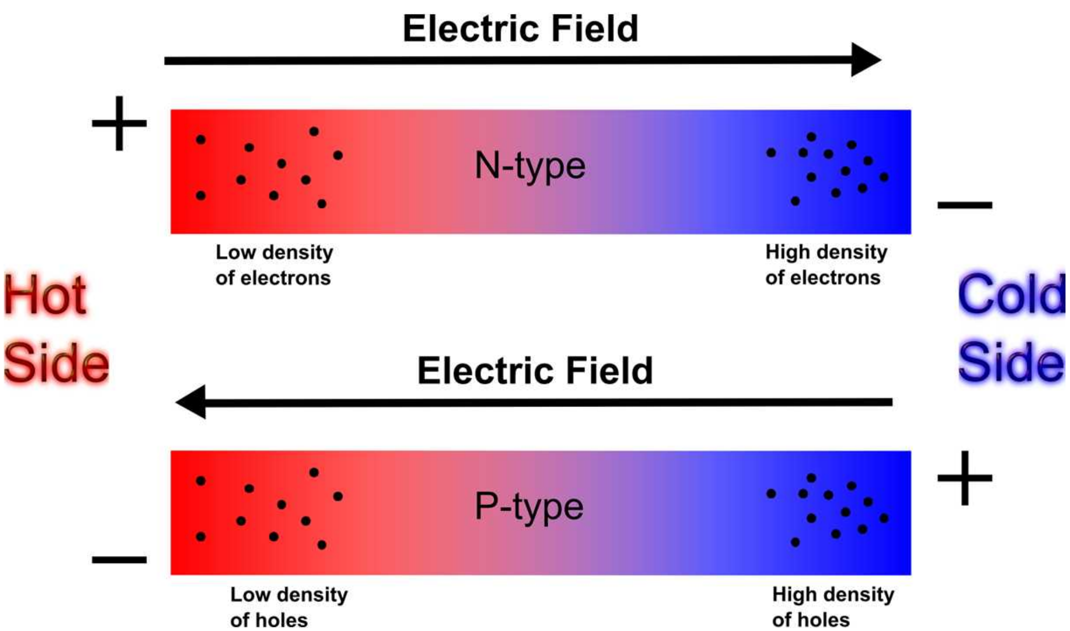
$$H_{AB} = \langle \Psi_A | H | \Psi_B \rangle$$

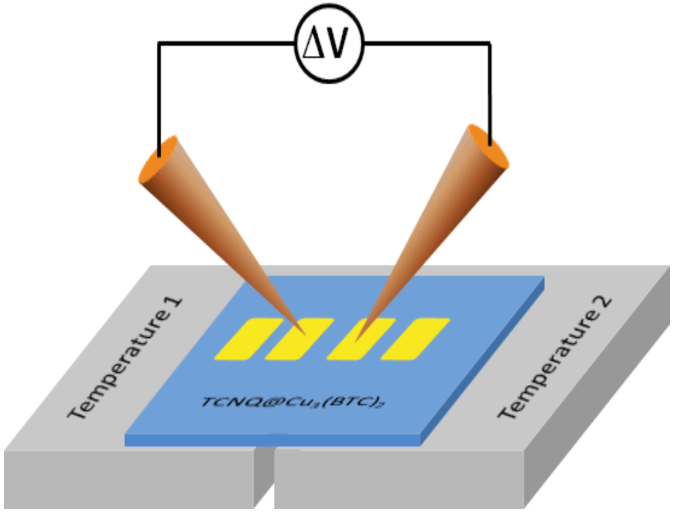
Computed by Constrained DFT:

H_4-TCNQ < F_4-TCNQ < TCNQ

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

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



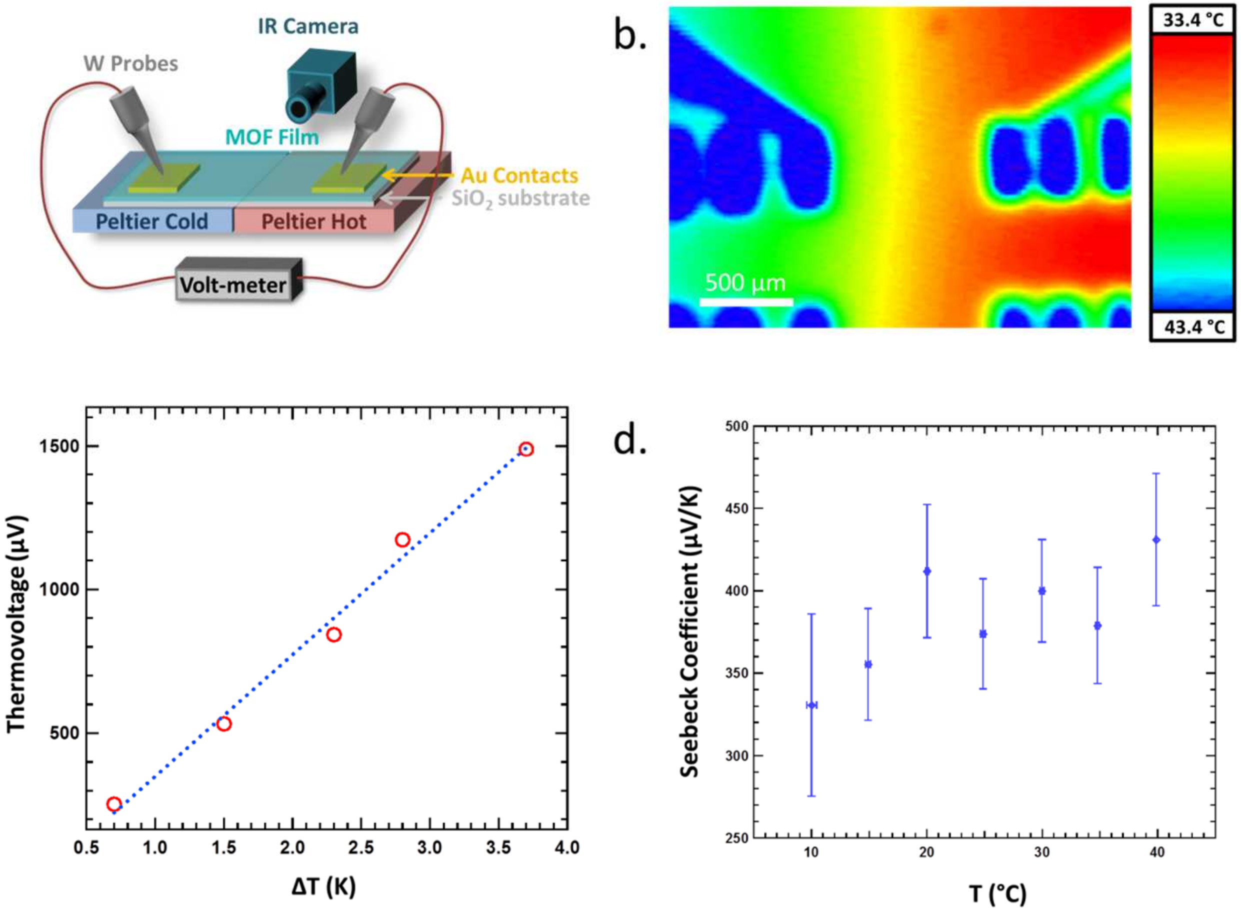


http://www.mn.uio.no/fysikk/english/research/projects/bate/thermoelectricity/

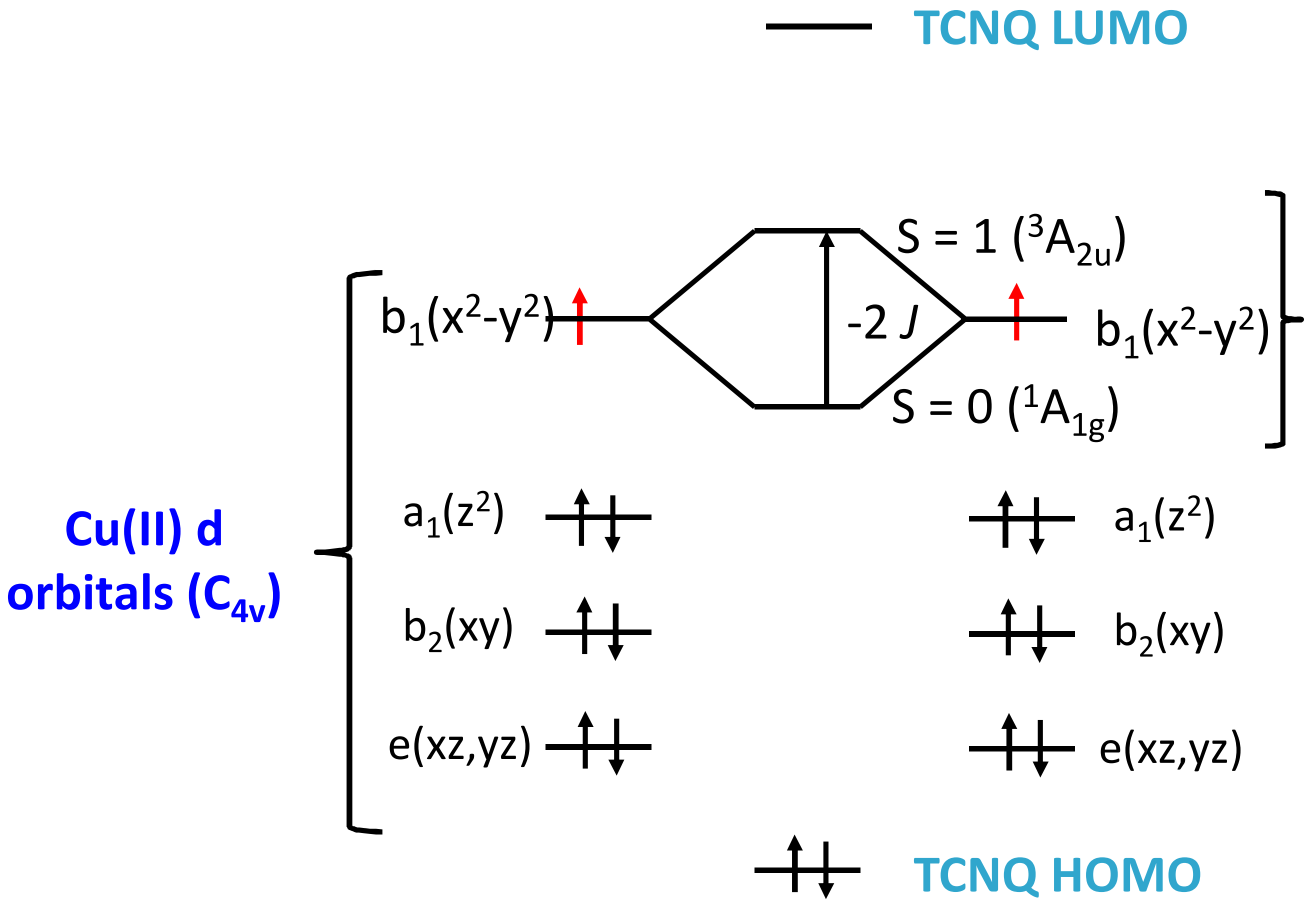
Thermoelectric measurements of $TCNQ@Cu_3(BTC)_2$

- **Majority carrier: holes**
- **<u>High Seebeck coefficient</u>**
  ~400 µV/K vs.
  170 µV/K for Bi_2Te_3

→ promising material for thermoelectrics



Electronic structure of TCNQ@$Cu_3(btc)_2$



MOF SBU ground state (~ D_{4h})

$-2J$ = ~ 340 cm^{-1}

= 0.042 eV

(same as Ea measured for conductivity)

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

Acknowledgements

Sandia National Laboratories

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- Catalin Spataru
- Vitalie Stavila
- Alec Talin
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SunShot U.S. Department of Energy

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LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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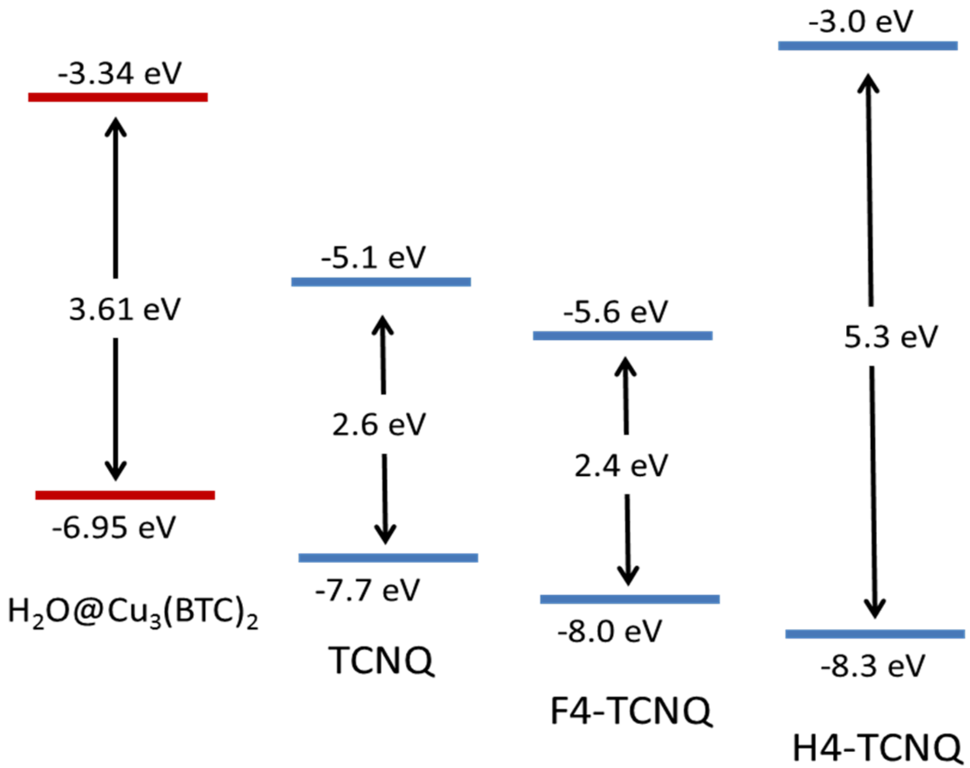
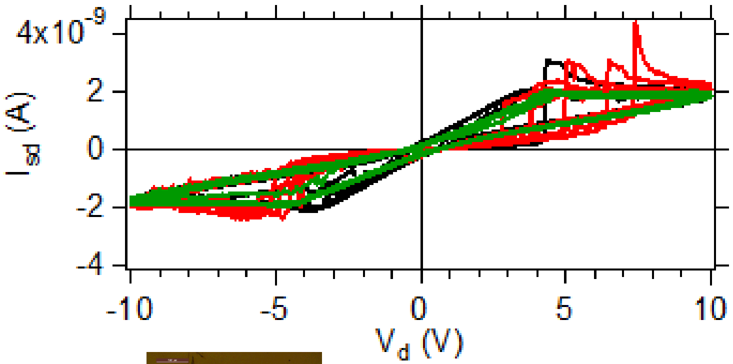
Backup Slides

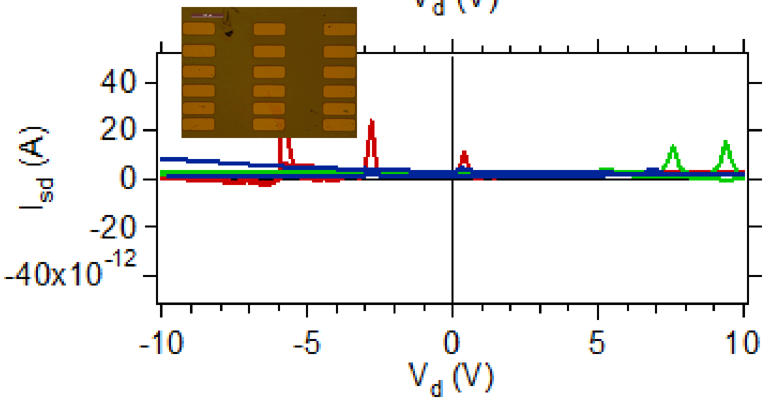


A schematic representation of the alignment of the HOMO/LUMO orbitals and bandgaps of H_2O@CuBTC, TCNQ, F4-TCNQ, and H4-TCNQ determined at the UB3LYP/VTZP level of theory.

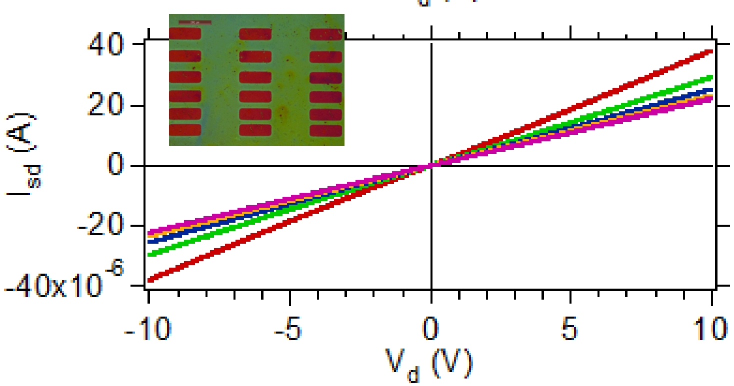
Solvent, precursor likely responsible for conductivity in as deposited $Cu_3(BTC)_2$



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



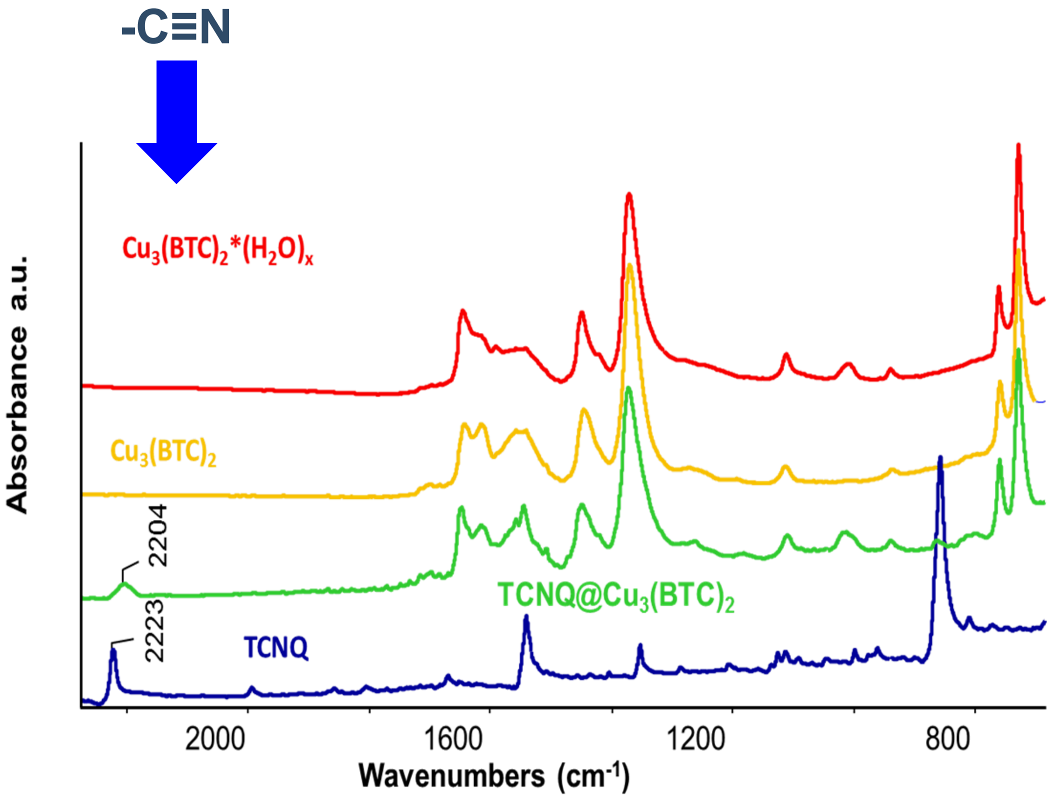
Activated, exposed to ambient: No measurable conductivity at 10 V ($<10^{-12}$ A)

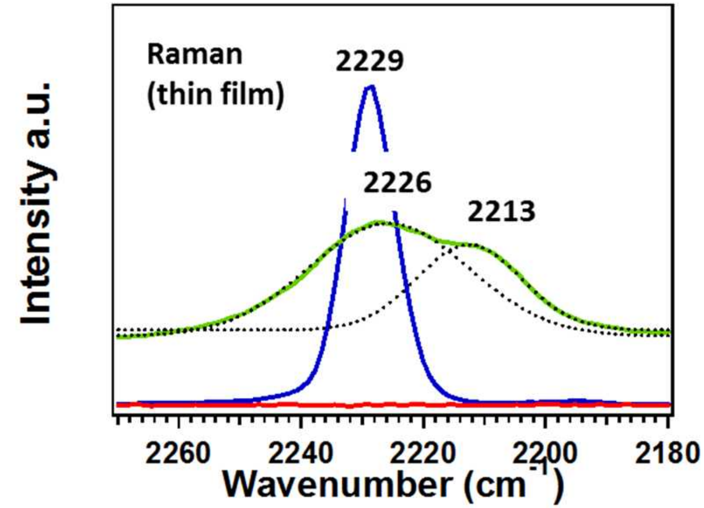


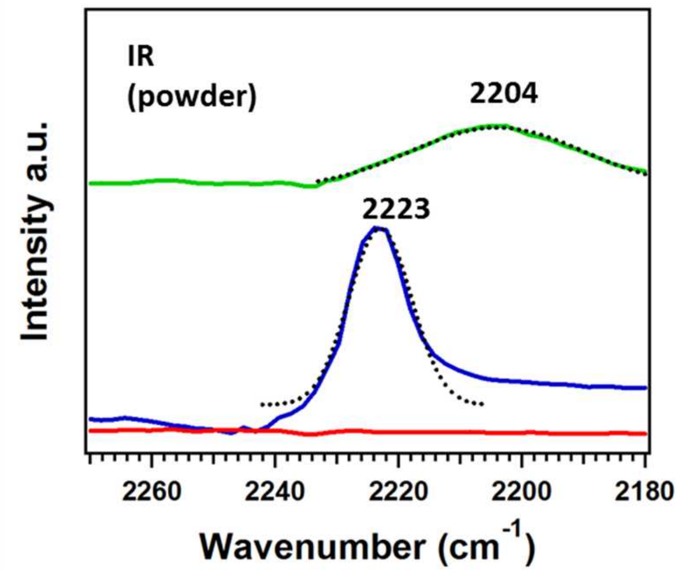
Infiltrated MOF (trace water): s~0.1 S/cm, $\sim 10^8$ increase

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

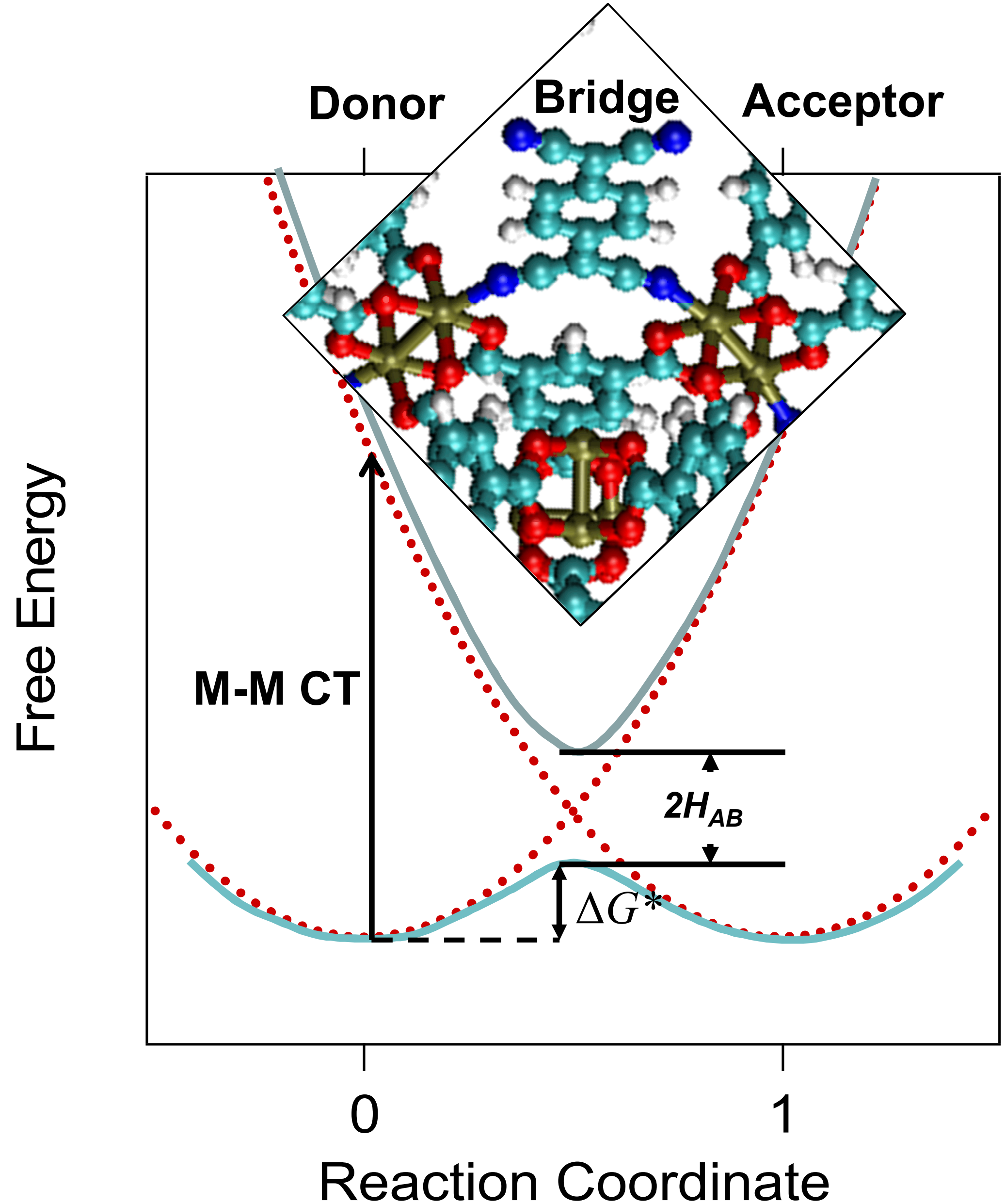
$$z = (\nu_o - \nu)/44cm^{-1} \approx \mathbf{0.43e}$$





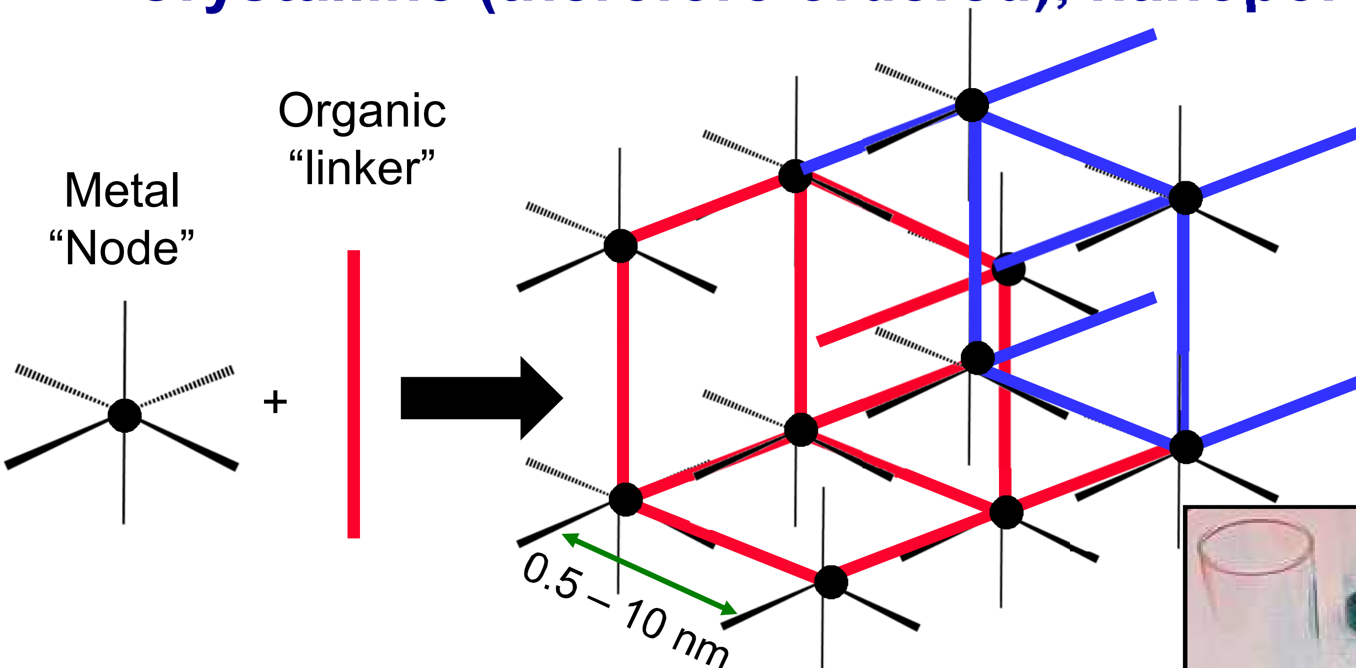


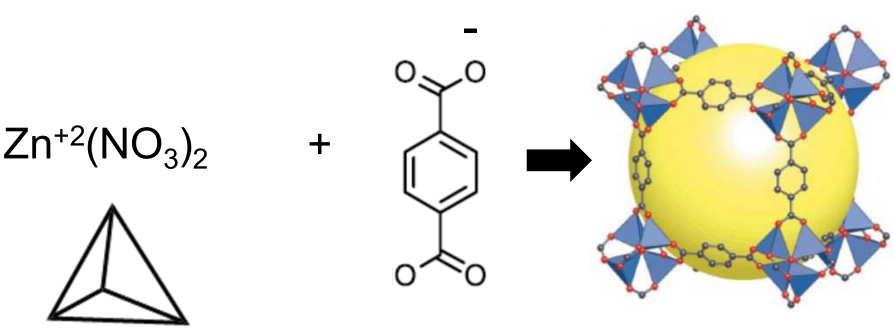
Raman peak splitting indicates 2 inequivalent CN groups


Donor
Bridge
Acceptor
Free Energy
M-M CT
2H_AB
ΔG*
0
1
Reaction Coordinate

What is a Metal-Organic Framework?

Crystalline (therefore ordered), nanoporous structure





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

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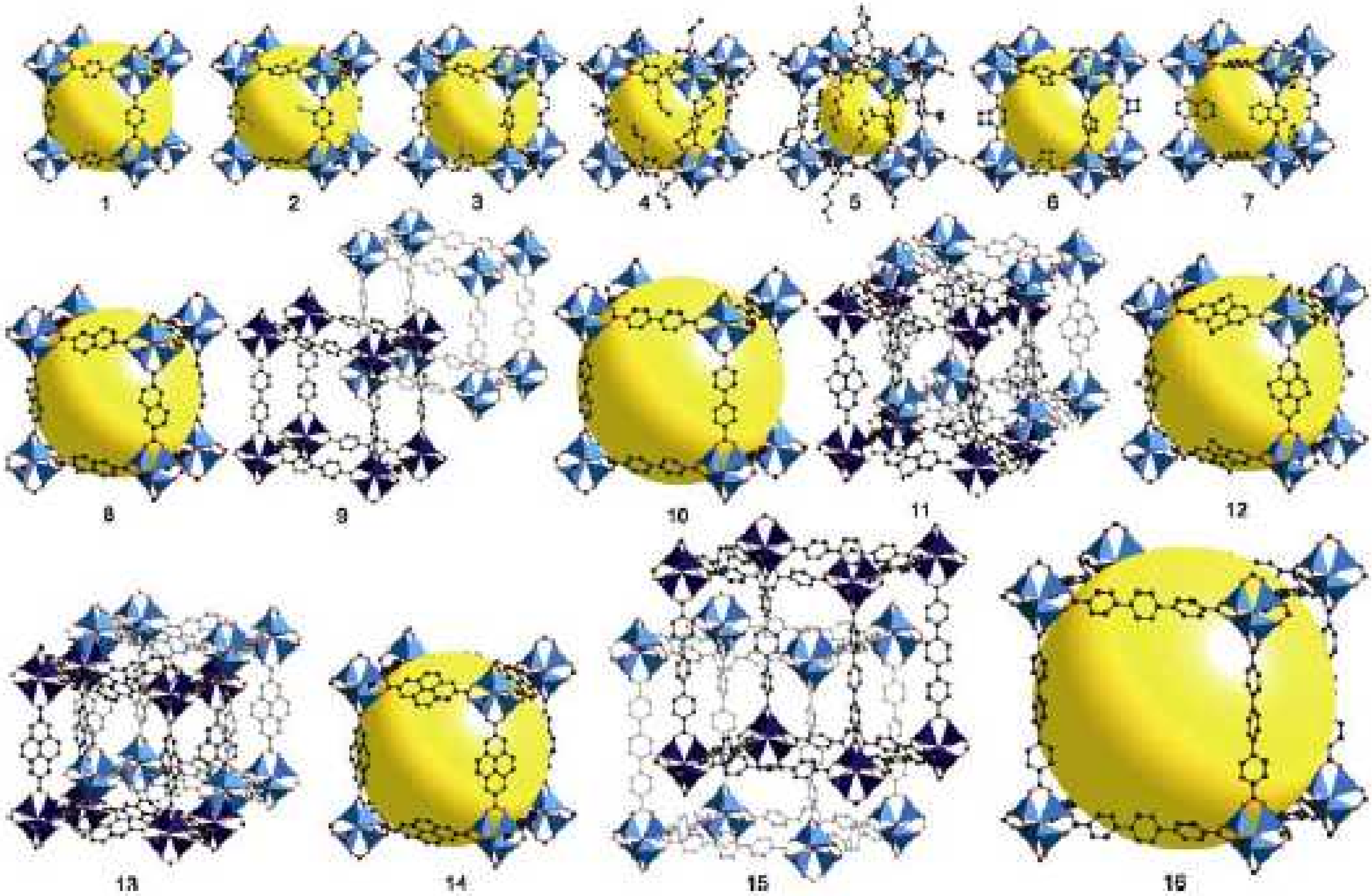
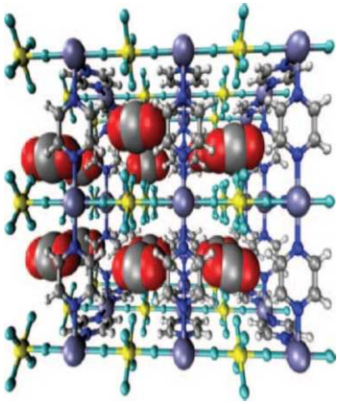
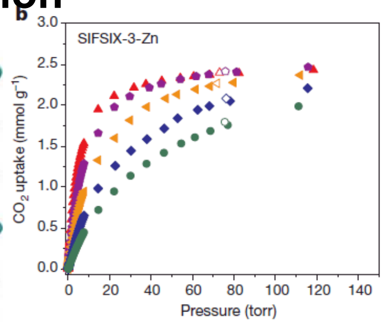


MOFs are attractive for gas storage, catalysis, separations, ionic conductors

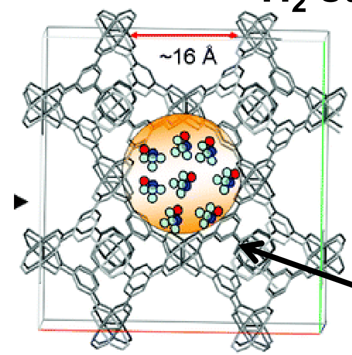
CO_2 sequestration





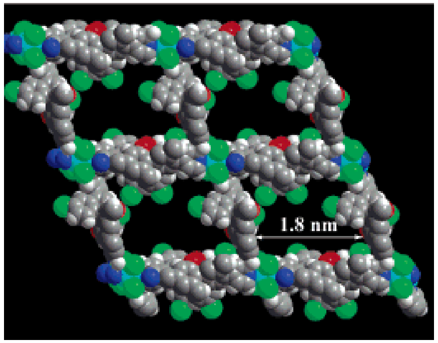
Nugent et al., Nature 495, 83 2013

H_2 storage

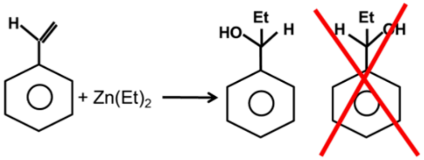


Bhakta, Allendorf et al., JACS 131, 13198, 2009

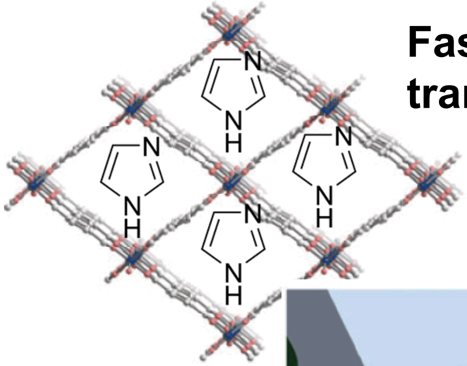
Catalysis

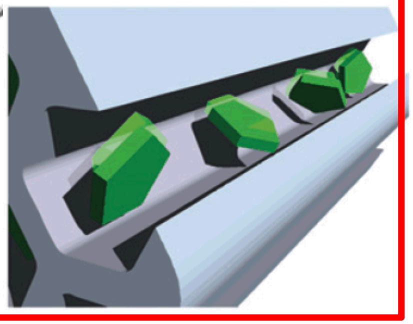


Wu, Hu, Zhang, Lin JACS 127, 8940, 2005



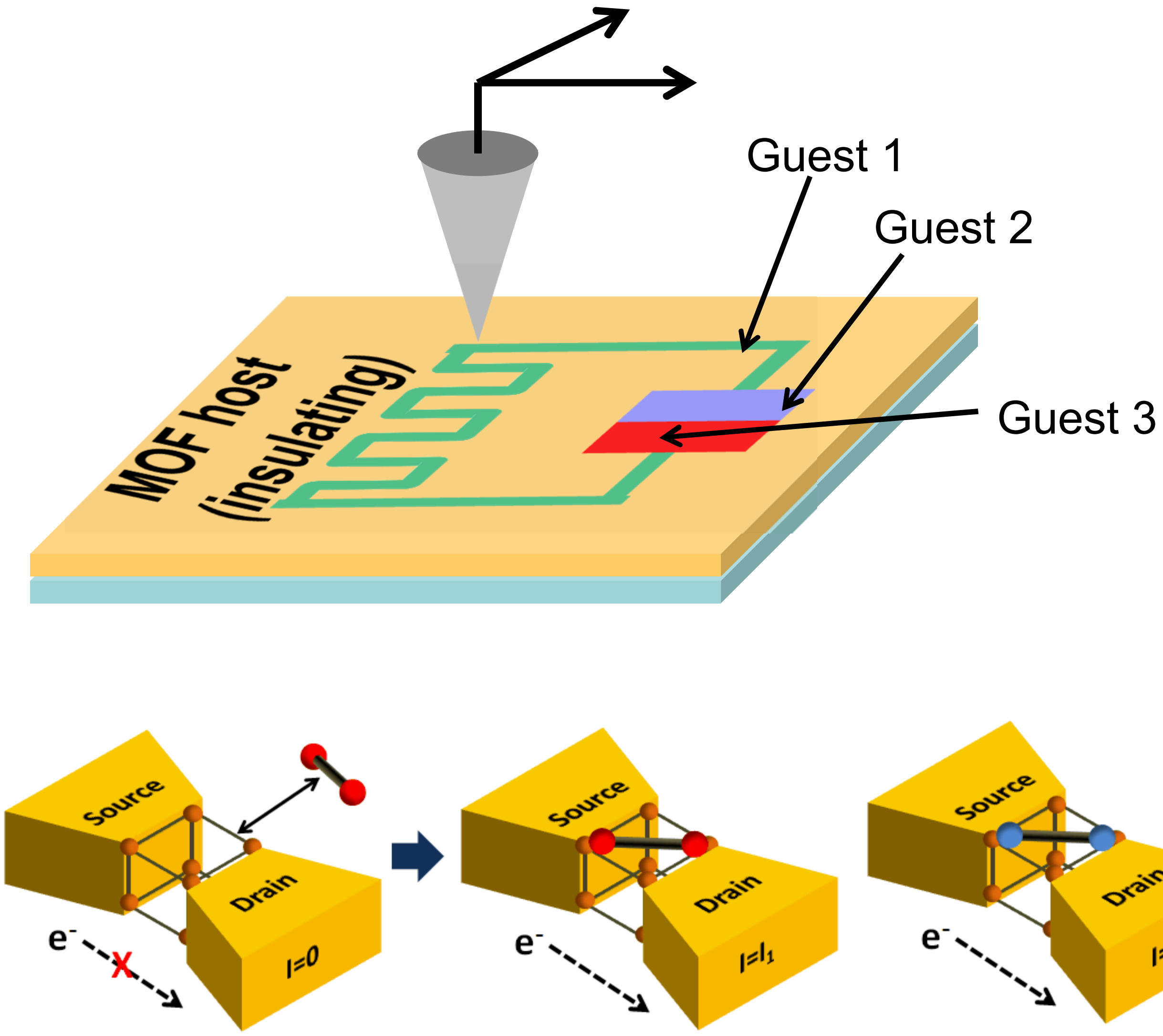
Fast H^+ transport





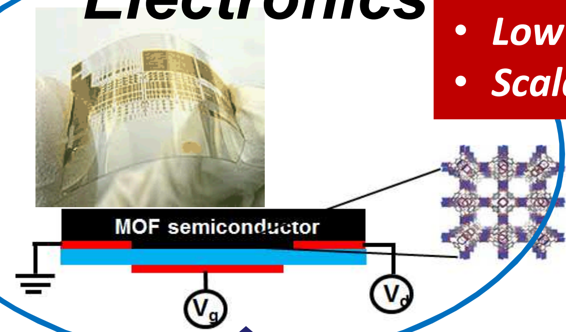
Bureekaew et al., Nat. Mat. 8, 831, 2009

Vision for Molecule@MOF ICs, nanodevices

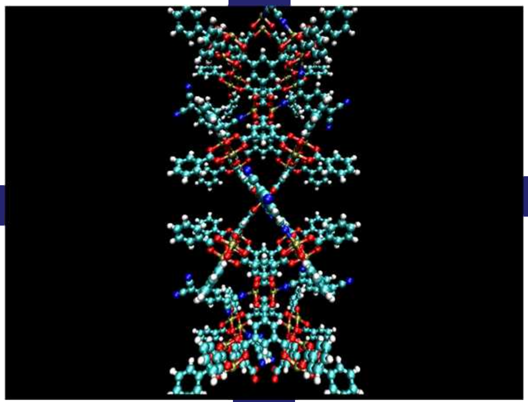


Sandia National Laboratories

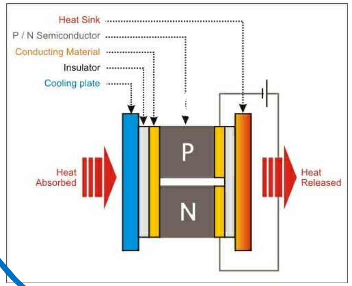
Electronics



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

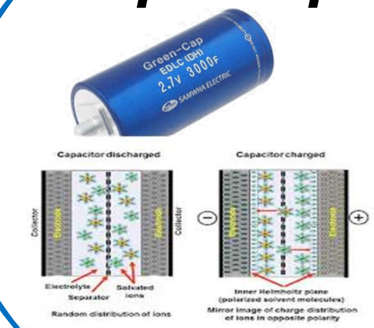


Thermoelectrics



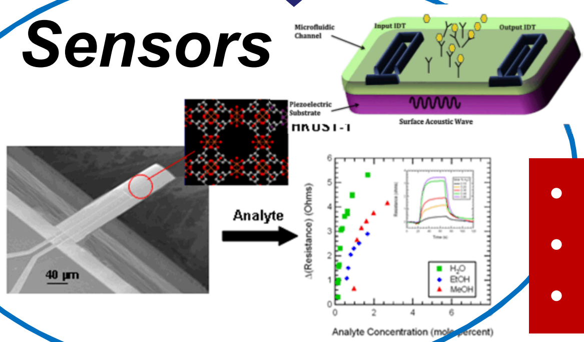
- *Ultrahigh surface area*
- *Redox active centers*

Supercaps



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

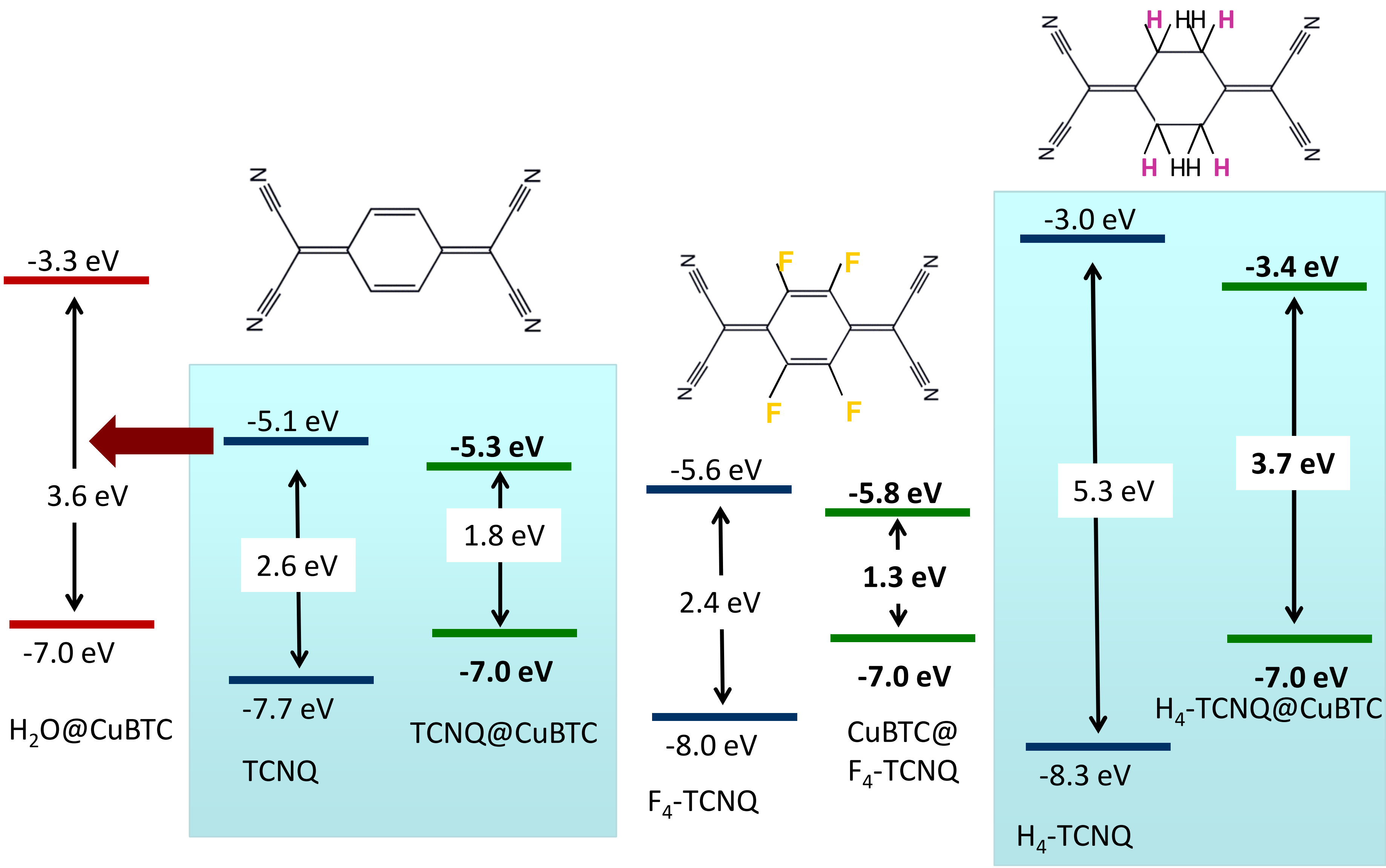
Sensors



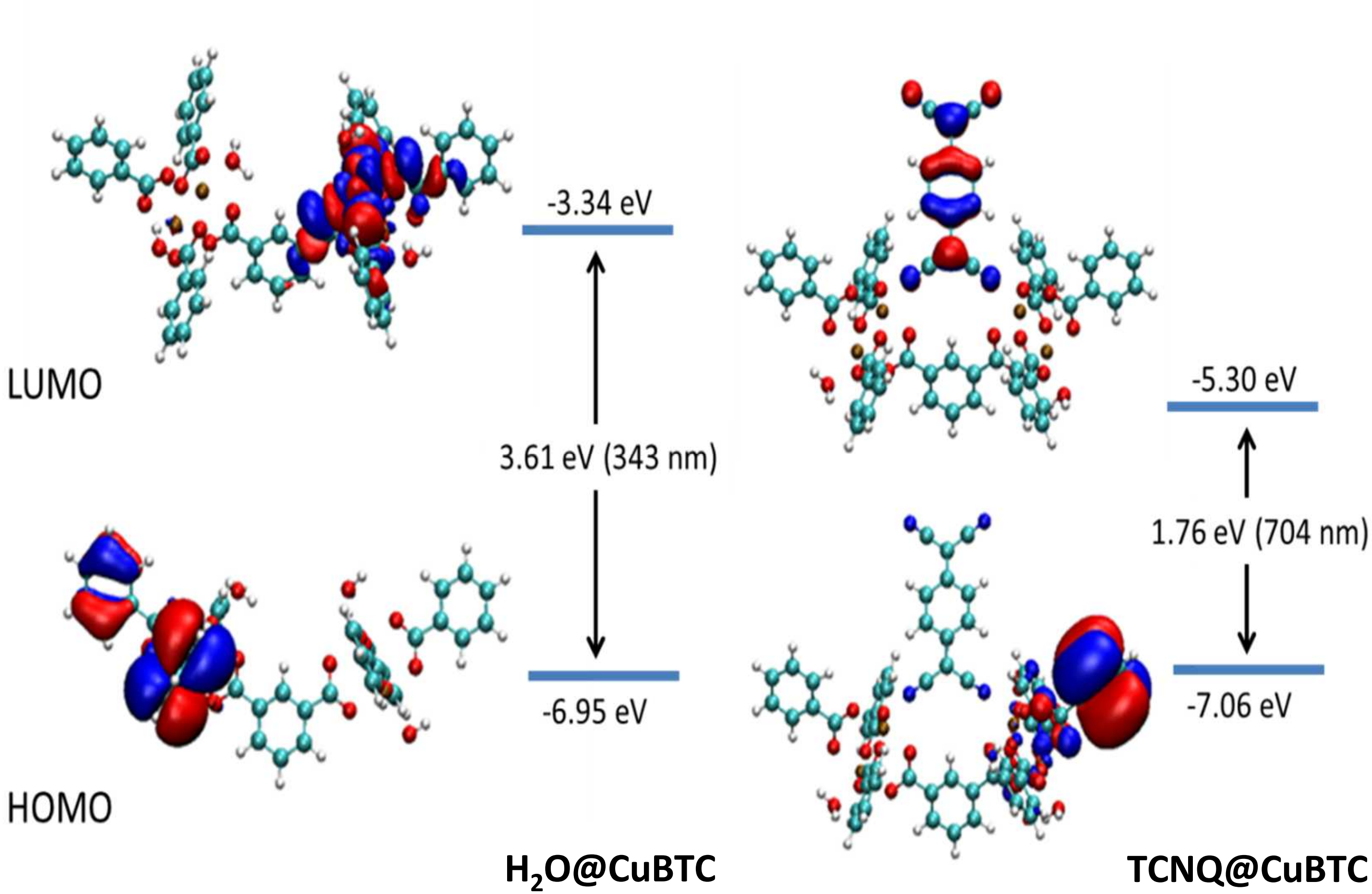
- *Multi-axis response*
- *Chemical specificity*
- *High surface area*

Cu-BTC band alignments: DFT/PBEsol calculations

Effect of fluorination and hydrogenation of TCNQ

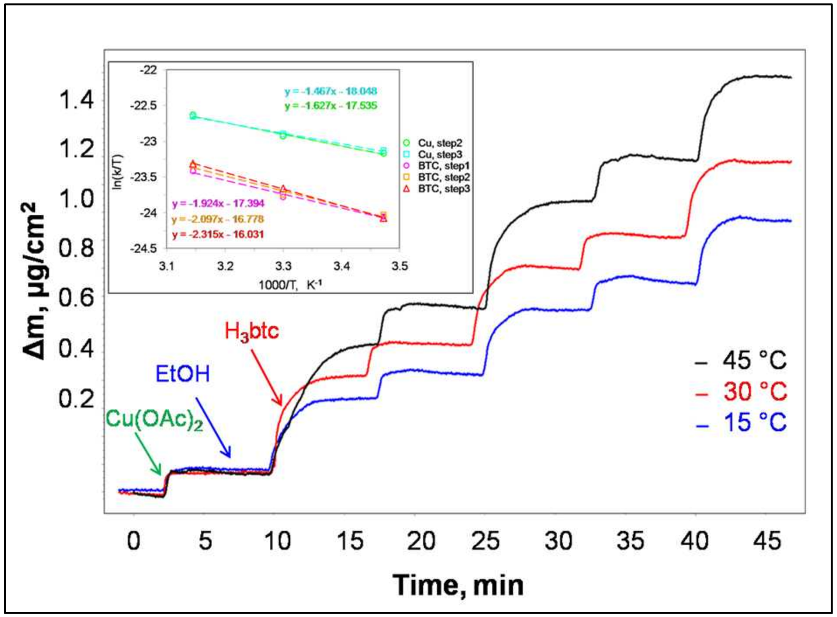


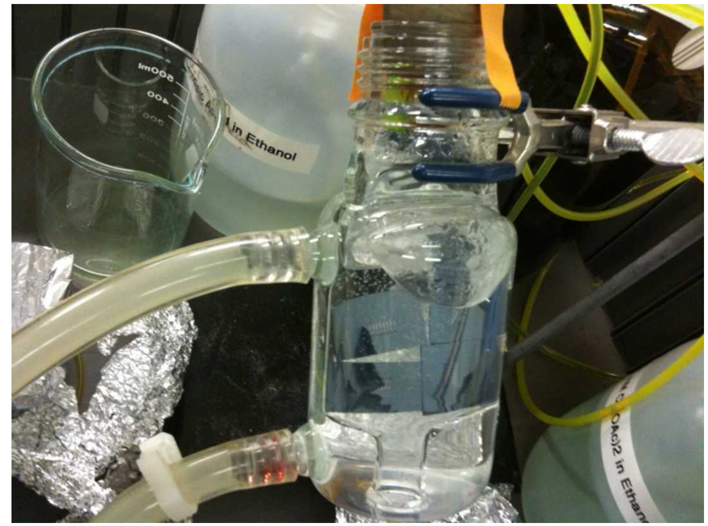
Bridging TCNQ molecules create new charge transfer states

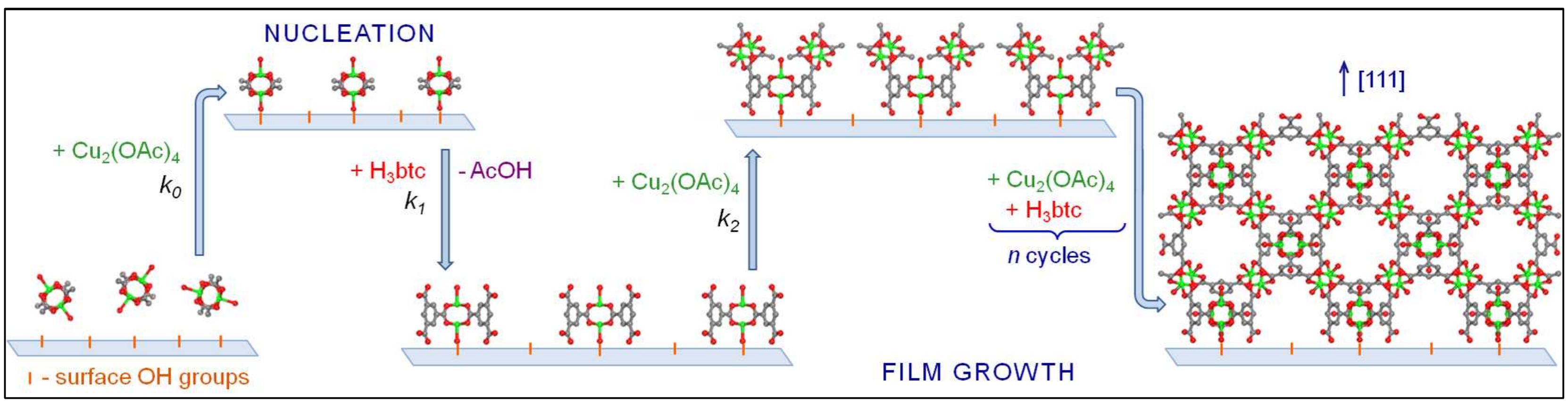


DFT/PBEsol calculations

Thin film growth for MOF device applications

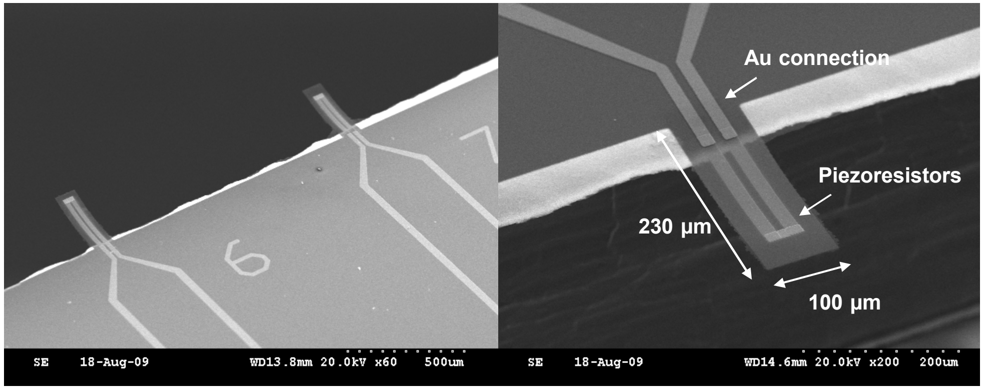


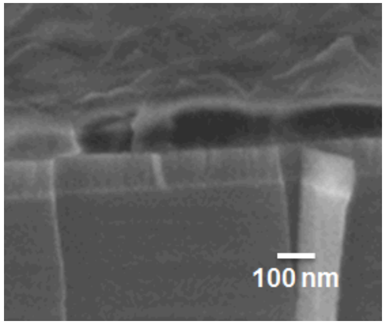




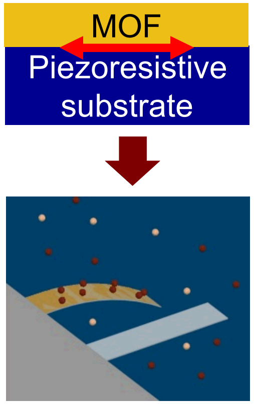
V. Stavlia et al. *Chem. Sci.* **3** (2012), 1531–1540

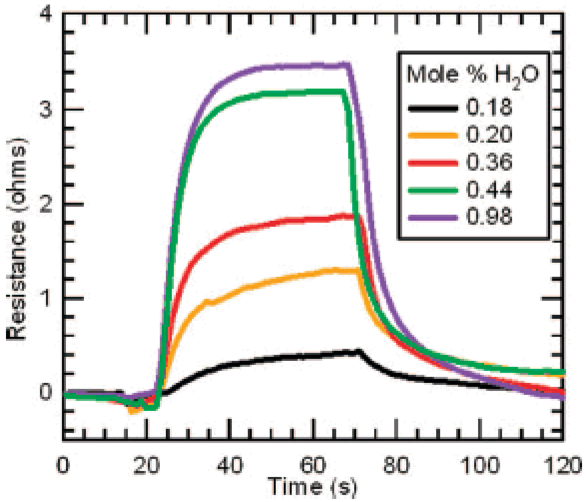
MOF films make sensitive, selective gas sensors

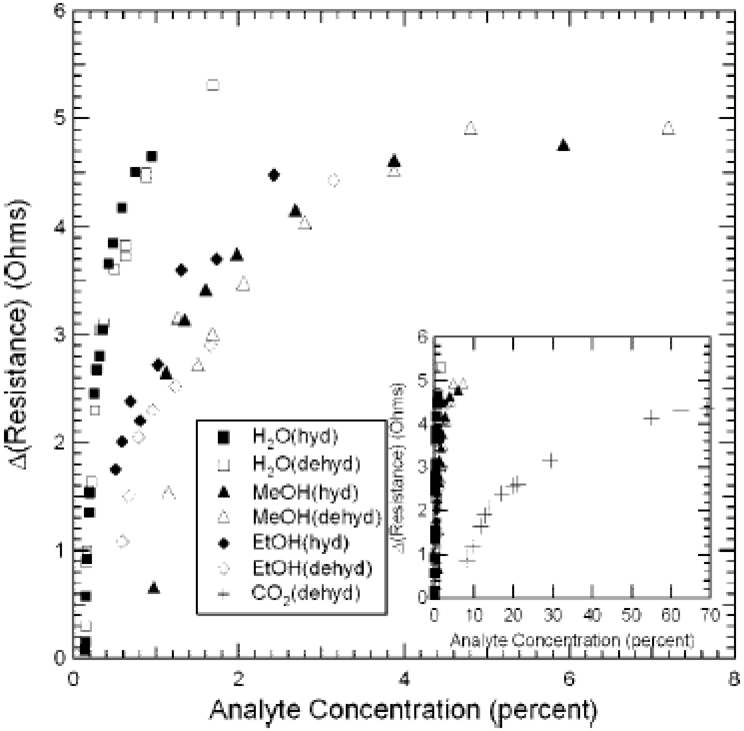




Microcantilevers (fg sensitivity)







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