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Exceptional service in the national interest

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Molecule@MOF: A New Class of Electronic Materials

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Remember these?

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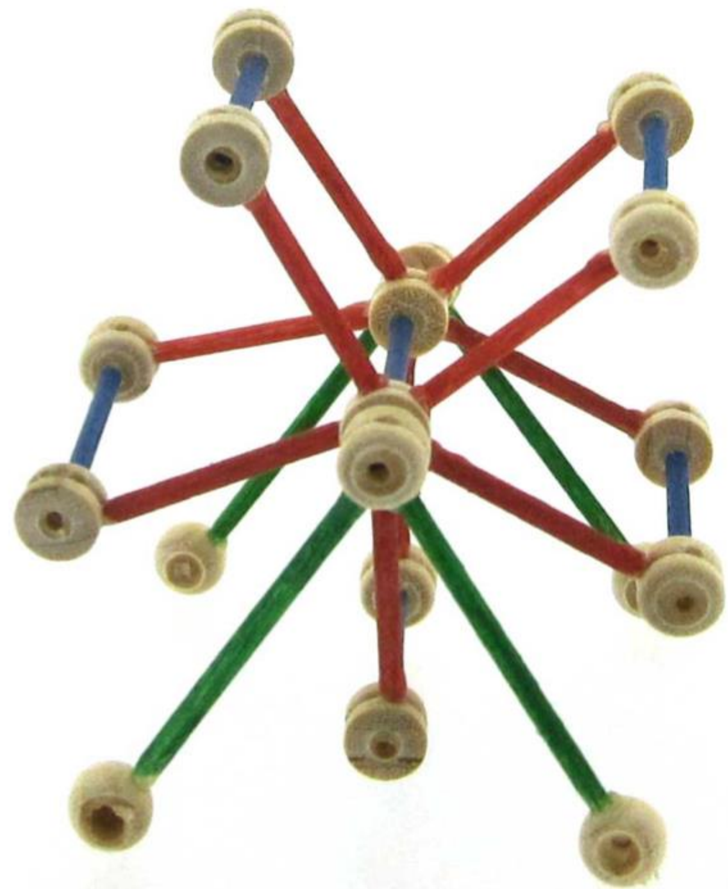

Knowing structure is POWER…because you can relate it to function!

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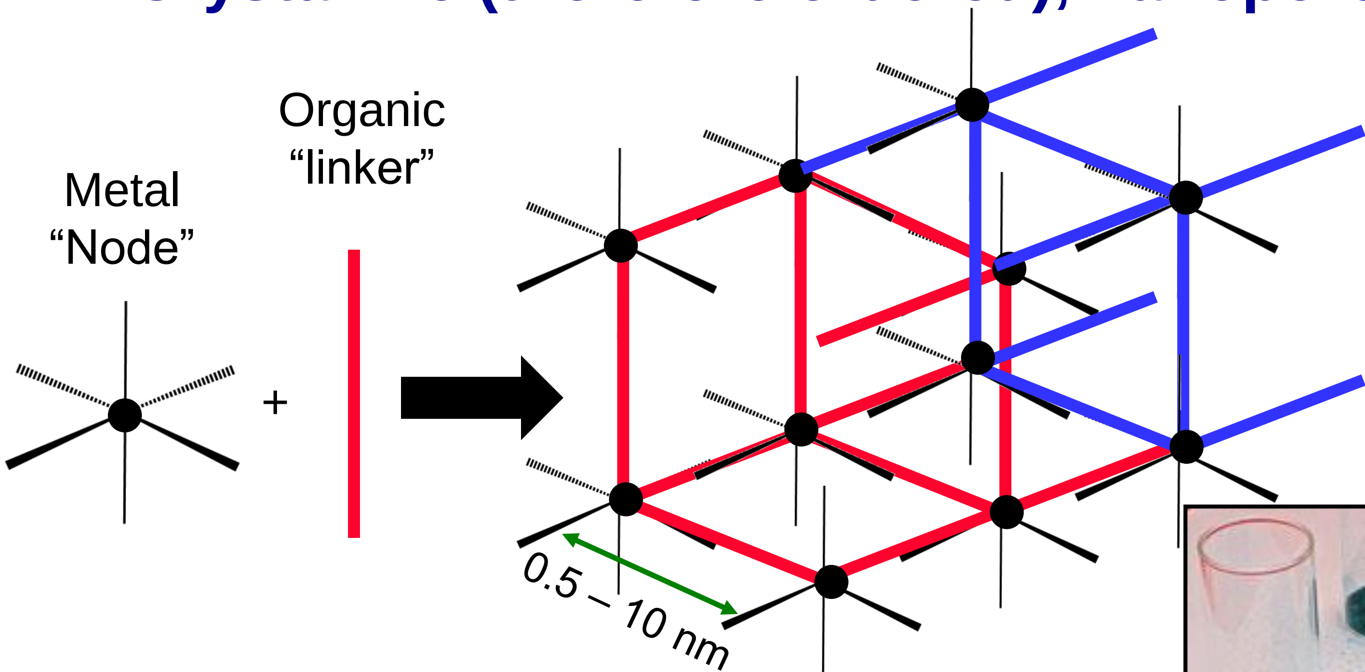
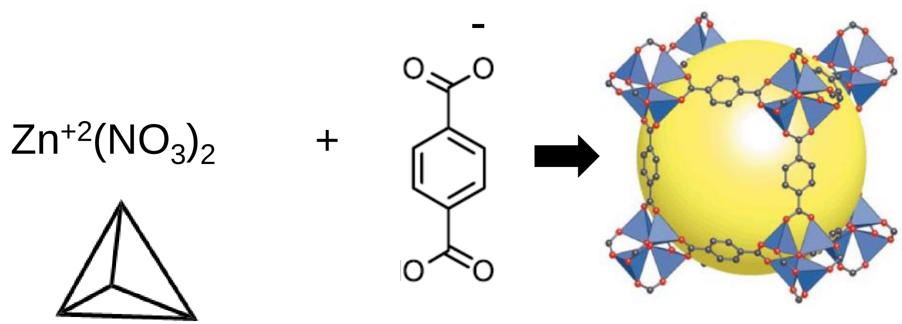
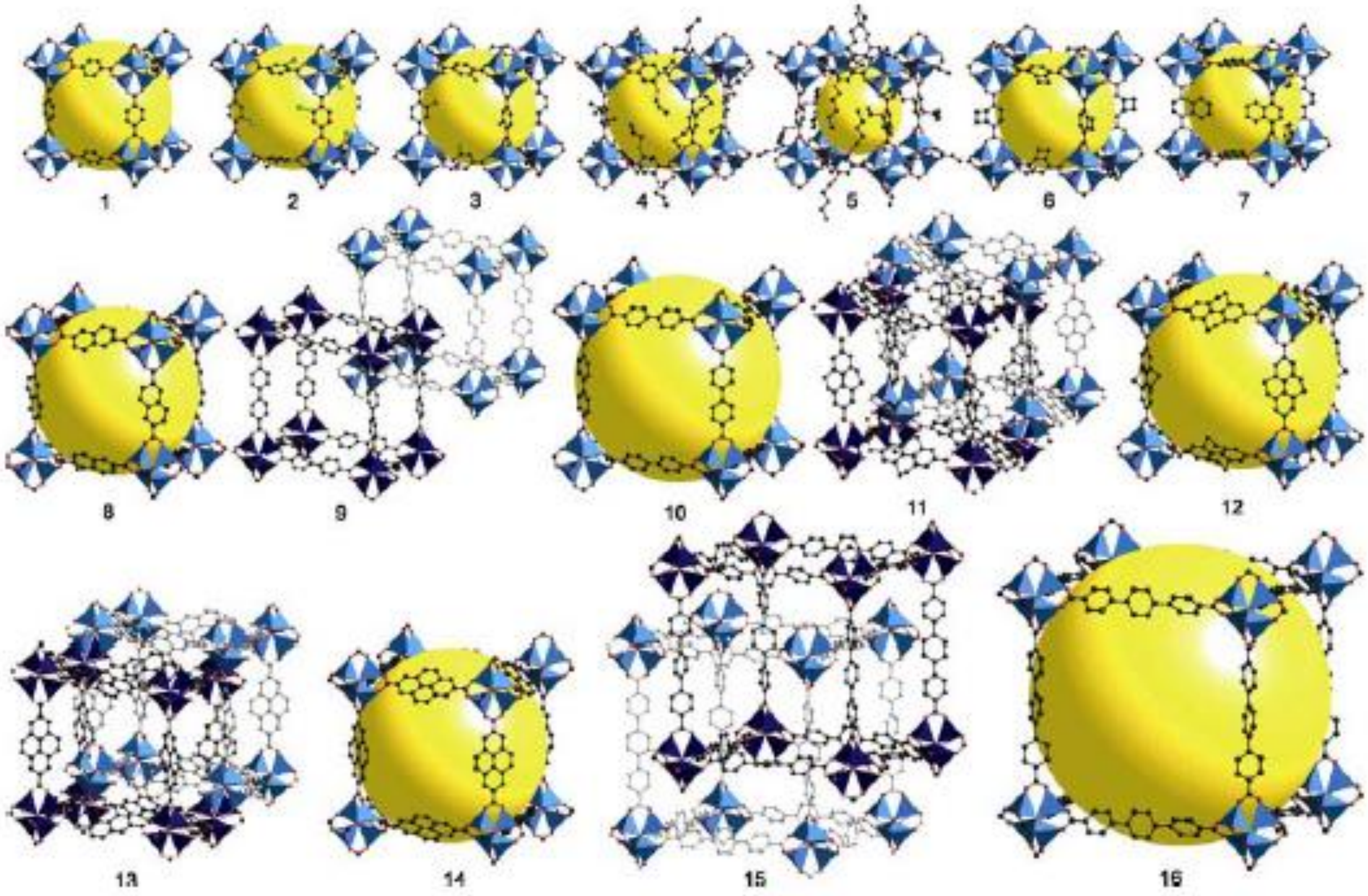
What is a Metal-Organic Framework?

Crystalline (therefore ordered), nanoporous structure





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



How big are the pores?

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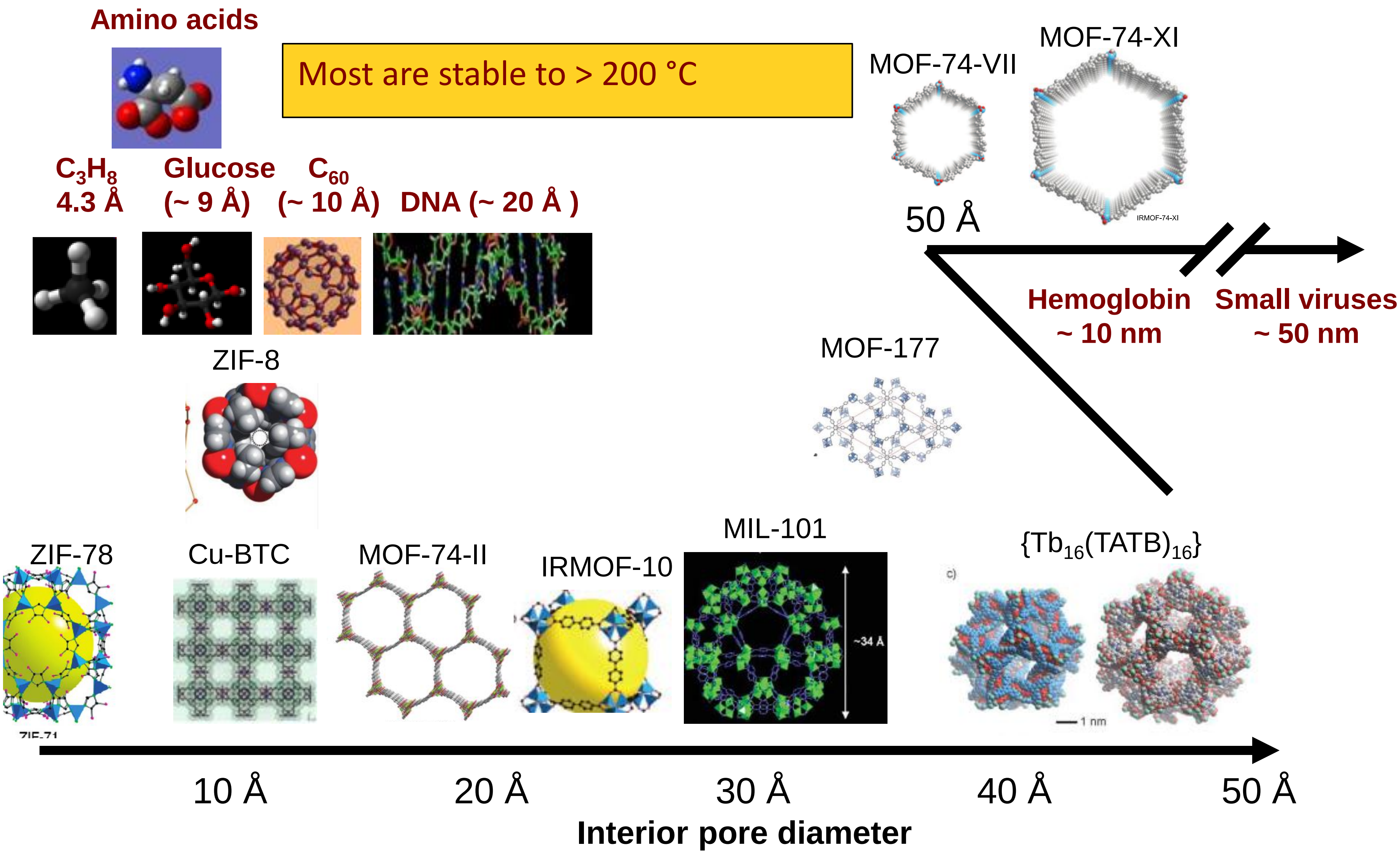

Let's think about the surface area of MOF pores

Surface area of a sphere = $4\pi r^2$

Surface area of tennis ball ≈ 140 cm^2 ≈ 0.01 m^2

What's the surface area of 1 cm^3 of a MOF (approximately)?

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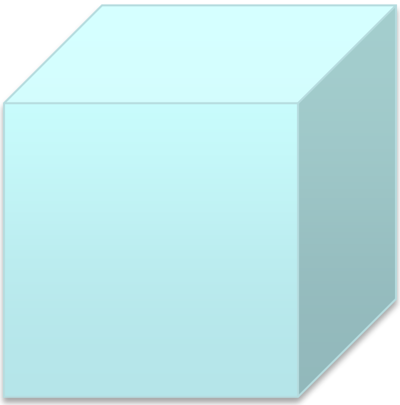
MOF pore diameters are ~ 1 – 3 nm

→ r(pore) ≈ 1 nm = 10^{-9} m

Pore volume = $(4/3)\,\pi r^3 = 4\text{x}10^{-27}\ m^3 = 4\ nm^3$

Surface area = $4\pi r^2 \approx 10^{-17}\ m^2$



How many pores in 1 cm^3 ?

$1\ cm^3 = (10^7\ nm)^3 = 10^{21}\ nm^3$

$10^{21}\ nm^3/(4\ nm^3/\text{pore}) = 2.5\text{x}10^{20}$ pores

Total surface area = $(2.5\text{x}10^{20}$ pores$)\text{x}(10^{-17}\ m^2/\text{pore})$

= $2{,}500\ m^2/cm^3$

If density = $0.5\ g/cm^3$, then **$5{,}000\ m^2/g$!**

(the tennis ball is ~ $0.0002\ m^2/g$)

1 football field = 5,351 m^2

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

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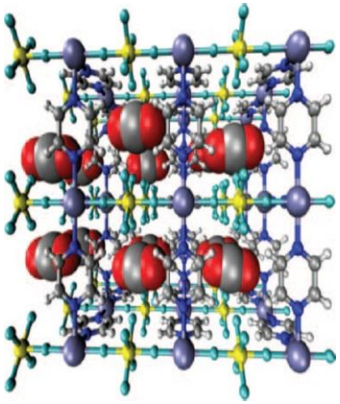
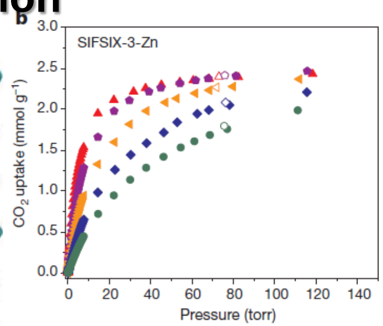
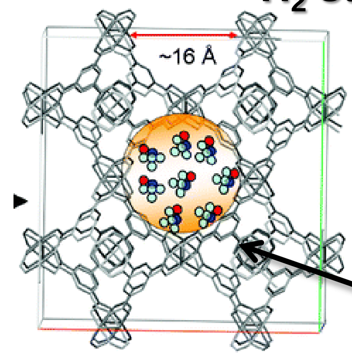
CO_2 sequestration





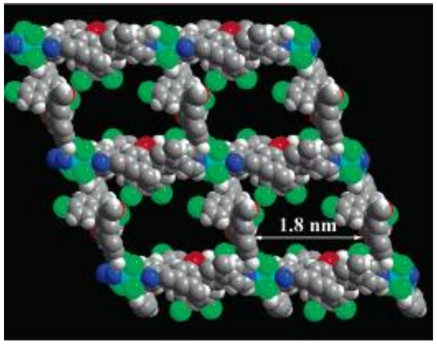
Nugent et al., Nature 495, 83 2013

H_2 storage

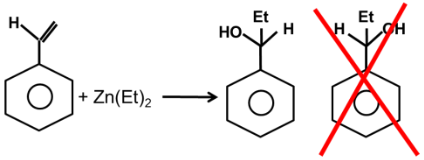


Bhakta, Allendorf et al., JACS 131, 13198, 2009

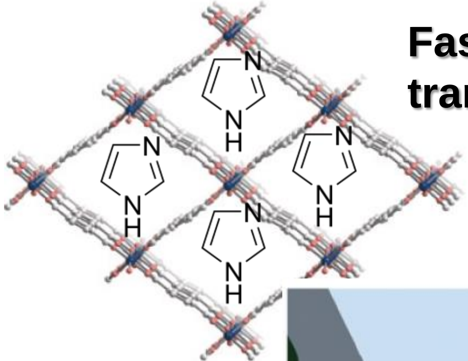
Catalysis

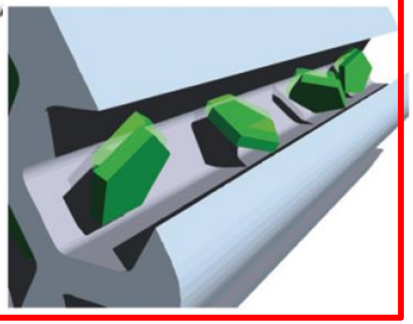


Wu, Hu, Zhang, Lin JACS 127, 8940, 2005



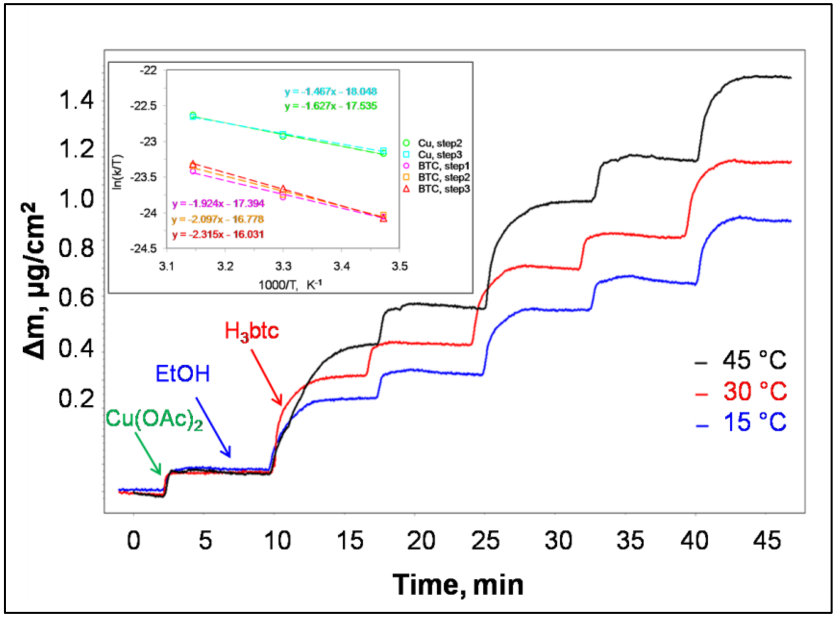
Fast H^+ transport

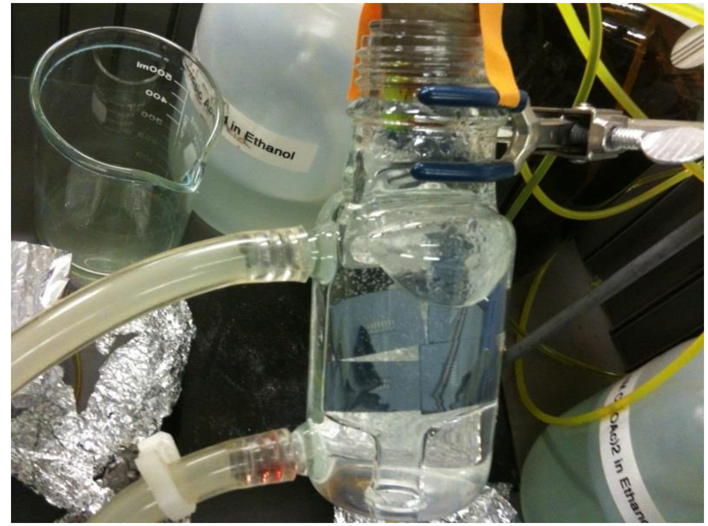


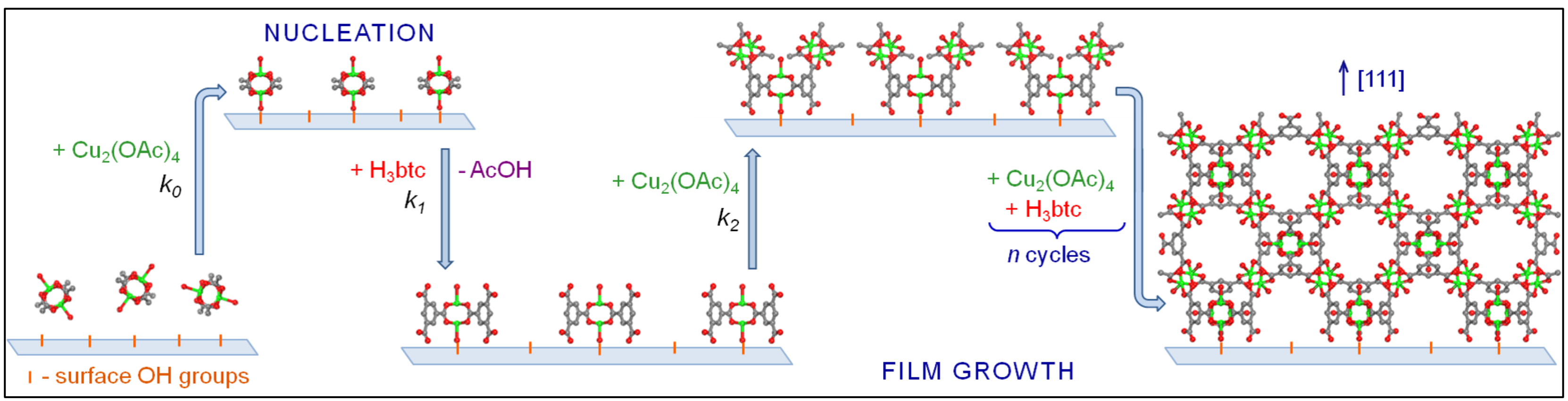


Bureekaew et al., Nat. Mat. 8, 831, 2009

Thin film growth for MOF device applications







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

MOF films make sensitive, selective gas sensors

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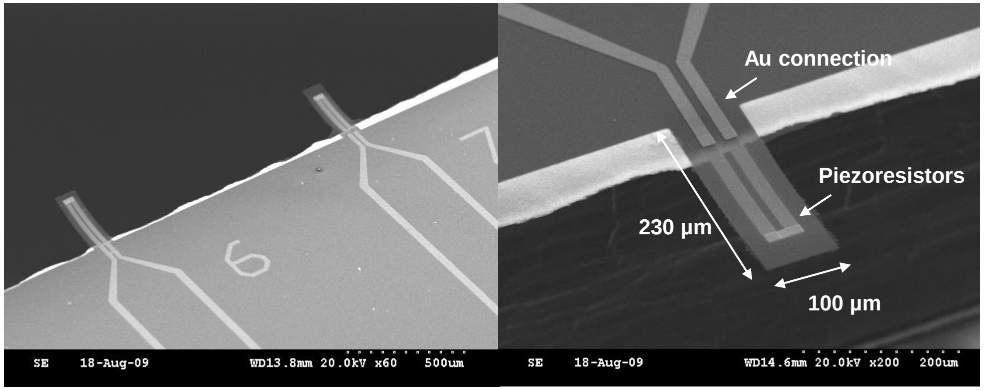
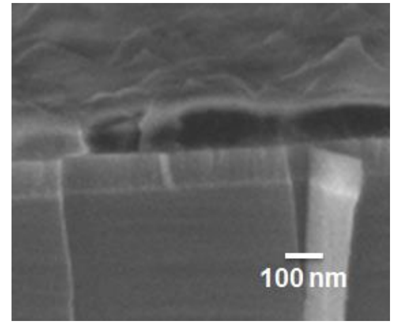
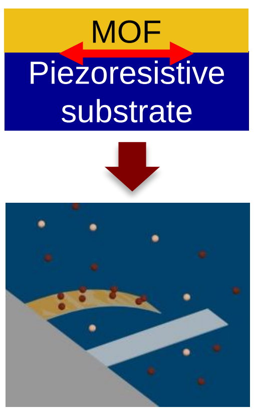
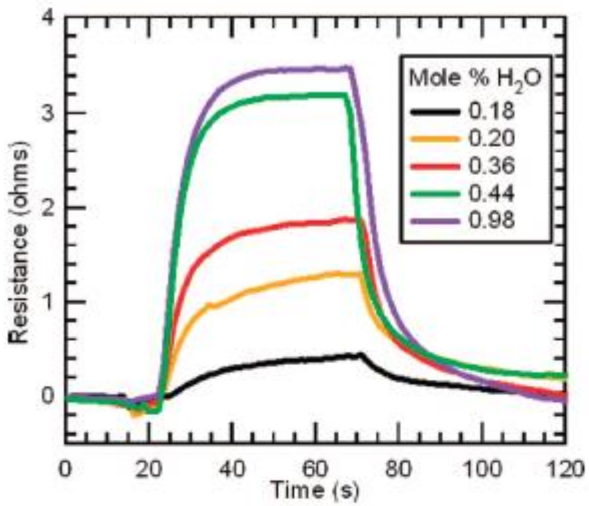
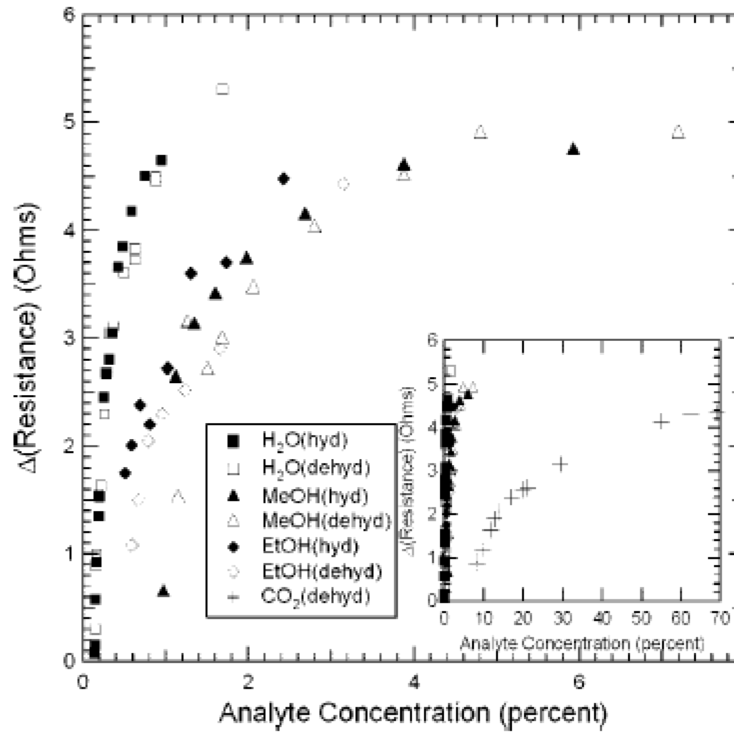




Microcantilevers (fg sensitivity)

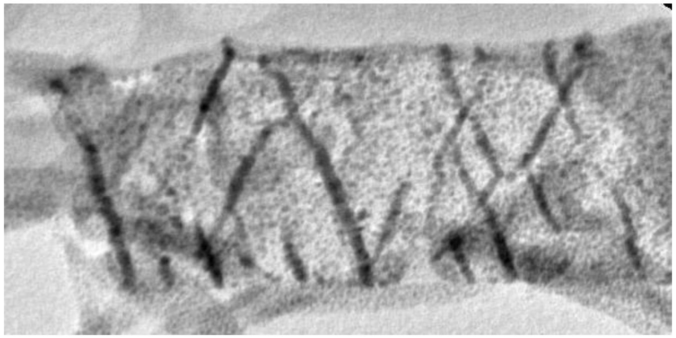


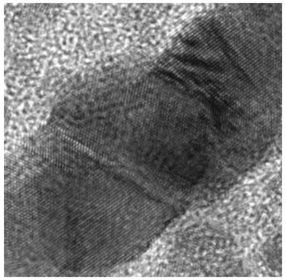


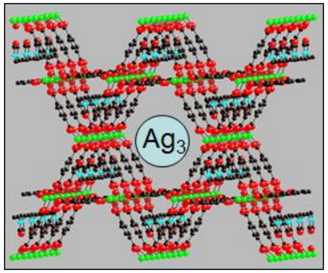


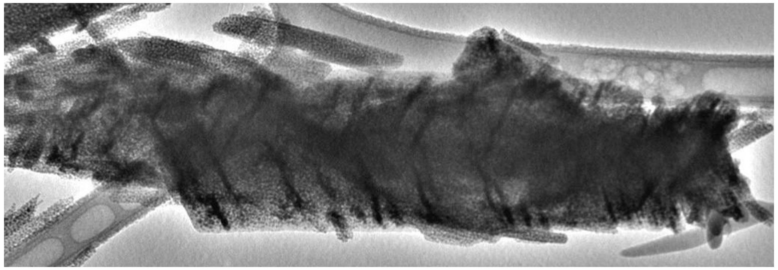
Allendorf, Talin, Hesketh, et al., *J. Amer. Chem. Soc.* 130, 14404 (2008)

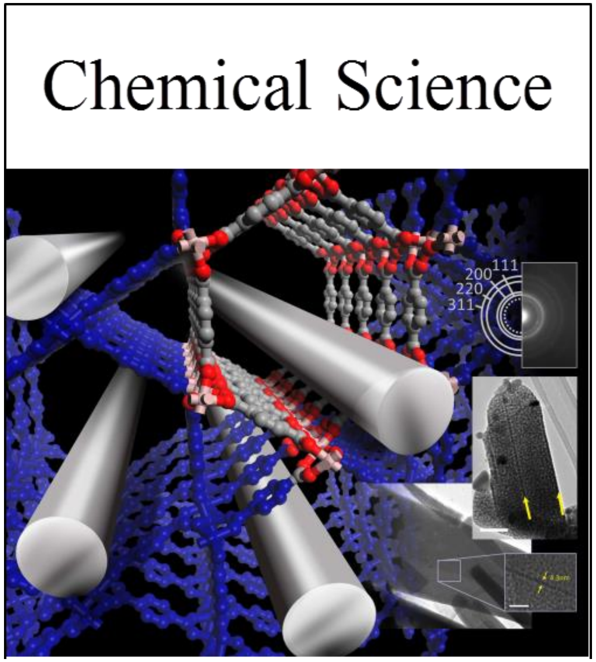
MOFs guide Ag nanowire growth

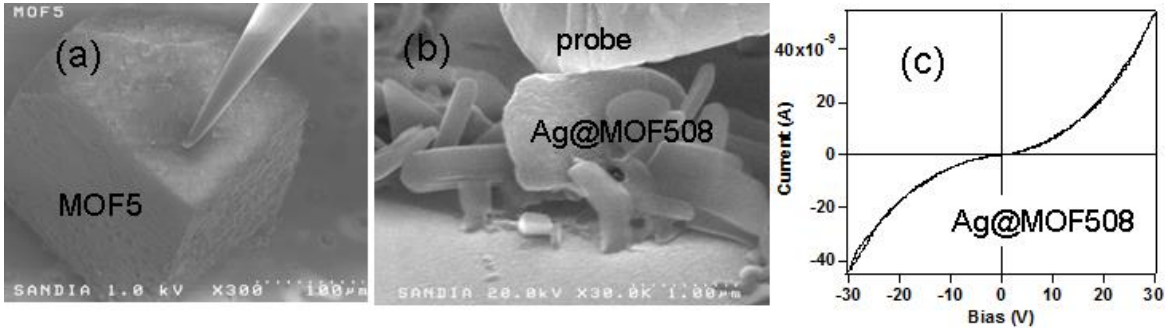








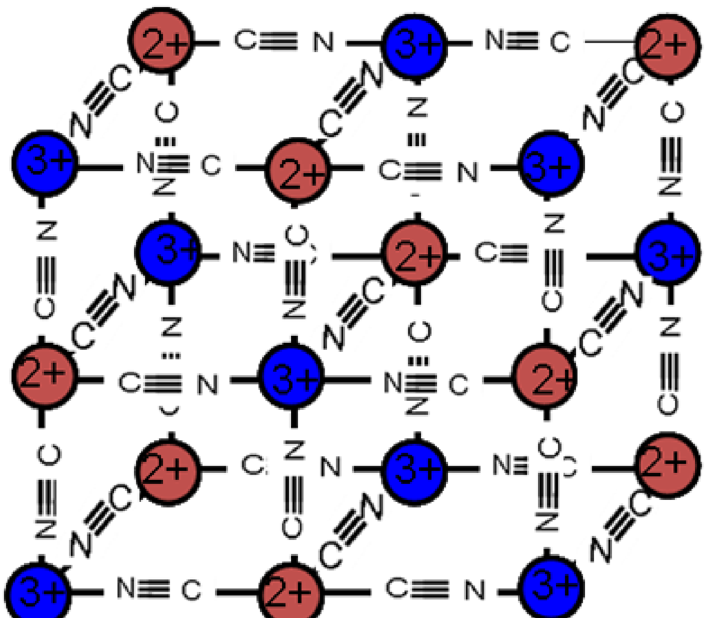


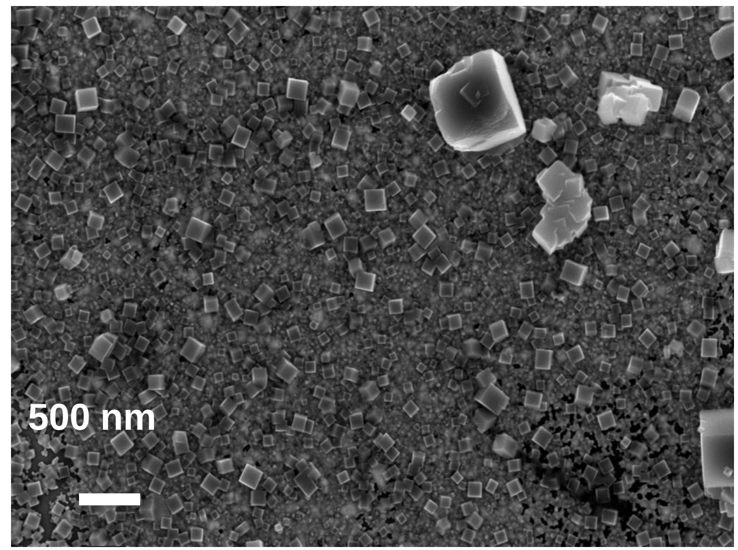


Houk, Jacobs, Allendorf, Talin et al.
Nano Lett., 9 3413, (2009)
Chemical Science 2, 411, (2011);
Chemistry 17, 11372 (2011).
;

Non-porous CPs have been used for centuries (i. e. Prussian blue)

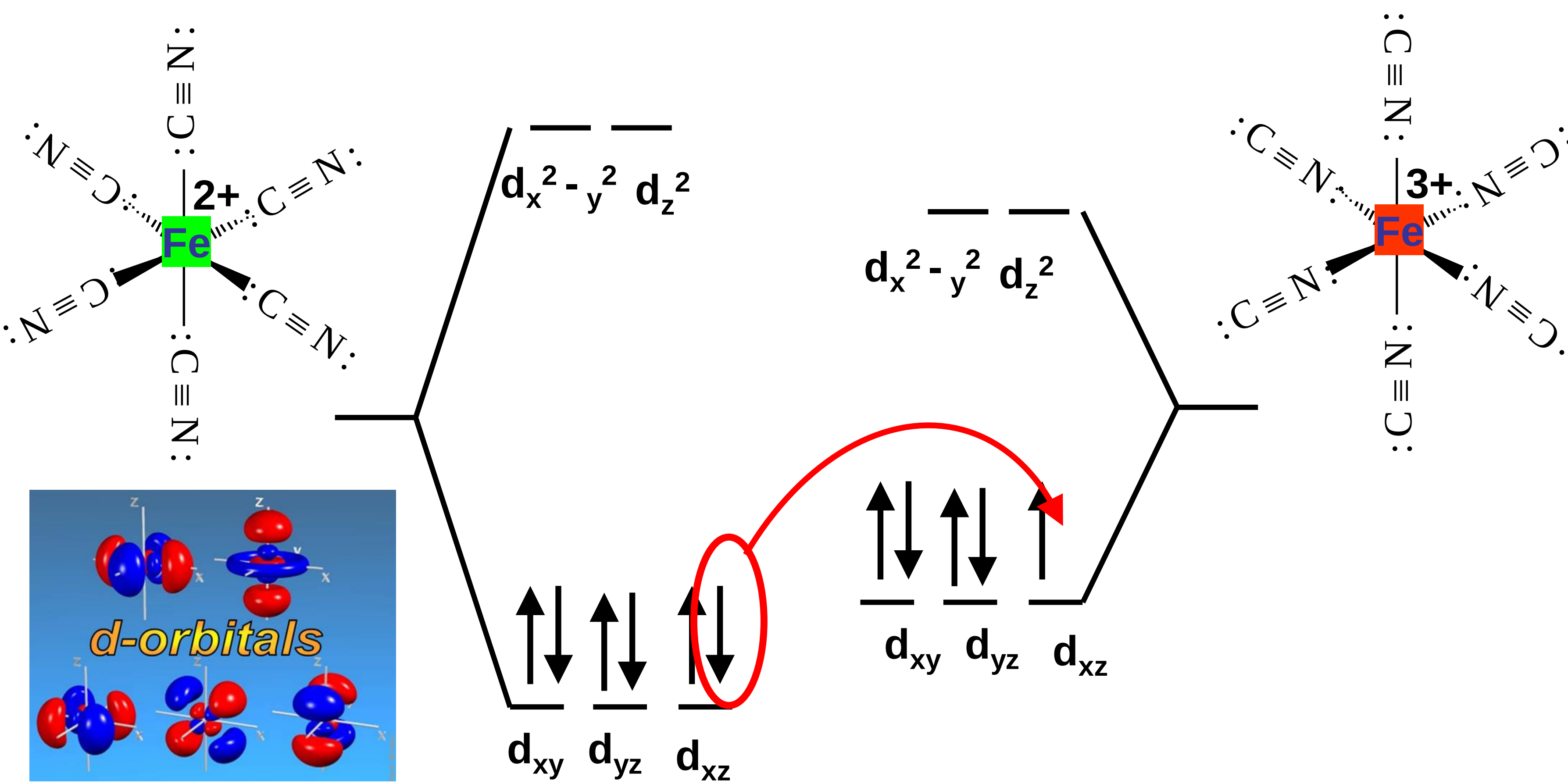
“The Great Wave of Kanagawa” by Hokusai





A. Agrawal, C. Susut, G. Stafford, U. Bertocci, B. McMorran, H. Lezec, A. A. Talin, Nano Lett. 11, 2774, 2011.

The PB red absorption band due to IVCT (Intervalence Charge Transfer)



Prussian blue is a 'class II' system according to donor-bridge acceptor model

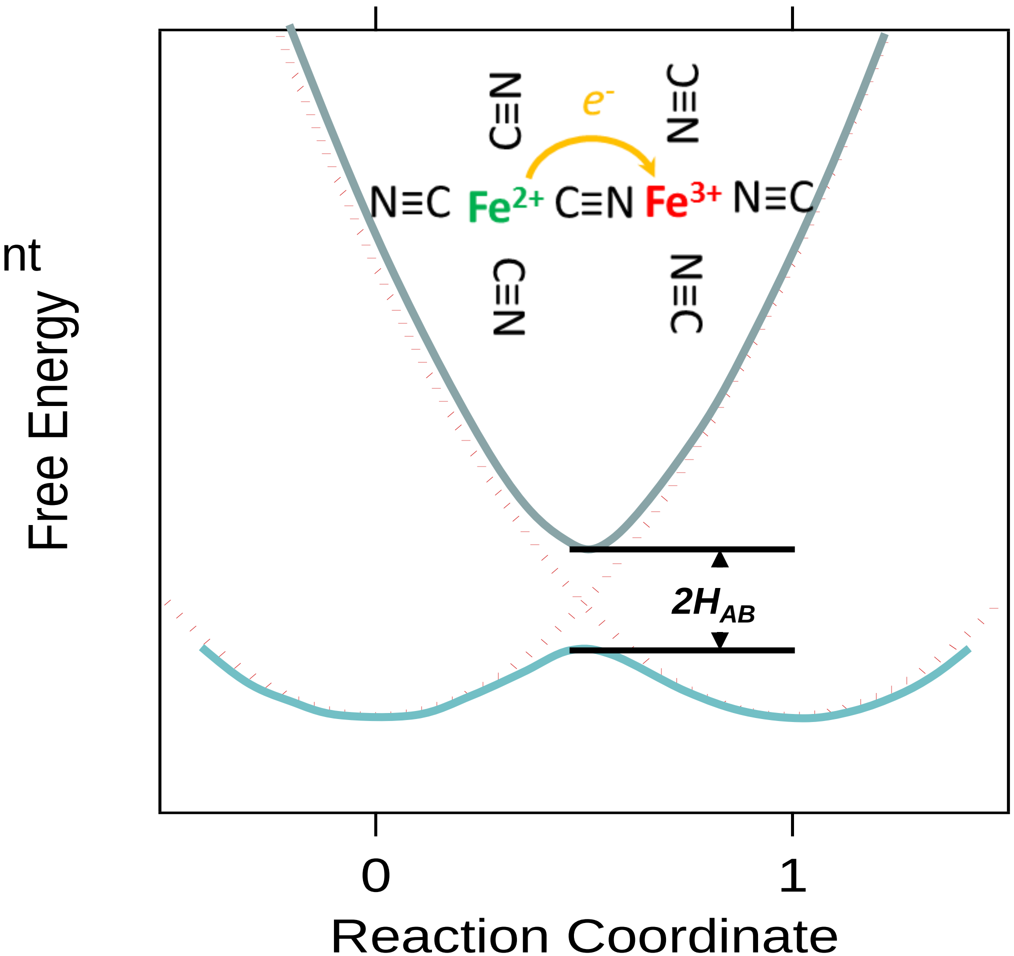
$$\Delta G^{*} = {(\lambda - 2H_{AB})^2}/{4\lambda}$$

H_{AB}-Electronic coupling matrix element

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

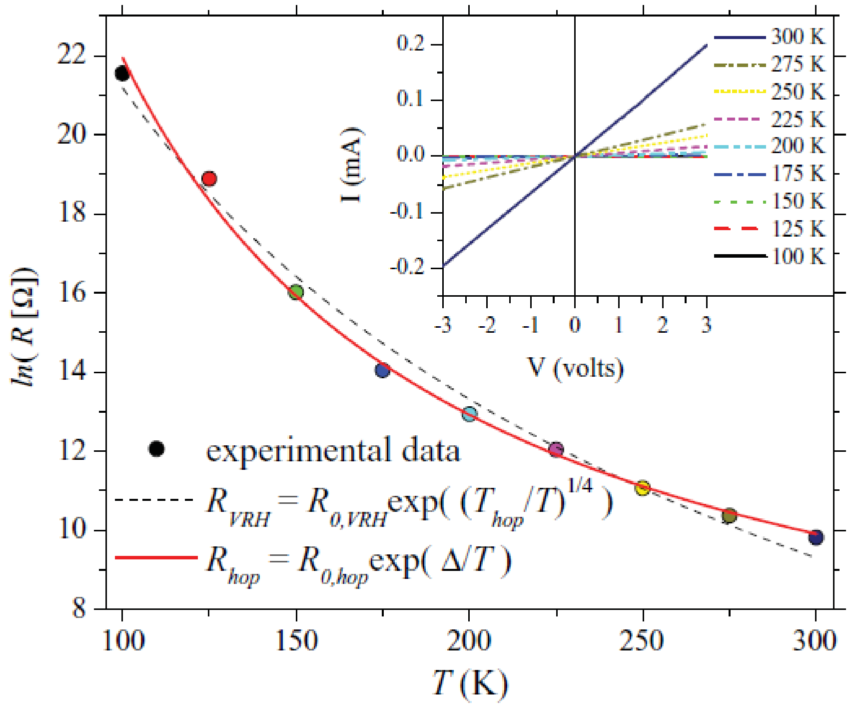
λ-Reorganization energy

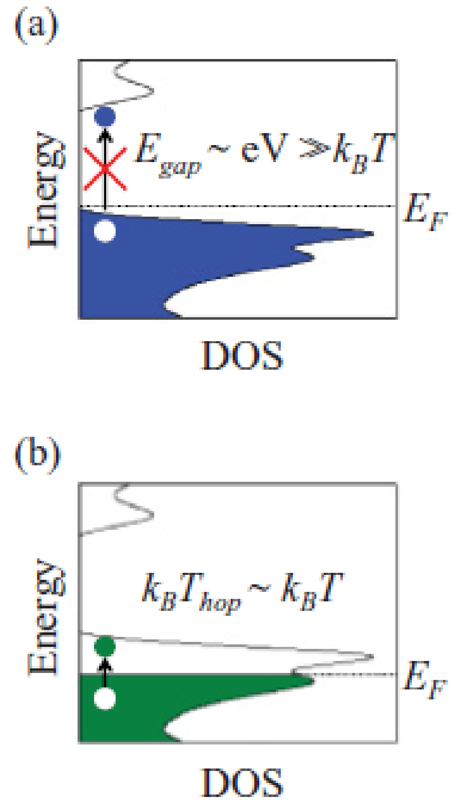
Class I: ~ weak/no coupling
Class II ~ moderate coupling
Class III ~ strong coupling



B. S. Brunschwig, C. Creutz and N. Sutin, *Chemical Society Reviews*, 2002, **31**, 168

Hopping conduction in oxidized or reduced PB consistent with intermediate coupling





D. M. Pajerowski, T. Watanabe, T. Yamamoto, Y. Einaga, Phys. Rev. B **83**, 153202 (2011)

Can guest molecules induce electrical conductivity in an insulating MOF?

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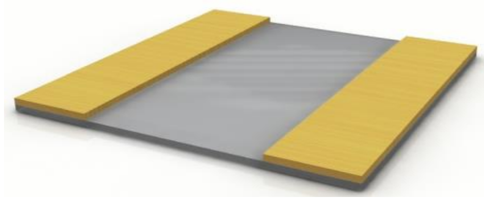
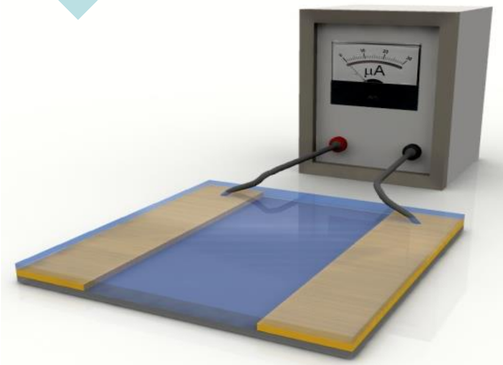
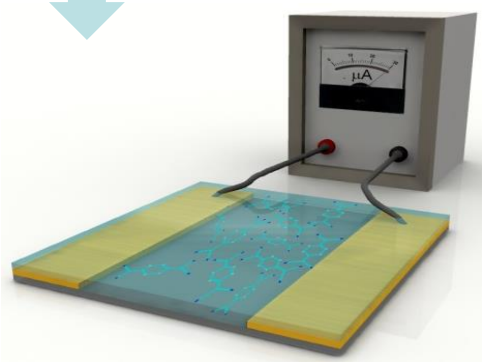
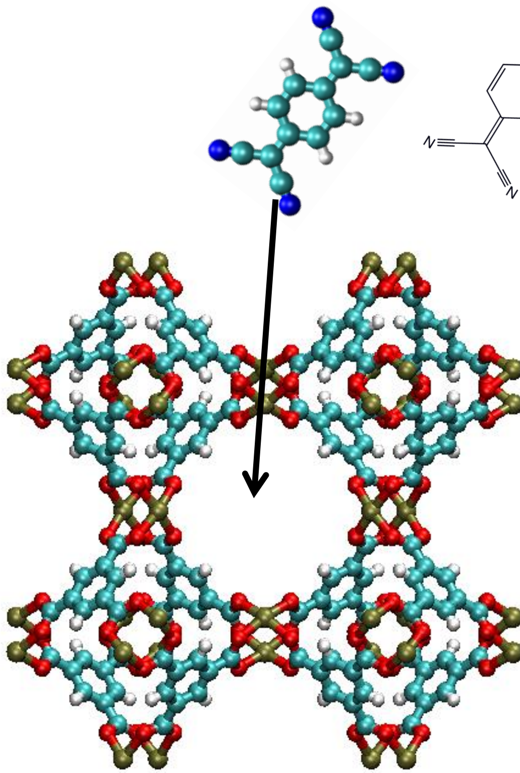


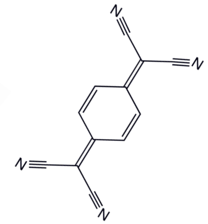
MOF growth

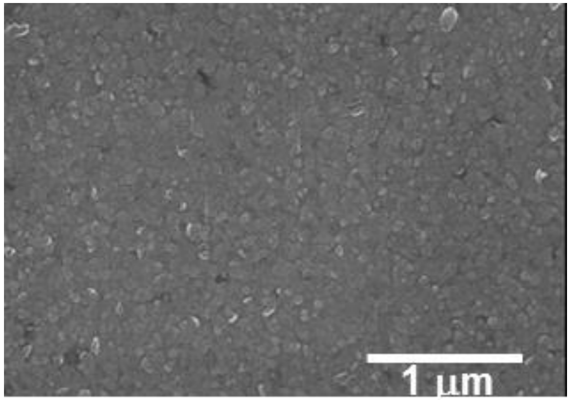


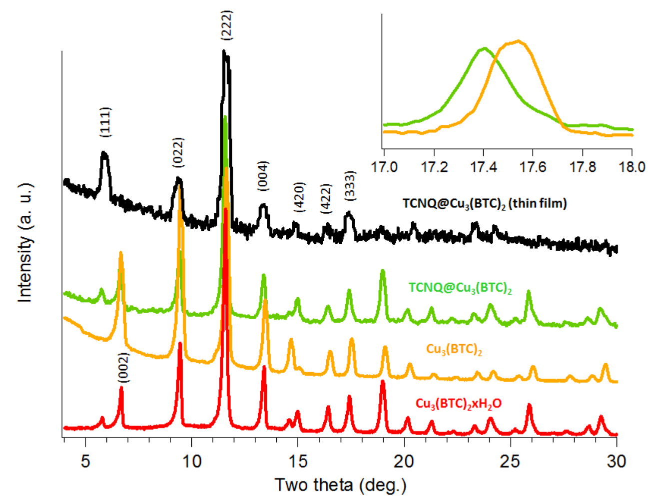
Molecule infiltration











Cu-TCNQ is a well-known conducting CP

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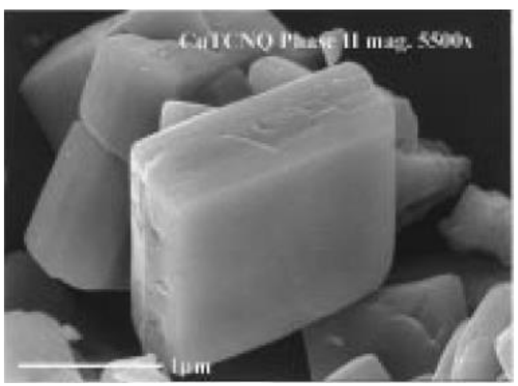
144 *Inorg. Chem.* **1999**, *38*, 144−156

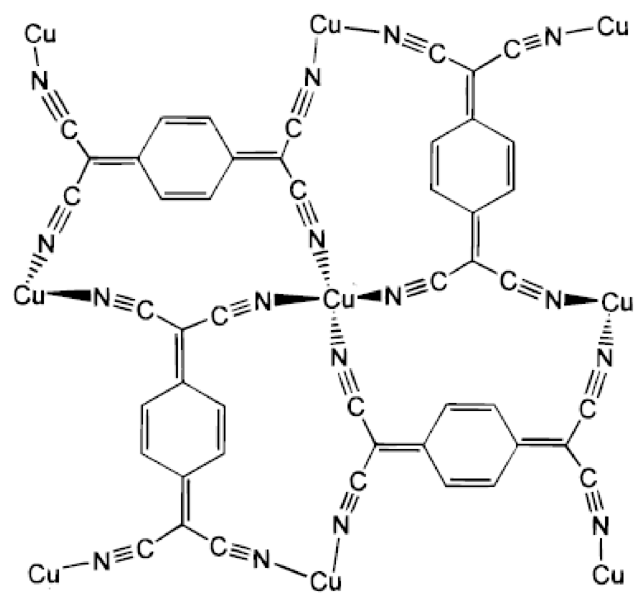
New Insight into the Nature of Cu(TCNQ): Solution Routes to Two Distinct Polymorphs and Their Relationship to Crystalline Films That Display Bistable Switching Behavior

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

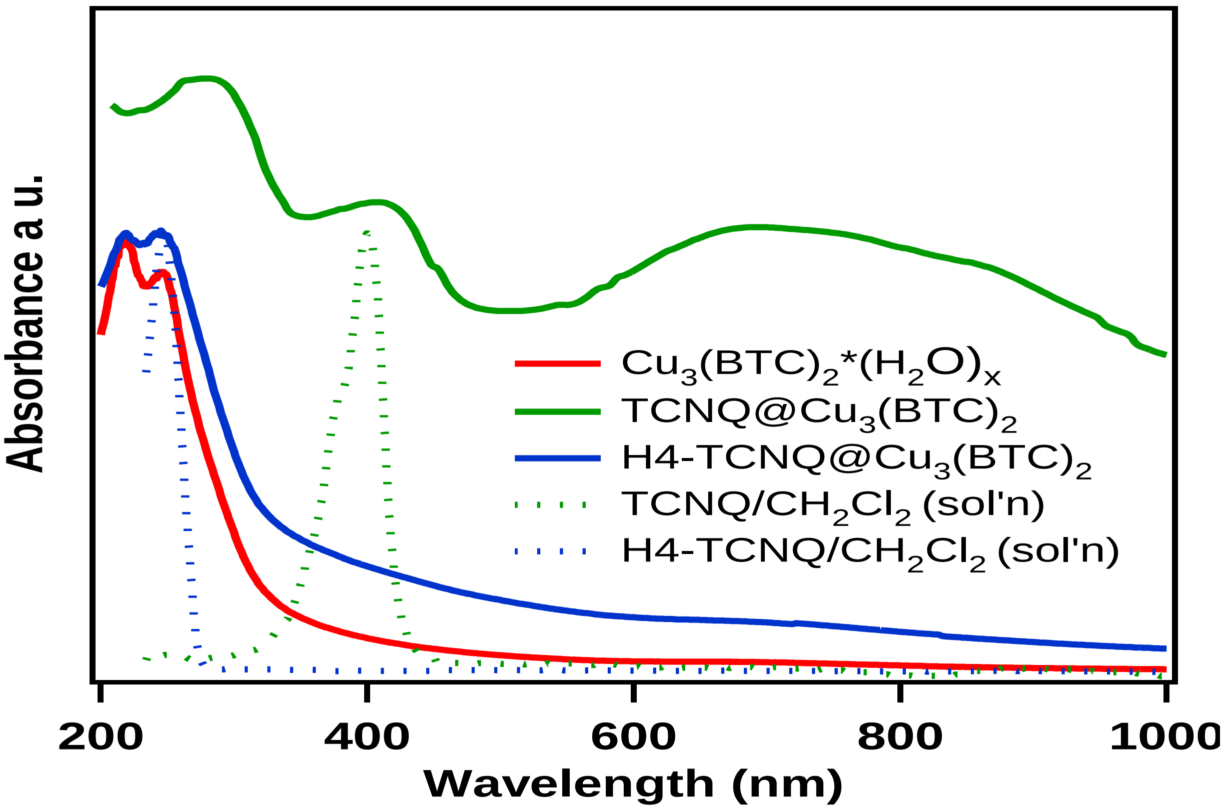
$$[\mathrm{Cu}^{+}(\mathrm{TCNQ}^{-})]_{n} \leftrightarrow [\mathrm{Cu}^{0}]_{x} + [\mathrm{TCNQ}^{0}]_{x} + [\mathrm{Cu}^{+}(\mathrm{TCNQ}^{-})]_{n-x} \quad (1)$$

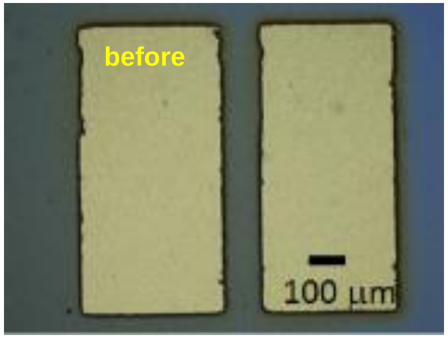
"OFF" state — "ON" state

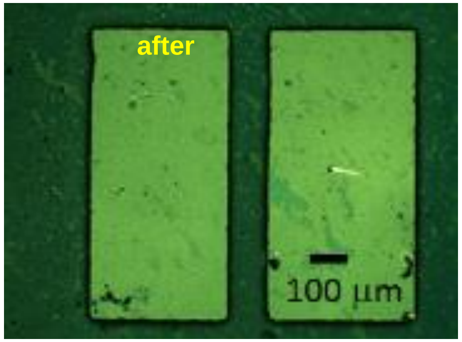




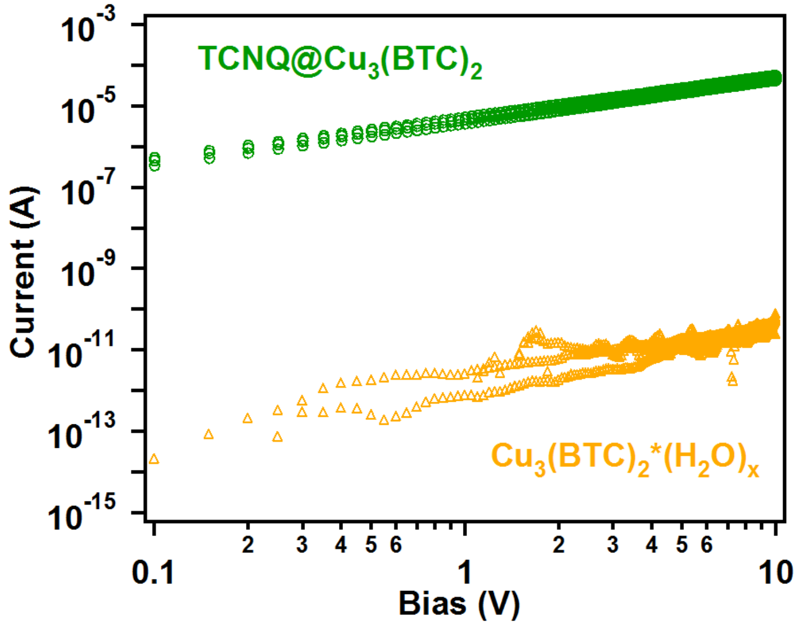
TCNQ@$Cu_2(BTC)_3$ leads to color change

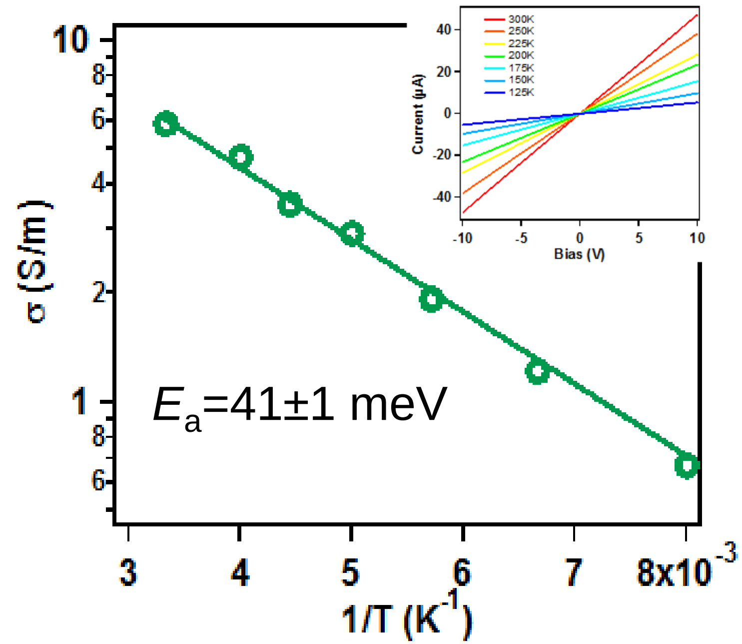


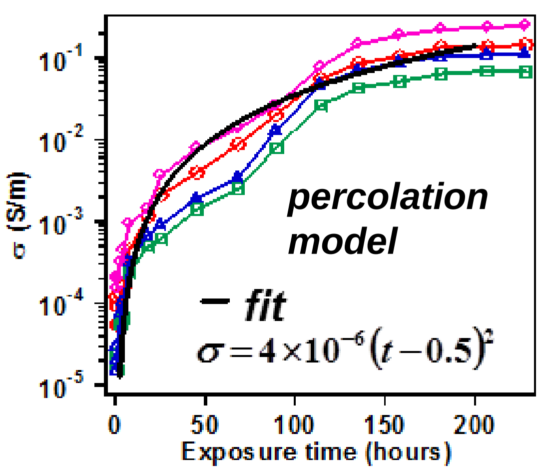




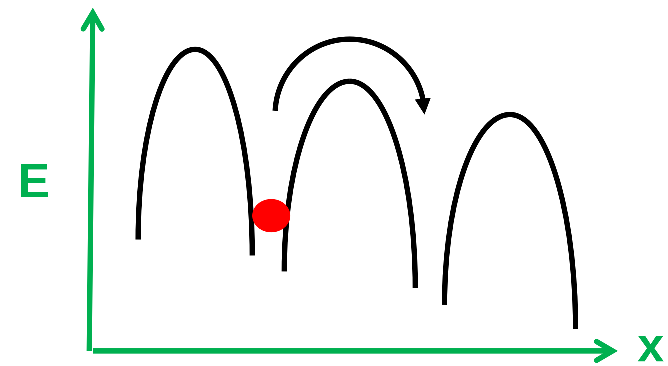
… and >10^6 increase in conductivity, air stable > 1 year



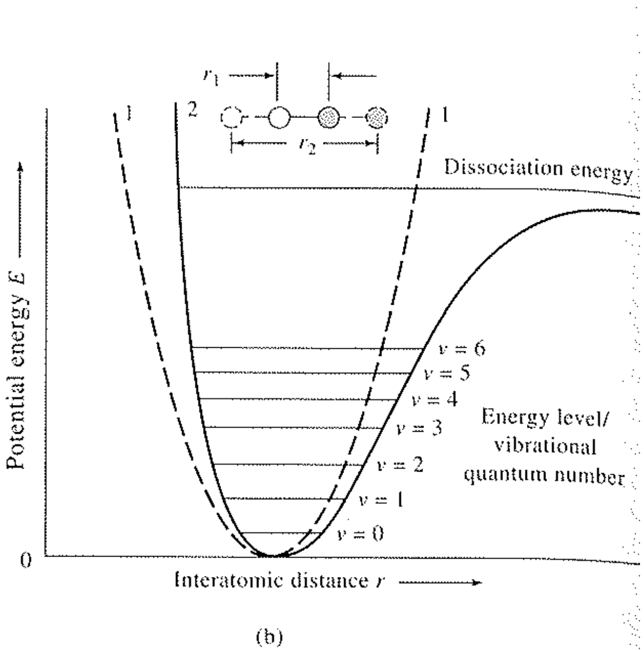




Hopping conduction

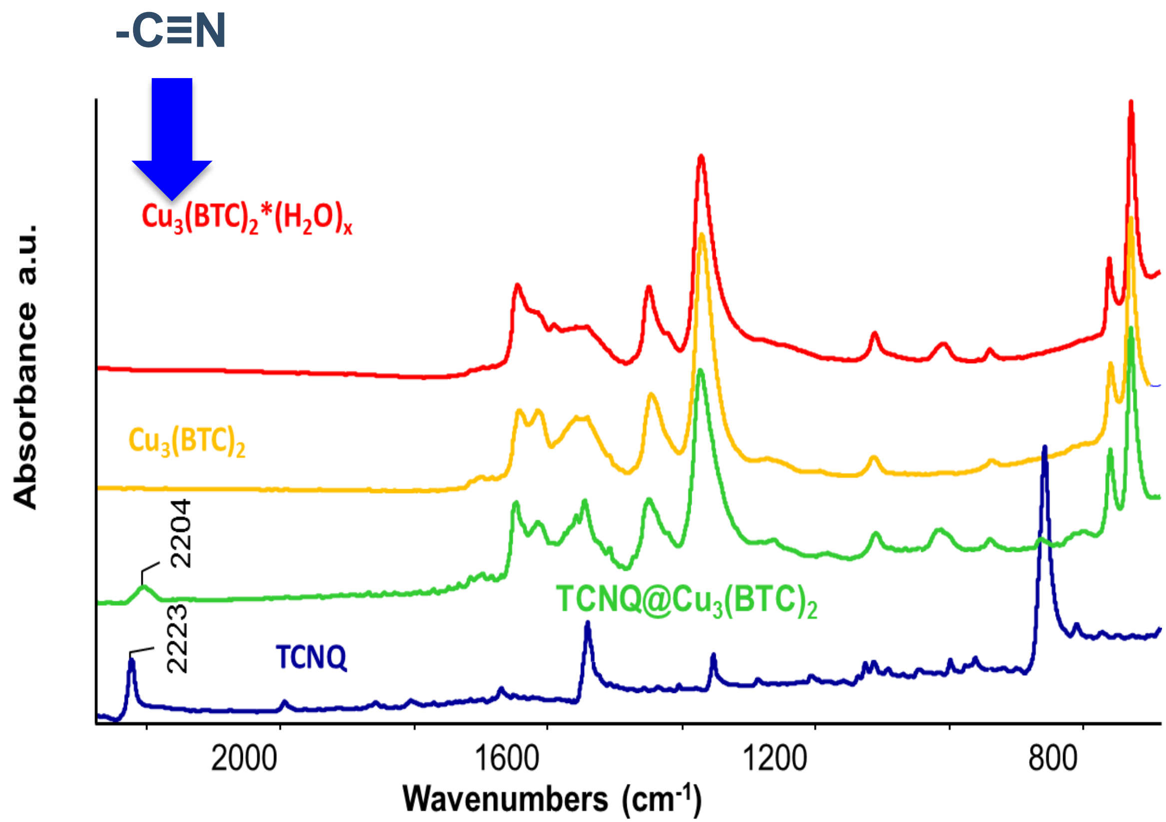


IR shift of -C≡N indicates charge transfer

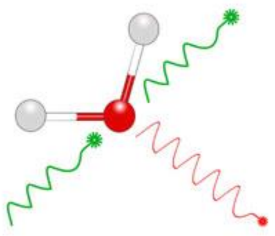


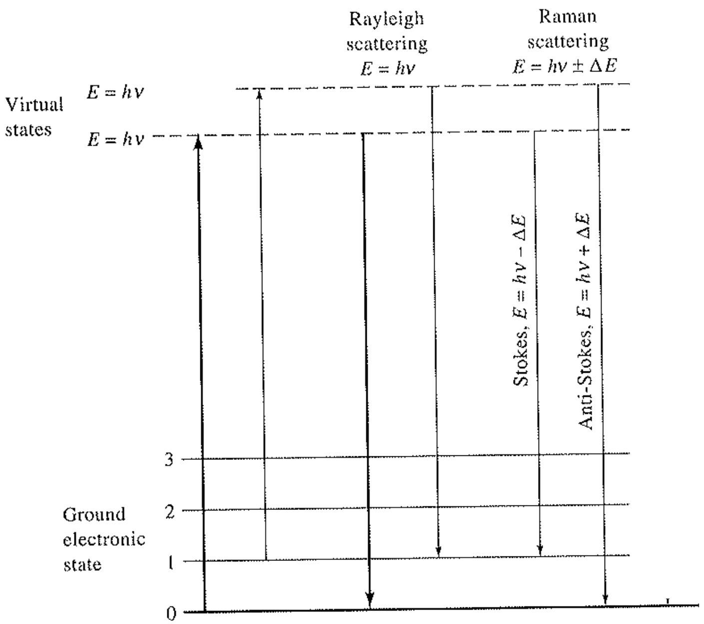
Skoog, Holler, Nieman,
Instrumental Analysis

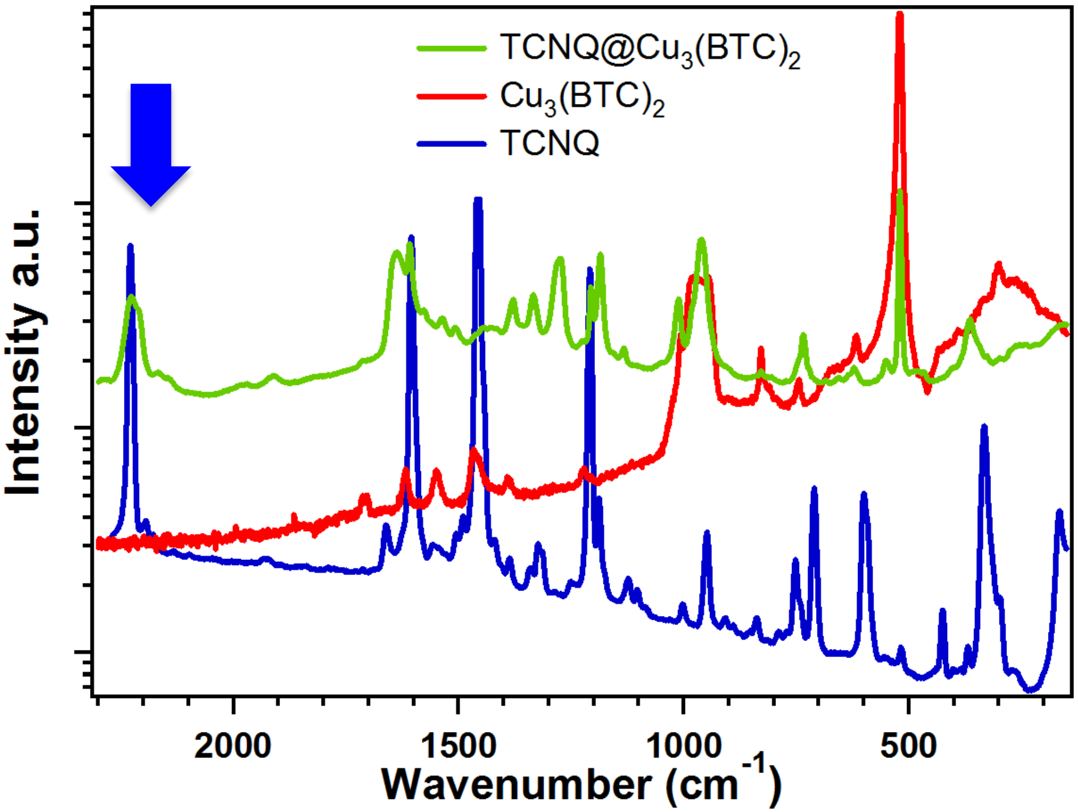
$$z = \left(\nu_o - \nu\right)/\,44cm^{-1}$$



Raman also shows shift of -C≡N







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

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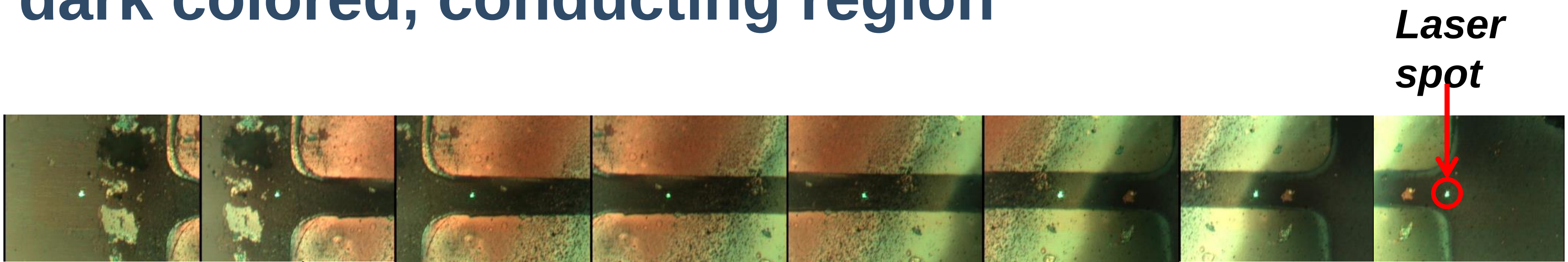
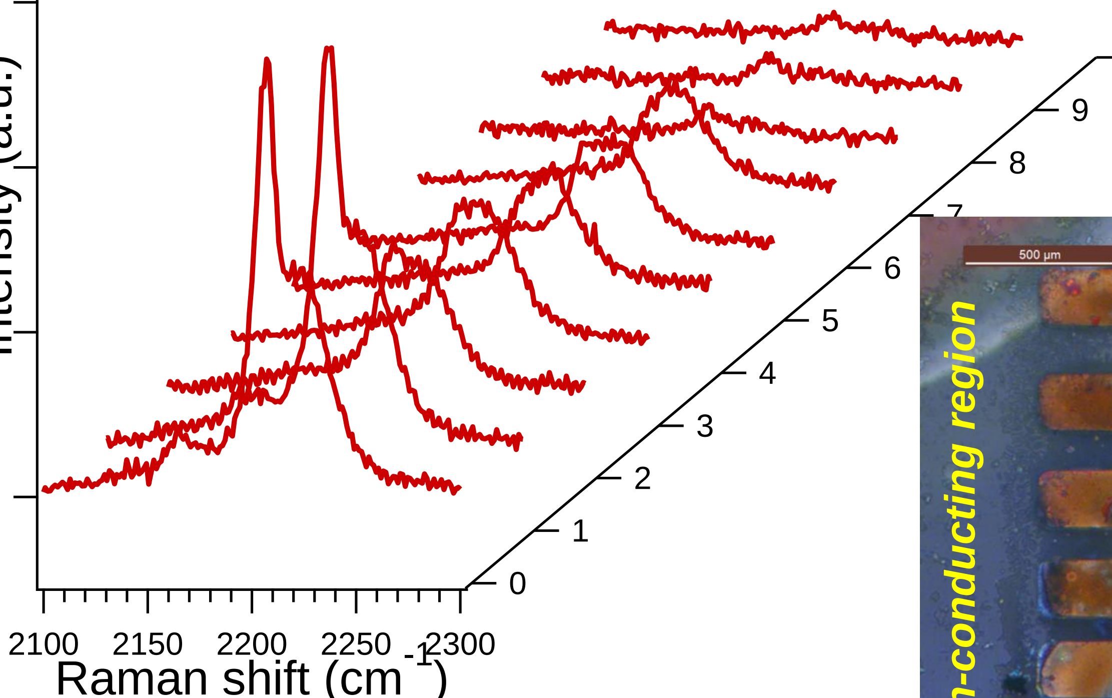
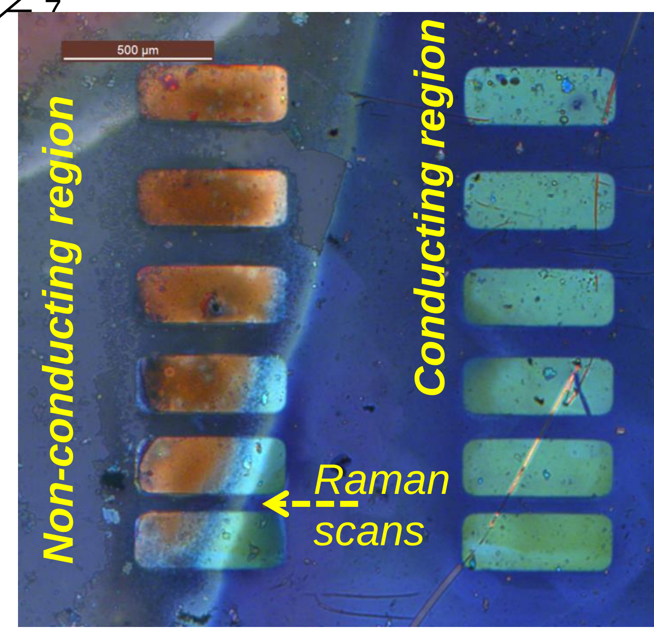
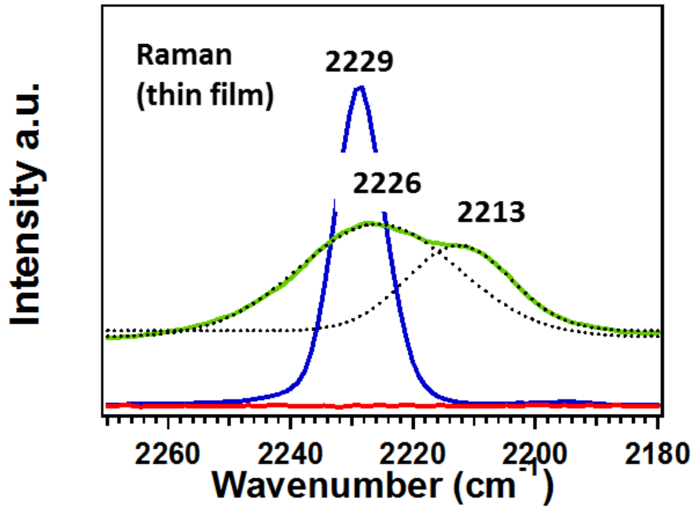
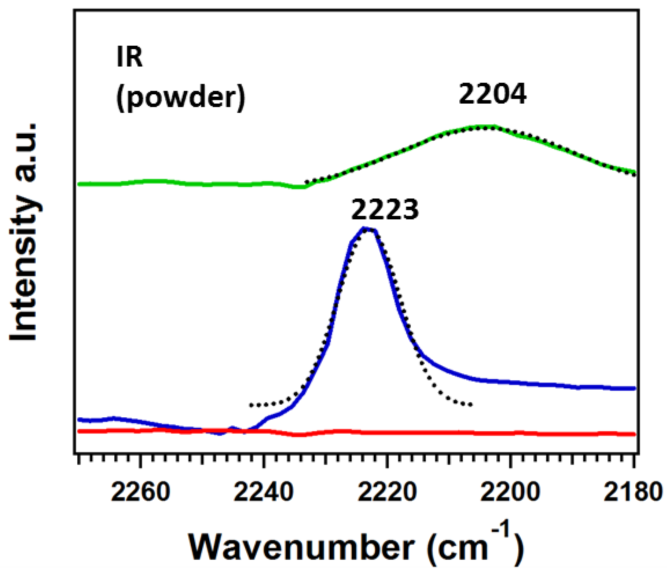


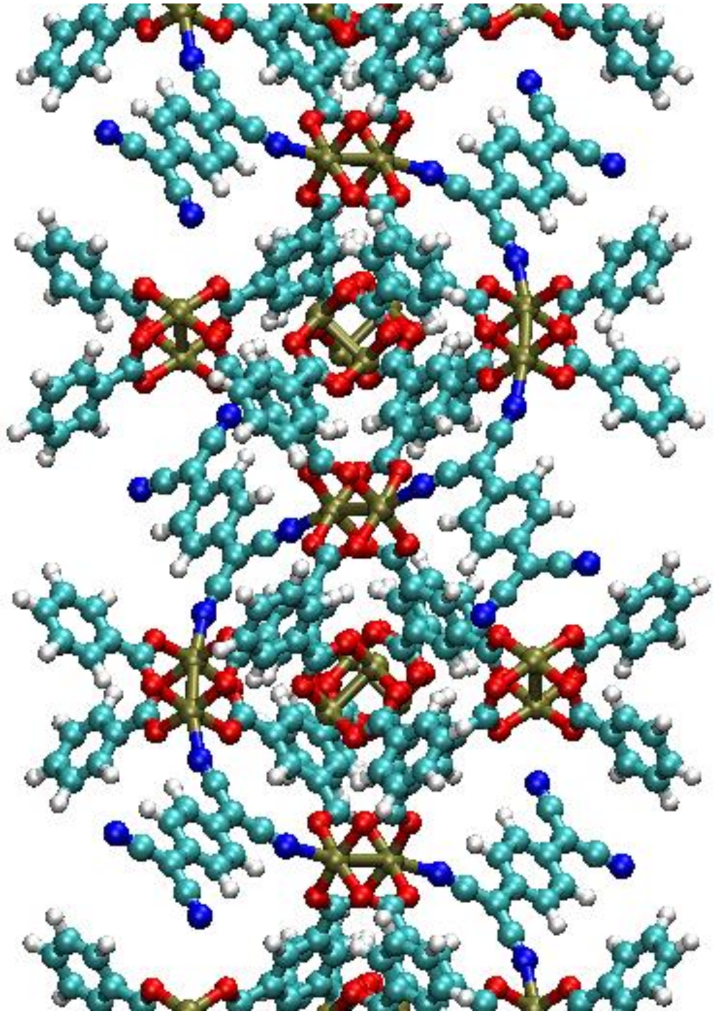




Peak splitting indicates 2 inequivalent -C≡N groups

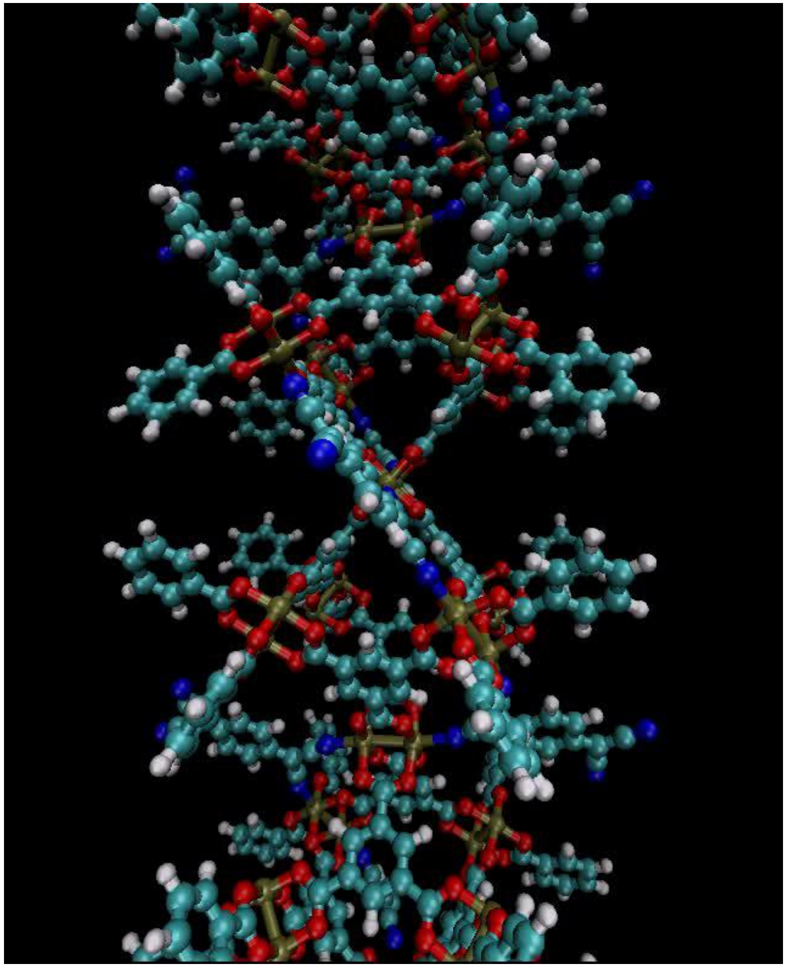






DFT: Cu dimers linked by TCNQ

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



Guest aromaticity, electronegativity affect conductivity

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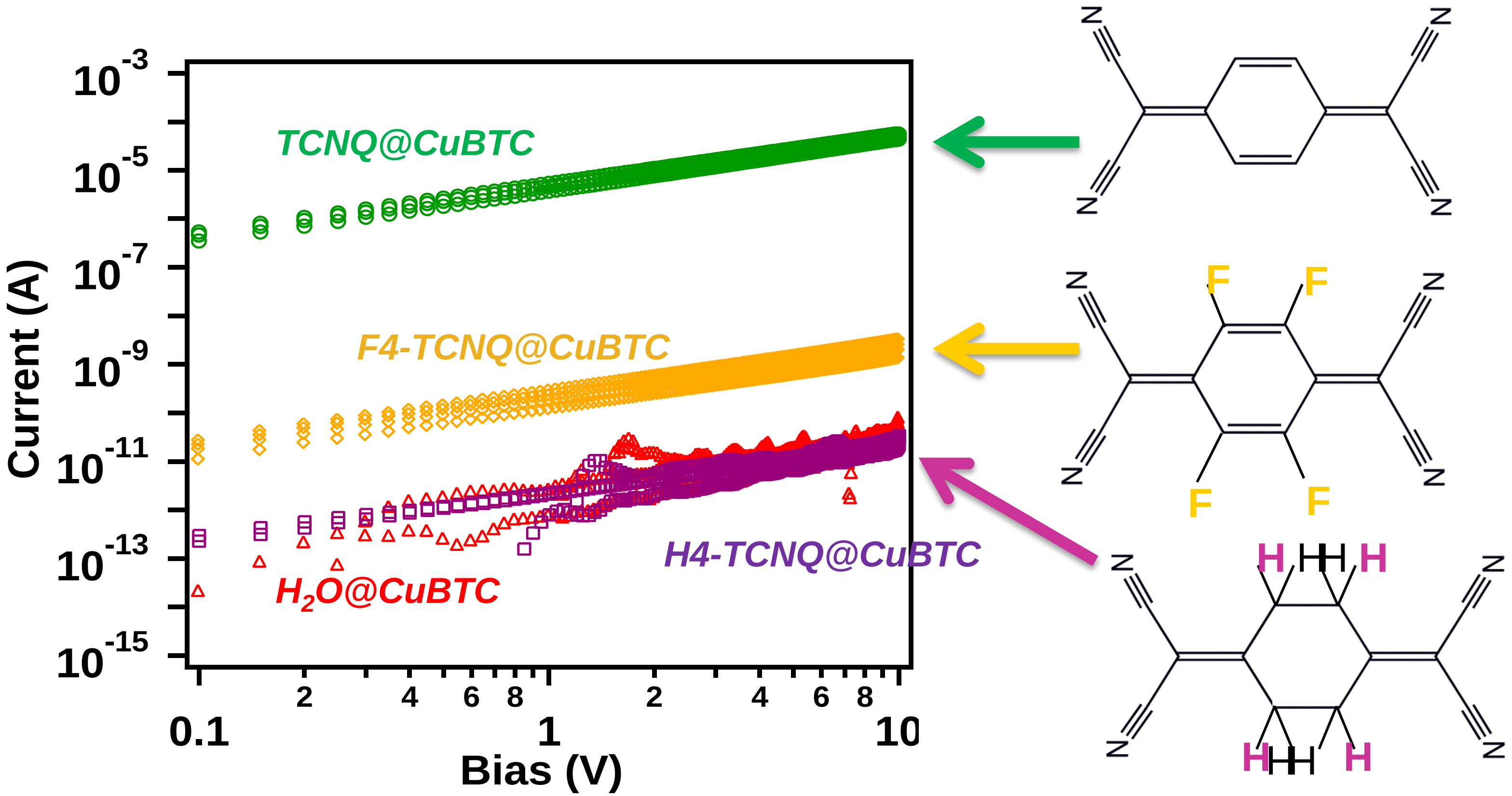
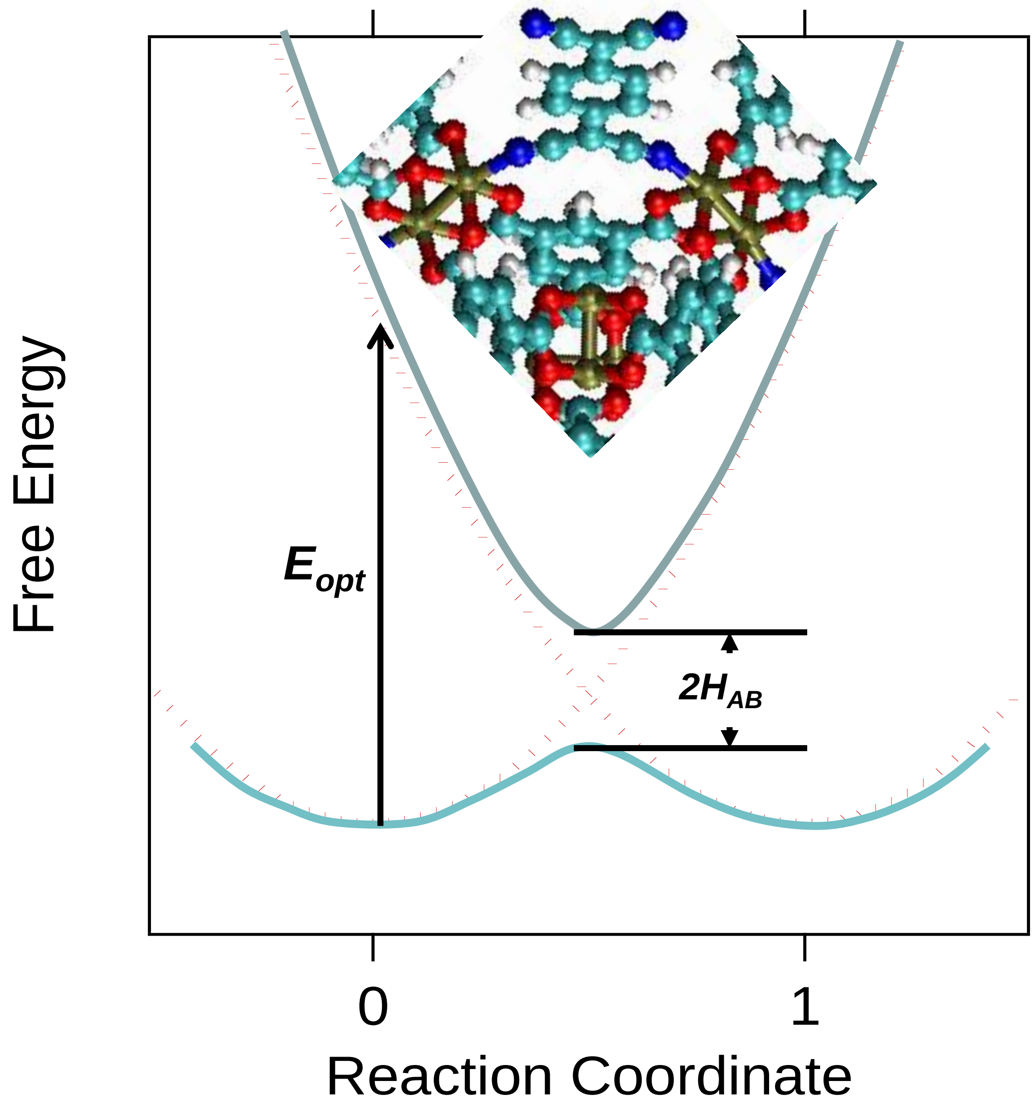


Increased coupling between neighboring Cu dimers lowers barrier to charge transfer



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

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

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

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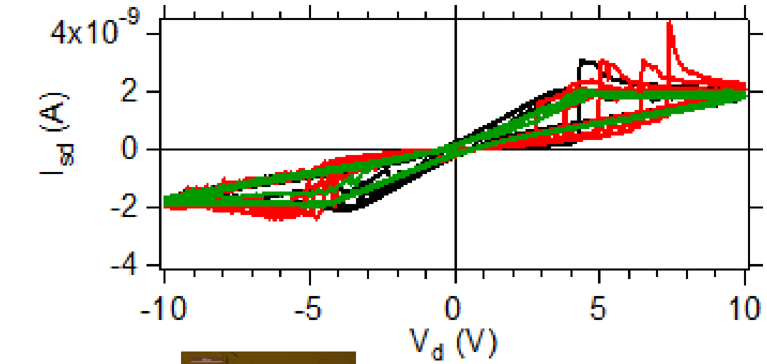
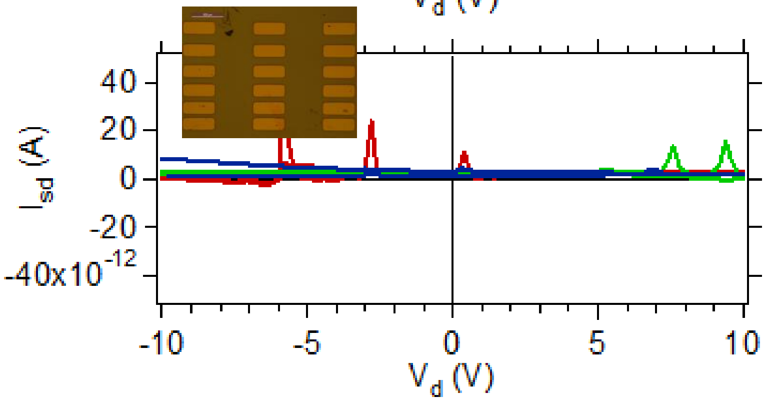
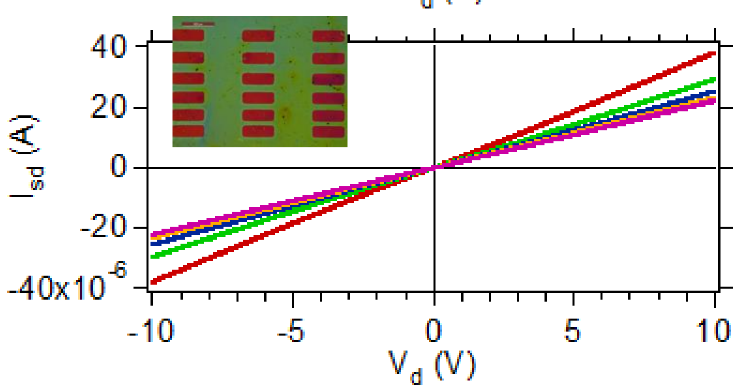


As deposited: Low but measurable conductivity, ionic/electronic?

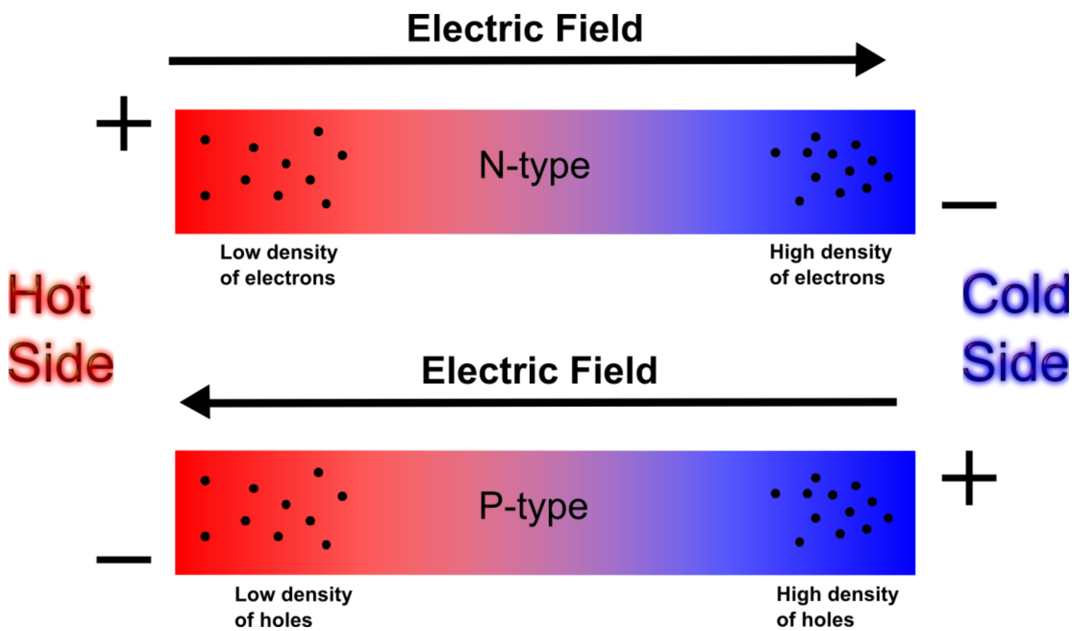


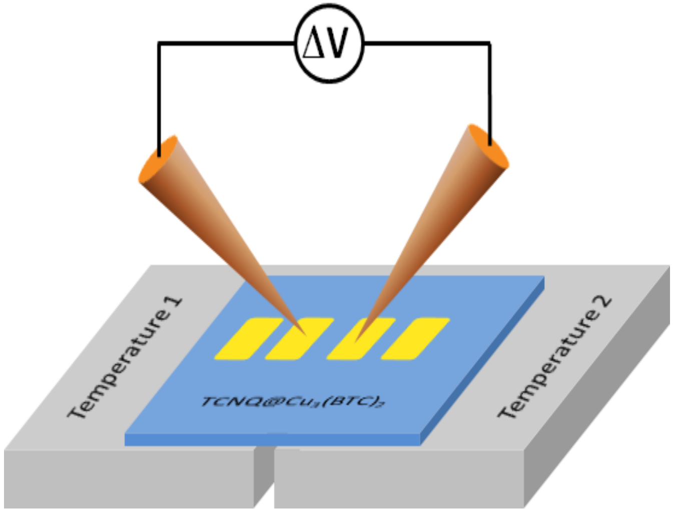
Activated, exposed to ambient: No measurable conductivity at 10V (<10^{-12} A)



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…

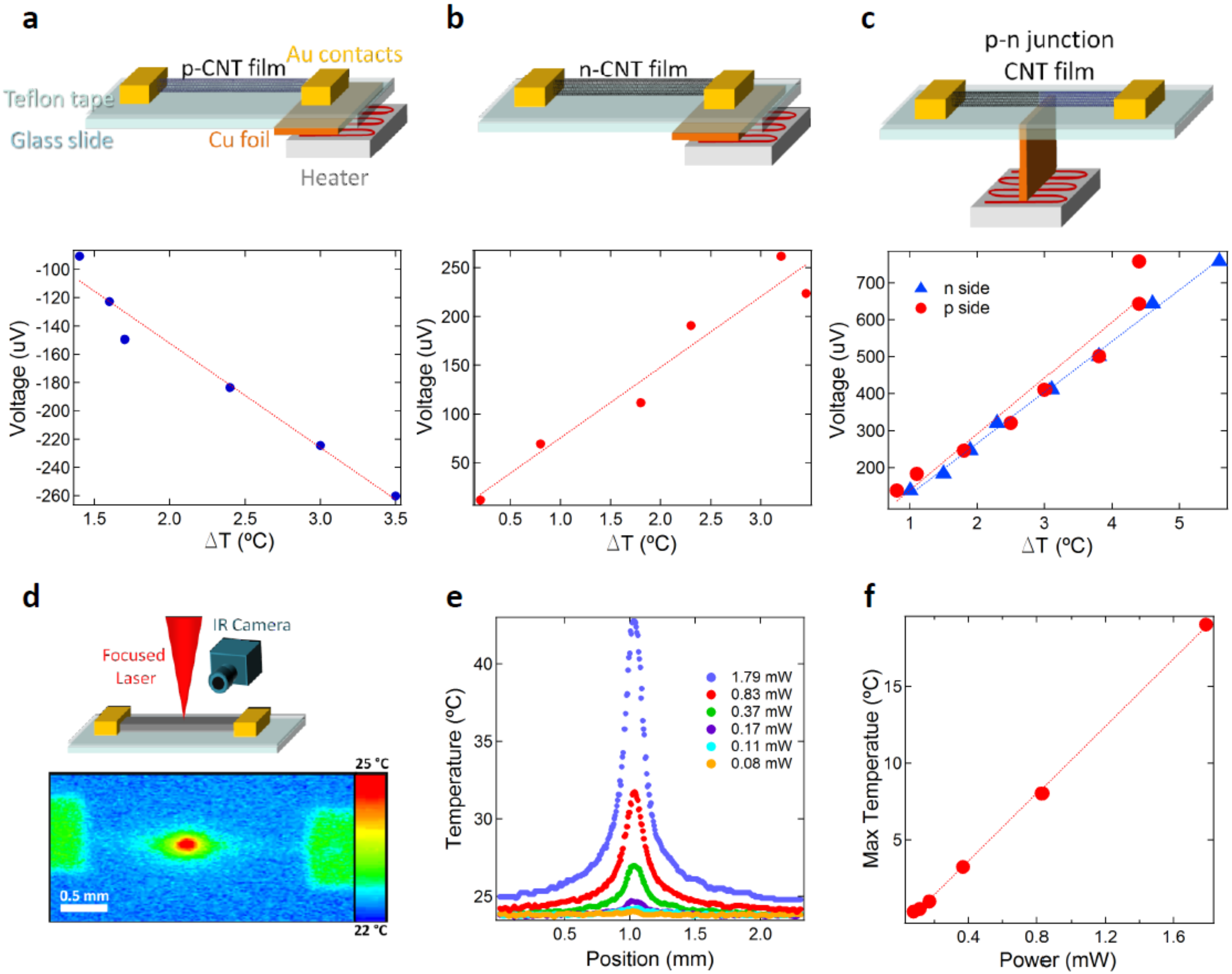




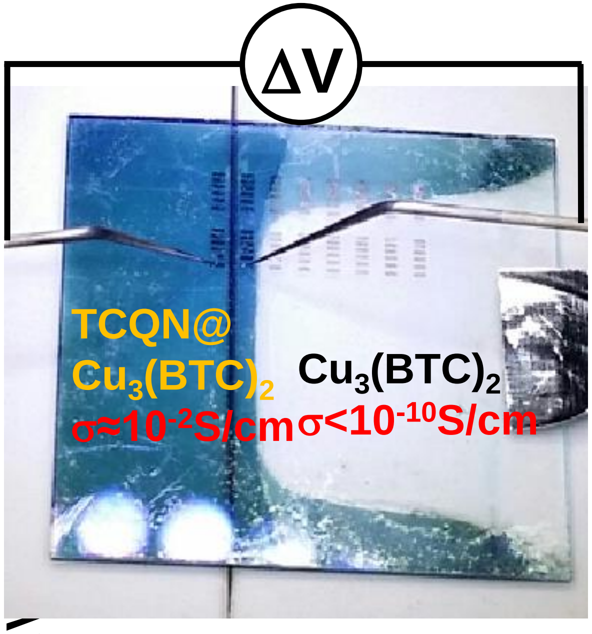
http://www.mn.uio.no/fysikk/english/research/projects/bate/thermoelectricity/

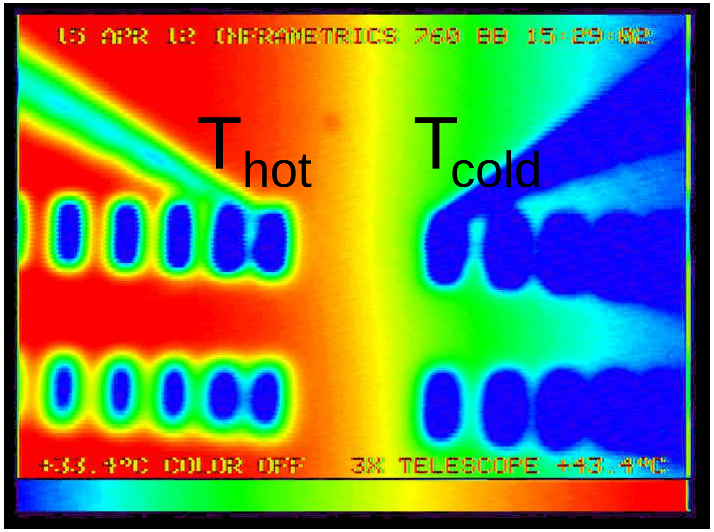
Example from recent work with CNT films

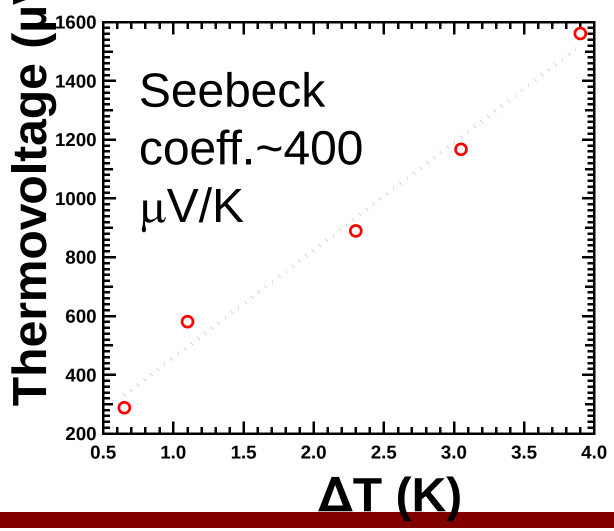
X. He, N. Fujimura, J. M. Lloyd, K. J. Erickson, A. A. Talin, Q. Zhang, W. Gao, Q.Jiang, Y. Kawano,R. H. Hauge, F.Léonard, J. Kono, CNT THz detectors, Nano Lett., just accepted

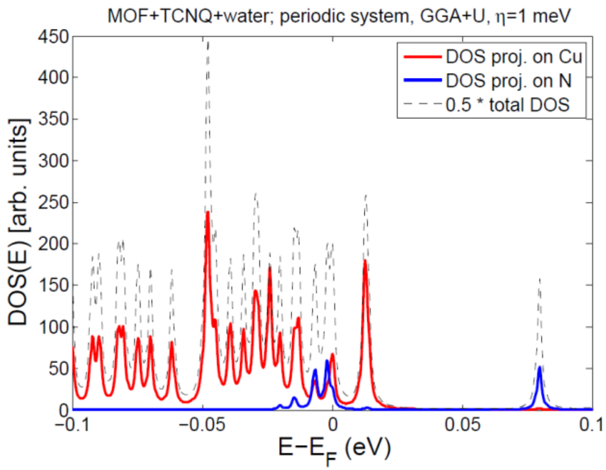


High, positive Seebeck coeff. (i.e Fermi level in VB)

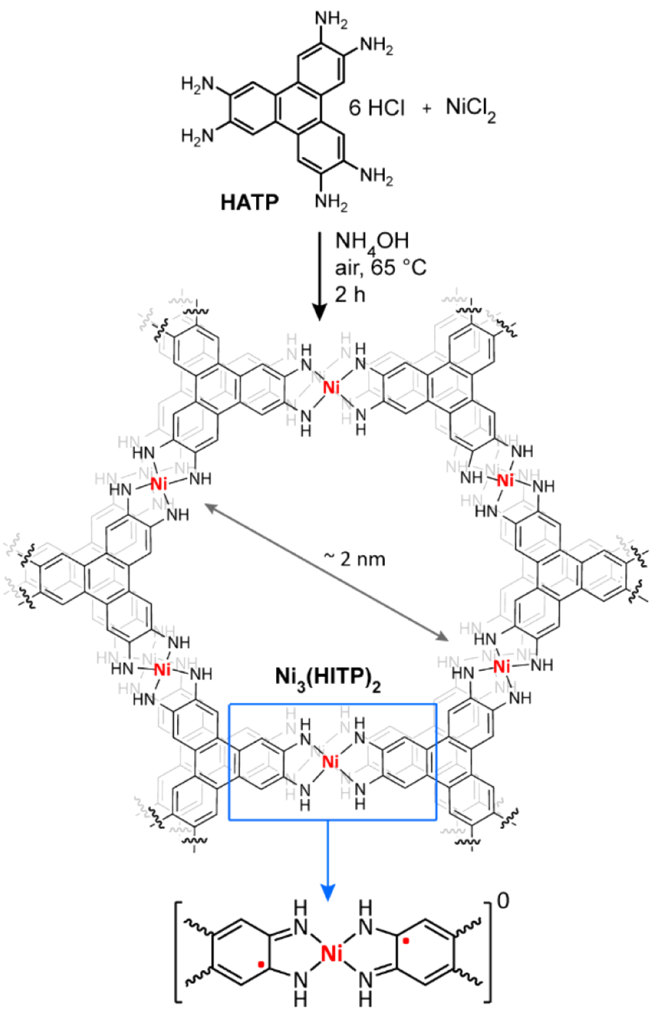


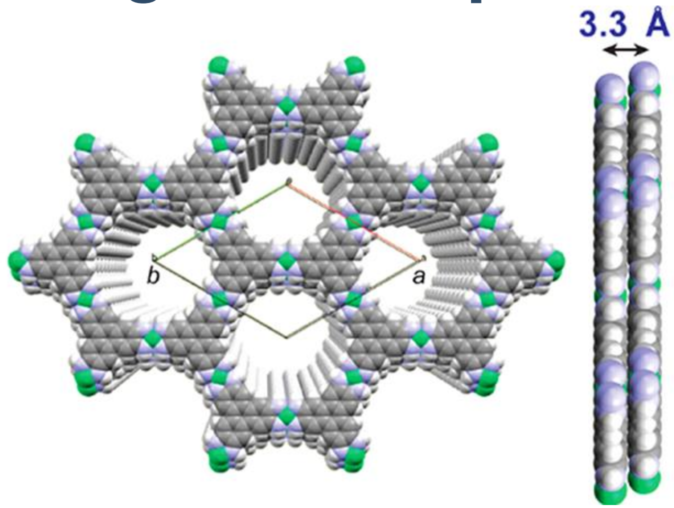


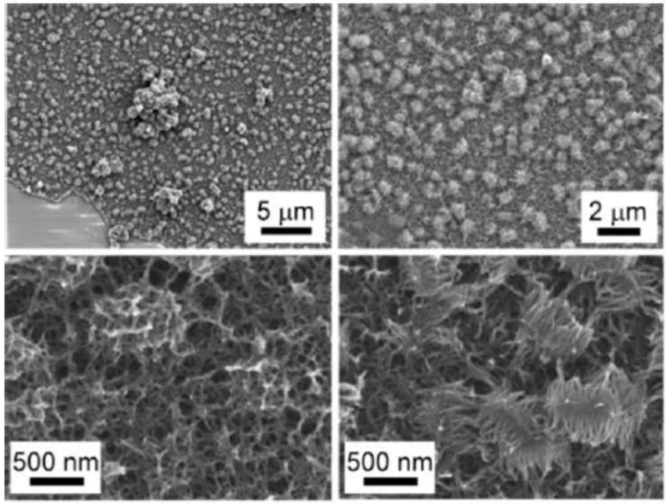




Semiconducting Metal Organic Graphene Analogues (SMOGs)

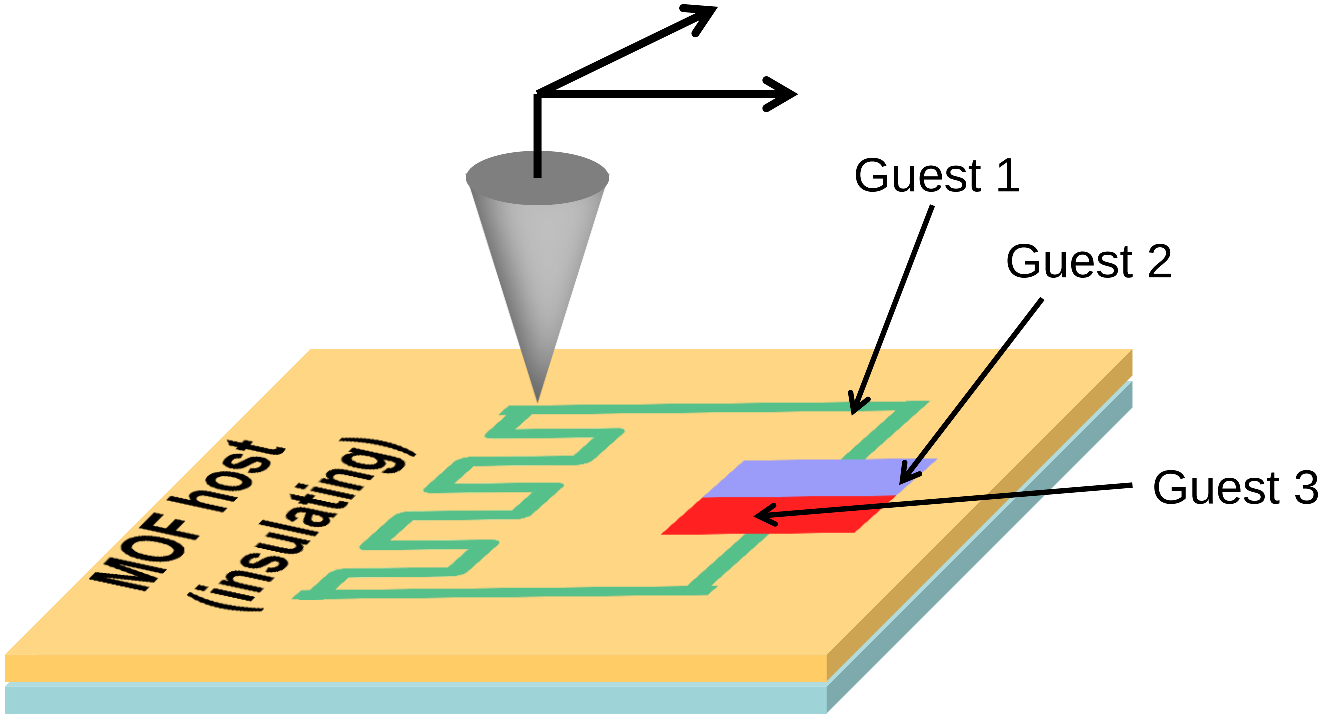


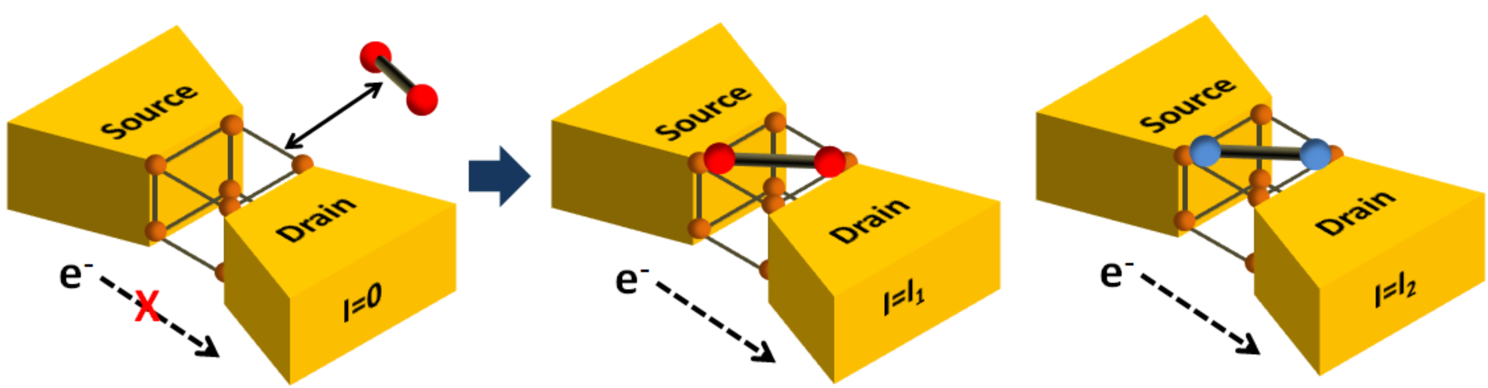




D. Sheberla, L. Sun, M. A. Blood-Forsythe, S. Er, C. R. Wade, C.K. Brozek, A. Aspuru-Guzik, M. Dincă, JACS ASAP

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

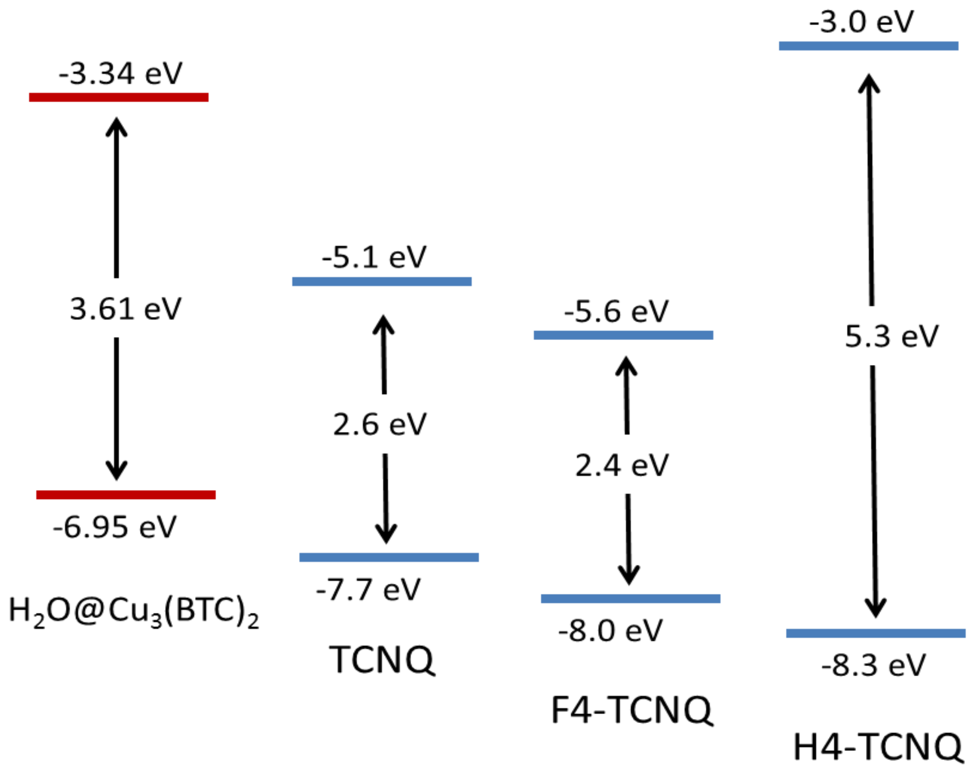
A. A. Talin, A. Centrone, M. E. Foster, V. Stavila, P. Haney, R. A. Kinney, V. Szalai, F. El Gabaly, H. P. Yoon, F. Léonard, M. D. Allendorf, *Science* **343**, 66 (2014);

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

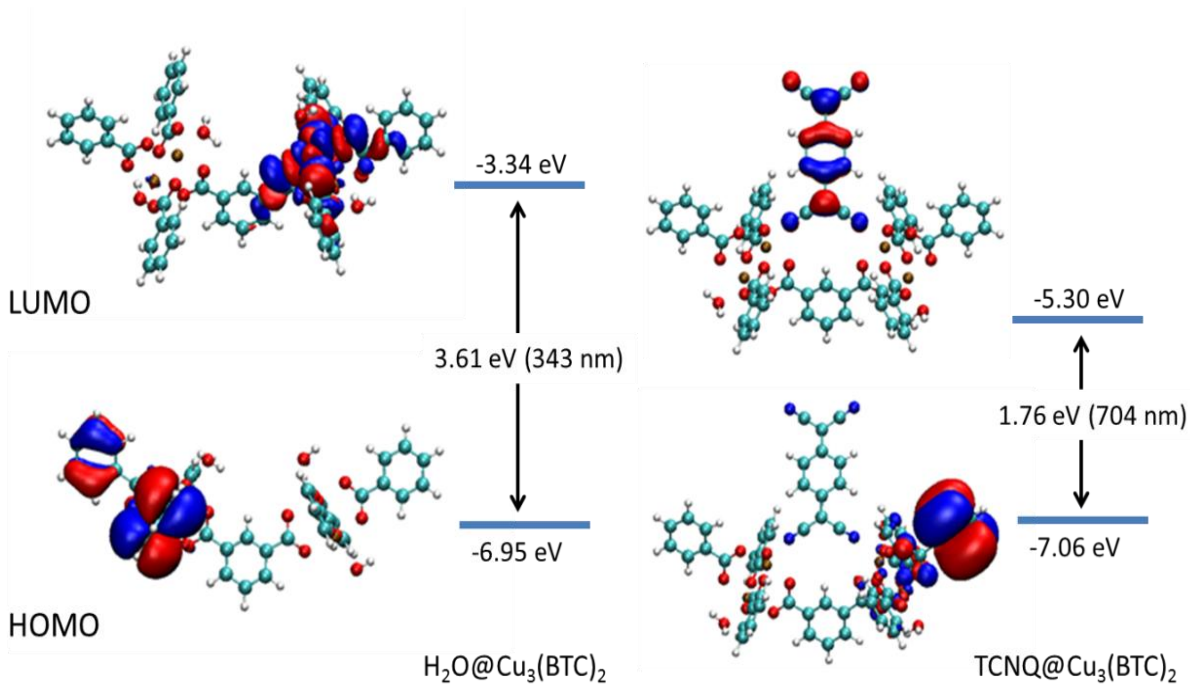
Contributors

Sandia: Vitalie Stavila, Alexandra C. Ford, Michael E. Foster, Catalin Spataru, Farid El Gabaly, François Léonard, Mark Allendorf

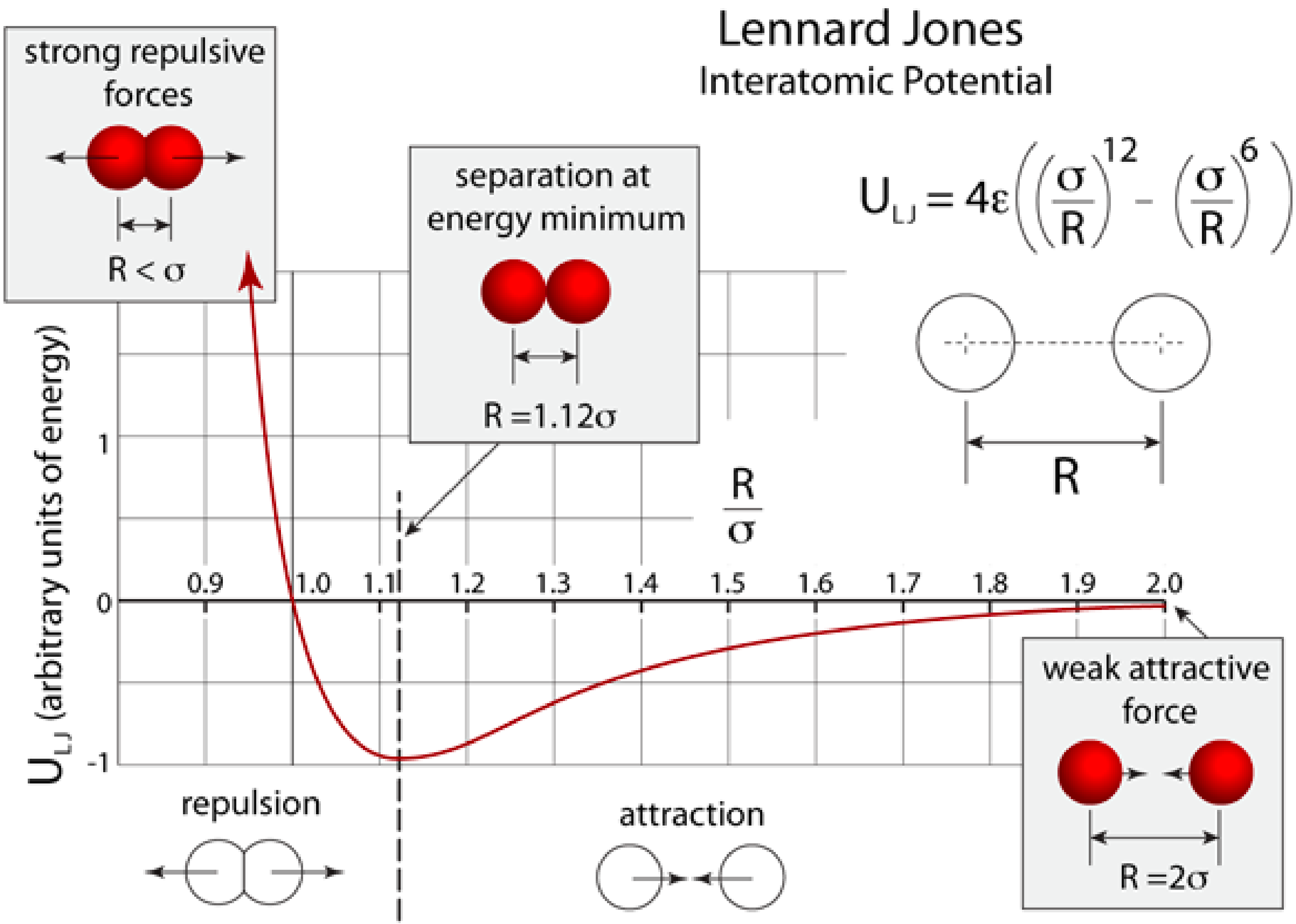
NIST: Andrea Centrone, Paul Haney, R. Adam Kinney, Veronika Szalai, Heayoung P. Yoon



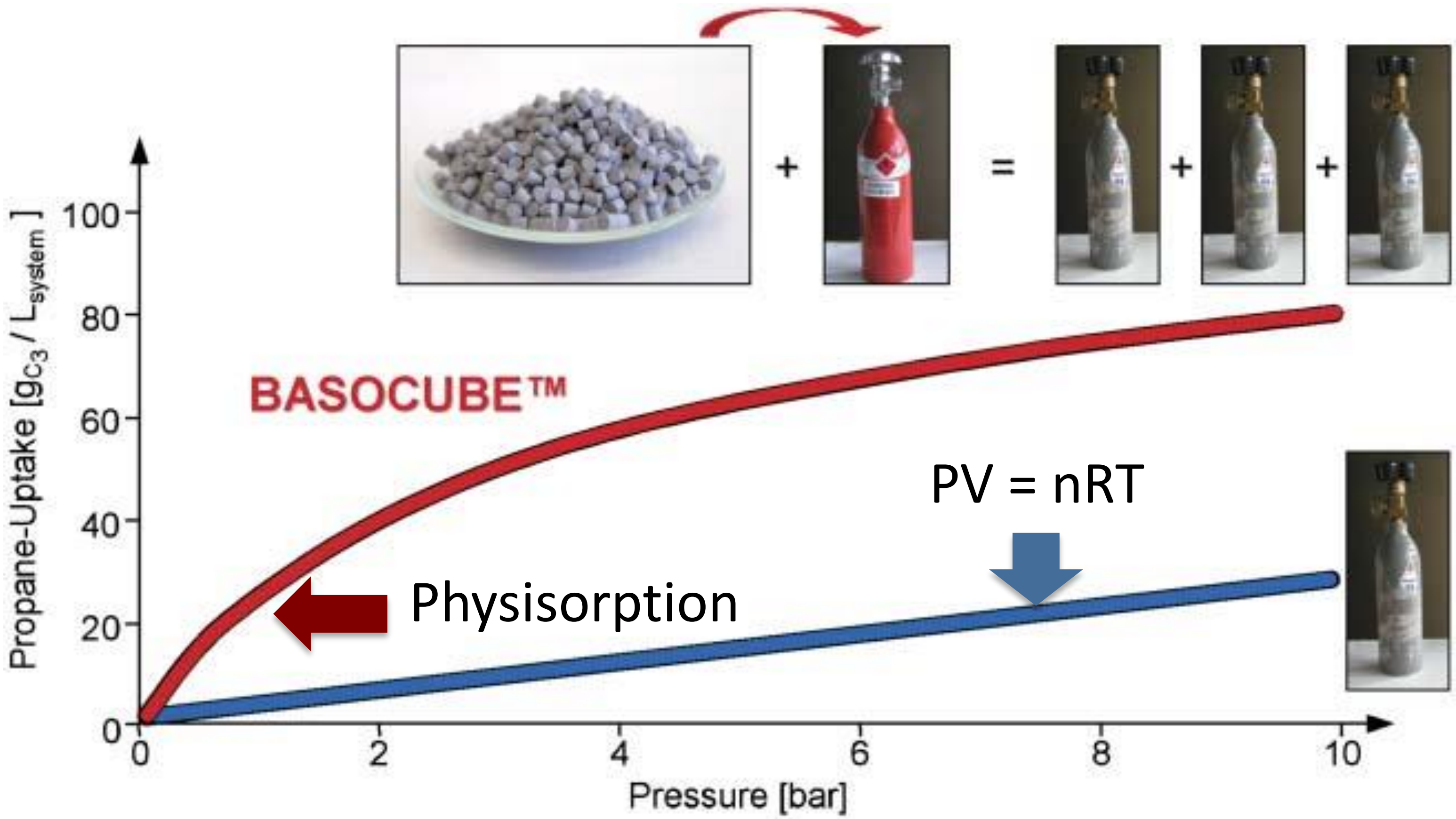
A schematic representation of the alignment of the HOMO/LUMO orbitals and bandgaps of H_2O@CuBTC, TCNQ, F4-TCNQ, and H4-TCNQ determined at the UB3LYP/VTZP level of theory.


LUMO
-3.34 eV
3.61 eV (343 nm)
-6.95 eV
HOMO
H2O@Cu3(BTC)2
-5.30 eV
1.76 eV (704 nm)
-7.06 eV
TCNQ@Cu3(BTC)2

Van der Waals forces govern the interaction of molecules such as H_2, He, and CH_4, with surfaces



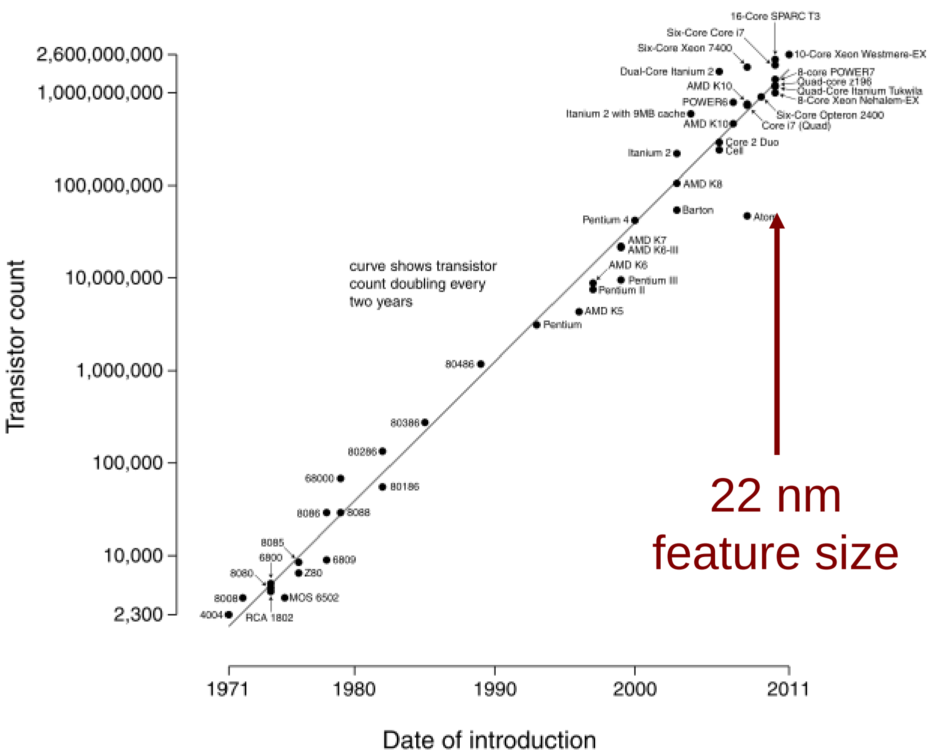
How does surface area affect gas storage?

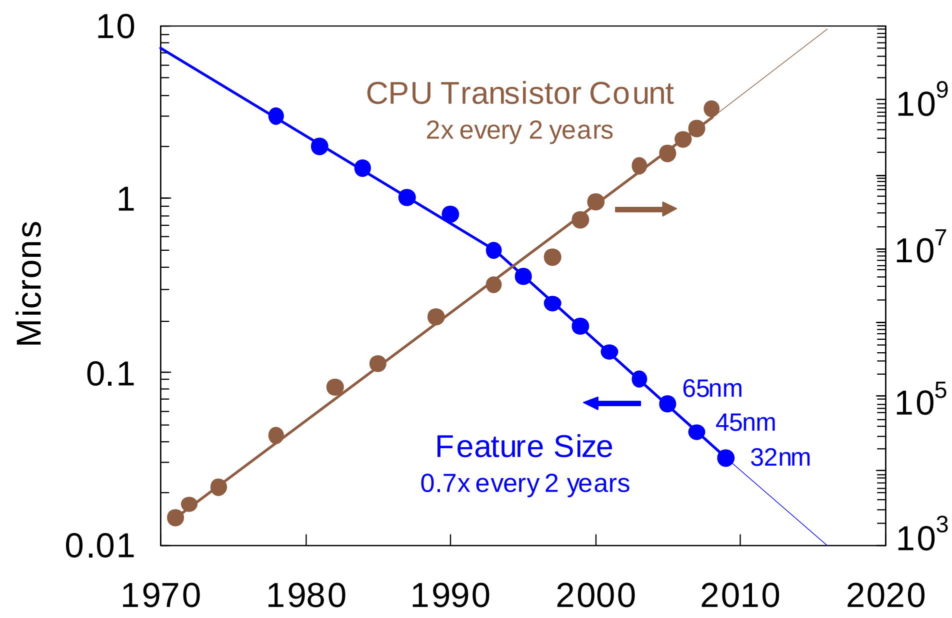


Compression of propane into gas container with and without MOF-filling (MOF-5 tablets in lecture bottles, room temperature) – U. Mueller et al. *J. Mater. Chem.*, 2006, 16, 626–636

The demise of Moore's Law?

Microprocessor Transistor Counts 1971-2011 & Moore's Law

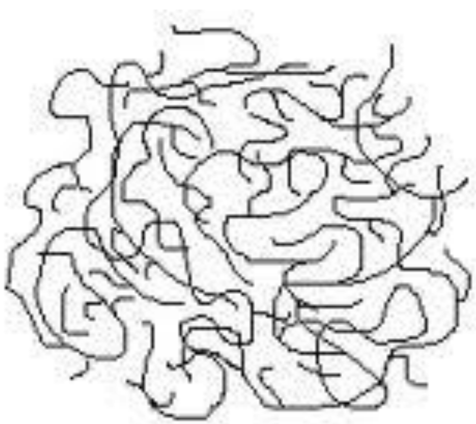


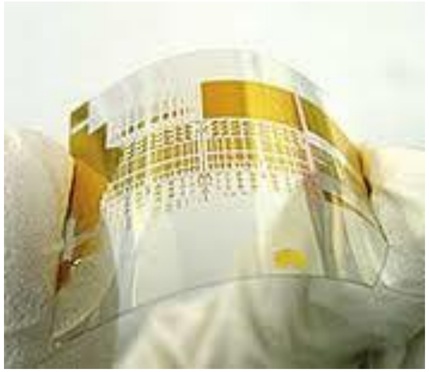


Could polymer or molecule-based electronics be the answer?

Sandia National Laboratories

Organic semiconductors: cheap, tunable properties, mechanically flexible, but…

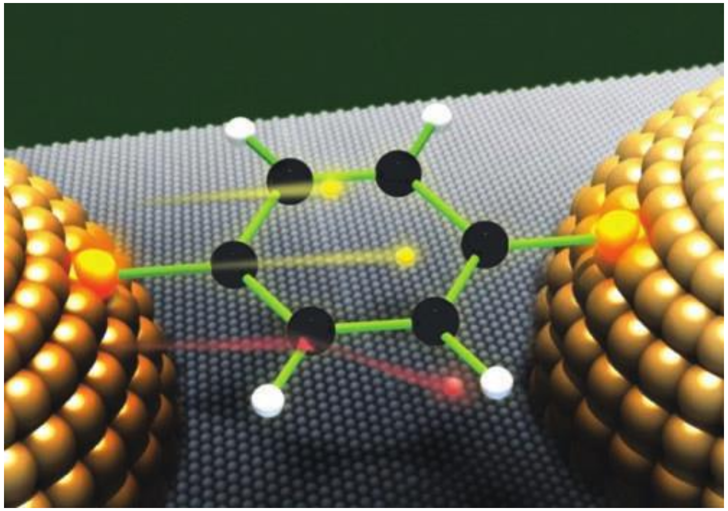




DIsordered structure leads to chain-to-chain hopping, causing:

- ➡ **Poor mobility**
- ➡ **Low free carrier lifetime**
- ➡ **Chemical & thermal Instability**

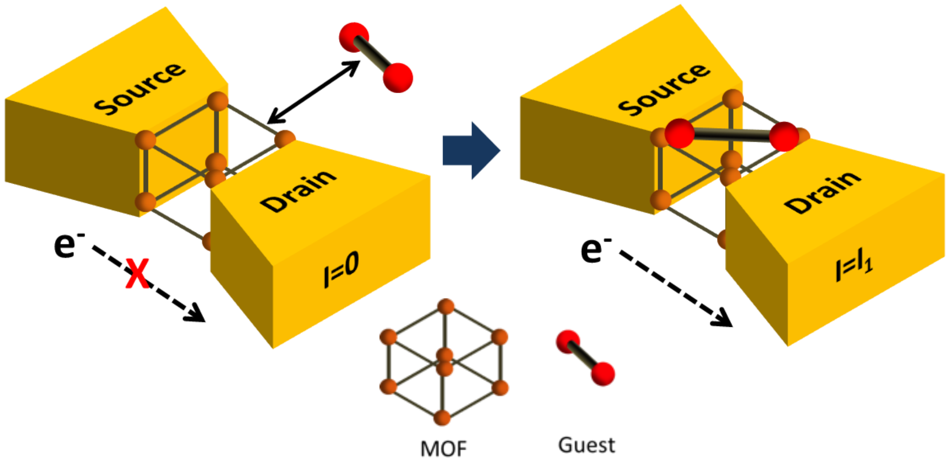
Molecular electronics: the ultimate in tunability and scalability, but…

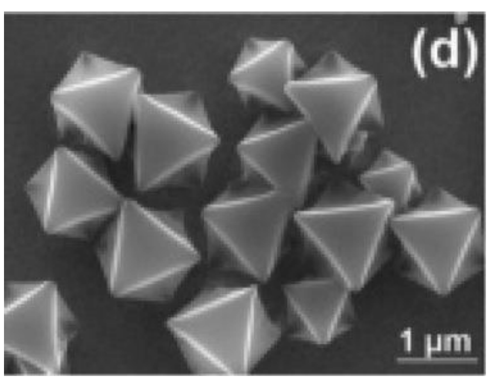


Extremely difficult fabrication stalls advances

At these length scales, “bottom-up” fabrication beats “top down”…

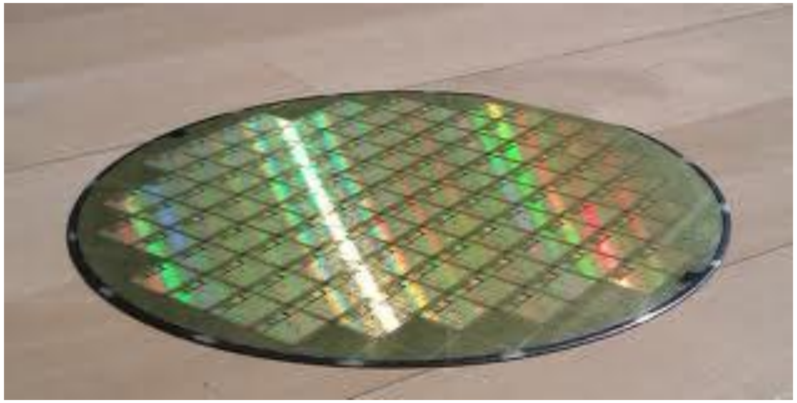
New device concept based on Guest@MOF materials: Reconfigurable Electronics





E. Biemmi, C. Scherb, T. Bein, J. AM. CHEM. SOC. 2007, 129, 8054

?

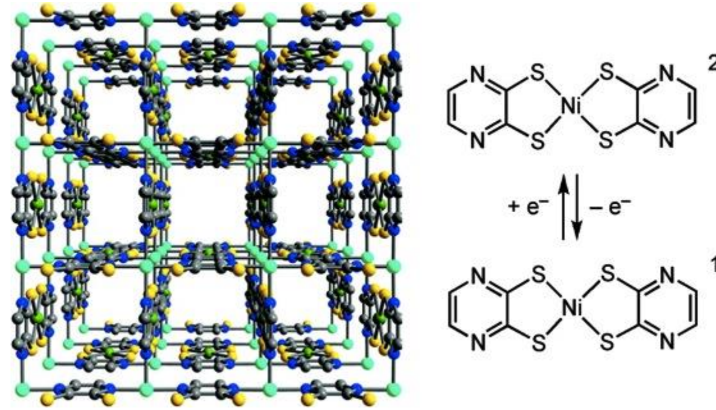


Electrically conducting porous MOFs are rare

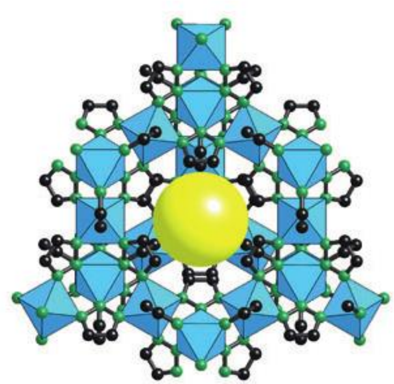
- **p-type Cu-Ni Dithiolene MOF**
  - First semiconducting, porous MOF
  - Conductivity increases with oxidative doping
  - Original Cu-Cu version is not porous (*Inorg. Chem.* 2009, 48, 9048)

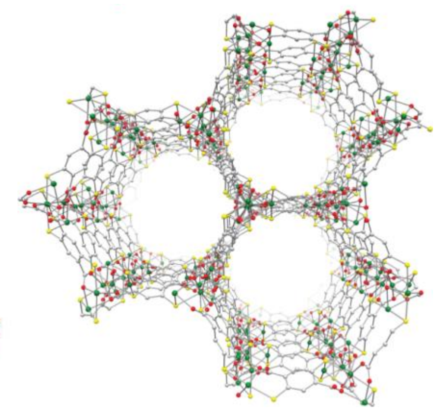
- **Other examples**
  - MET-3 (Fe-triazolate MOF)
  - Mn(thiophenol) MOF: (−Mn−S−)∞ Chains

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



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


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


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