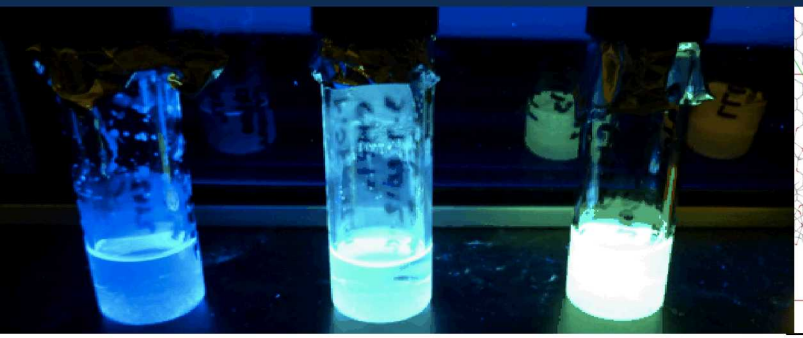
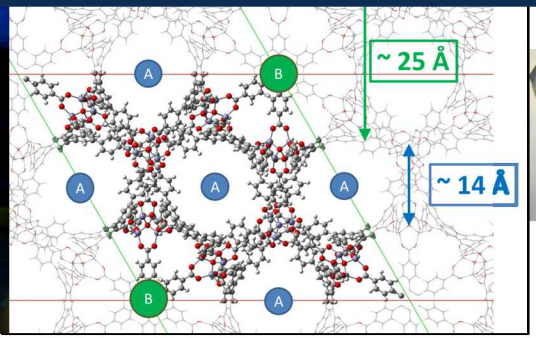
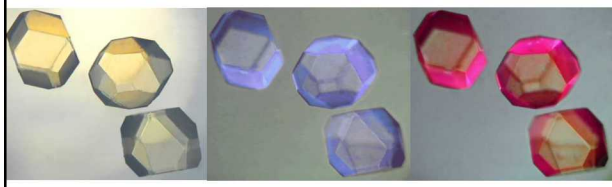
SAND2019-8390PE







Defects in Metal-Organic Frameworks: blessing or curse?

Mark D. Allendorf

Sandia National Laboratories, Livermore, CA 94551-0969

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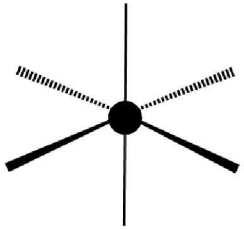
MOF self assembly

Sandia National Laboratories

Organic
"linker"

Metal
"Node"



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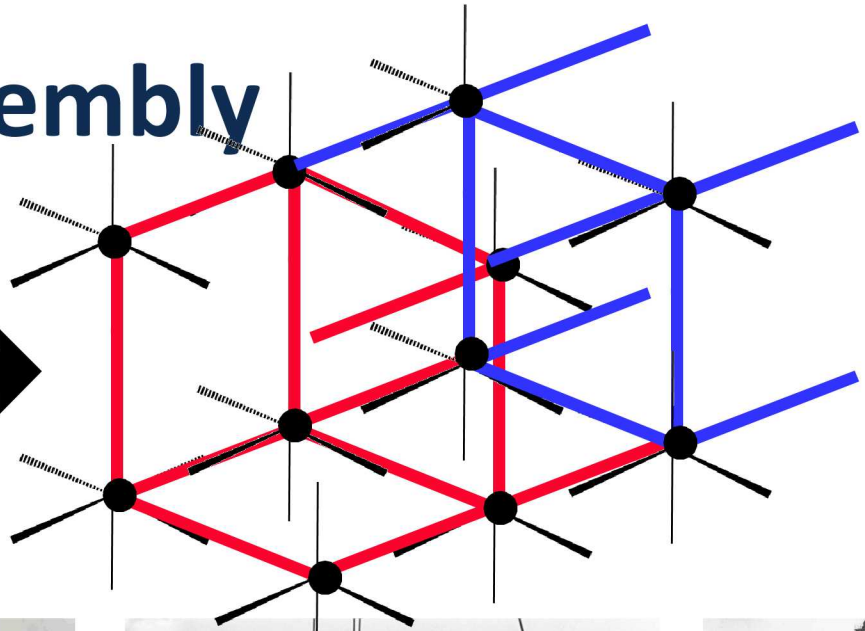
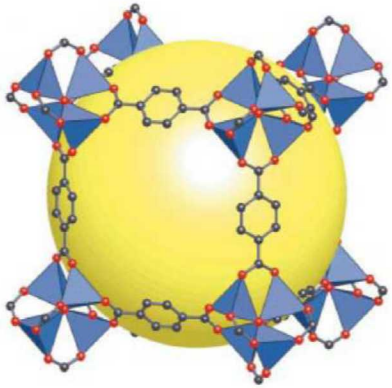


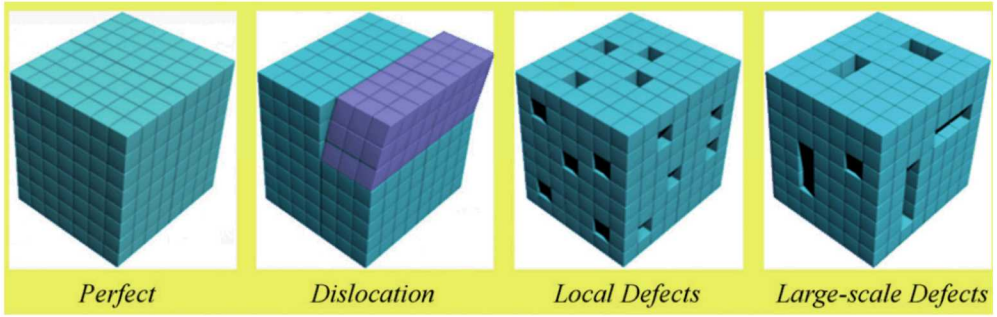


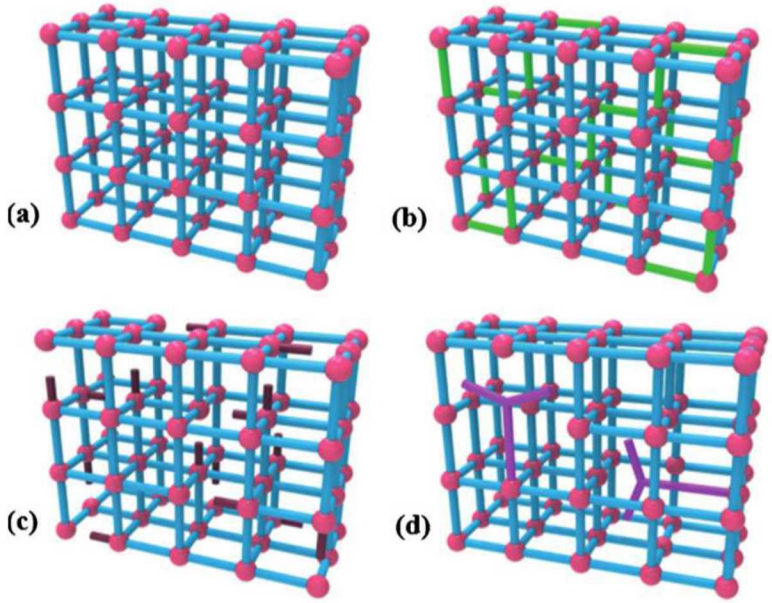
Things don't always go as planned…

Defects in MOFs are now well known

Effects include:

- Gas storage/separations: altered mass transport
- Catalysis: Brønsted or Lewis acid sites
- Luminescence: modified band gaps
- Magnetic properties: ferromagnetism introduced by point defects
- Mechanical properties: reduced stiffness





Fischer et al. *Angew. Chem. Int. Ed.* 2015, **54**, 7234

When defects turn into virtues: The curious case of zirconium-based metal-organic frameworks

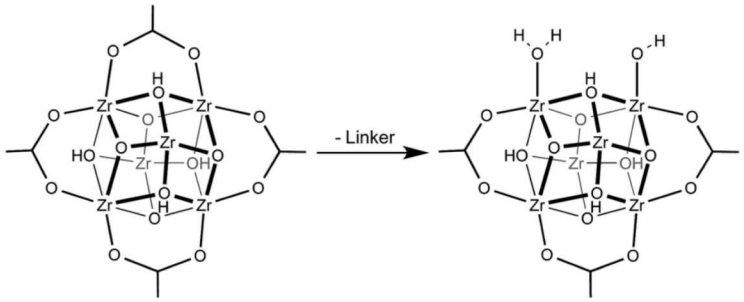
Marco Taddei

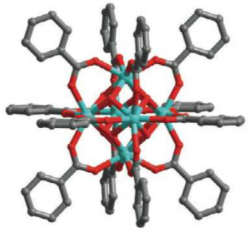
Energy Safety Research Institute, College of Engineering, Swansea University, Fabian Way, Swansea SA1 8EN, United Kingdom

Sandia National Laboratories

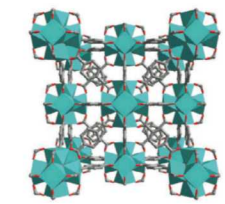
Coordination Chemistry Reviews 343 (2017) 1–24

MOFs with tunable acid site concentrations and pore size

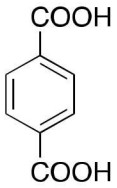




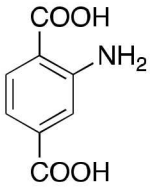
12-connected



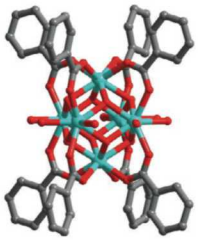
7Å and 9Å



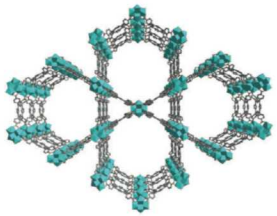
UiO-66



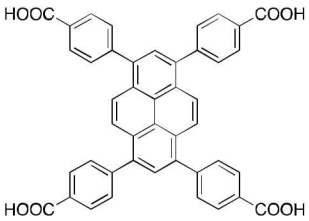
UiO-66-NH$_2$



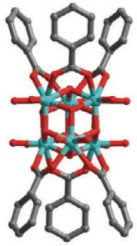
8-connected



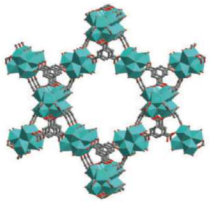
30 Å and 15 Å



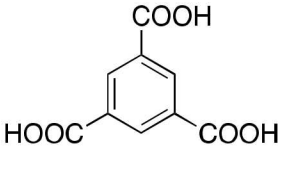
NU-1000



6-connected



17 Å



MOF-808(Zr, Hf)

Defects and optical and electrical properties

- **Defects in a 3D MOF: HKUST-1**
  - Defects as color centers: colorimetric sensing of water vapor
  - Guest molecules as dopants (or are they?)

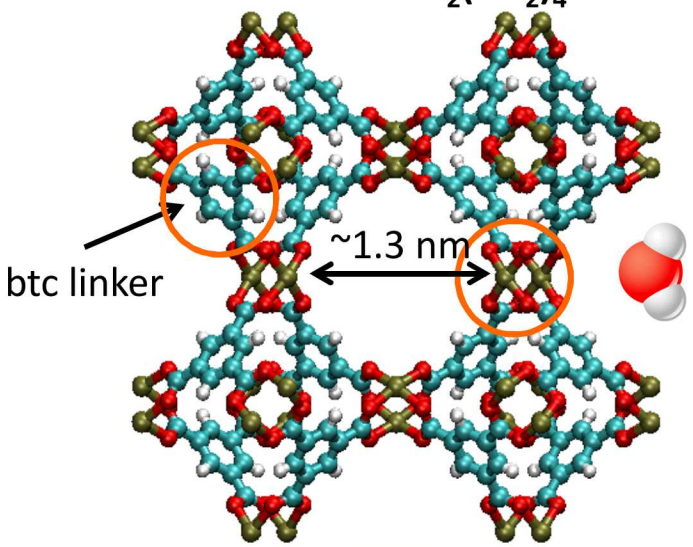
- **Defects in 2D MOFs: $Ni_3(HITP)_2$ a "Metal-Organic Graphene Analog"**
  - Semiconducting vs. metallic: a DFT-experimental conflict
  - Polycrystallinity and growth mechanism
  - Pd- and Pt-substituted MOGs: tunable semiconductivity

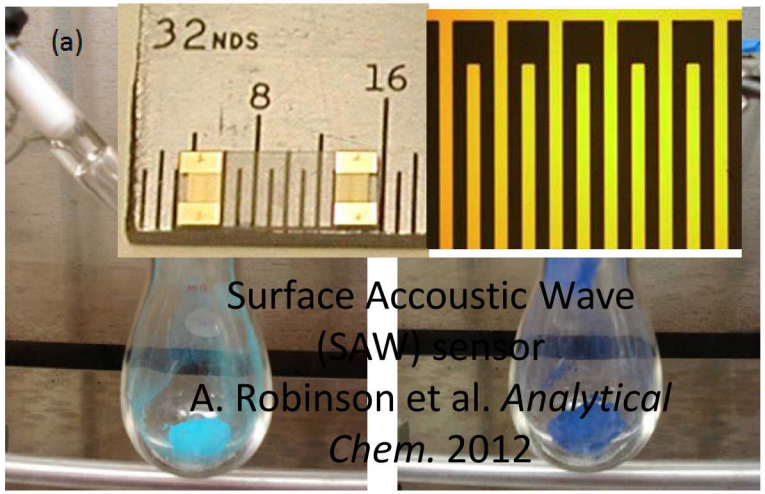
Many manufacturing processes require rigorous control of humidity levels, but low-cost, compact sensing packages

Pharmaceuticals: 3%RH at 25 °C

Li battery manufacturing:
Dew point -40 – -45 °C (< 0.5%RH)

HKUST-1: $Cu_2(CO_2)_4$

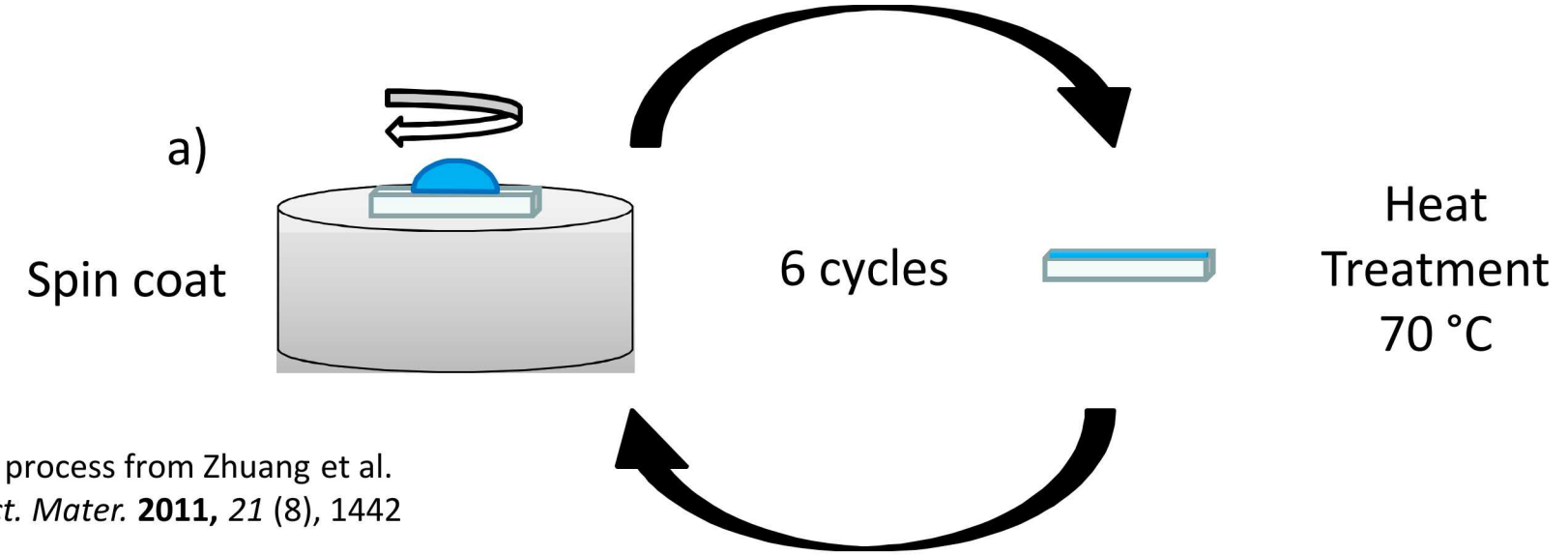




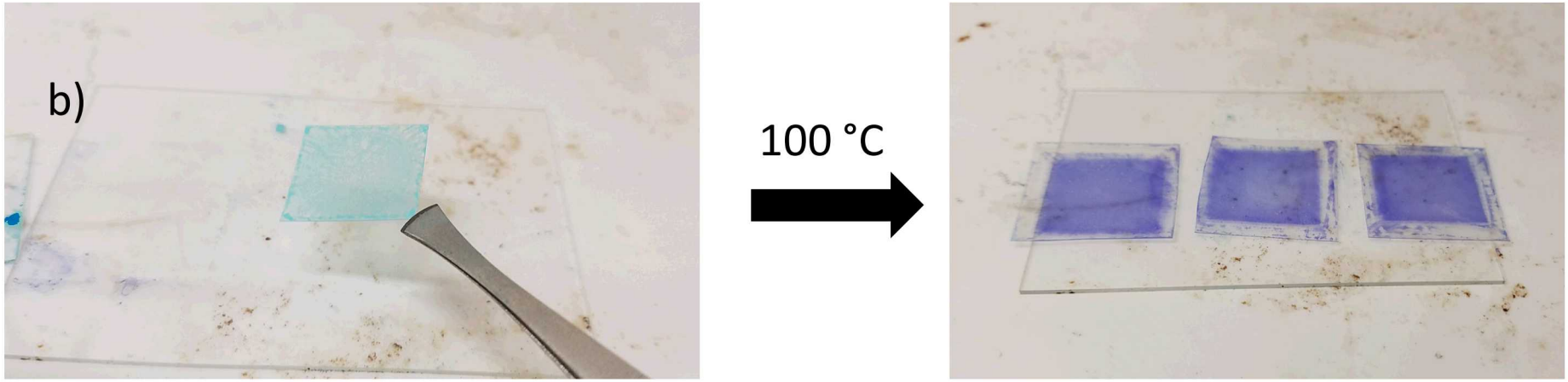
Surface Accoustic Wave (SAW) sensor
A. Robinson et al. *Analytical Chem.* 2012

As synthesized Heated to 180 °C/vacuum

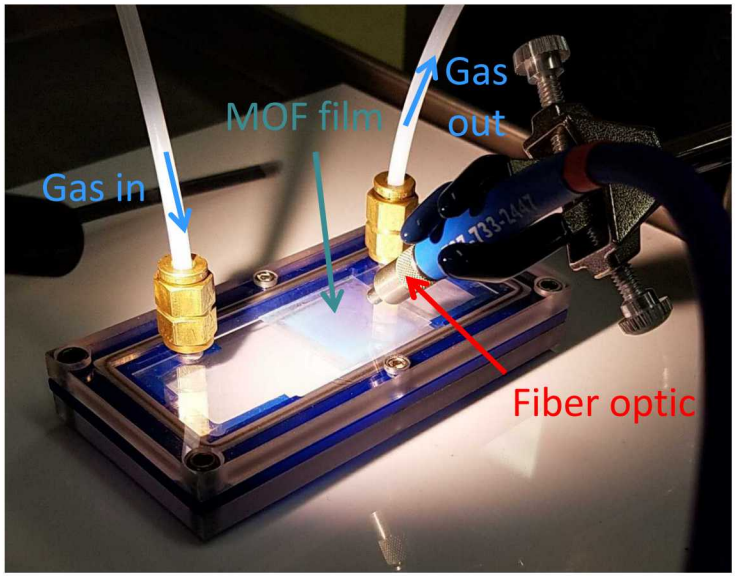
Spin coat and evaporative heating scheme for growth of HKUST-1 thin films on glass or plastic substrates

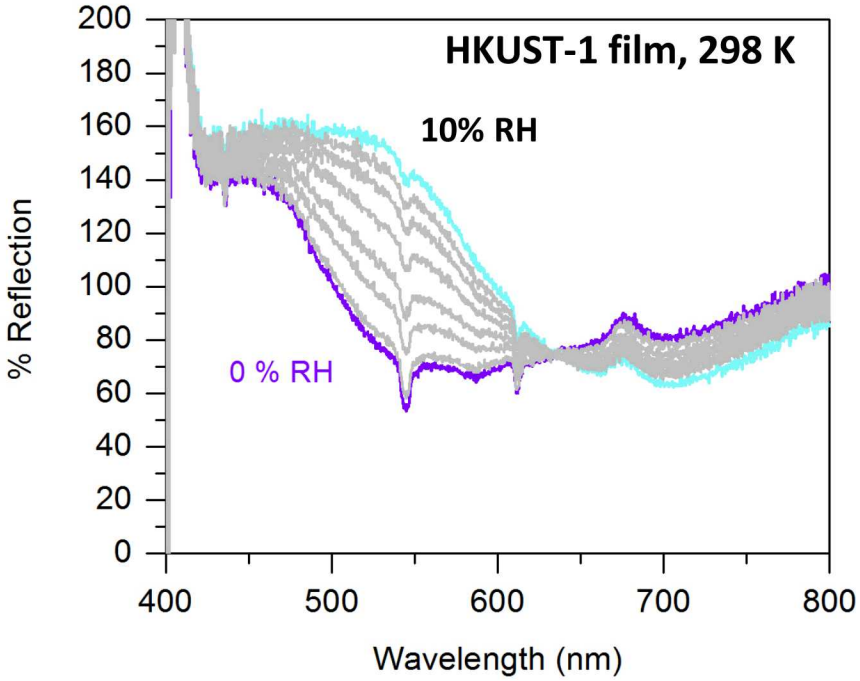


Modified process from Zhuang et al.
Adv. Funct. Mater. **2011,** *21* (8), 1442



Water vapor is easily detected and quantified by changes in the optical reflectance spectrum of HKUST-1



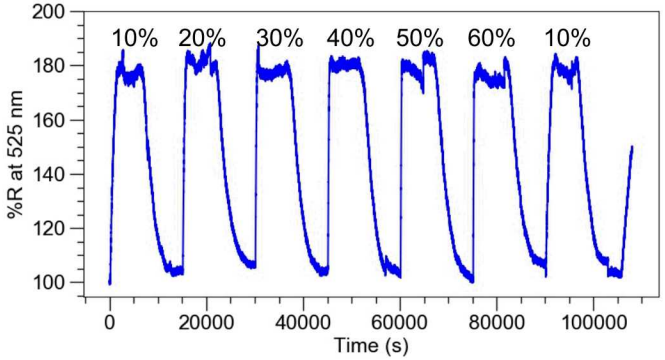


Ullman et al. *ACS Appl. Mater. Interfaces* 2018, 10, 24201

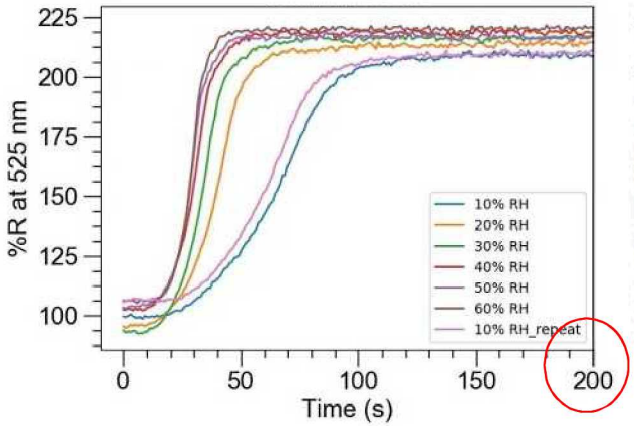
Hybrid MOF/polymer films detection at RH ≥ 10% using time-dependent reflectance

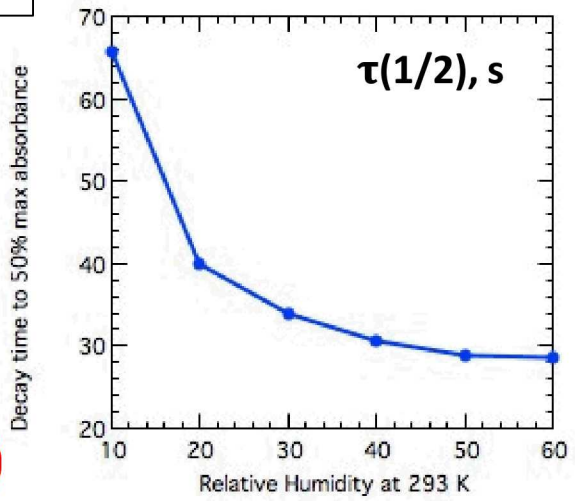
Sandia National Laboratories

MOF only

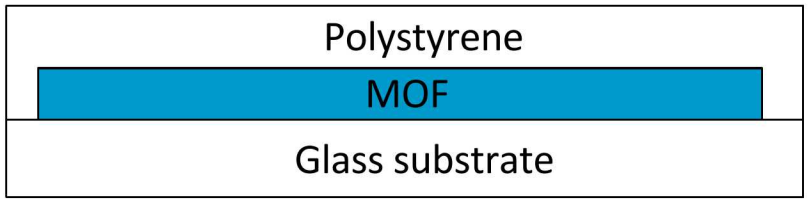


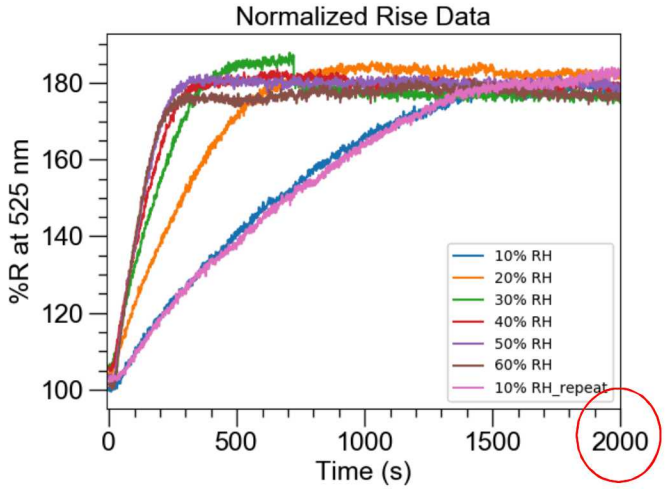
Normalized signal



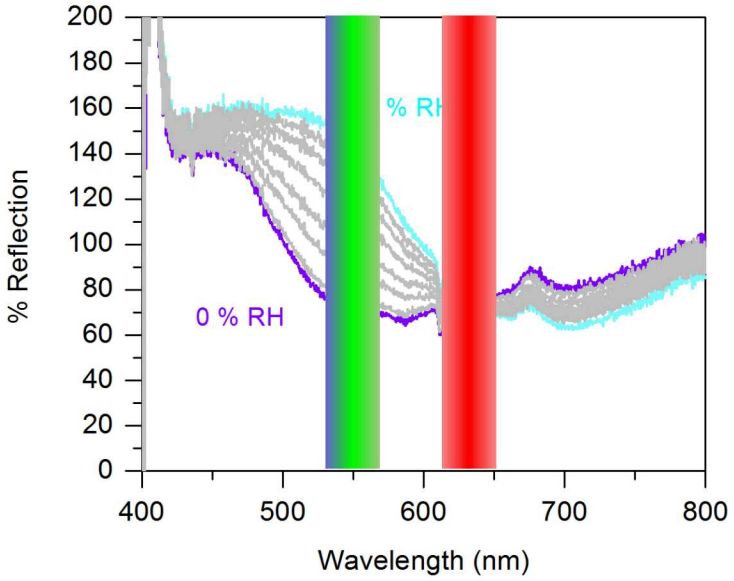


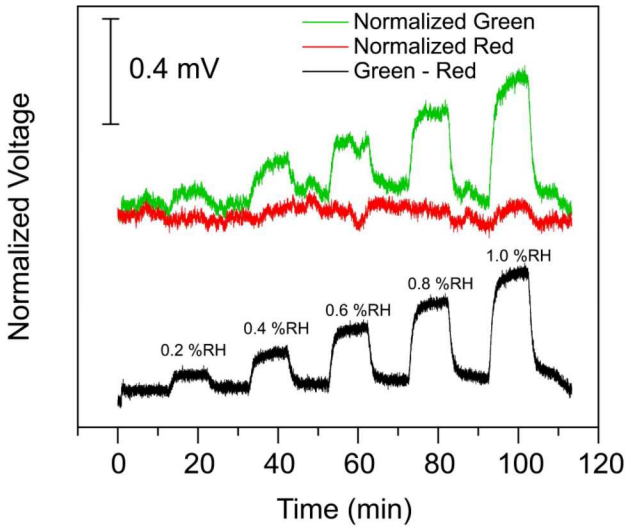
MOF-polymer composite

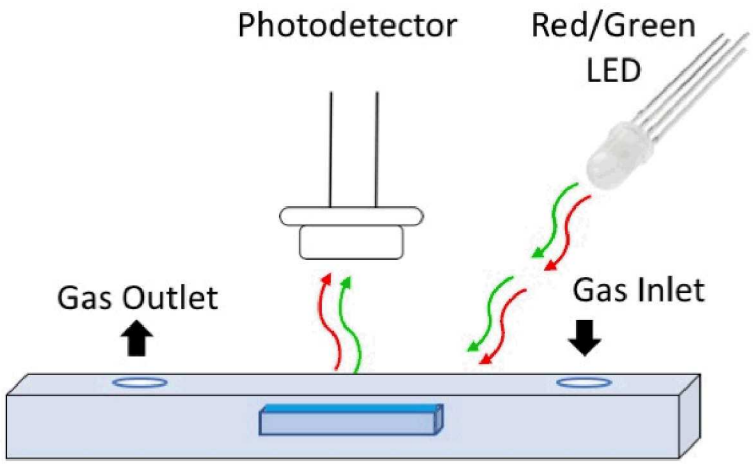




Practical implementation: a low-cost, compact sensor







- Reflectance measurement
- Δλ(max), 525 nm: green LED
- λ(isosbestic), 635nm: red LED
- Average photovoltage during alternating 200-µs pulses of green and red light
- 5 data points/ 2 s
- Normalized, subtracted data << noise than the green signal alone
- Detection limit < 0.2 %RH

The origin of the HKUST-1 color change with H_2O is a mystery

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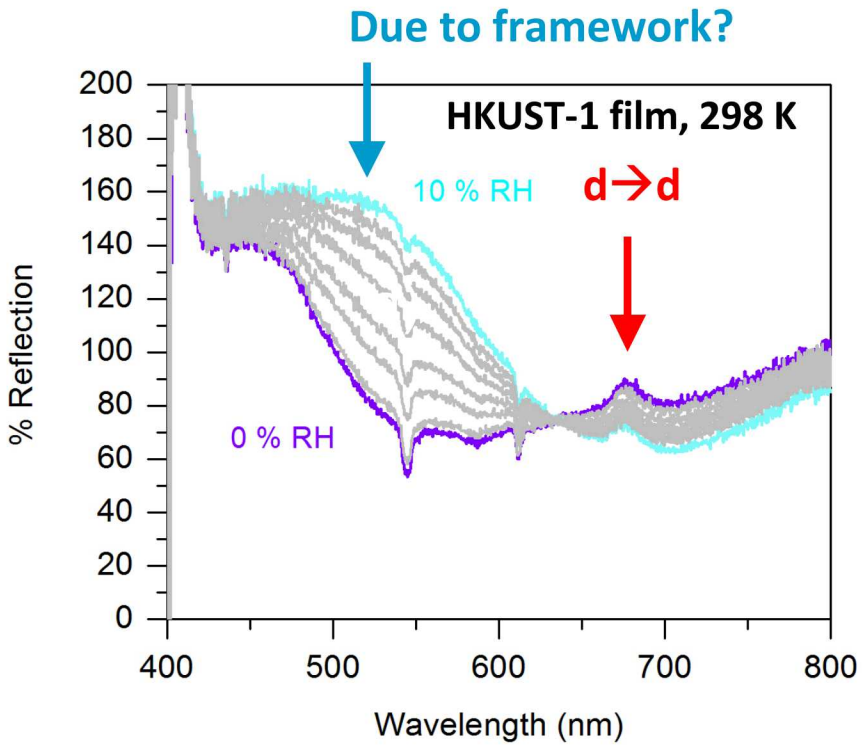
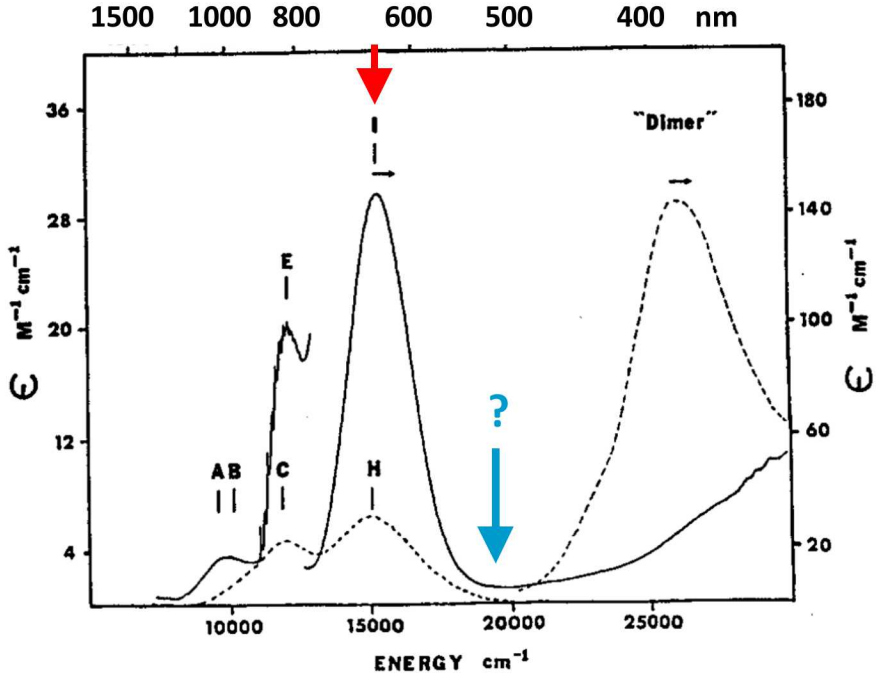


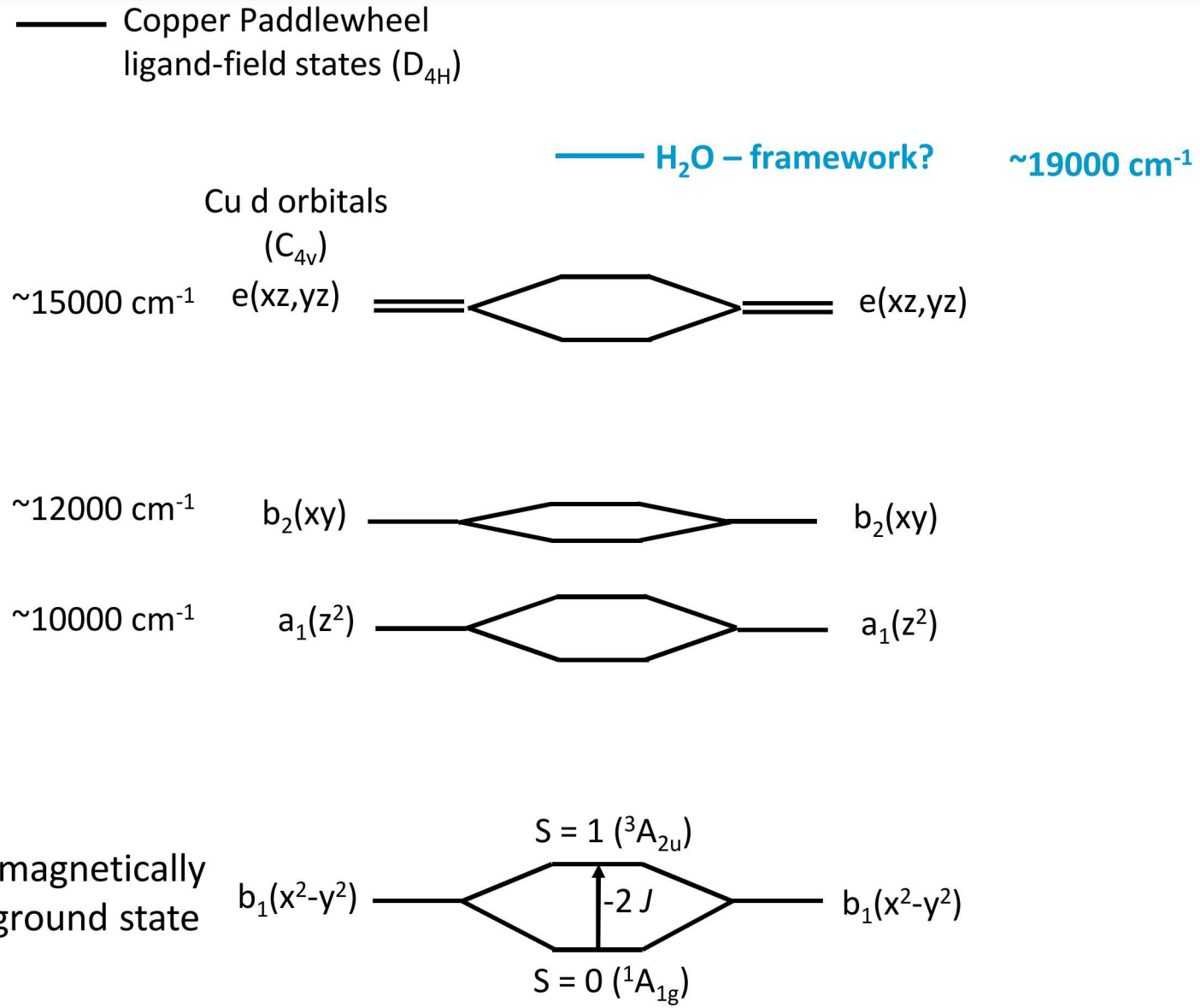
Molecular analogue of MOF of $Cu(acetate)_2(pyrazine)$

$d(x^2-y^2) \rightarrow d(xz,yz)$



Low-T (5 K) single-crystal absorption spectra
Ross, Allendorf, and Solomon *JACS* **1989,** *111,* 4009

Electronic excited states of $TCNQ@Cu_3(btc)_2$

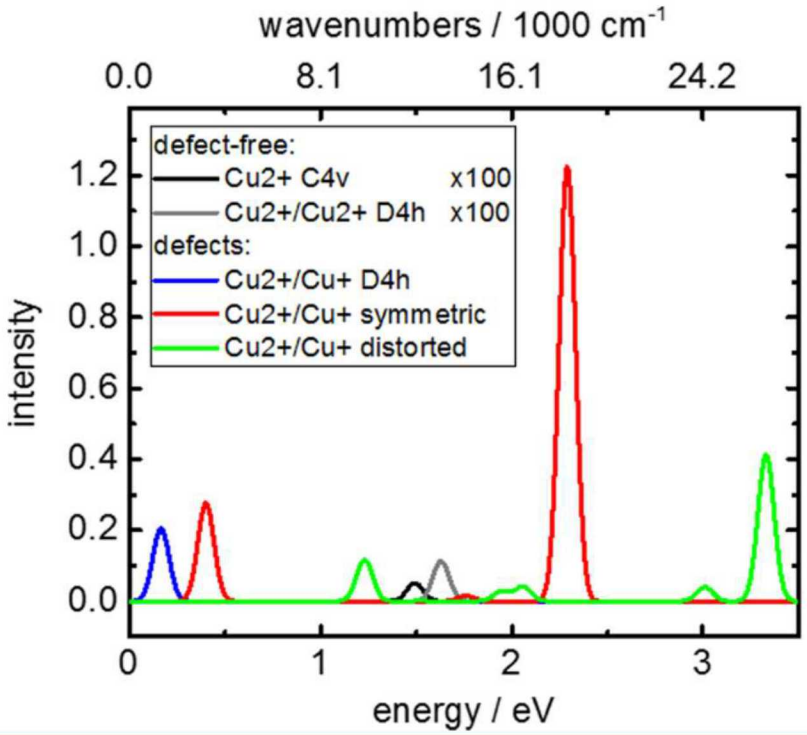


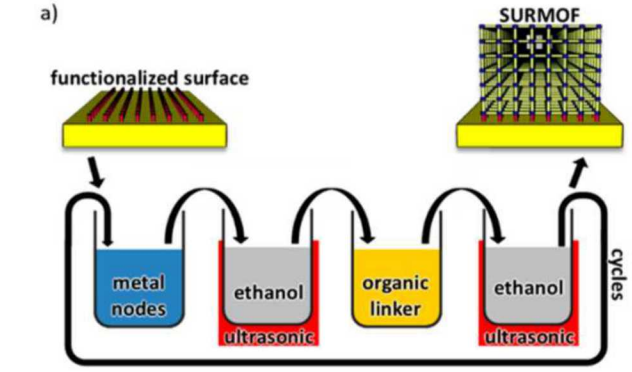
MOF color centers: partial reduction of Cu dimers in HKUST-1

- "High-quality" (low defect) thin films are colorless
- Pristine MOF: high symmetry reduces oscillator strength of d-d transitions

- Theory (CASSCF): Cu^{1+} – Cu^{2+} defects
  - Symmetry is reduced

  → d-d absorptions localized on Cu^{2+} increase

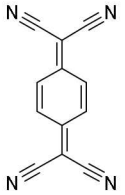




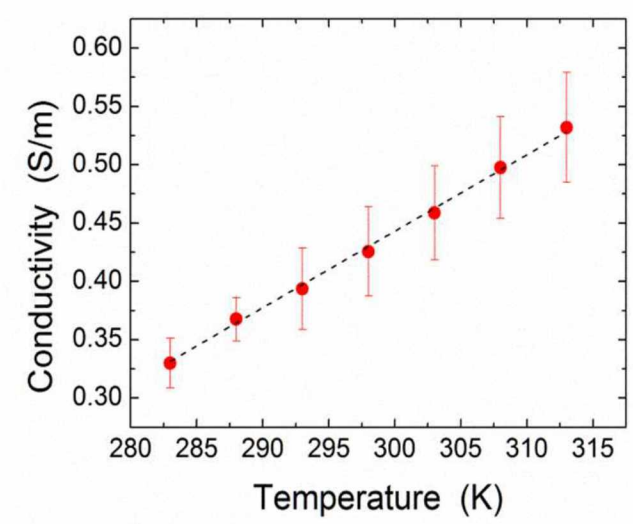
C. Wöll et al.
ACS Appl. Mater. Interfaces 2017, **9**, 37463

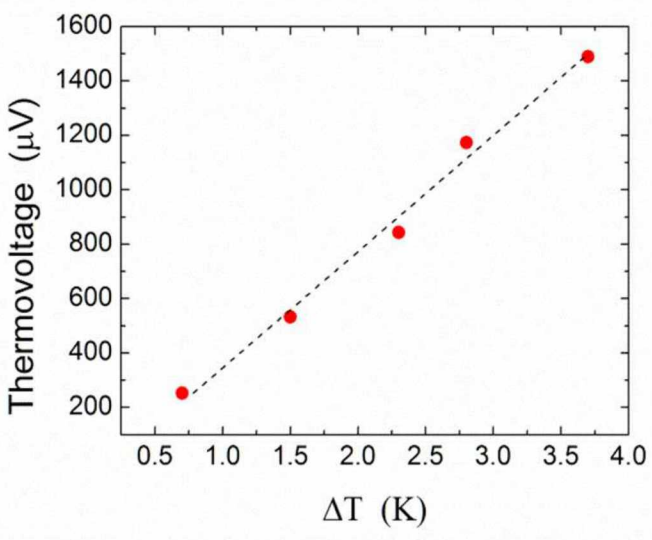
$TCNQ@Cu_3BTC_2$: bridging ligand or dopant?

Cu_3BTC_2 —TCNQ, solvent→ $TCNQ@Cu_3BTC_2$



TCNQ: 7,7,8,8-tetracyanoquinodimethane





σ = 0.07 S/cm

S = +375 μV/K

→ Holes are the majority carrier

M. D. Allendorf *et al.*, *Science* **2014**, *343*, 66

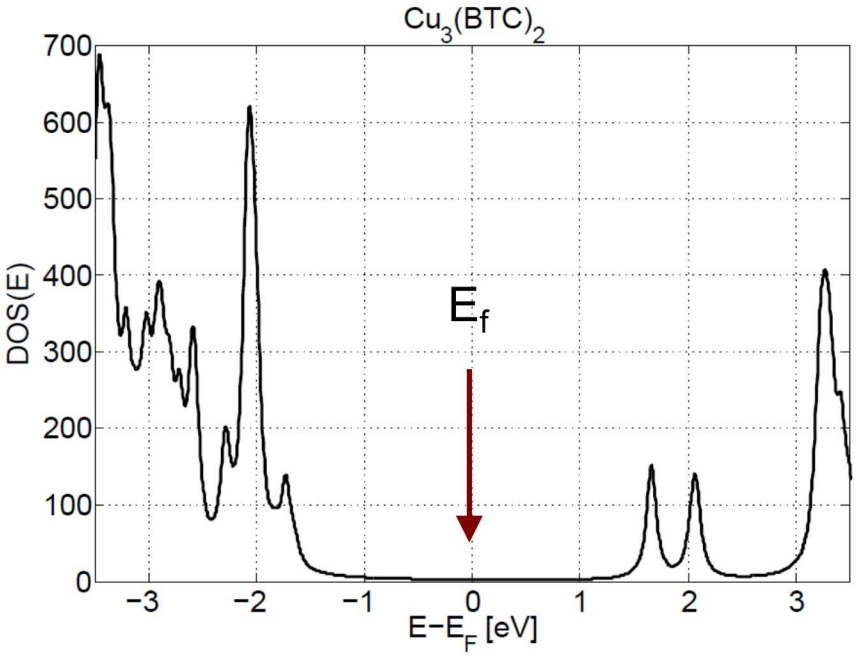
A. Talin *et al.*, *Adv Mater* **2015**, *27*, 3453

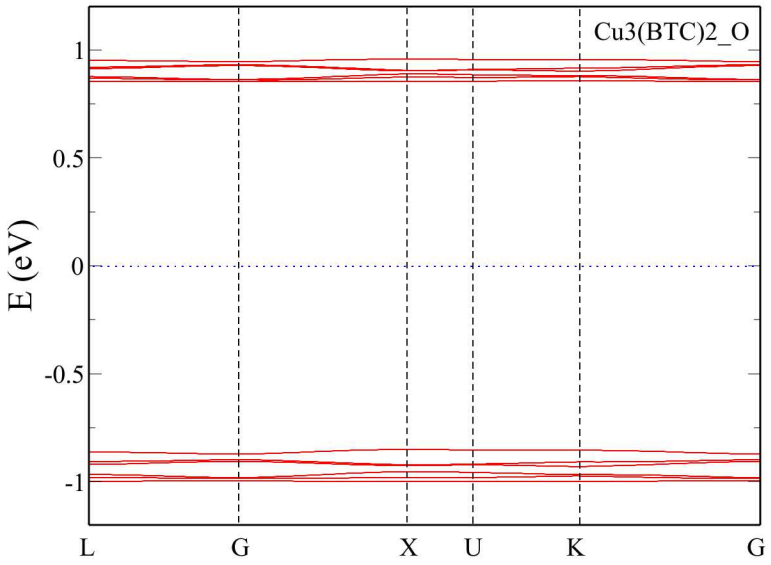
M. Dincă *et al.*, *Angew. Chem.* **2016**, *55*, 3566

H. Baumgart *et al.*,
ECS J. Sol. State Sci. Technol., **2017**, *6*, 150

The case for TCNQ as dopant: band structure of $Cu_3(BTC)_2$ shows little or no delocalization

Predicted DOS for $Cu_3(BTC)_2$, computed by DFT using the hybrid functional HSE06

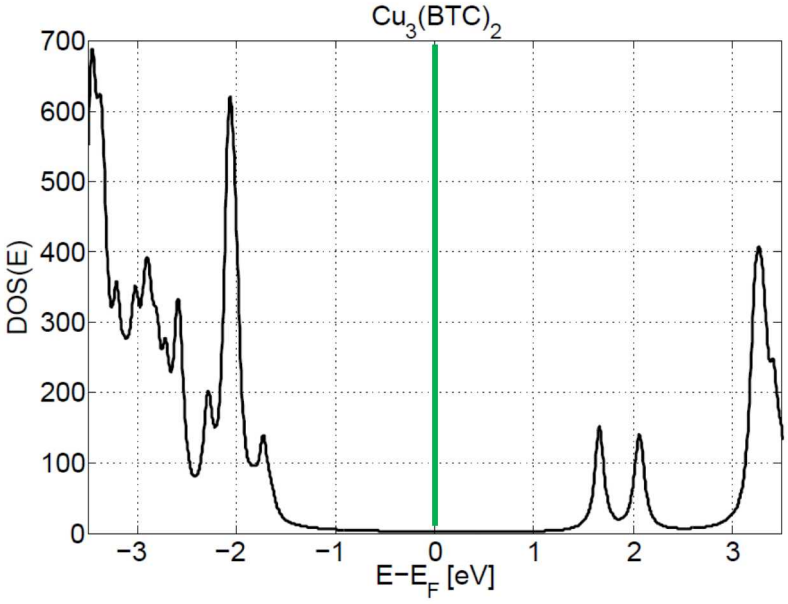


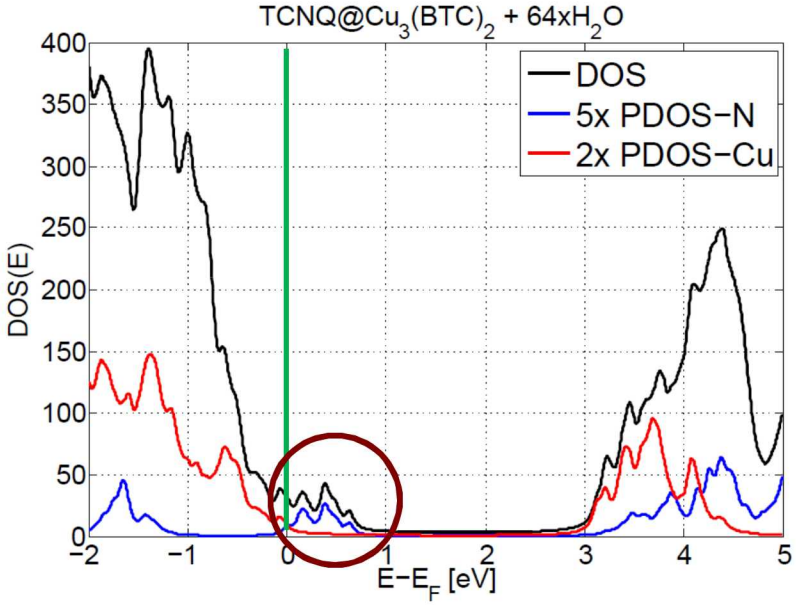


This picture is consistent with insulating nature of this MOF

The case for TCNQ as dopant: infiltration with TCNQ moves E_f close to MOF V_b

Predicted DOS for $Cu_3(BTC)_2$, computed by DFT using the hybrid functional HSE06



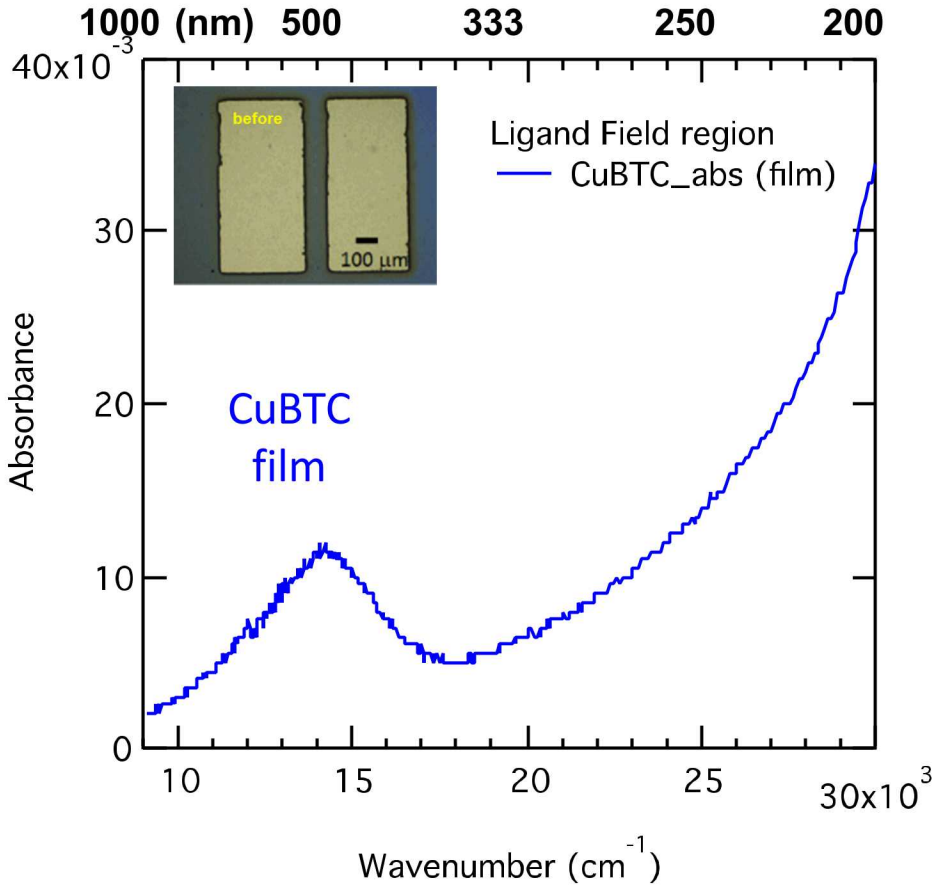


K. J. Erickson, et al., *Adv. Mater.*, **27** (2015), 3453

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

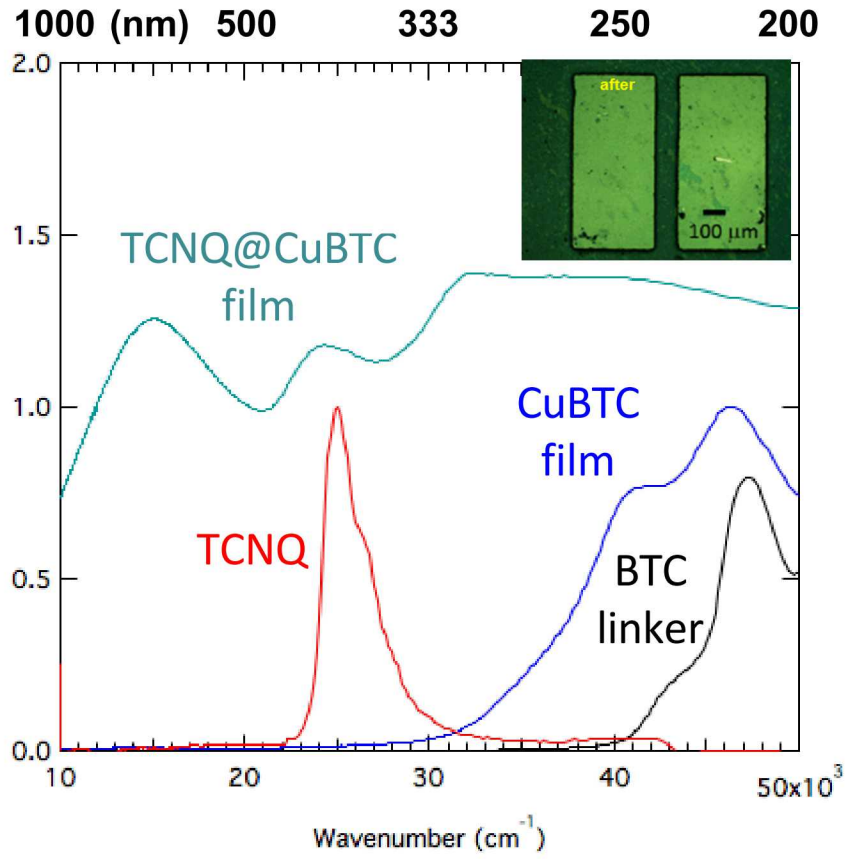
$H_2O@Cu_2(BTC)_3$

Cu(II) d-d transitions (weak)

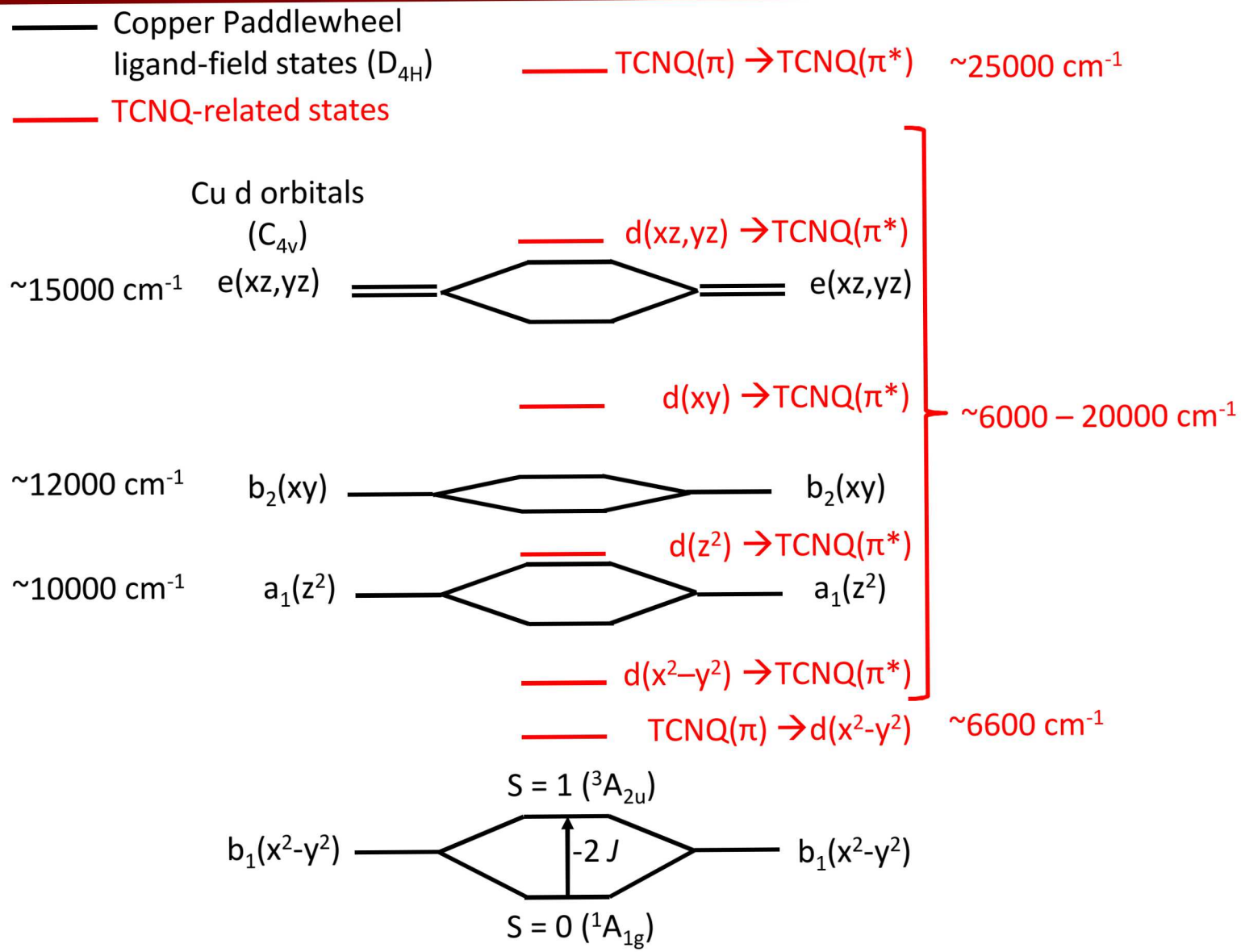


$TCNQ@Cu_2(BTC)_3$

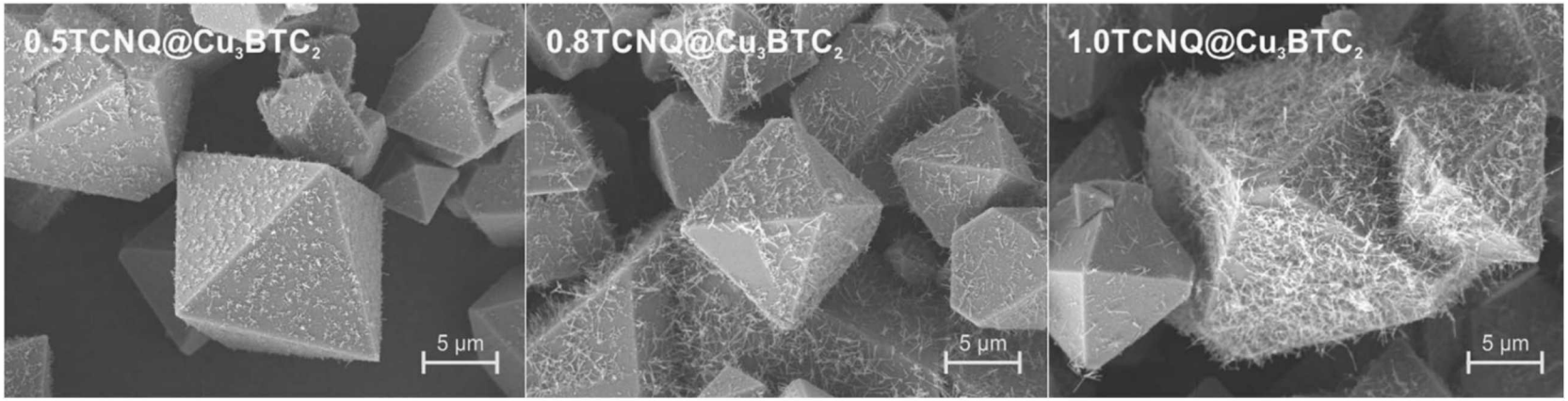
Charge transfer transitions



Electronic excited states of $TCNQ@Cu_3(btc)_2$



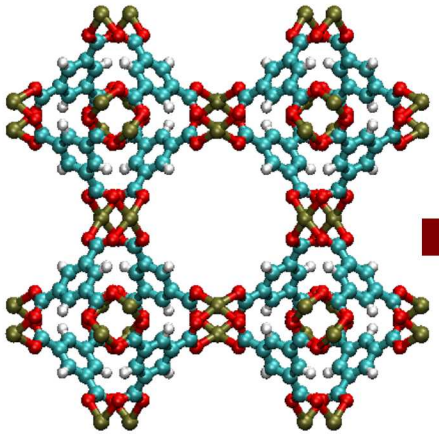
Vapor-phase TCNQ infiltration creates C(TCNQ) nanowires on particle surfaces

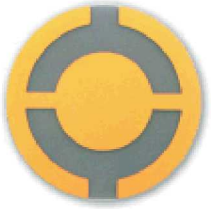


C. Schneider et al. *Chem. Sci.*, 2018, 9, 7405–741

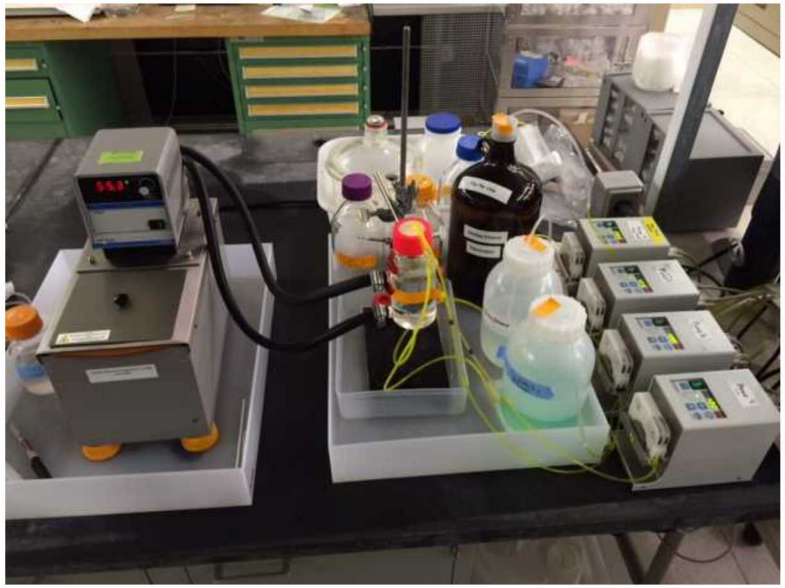
Layer-by-layer MOF film growth: liquid-phase epitaxy

HKUST-1



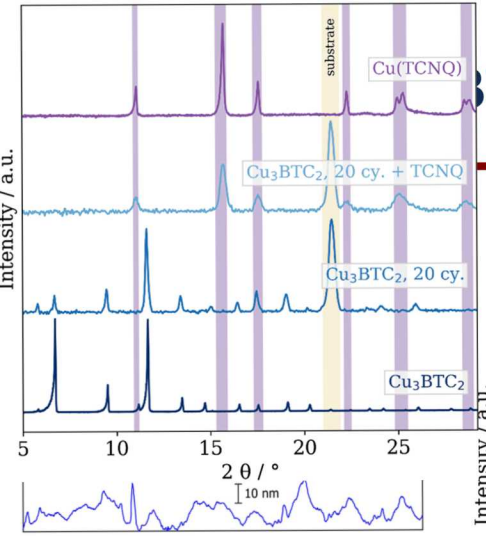


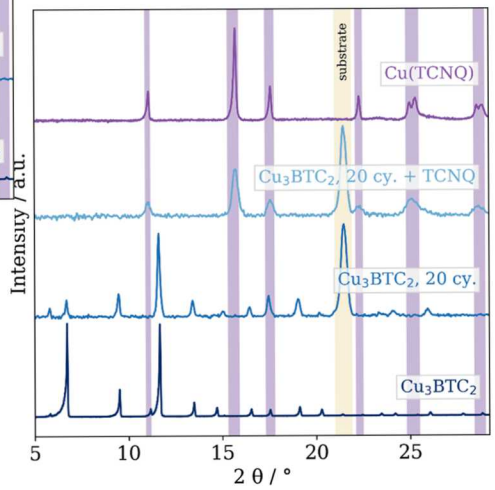
QCM crystal



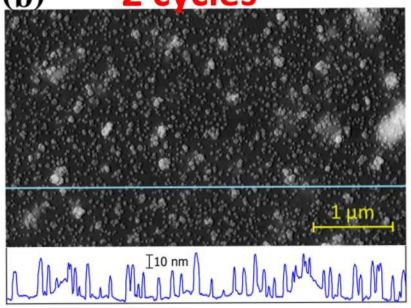
Automated MOF film growth with QCM capability

$_3BTC_2$ to form Cu(I)TCNQ

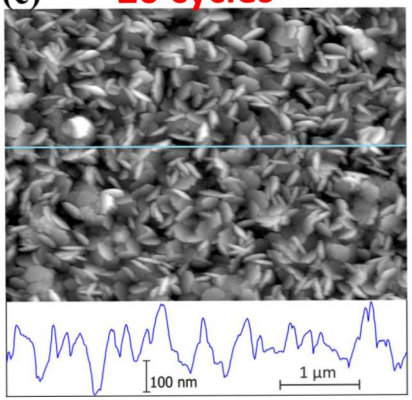


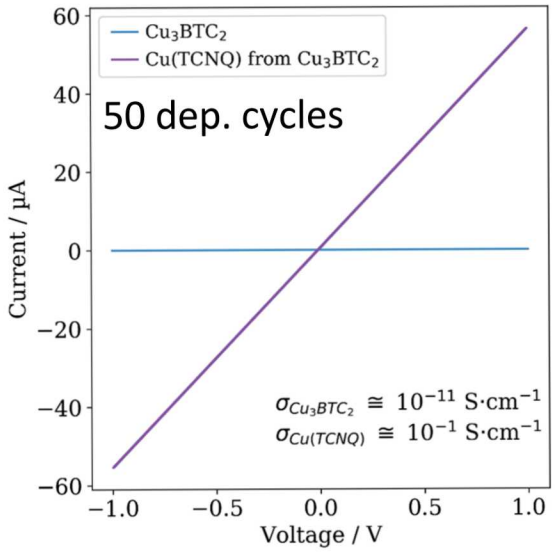


(b) 2 cycles



(c) 20 cycles





Cu(II) and TCNQ reduced by MeOH/H_2O:

CuBTC +3TCNQ+6H^++6e-
→ 3Cu(TCNQ) + 2H_3BTC (2)

CH_3OH → CHOH + 2H^+ + 2e^- (3)

Cu_3BTC_2 + 3TCNQ + 3CH_3OH
→ 3Cu(TCNQ) + 2H_3BTC + 3CHOH (4)

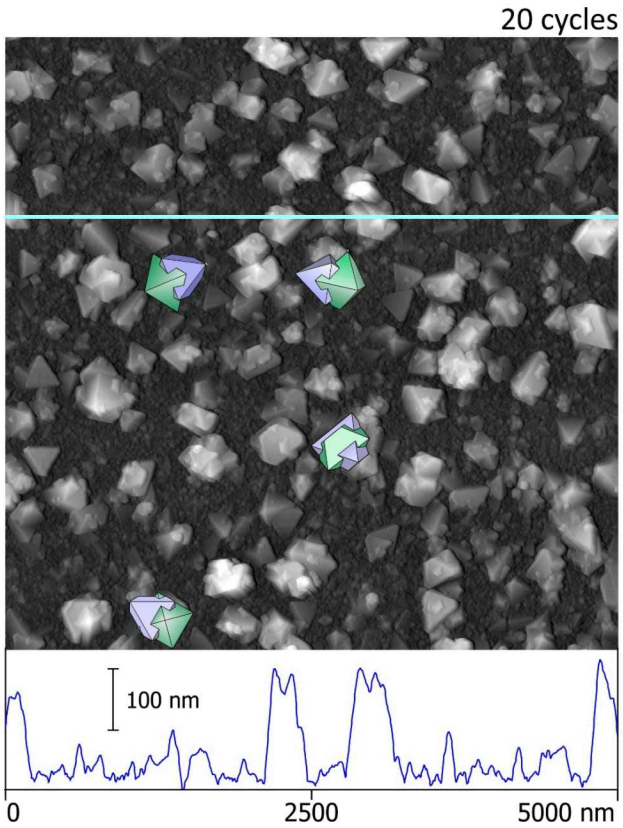
- **Cu(TCNQ) is n type vs. TCNQ@Cu_3BTC_2 is p type**
- **New method for depositing Cu(TNCQ) on patterned substrates: MOF provides template**

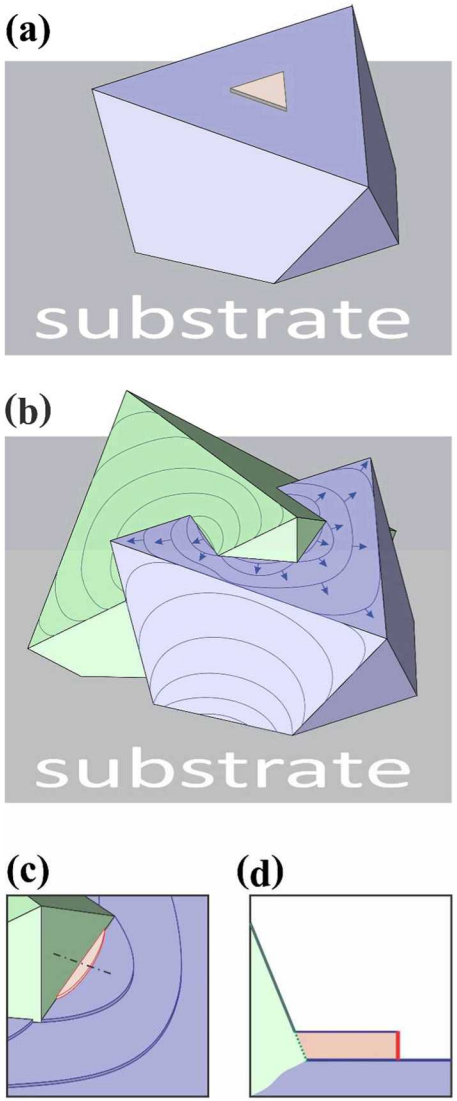
Mechanism of bimodal crystallite growth

a). Monocrystal via nucleation of new 2D layers E_{step}
Accelerated growth of compound crystals:
b) and c). New 2D layers formed at domain boundary between 2 crystallites
d). New surface step energetics

$E_{nuc2D} \approx E_{step} + E_{if} - E_{Surf}$

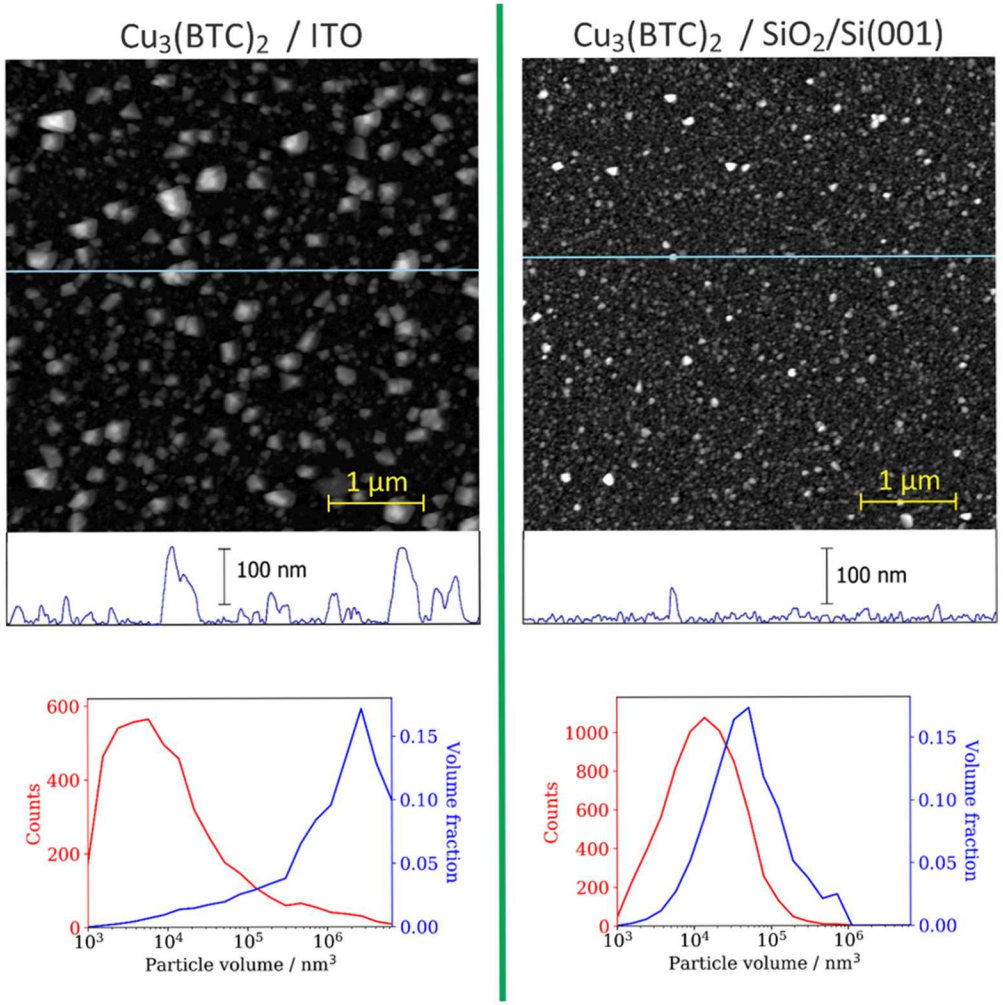
If $E_{step} \approx E_{surf}$
→ Bimodal distribution implies E_{if} is small



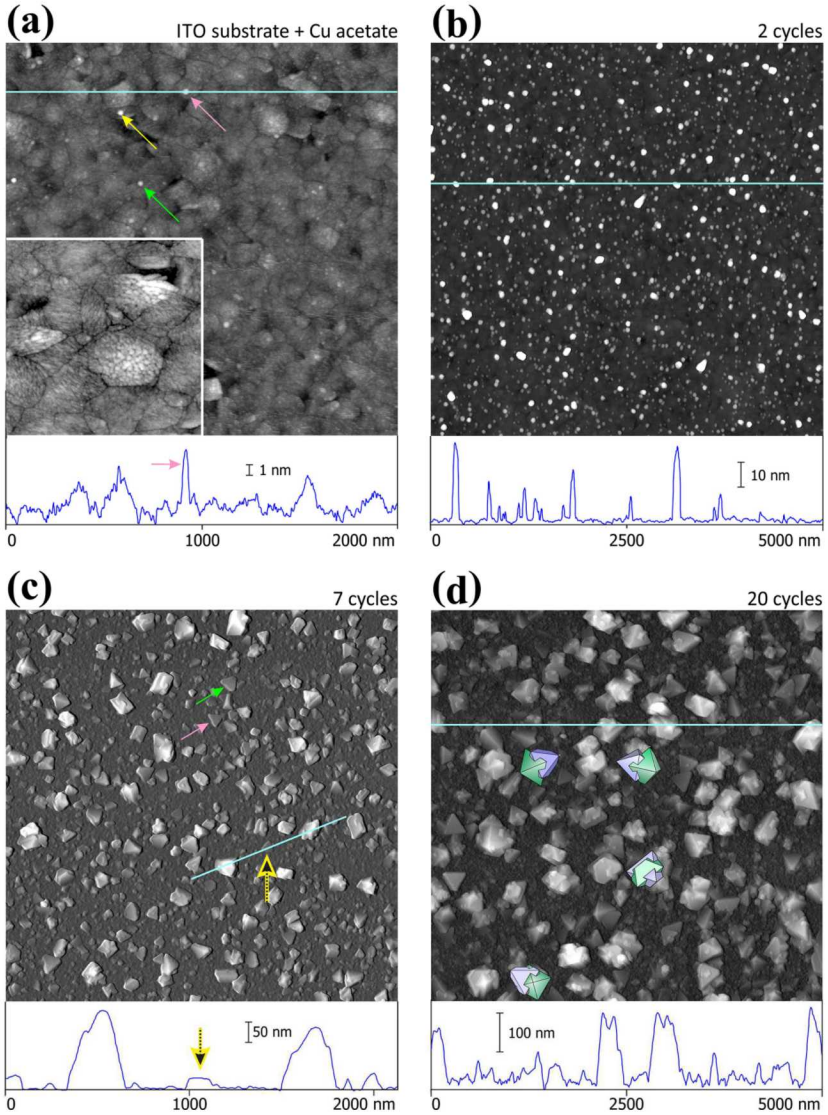


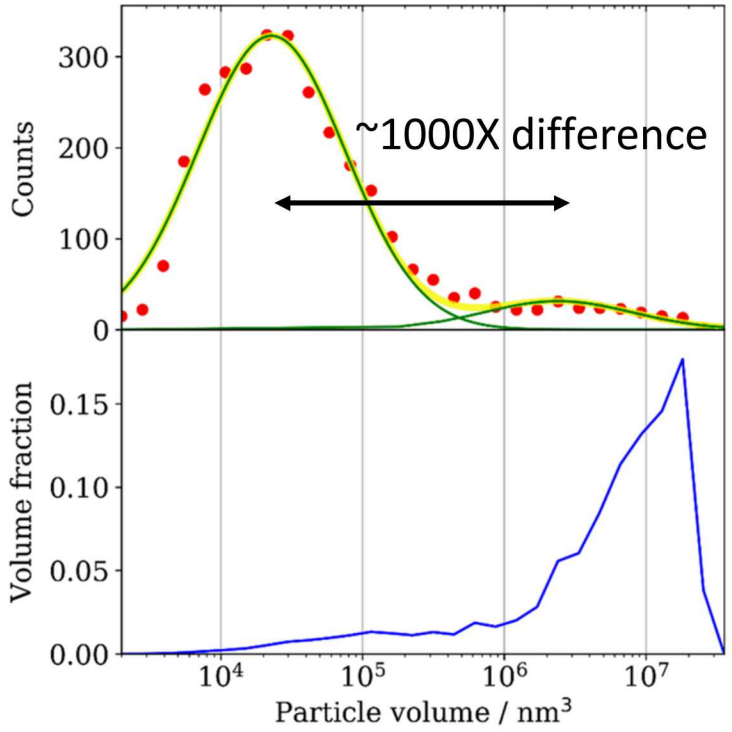
K. Thürmer, C. Schneider *et al.*, *ACS Appl. Mater. Interfaces*, **2018**, *10* (45), 39400–39410

Amorphous substrates promote random growth directions, leading to narrower crystallite size distributions



Cu_3BTC_2 film morphology evolves as the number of deposition cycles increases





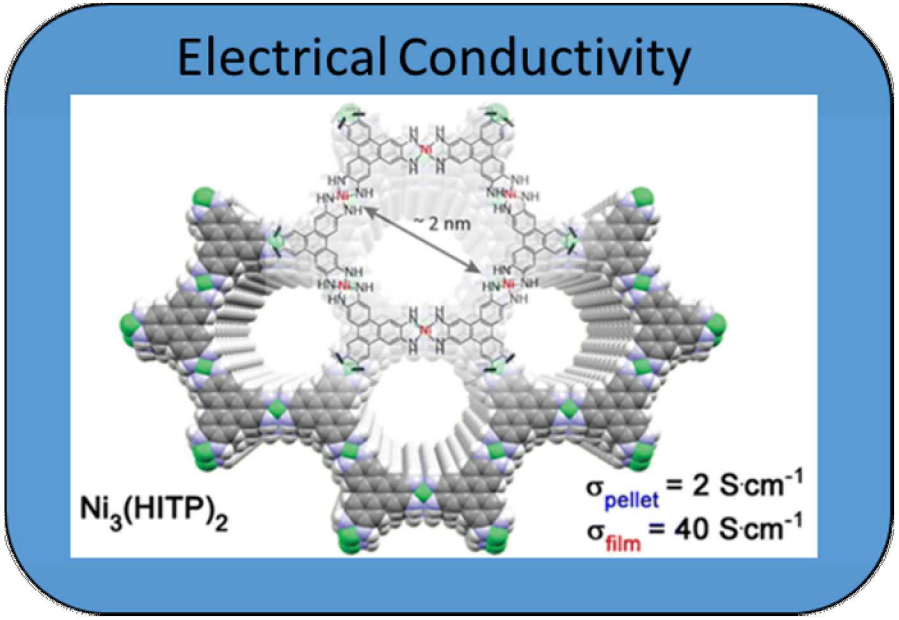
From the unusual bimodal, non-log-normal distribution of crystal domain sizes, we conclude that the nucleation of new layers of Cu_3BTC_2 is greatly enhanced by surface defects and thus difficult to control

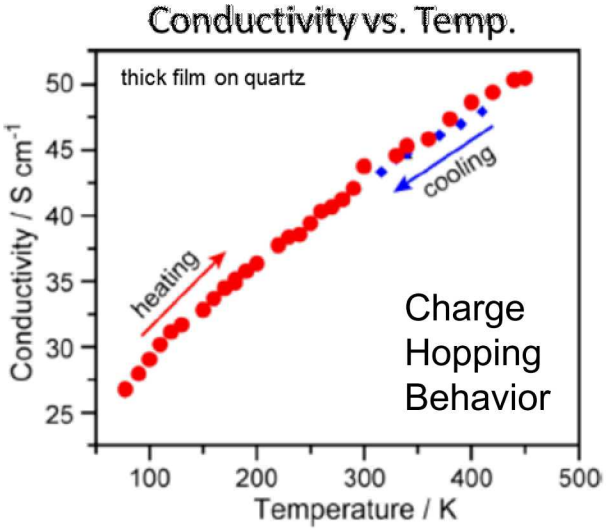
K. Thürmer, C. Schneider *et al.*, *ACS Appl. Mater. Interfaces*, **2018**, *10* (45), 39400–39410

Defects in 2D MOFs: metallic vs. semiconducting behavior

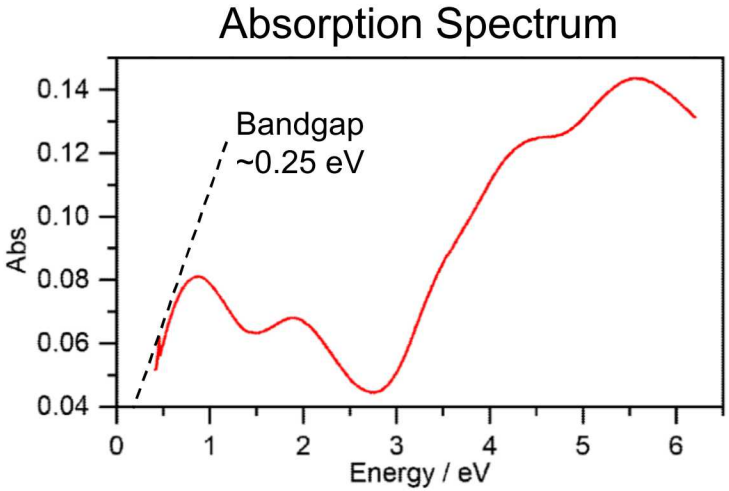
Metal-Organic Graphene Analogues (MOGs): promising MOFs for device applications

$Ni_3(HITP)_2$ – Experimental conductivity data





- Experimental evidence suggests that the material is semiconducting.
- Absorption spectrum – optical gap of ~0.25 eV
- Conductivity increases with temperature – charge hopping mechanism

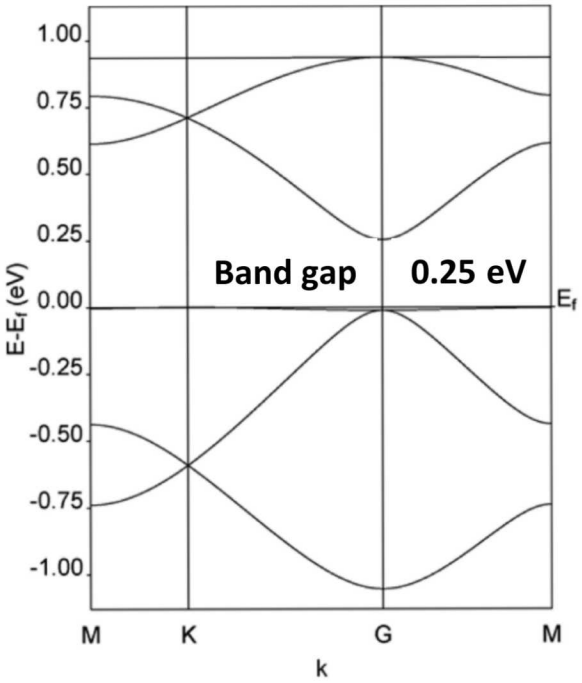


Sheberla et al. *J. Am. Chem. Soc.* 2014, **136**, 8859−8862

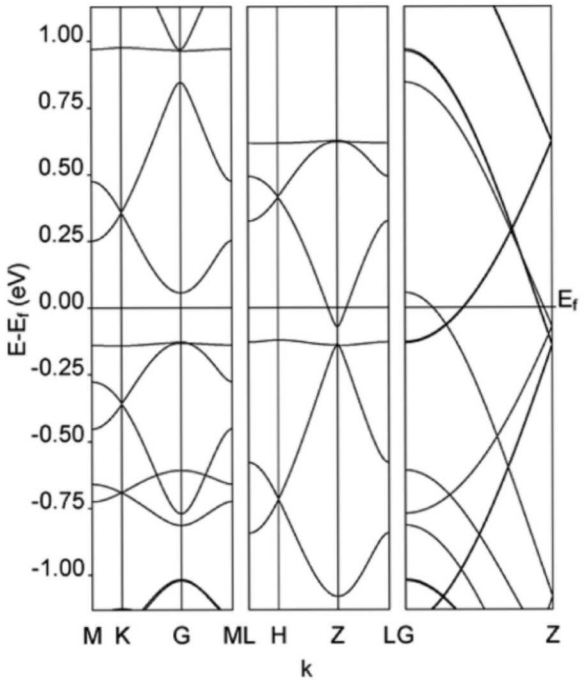
Theory predicts bulk $Ni_3(HITP)_2$ to be metallic; experiment indicates a narrow bandgap semiconductor

Sandia National Laboratories

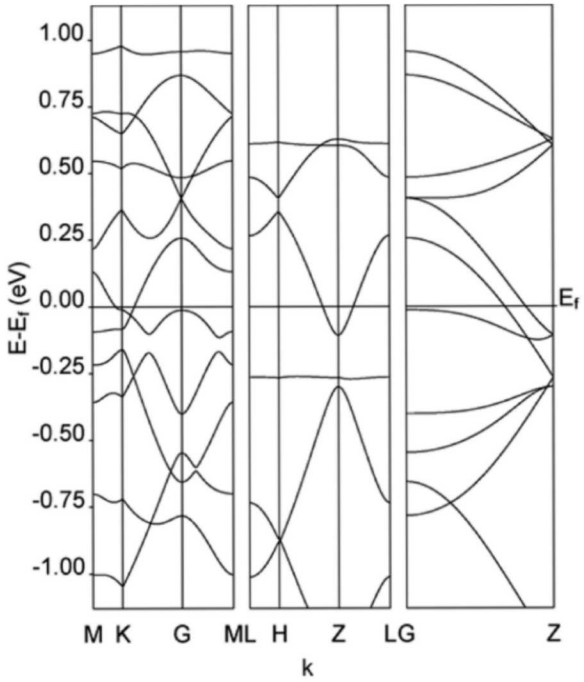
Band structure of $Ni_3(HITP)_2$



Monolayer

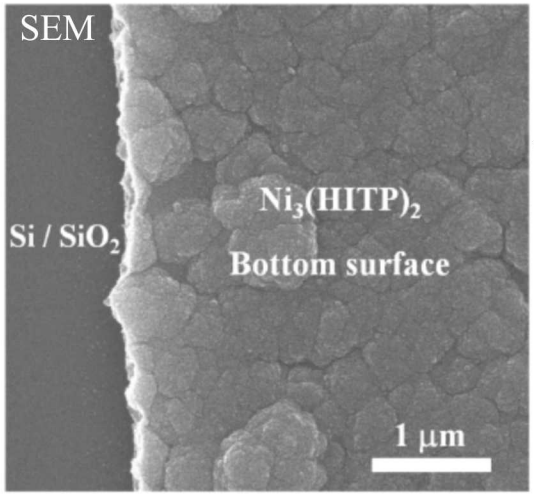


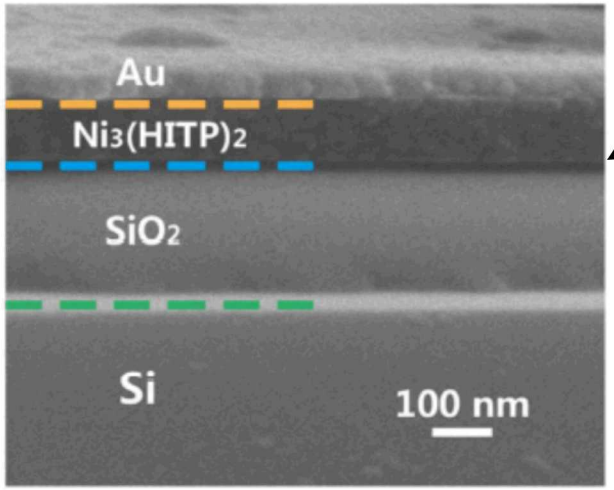
Bulk parallel stacked

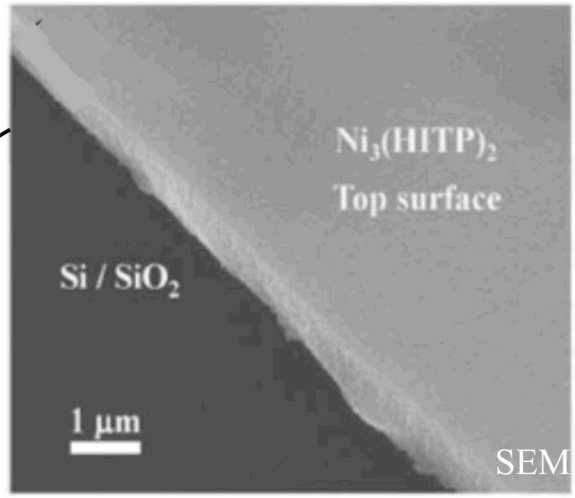


Parallel displaced to minimum-energy structure

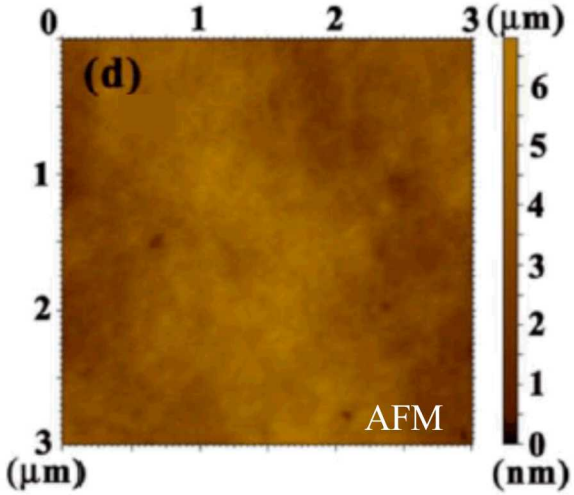
Hypothesis: material performance is governed by defects





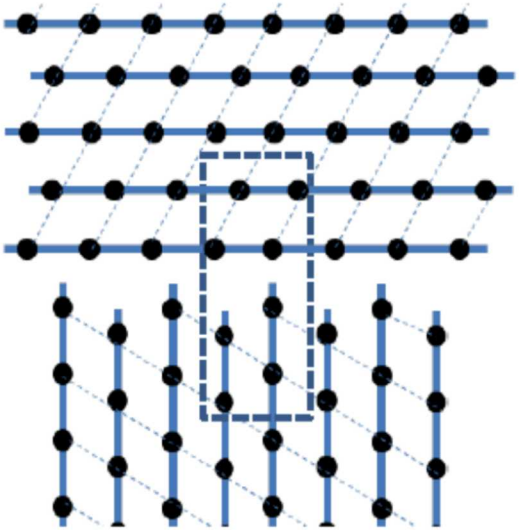


- Pure or low defect material should have much higher conductivity and mobility
- 100 nm thick film is approximately 303 layers
- Avg. Surface Roughness: 1.05 nm (3 layers) to 1.43 nm (4 layers)
- Device channel length 100 µm

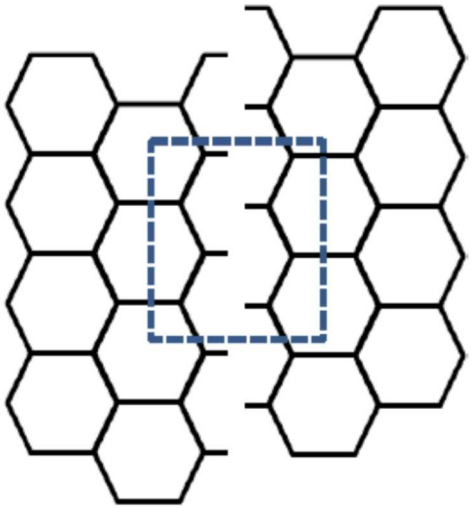


G. Xu and coworkers *JACS*, **2017**, 139 (4), pp 1360–1363

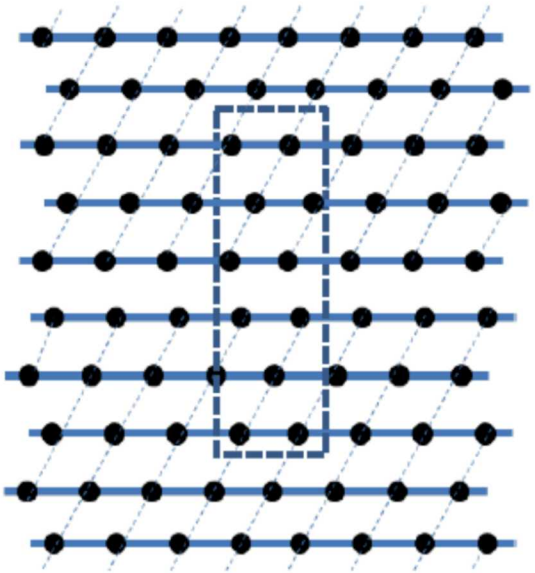
Potential interface defects



Perpendicular Grain Boundary



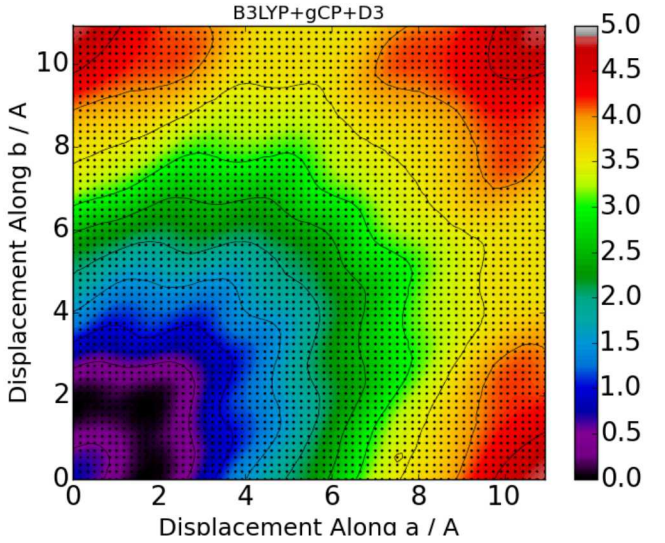
Strike-Slip Fault



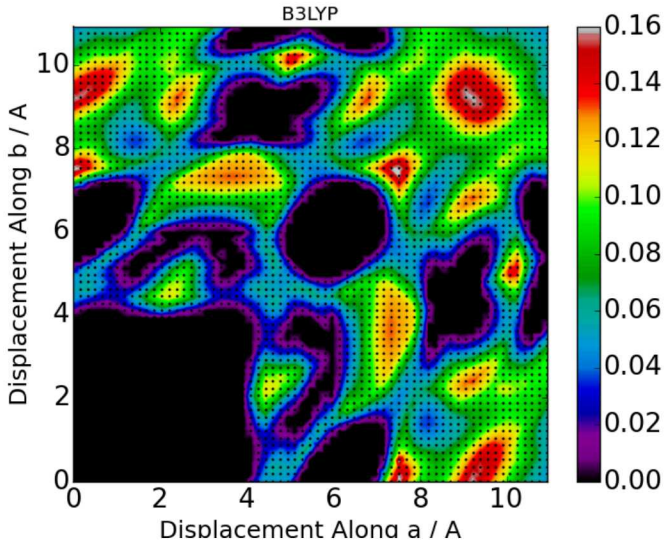
Layer-Layer Displacement Defect

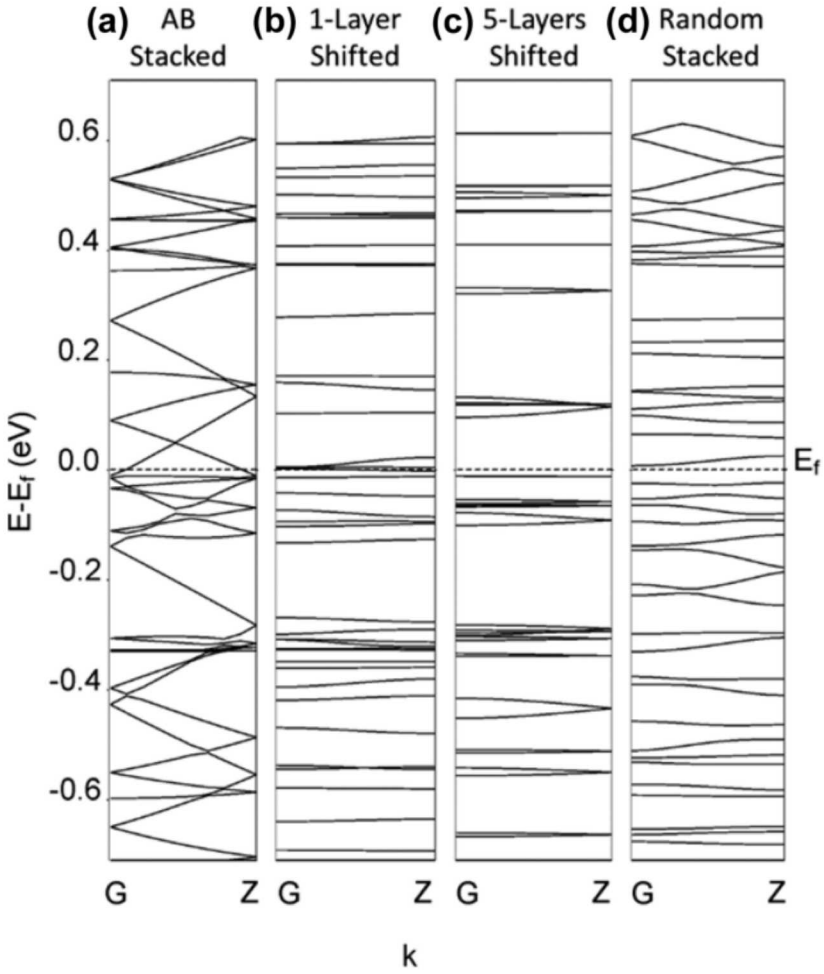
Layer-layer displacement defect can give rise to a bandgap for sufficiently large displacements (typically > 4 Å)

Total energy



Band gap





Defects can be interdependent; one type of defect leads to formation of others

- Example: strike−slip fault in one layer forces the presence of a layer−layer displacement in half of the material

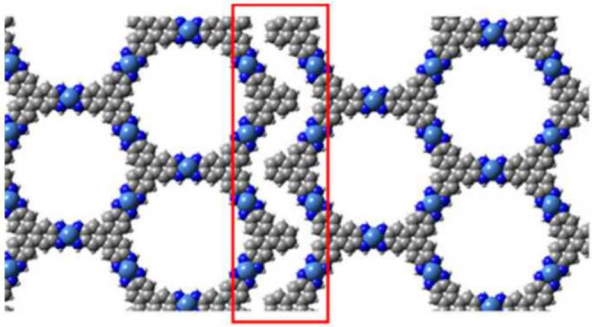
→ **A single defect can break the conjugation pathway within the bulk**

→ Opens a band gap in one direction

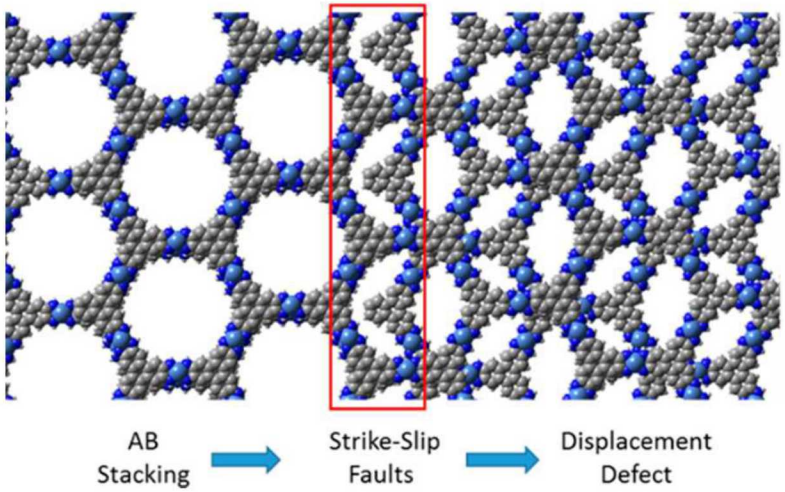
→ Drastically reduces electron momentum

→ Leads to a hopping barrier

Top-down view: **Monolayer** with Strike-Slip Fault



Top-down view: **Bilayer** with Strike-Slip Fault



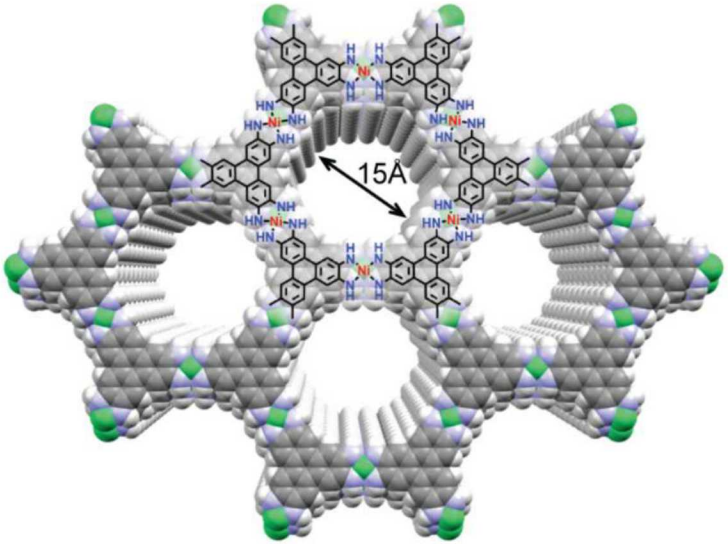
M.E. Foster et al. *J. Phys. Chem. Lett.* 2018, 9, 481−486

MOF thermoelectric materials: two prototypes

$Ni_3(HITP)_2$

2D "Metal-Organic Graphene Analogue" (MOG)

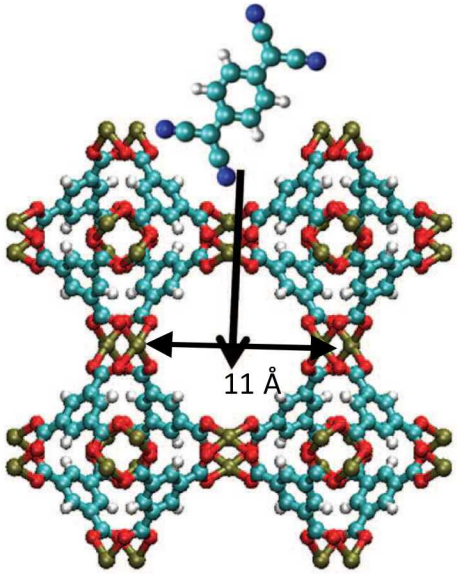
L. Sun et al. *Joule* 2017



$Cu_3(btc)_2$

3D Metal-Organic Framework

K. Ericksson et al. *Adv. Mater.* **2015**, *27*, 3453



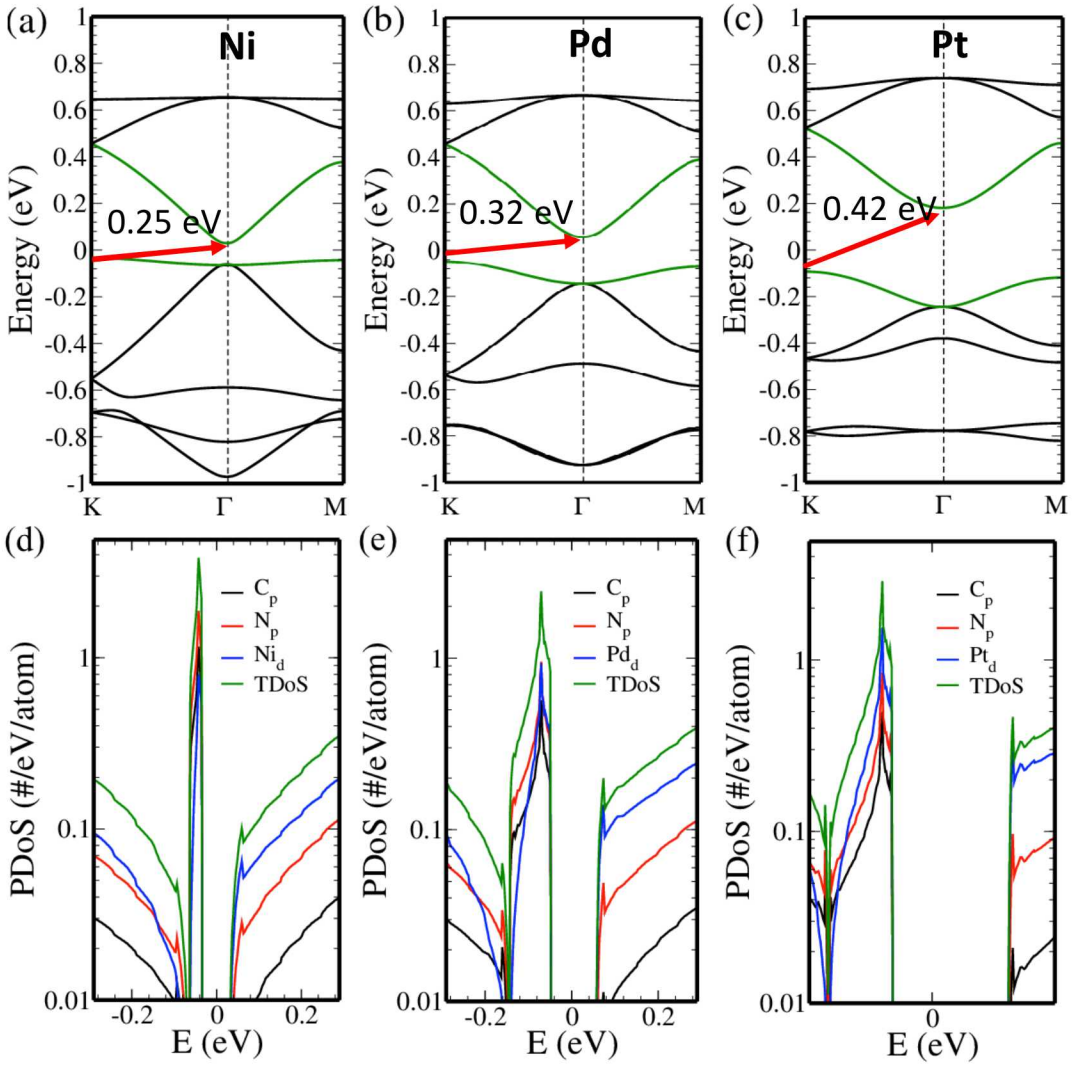
Material	Type	σ (S/cm)	κ (W/m · K)	*S* (μV/K)	*PF* (μW/m · K²)	ZT (300K)
$TCNQ@Cu_3(BTC)_2$ [1]	*p*	0.0045	0.27	+375	0.057	7.0×10^{-5}
$Ni_3(HITP)_2$ [2]	*n*	58.8	0.2	-11.9	8.31×10^{-3}	1.19×10^{-3}

Values at 25 ∘C. [1] K. J. Erickson et al. *Adv. Mater.* **2015**, *27*, 3453. [2] L. Sun et al. *Joule* 1 (2017), 168.

How can we improve the thermoelectric properties of MOFs?

Tuning $M_3(HITP)_2$ band structure by metal ion substitution

Increasing VB dispersion



Large CB and VB dispersion

- Both ligand and metals contribute
- Indirect bandgap
  - Small compared to most MOFs
  - Increases Ni → Pd → Pt

Density of states:

- Singularities: characteristic of 2D materials
- Linear behavior on either side of bandgap representative of 3D materials

What is the structure of the Pd and Pt materials

Sandia National Laboratories

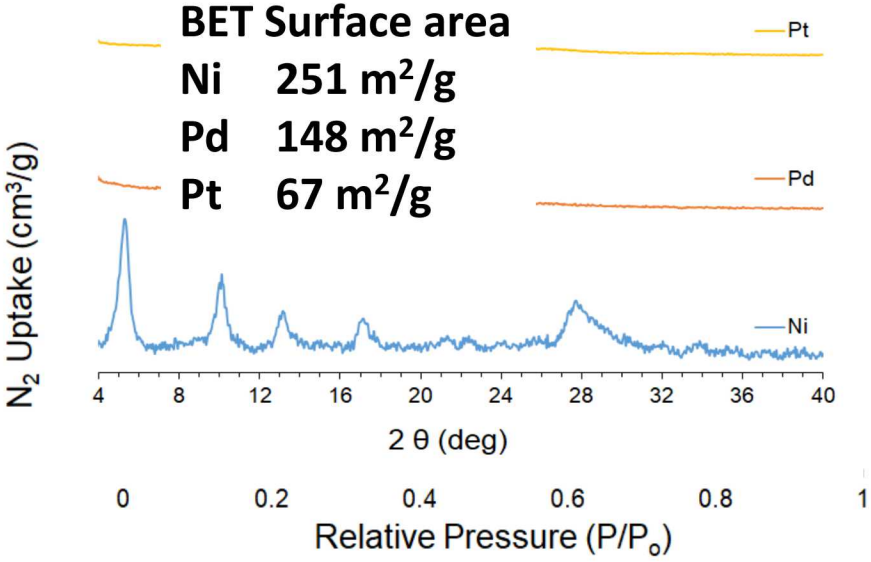
Pd and Pt MOGs lack long-range order

BET Surface area

Ni 251 m^2/g

Pd 148 m^2/g

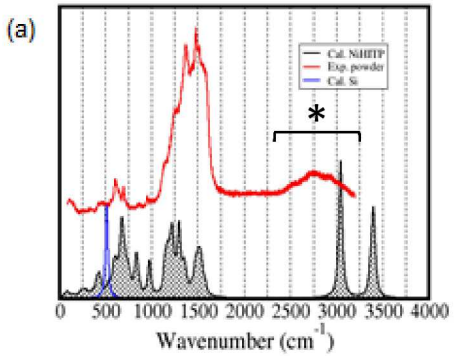
Pt 67 m^2/g



L:M ratios from elemental analysis

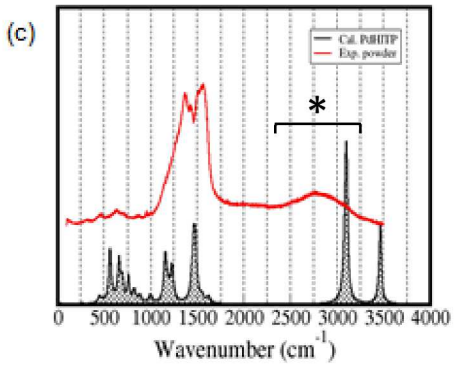
	C basis	N basis
Theoretical ($Ni_3(HITP)_2$)	0.67	0.67
Pd_xL_y	1.13	1.02
Pt_xL_y	0.73	0.73

Does the Pd version have missing metal ions or different structure?

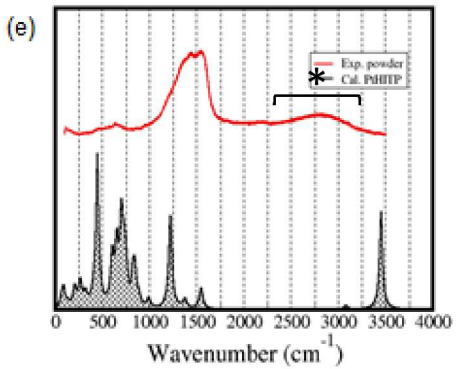


$Ni_3(HITP)_2$

*** Graphene-like**

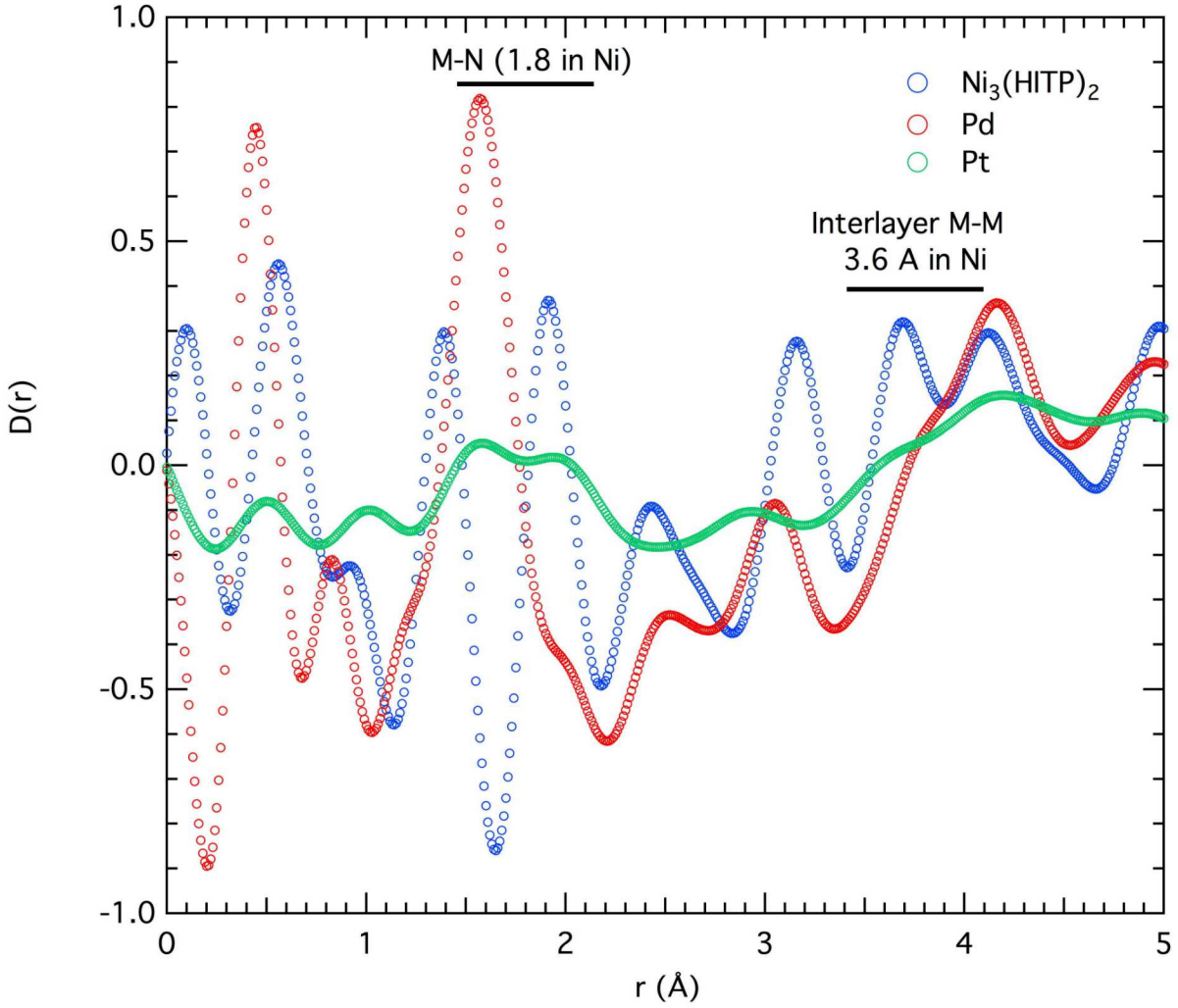


$Pd_x(HITP)_y$

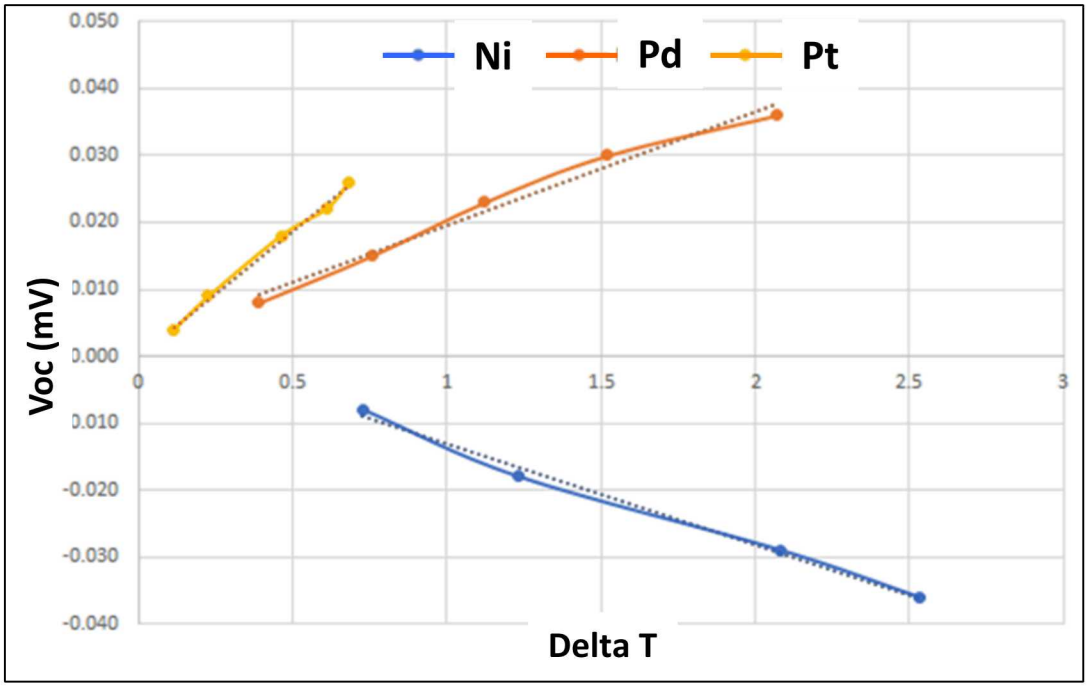


$Pt_x(HITP)_y$

PDF: evidence of M-M and M-N bonding in all three $M_3(HITP)_2$



Measured thermoelectric data for Ni, Pd, and Pt structures show both p- and n-type are possible



- Ni is n-type
- Pd and Pt are p-type materials

→ consistent with predicted bandgap trend

- σ and S^2 both increase → *PF* also increases
- Power factor: Ni < Pd < Pt

Sample	R (Ω)	ρ (Ω•cm)	σ (S/cm)	S (μV/K)	Power Factor (μW/mK²)
Ni	48.2	5.123	0.195	-13.46	3.54×10^{-3}
Pd	43.7	3.835	0.261	+19.63	10.05×10^{-3}
Pt	40.0	3.060	0.327	+37.69	46.42×10^{-3}

Conclusions

- Modifying metal ion and/or linker are effective strategies for tailoring MOF electrical properties
- Control of film thickness could be critical to achieving desired electronic properties
  - MOG “monolayers” (non-interacting multilayers)
- Defects affect MOF charge transport properties
  - Grain boundaries
  - Stacking faults/polymorphs
  - Lattice mismatches
- We need synthetic methods to control and minimize defects
  - Defect formation might be a strategy for tailoring electrical properties

Acknowledgements

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Chris Hendon

Austin Mroz

Technical Univ. Munich

Prof. Roland Fischer

Christian Schneider

Gregor Kieslich

Univ. Cambridge

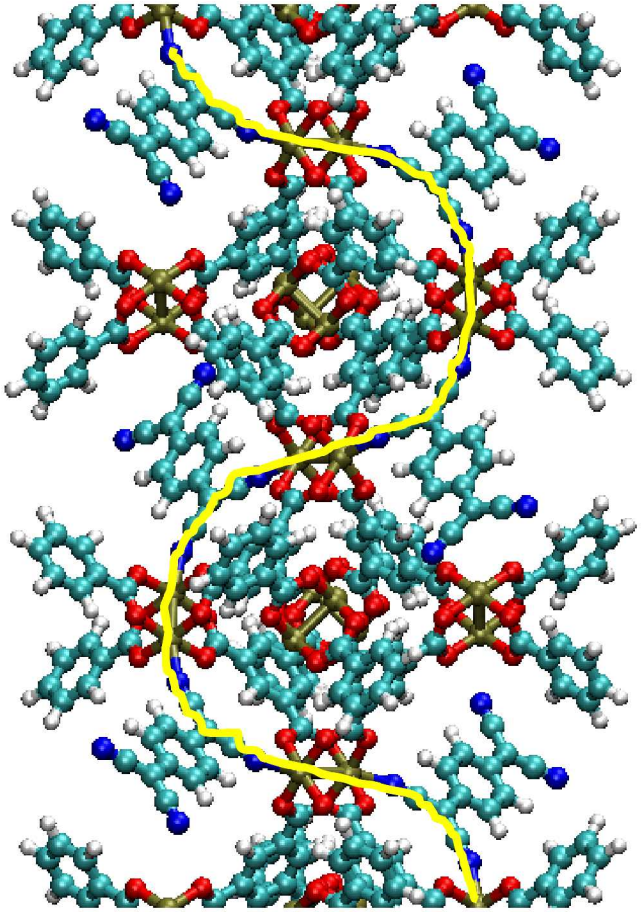
Tom Bennett

Louis Longley

David Keen

Backup Slides

Alternative role for TCNQ: $Cu_2(btc)_4$ paddlewheels bridged by TCNQ

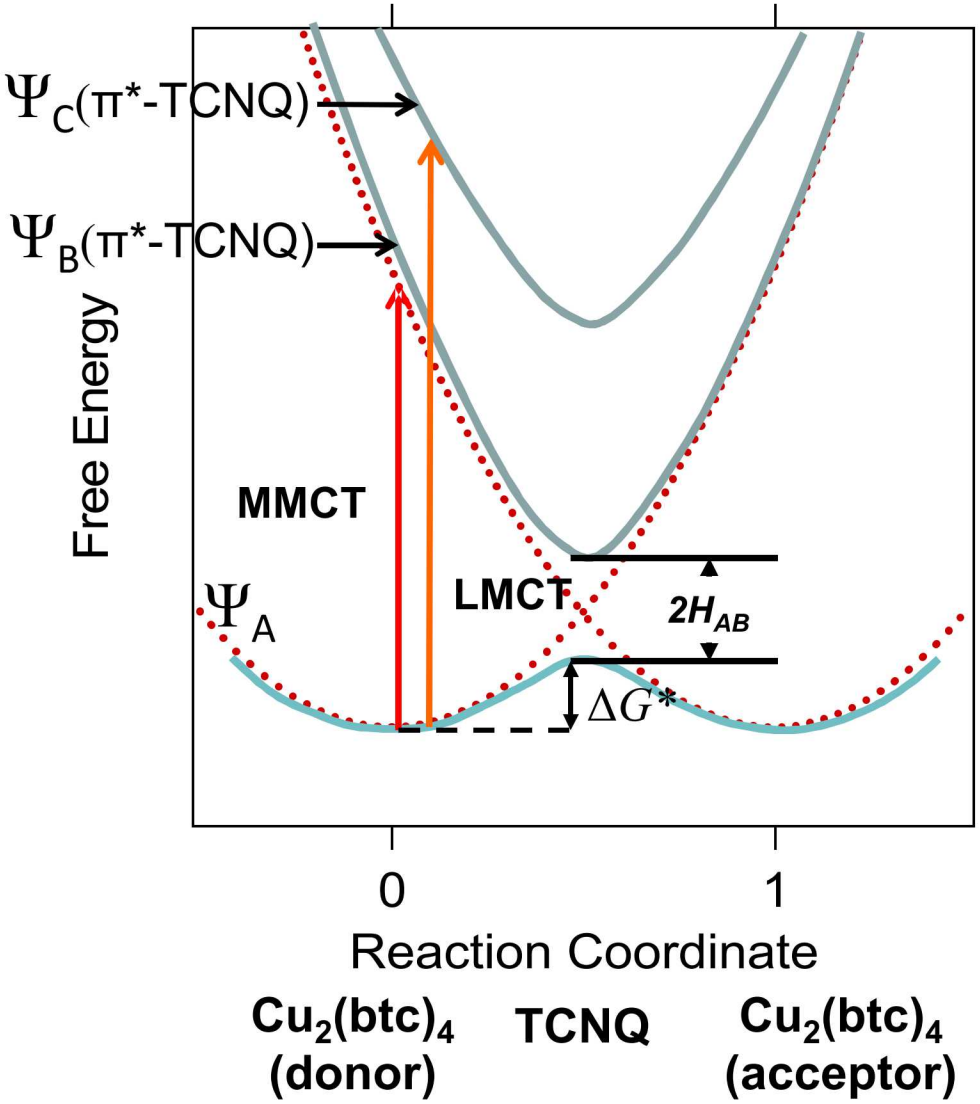


- 2 TCNQ will fit in each large pore (16 TCNQ/unit cell)

→ Continuous TCNQ-Cu2-TCNQ pathway with 1 TCNQ/large pore = 8 TCNQs/unit cell

- Measured loading = 8 TCNQs/unit cell
- IR, Raman, PXRD, UV/Vis, and EPR support this model

TBCNQ couples neighboring Cu dimers → lowers barrier to charge transfer



Three-site model: Donor-Bridge-Acceptor

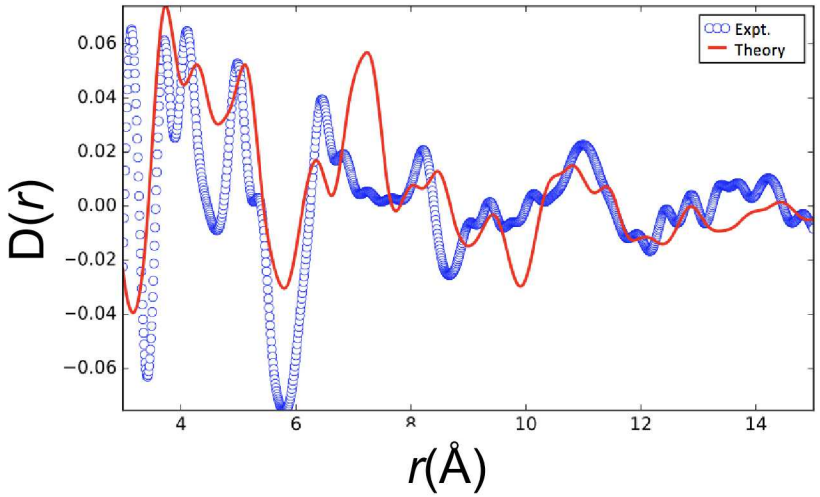
Superexchange mechanism:

H_{AB}-Electronic coupling matrix element

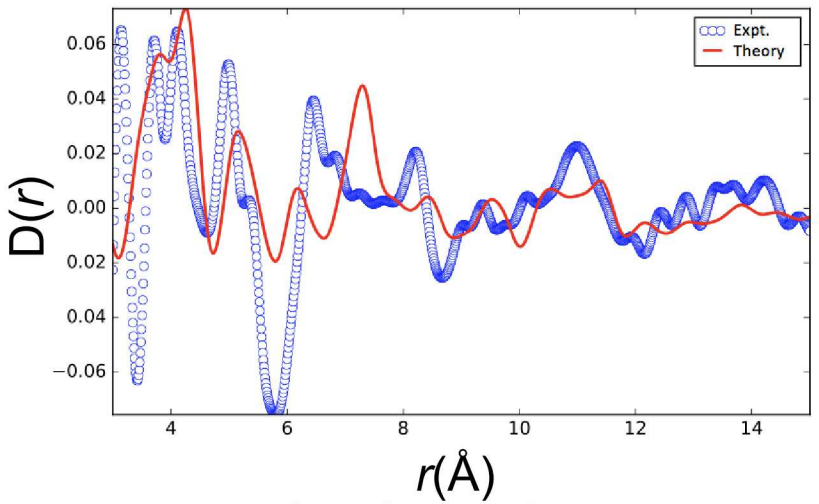
$$H_{AB} = \langle \Psi_A | H | \Psi_B \rangle$$

$$H_{AC} = \langle \Psi_A | H | \Psi_C \rangle$$

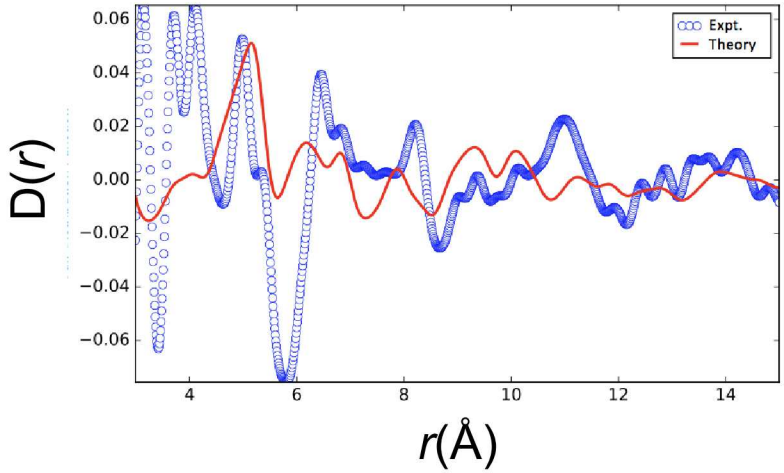
Experimental PDF data for $Ni_3(HITP)_2$ are in best agreement with a 2D structure with offset layers



$Ni_3(HITP)_2$ slipped-parallel bilayer



$Ni_3(HITP)_2$ monolayer



$Ni_3(HITP)_2$ monolayer with widened ligand binding angle

A pillared MOG may provide both charge transport tunability and reduce the effects of defects

Proposed Modification of the Graphene Analogue $Ni_3(HITP)_2$ To Yield a Semiconducting Material

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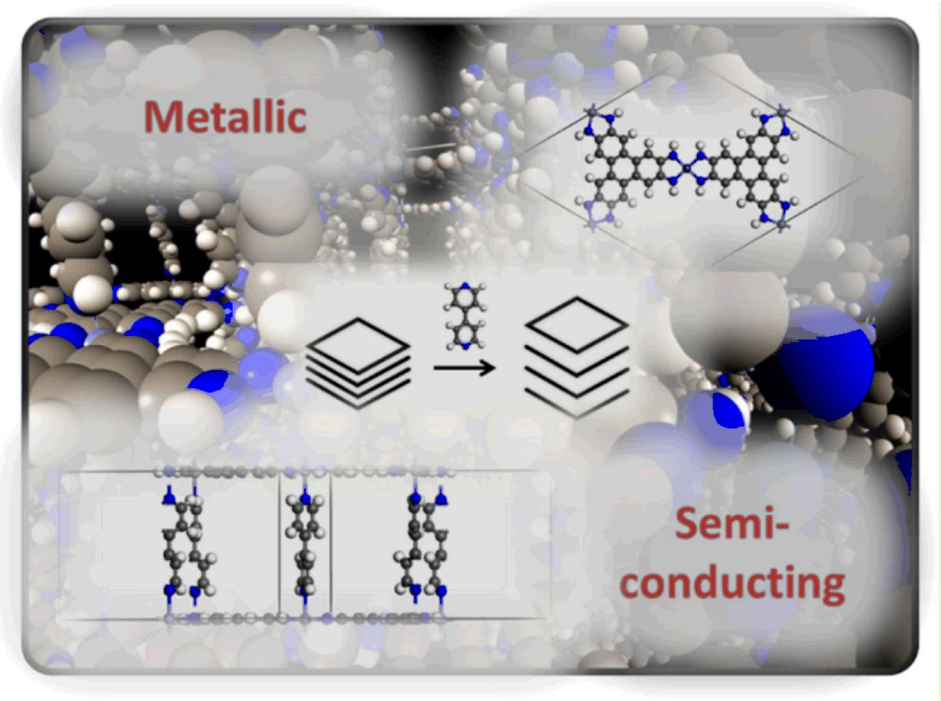
[‡]Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104, United States

J. Phys. Chem. C 2016, **120**, 15001.



Modifying the MOG interlayer spacing modifies the band gap

Sandia National Laboratories

$Ni_3(HITP)_2$ band structure as a function of interlayer spacing (slipped parallel structure)

Decreasing interlayer interaction

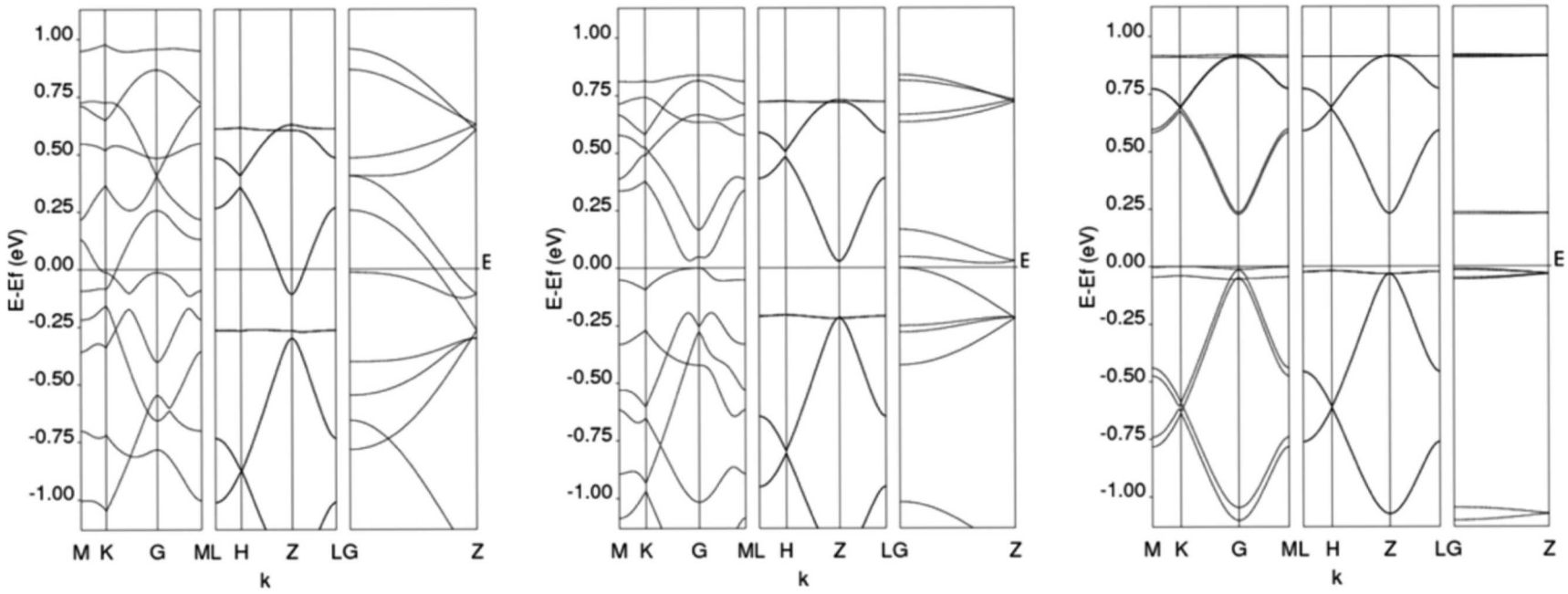
3.3 Å

3.8 Å

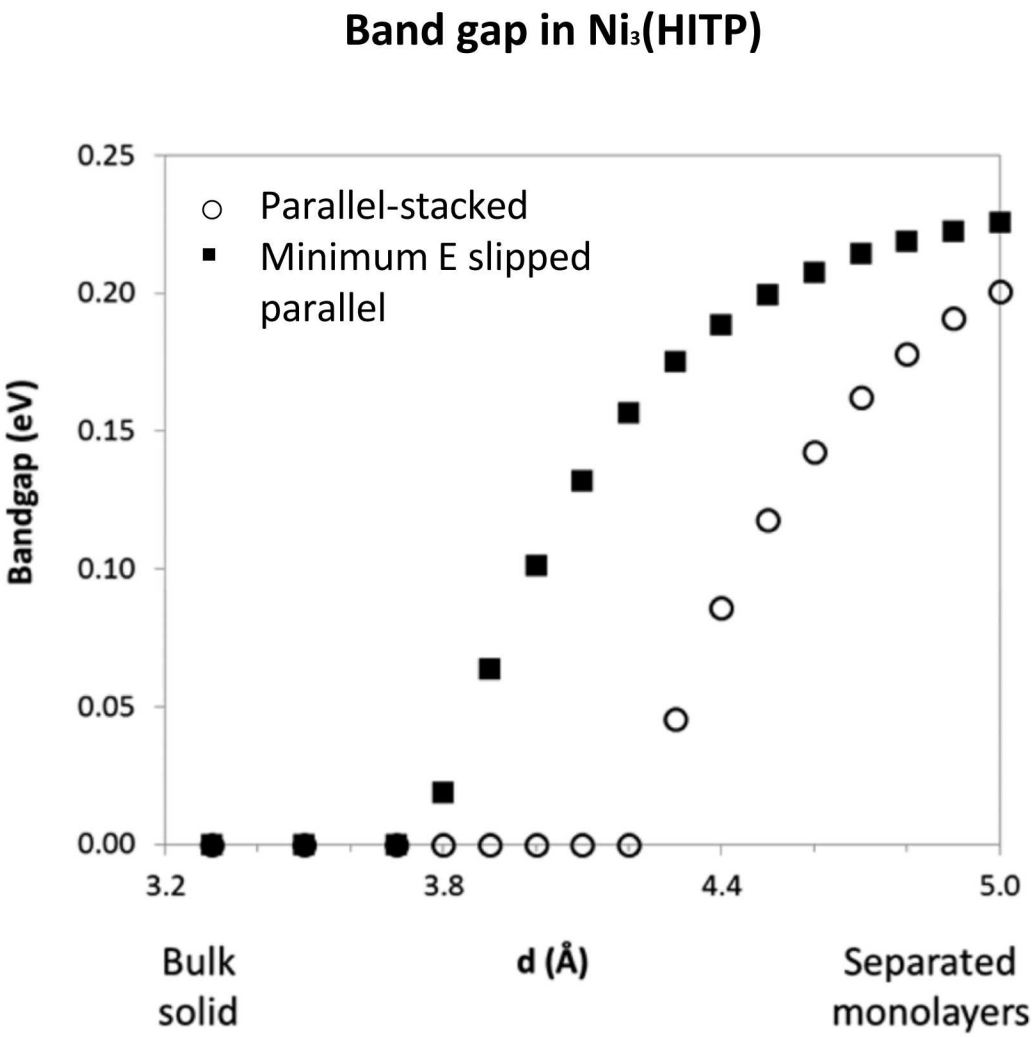
$E_{gap} > 0$

5.0 Å

$E_{gap} > 0$

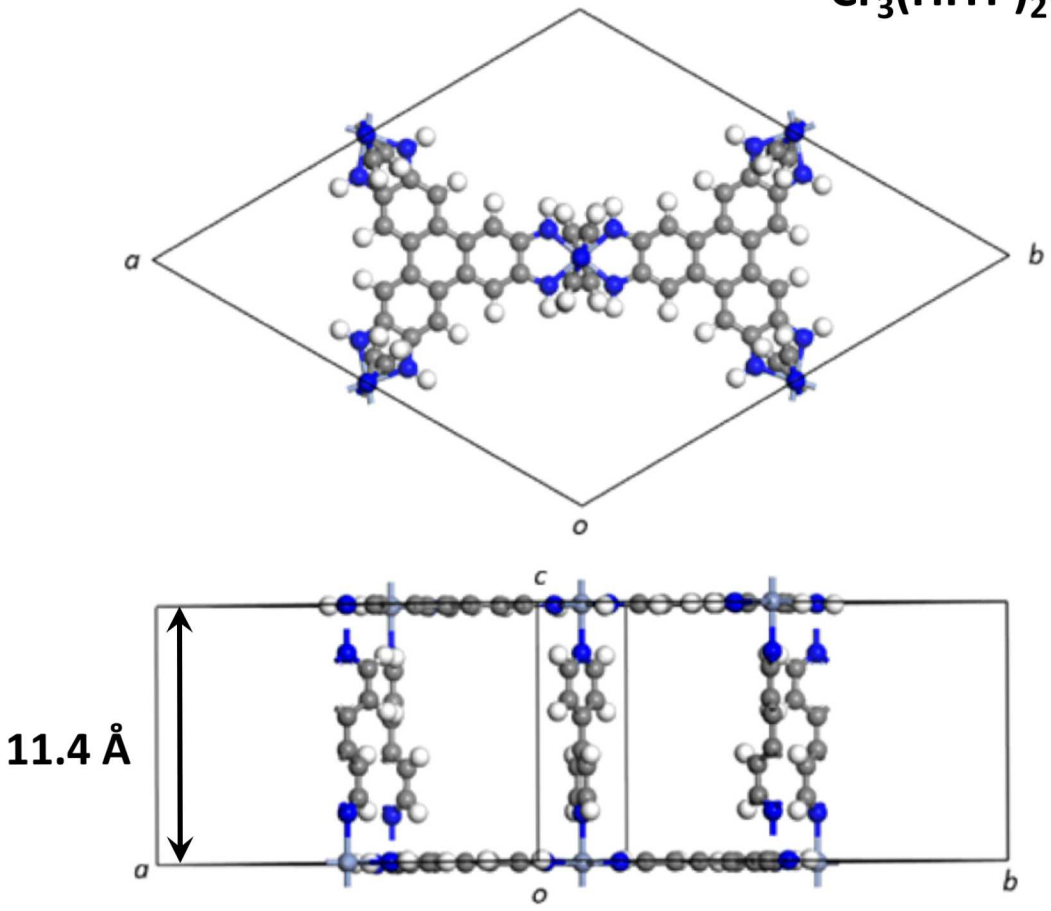


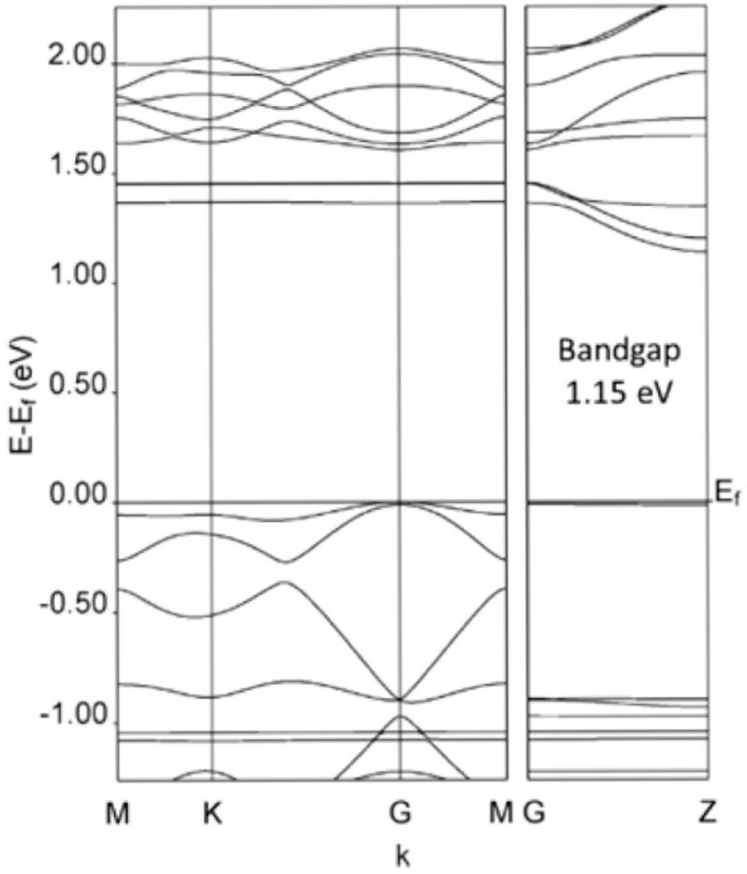
MOG Bandgap can be tuned by varying interlayer spacing



Substituting Cr(II) for Ni(II) and inserting a pillar ligand as a spacer (e.g. bpy) causes a bandgap to form

$Cr_3(HITP)_2(bpy)_3$

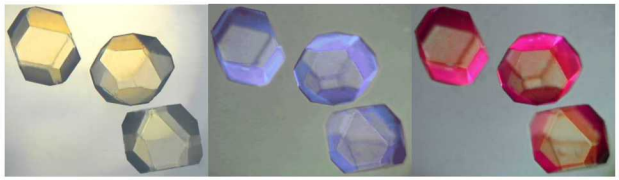




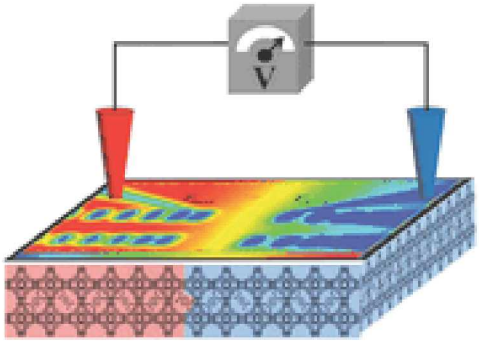
Pillar ligands also rigidify the structure and prevent formation of polymorphs

Presentation topics

- Luminsecent MOFs for solid-state lighting and radiation detection

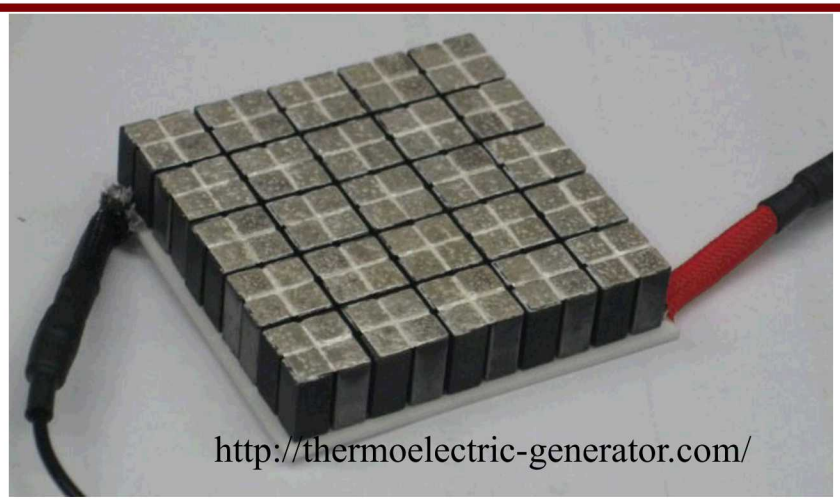


- Conducting MOFs



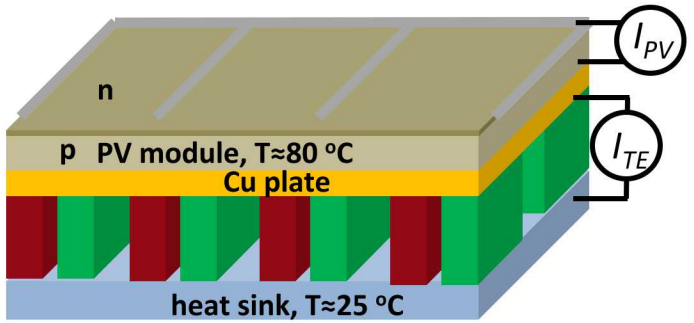
- **Defects and their influence on electrical conductivity**

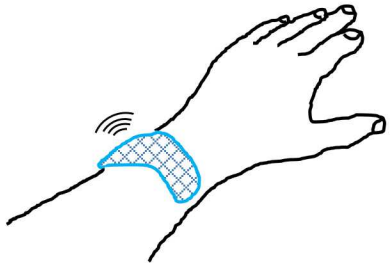
Cost, toxicity, and manufacturability limit applications thermoelectric (TE) generators




Mobicool

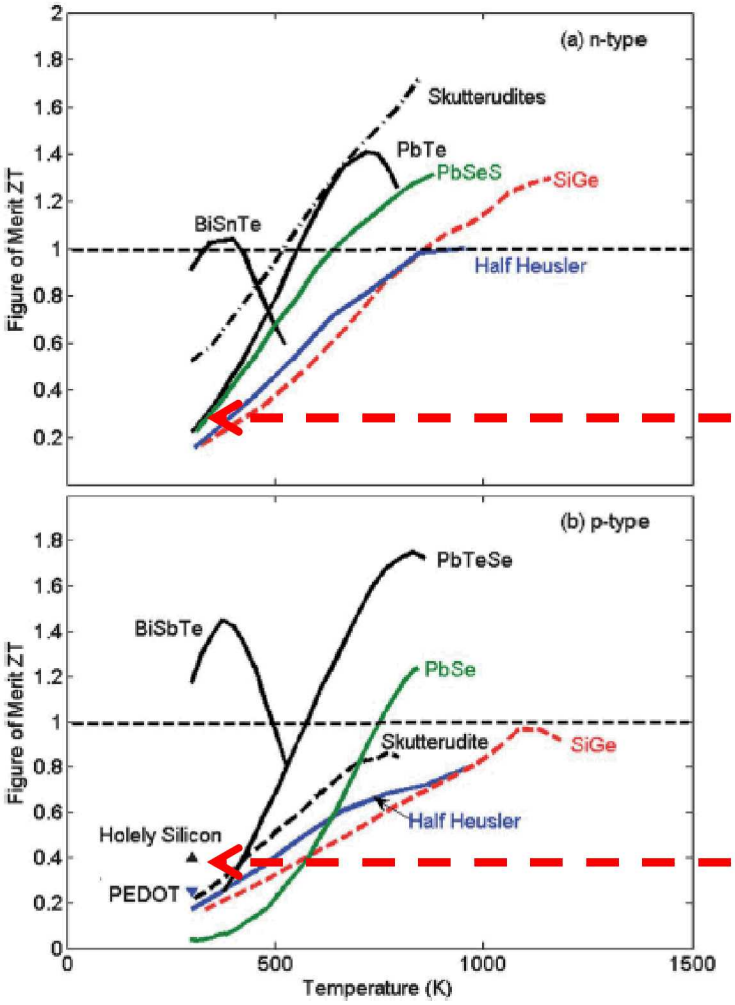

www.alphabetenergy.com



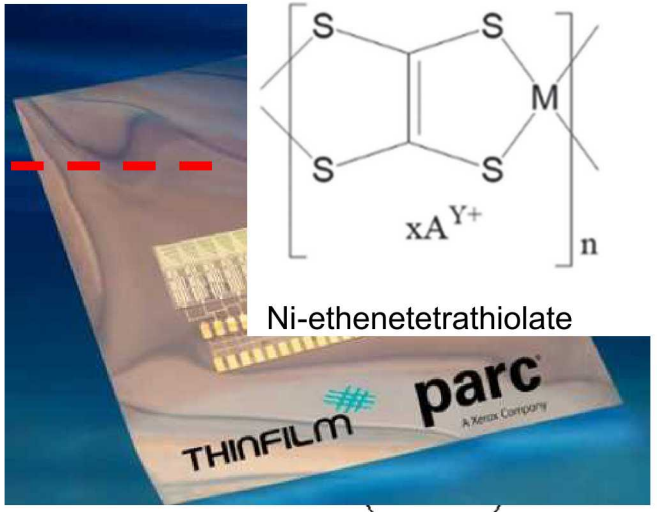


Cost, toxicity, and manufacturability limit applications of thermoelectric generators

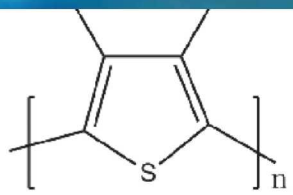
$$ZT = \frac{\alpha^2 \sigma T}{\kappa}$$



Polymer TEs could solve these challenges



Ni-ethenetetrathiolate

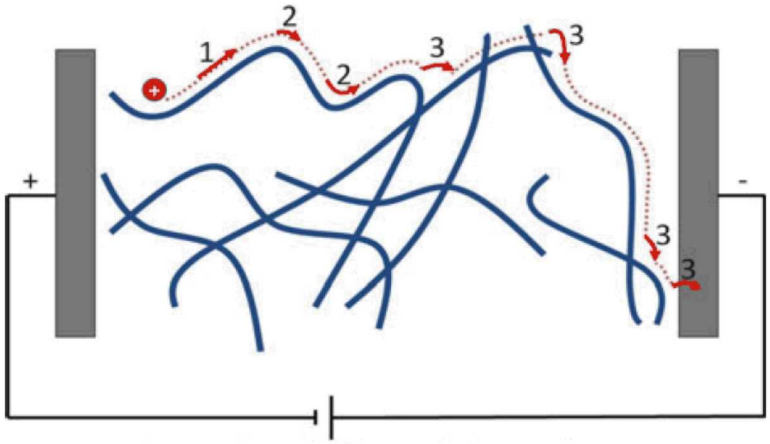


Poly(3,4-ethylenedioxythiophene)

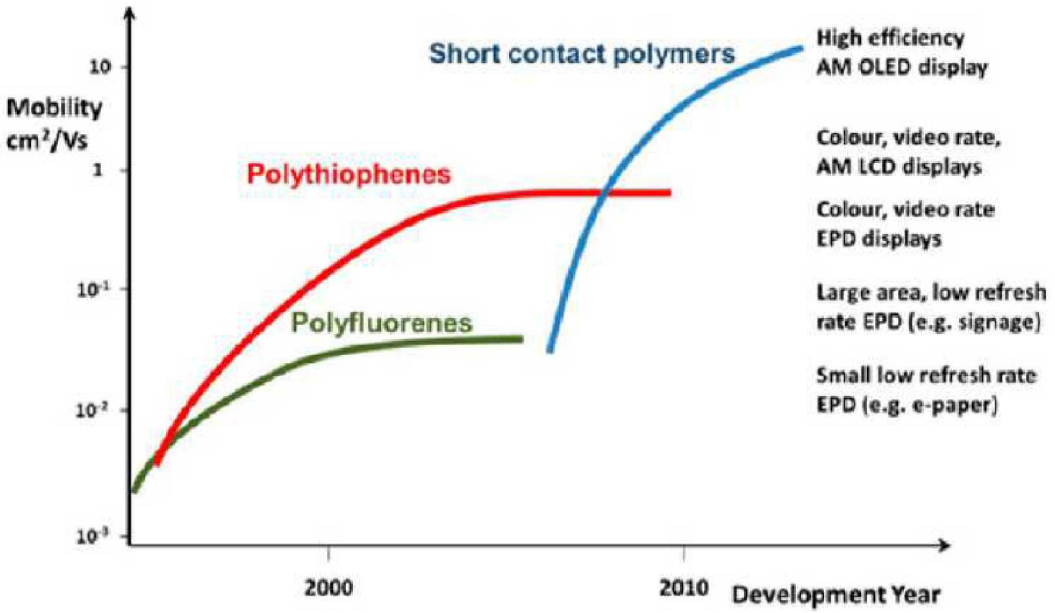
Zebarjadi et al., Energy Environ. Sci., 2012, 5, 5147

Disorder limits charge mobility in polymers

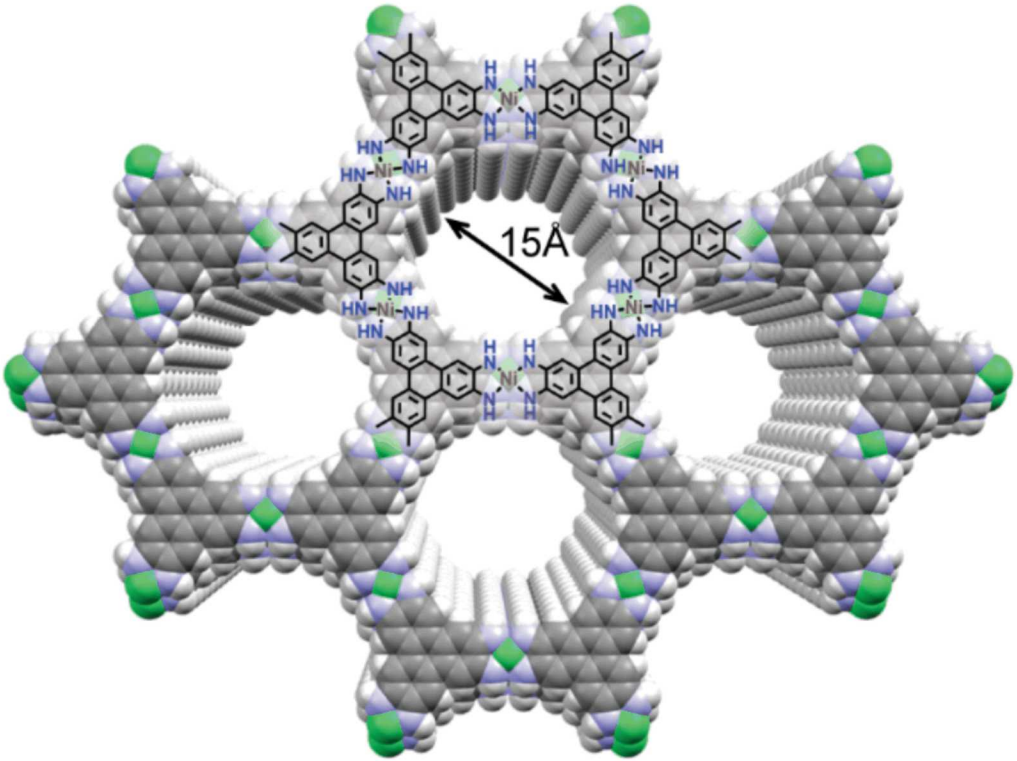
Si ~ 1000 cm^2/Vs



H. Bassler, A. Kohler, Top Curr Chem 312, 1, 2012



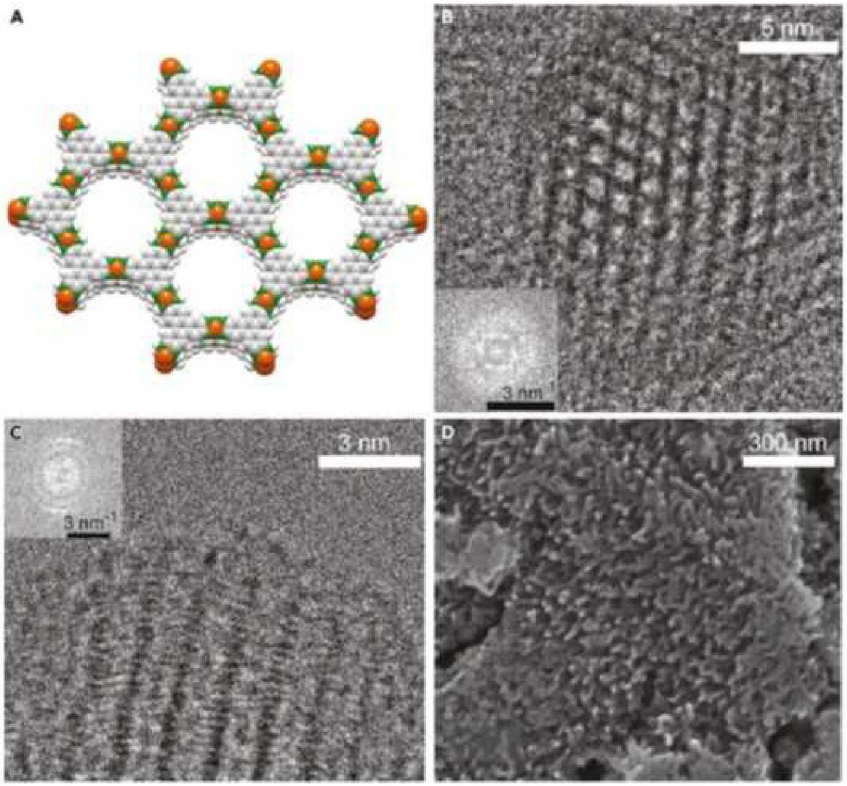
Holliday et al., Chem. Mater. 2014, 26, 647

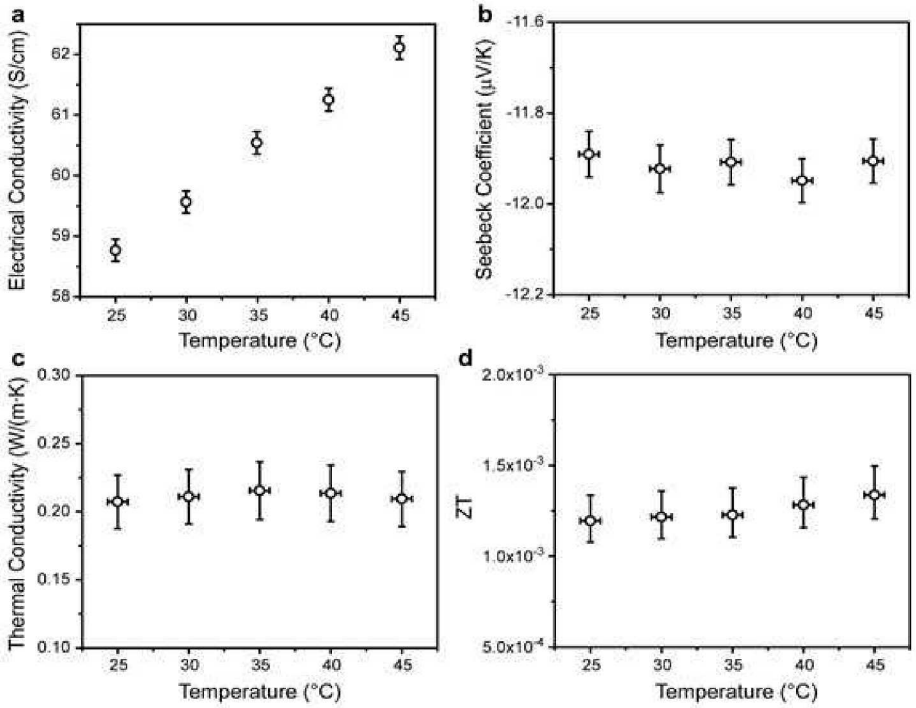


D. Sheberal, M. Dinca, et al. *J. Amer. Chem. Soc* 2014

“Metal-Organic Graphene Analogue” (MOG)

$Ni_2(HITP)_3$ powder is n-type, low thermal conductivity

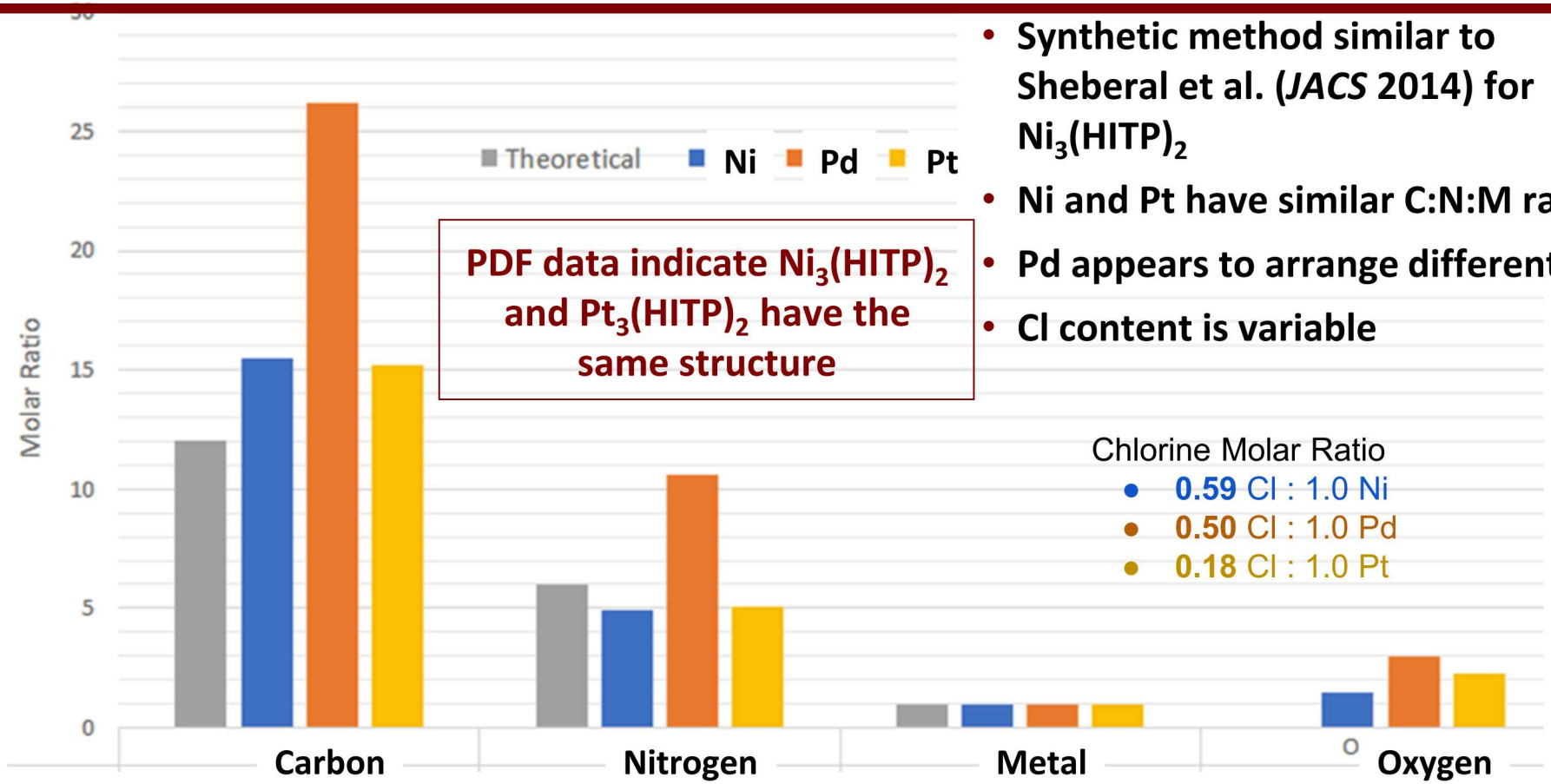




L. Sun, B. Liao, Y. He, D. Sheberla, D. Kraemer, J. Zhou, R. E. Jones, C. D. Spataru, E. A. Stach, D. Zakharov, M. E. Foster, V. Stavila, A. A. Talin, M. D. Allendorf, G. Chen, F. Léonard, M. Dincă, *Joule* **1**, 167, 2017

Can we synthesize the Pd and Pt versions to test theoretical predictions?

Synthesis of $Pd_3(HITP)_2$ and $Pt_3(HITP)_2$: Elemental analysis (EDX)



PDF data indicate $Ni_3(HITP)_2$ and $Pt_3(HITP)_2$ have the same structure

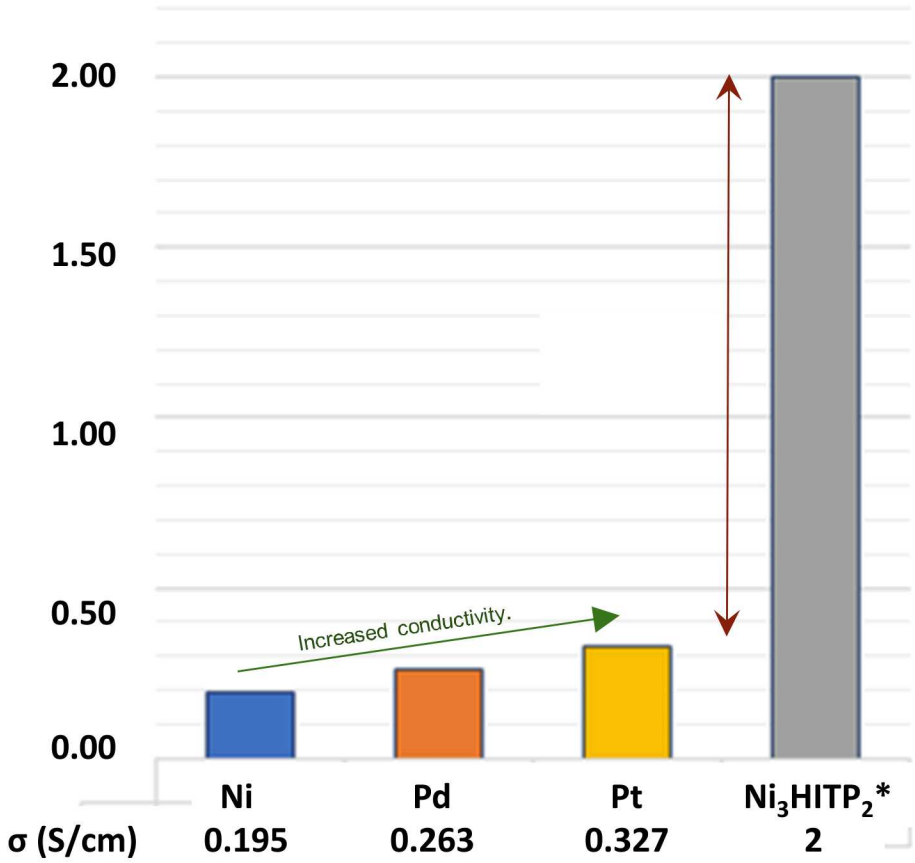
- Synthetic method similar to Sheberal et al. (*JACS* 2014) for $Ni_3(HITP)_2$
- Ni and Pt have similar C:N:M ratios
- Pd appears to arrange differently
- Cl content is variable

Chlorine Molar Ratio
- **0.59** Cl : 1.0 Ni
- **0.50** Cl : 1.0 Pd
- **0.18** Cl : 1.0 Pt

	Carbon	Nitrogen	Metal	Oxygen
Theoretical	12	4	1	0
Ni	15.5	4.9	1.0	1.5
Pd	26.2	10.6	1.0	3.0
Pt	15.2	5.0	1.0	2.3

Pd and Pt versions are electrically conducting

- Trend qualitatively supports theory
- Larger metal cation increases electrical conductivity
- Conductivity < reported by D. Sheberal et al. for $Ni_3(HITP)_2$
  - Very thin pellet
  - Electrical contacts sub-optimal



*D. Sheberal et al. *JACS* 2014

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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Porous Field-Effect Transistors Based on a Semiconductive Metal–Organic Framework

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[‡]School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, Guangdong 510006, China