SAND2020-9580C

Proton-Tunable Analog Transistor Using a Coordination Polymer

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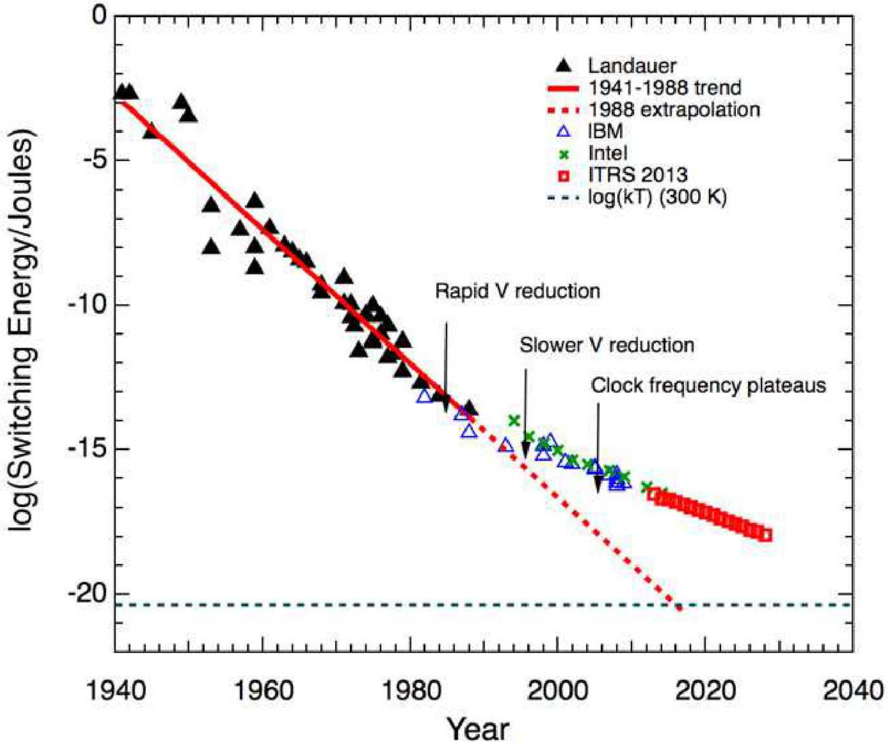
Symposium H05 - Metal Organic Frameworks (MOFs), Covalent Organic Frameworks (COFs) and Porous Hybrid Materials: Characterization, Technology, Bio-Applications, and Emerging Devices 2
PRiME 2020

Strong indications that certain fundamental and economic limits are being reached

- Smallest usable gate length, 5 nm (~90 silicon atoms), has been achieved
  - Taiwan Semiconductor Manufacturing Co. (TSMC) and Samsung 5-nm manufacturing
  - *IEEE Spectrum* **2019,** *56*, 9
- Switching energy also plateauing
- Heat generation may be dominant factor in the departure from Moore's Law

Historical data for switching energy*

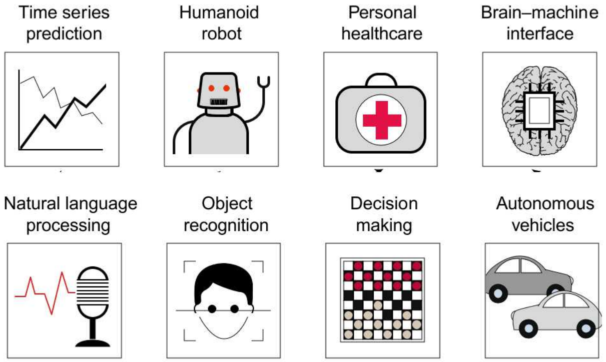


*Theis and Wong "The End of Moore's Law: A New Beginning for Information Technology" *Computing Sci. Eng.* **2017,** *19*, 41

Machine learning and artificial neural networks for computing

Application-specific computing capacity now exceeds general-purpose computing

- Internet of Things
- Edge computing
- Mobile
- Autonomous vehicles



Q. Xia, J. J. Yang *Nat. Mater.* 2019, **18**, 309

Humans excel at data processing
Machines do not

Which one of these images is a cat?

ML is energy-intensive
Example: autonomous vehicles:

J. Gawron et al.
Environ. Sci. Technol. 2018, 52, 3249–3256

Conventional von-Neuman digital architecture is energy inefficient

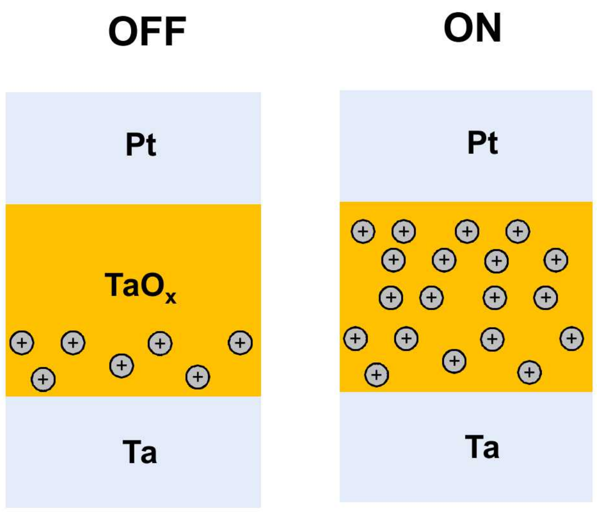
	Analog	Digital
Vector matrix multiply (read)	13 nJ	2600 nJ
Outer product update (write)	2 nJ	3600 nJ

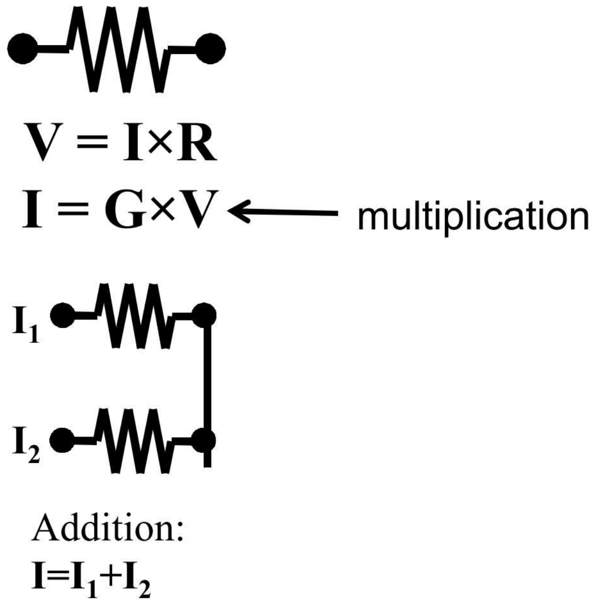
Energy/operation/array
1024X1024 synapses
1 million multiply-and-accumulate

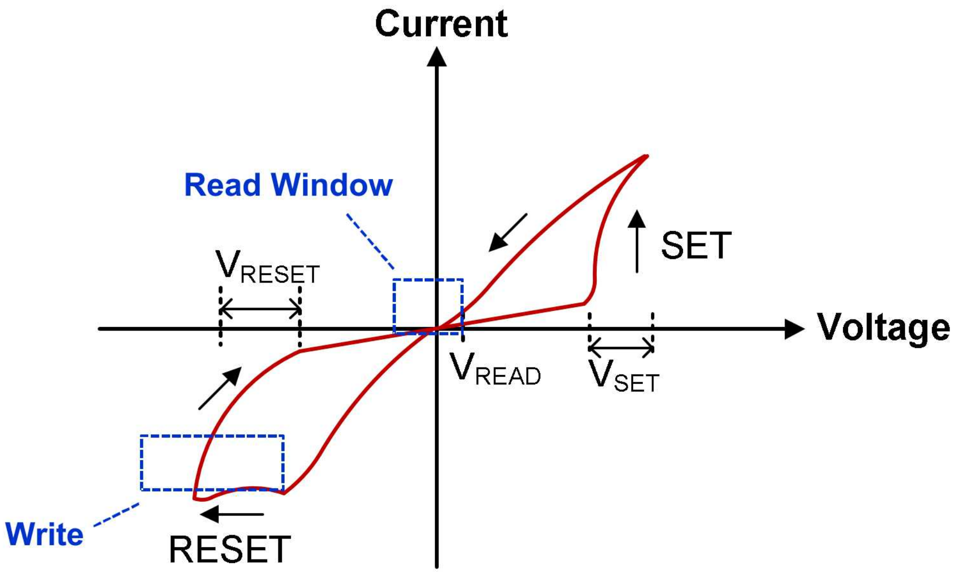
YiYang Li, Sandia National Labs. Personal communication

Use resistive memories for energy-efficient local computation

- A resistive memory or ReRAM is a programmable resistor
  - Applying small voltages allows the conductance to be read: I = G × V
  - Applying large voltages changes the resistance







Artificial neural networks (ANN) are compatible with low-power analog hardware that can reduce energy consumption

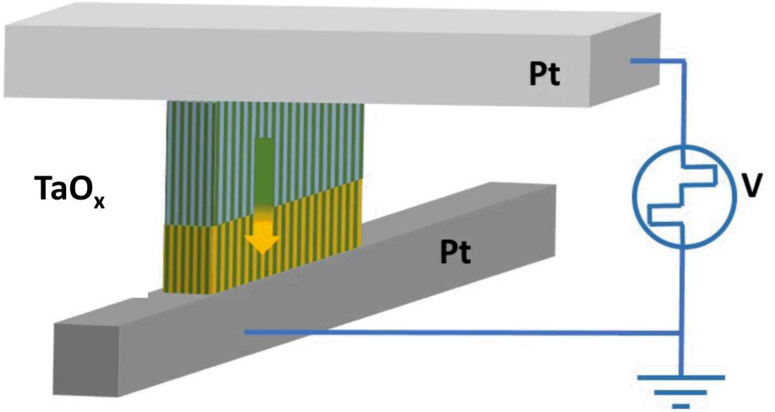
Key requirements for analog switches

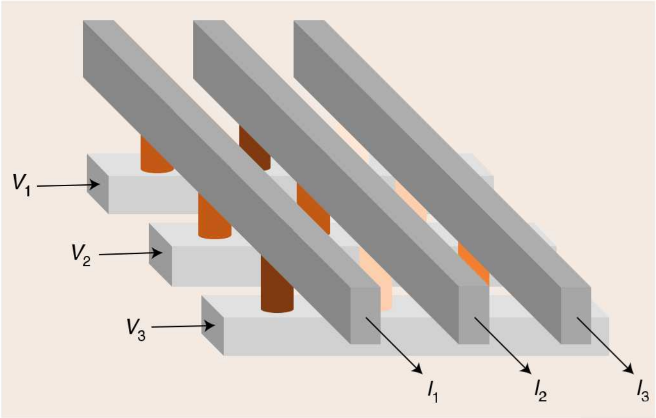
- High number of distinct conductance states
- Low fluctuation and drift in each state
- High endurance for repeated training
- Currents ≤ 10 nA to create large arrays (>1000 x 1000) without large voltage drops

2-terminal memristors

- Phase-Change Memory (PCM) and Filament-Forming Metal Oxides (FFMO)
- Stochastic switching mechanisms
- WRITE nonlinearities → degrades accuracy
- High WRITE voltages
- Excessive currents due to summation in crossbar arrays with memristors in series

Schematic of a typical 2-terminal memristor crossbar





Q. Xia, J. J. Yang *Nat. Mater.* 2019, **18**, 309

No resistive memory device has been demonstrated with adequate electrical characteristics to fully realize the efficiency and performance gains of ANN

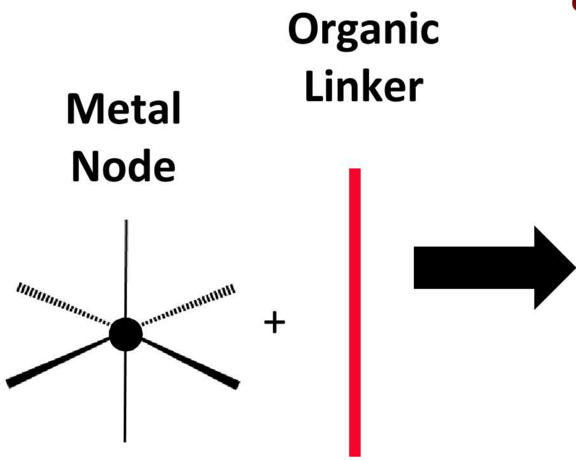
Nanoscale ordered structures could accelerate ionic and electronic transport

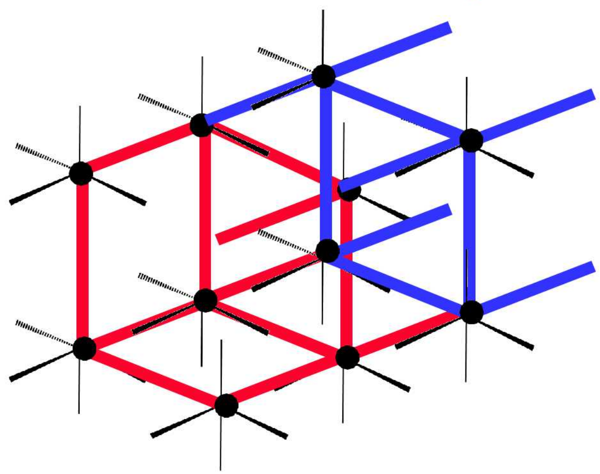
Knowledge gaps: Fundamentals governing charge and ion transport in organic mixed conductors are very poorly understood

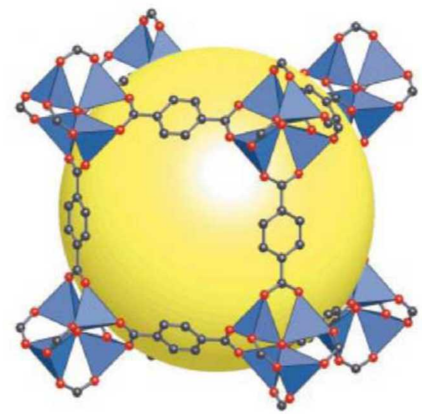
- Inadequate knowledge of local potentials
- Disorder within layers and at interfaces
- Lack of spatially resolved composition and microstructure
- No consensus regarding most effective modeling approach
- No structure-property relationships

Nanoporous MOFs are a class of coordination polymers provide atomic-scale clarity within a tunable structure

Ion and electronic charge transport are enhanced when the transporting medium is ordered with minimal defects



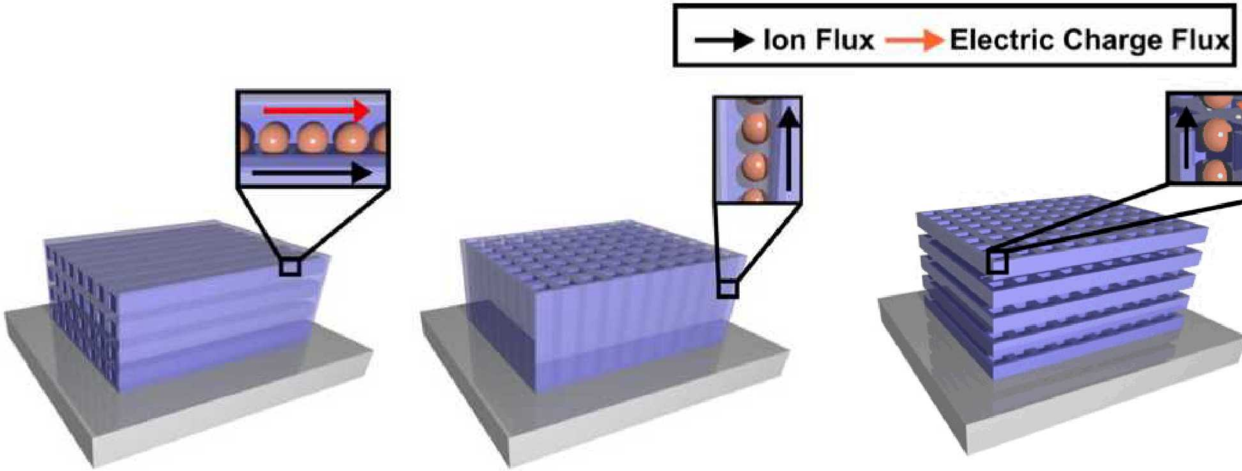




MOF-5

Advantages of MOFs for resistive switching

- Tailorable nanopore size, geometry, chemical functionality → fast, selective ion transport
- Guest molecules in nanopores are a new design element for enhancing ion transport
- Crystallinity can enhance electronic charge transport relative to disordere polymers
- 1D, 2D, and 3D porous networks are available, allowing anisotropic ion and electronic charge transport



Coaxial ion/charge flux
Conventional memristor

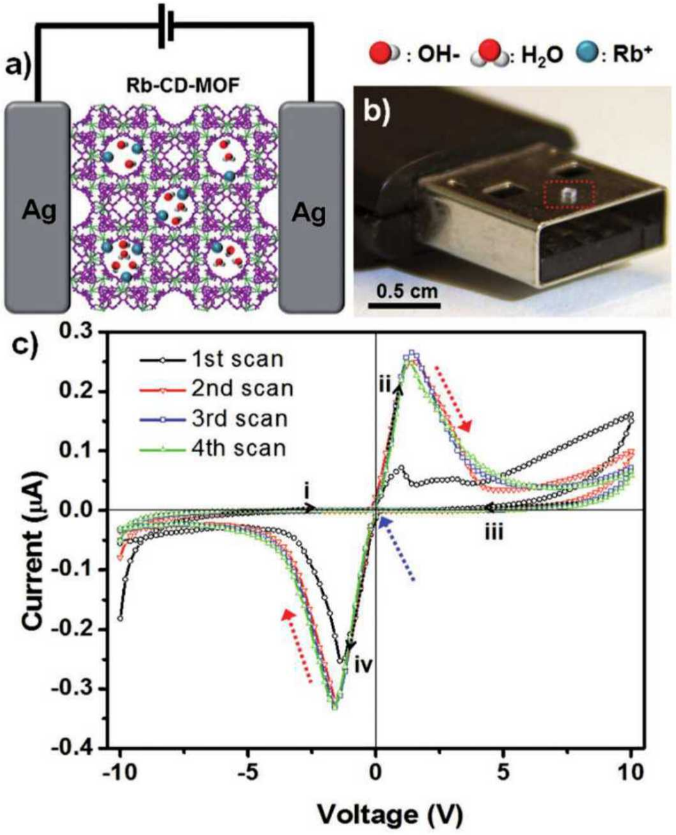
1D channels
Solid-state electrolyte

Anisotropic ion/electronic charge flux
Conducting channel

A few examples of MOF-based resistive switching have been reported

First demonstration of MOF-based chemical bipolar resistance switching

Storage of Electrical Information in Metal–Organic-Framework Memristors**



- Switching occurs by selective ion transport through the nanopores of a rubidium-cyclodextrin MOF
- Device: MOF sandwiched between silver electrodes
- Transport of Ag^+ facilitated under applied bias
- Mechanism of resistance modulation: hypothesized to be formation of a nanoscale passivating layer (AgO?) at the MOF-electrode interface.

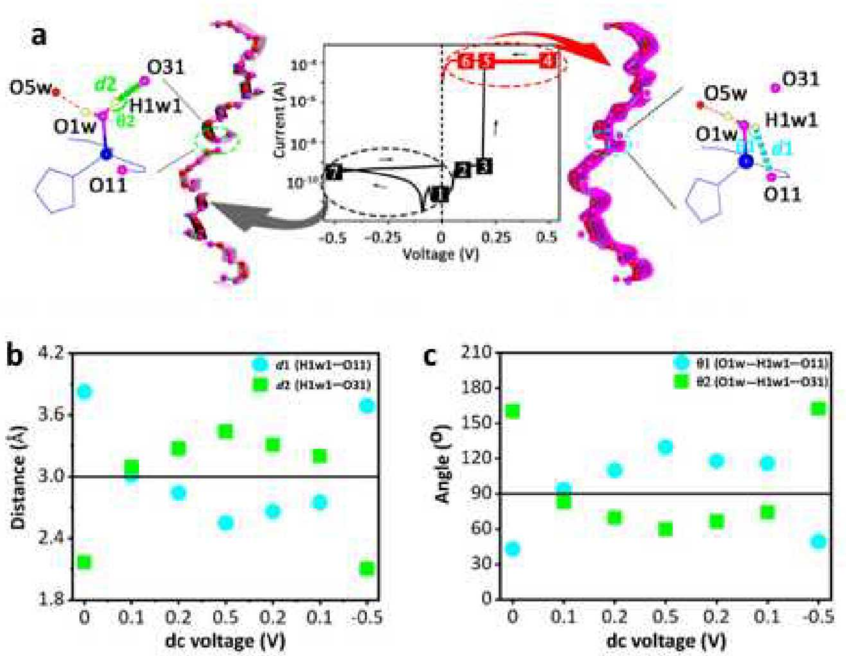
S. M. Yoon et al.
Angew. Chem. Int. Ed. 2014, 53, 4437

Proton-based resistive switching examples using MOFs

Simultaneous implementation of resistive switching and rectifying effects in a metal-organic framework with switched hydrogen bond pathway

Zizhu Yao[1]*, Liang Pan[2]*, Lizhen Liu[1], Jindan Zhang[1], Quanjie Lin[1], Yingxiang Ye[1], Zhangjing Zhang[1†], Shengchang Xiang[1†], Banglin Chen[3†]

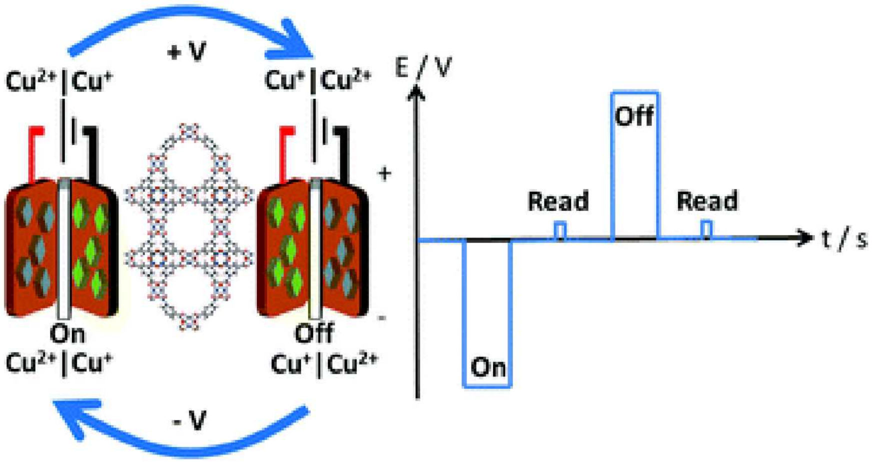
- Proton transport
- MOF single crystal bonded to two Ag electrodes
- Low set voltage (~0.2 V)
- ON/OFF ratio > 10
- Chiral structure → device is also a rectifier



Yao et al. proton-based switch 2019
Yao *et al.*, *Sci. Adv.* 2019; **5** 4515

Rewritable data storage device with copper paddlewheel MOF HKUST-1 as active material

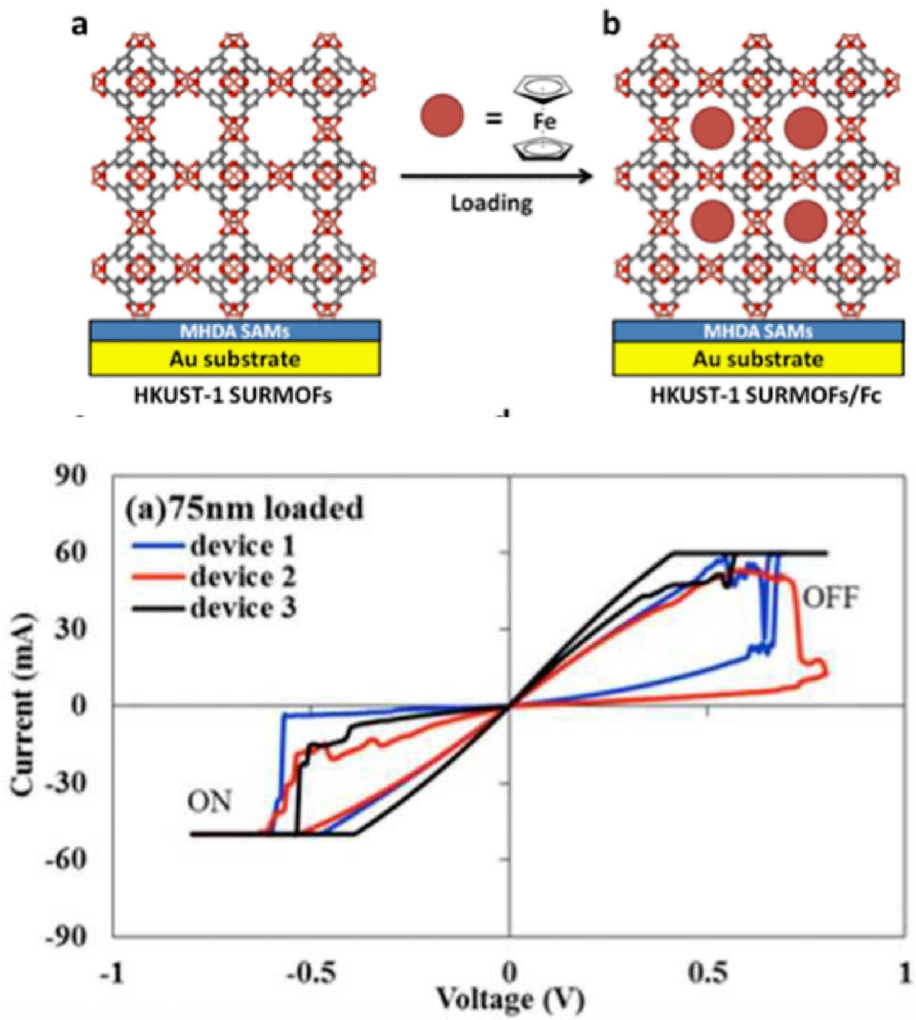
- Memory device involving cu^{2+}/$^{1+}$ reversible reduction
- Active metal cations are thought to be located near the interface of the MOF with the electrode
- Cycled 6000 times without apparent degradation
- Presence of methanol cause formation of some Cu(i)



S. D. Worrall et al. *J.Mater.Chem.C*,2016,4, 8687

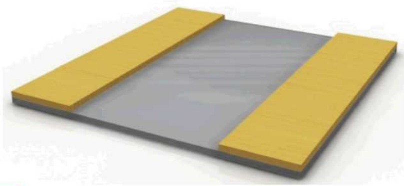
MOF-based switching facilitated by guest molecules

- **Ferrocene-loaded HKUST-1**
- **Reversible and repeatable low- and high-conductivity states**
- **Electrochemistry not consistent with filament-forming switching mechanism**
- **Possible switching mechanism: loosely bound ferrocene Fe^{2+} ions?**



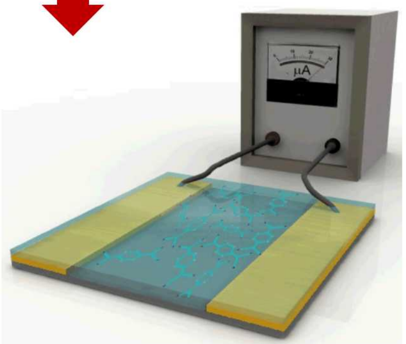
Z. Wang, E. Redel et al. *ChemNanoMat* 2016, 2, 67

Guest molecules can provide coupling between SBUs to create an electronic conduction path

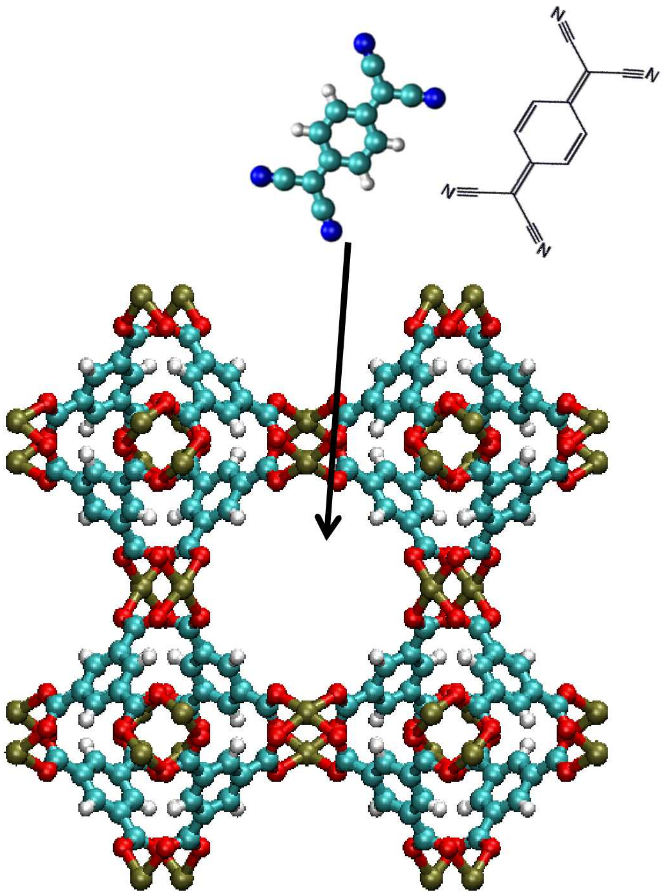


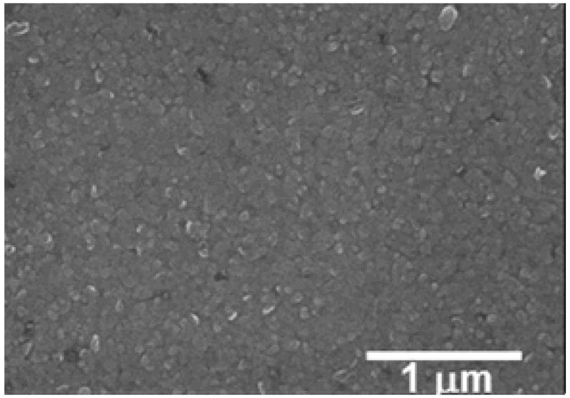
MOF growth

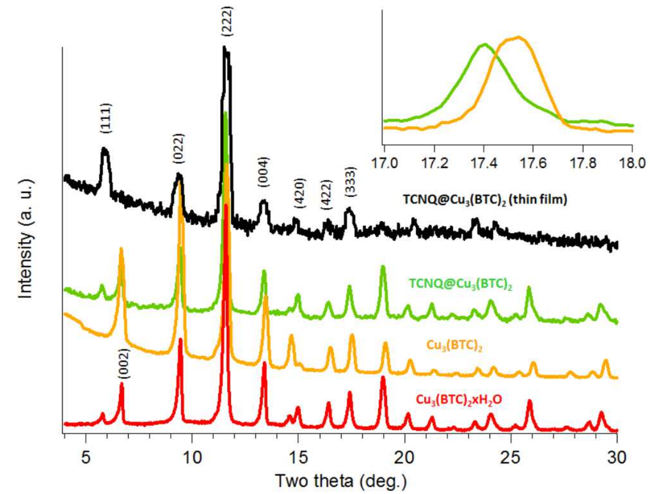
Molecule infiltration



TCNQ-infiltrated HKUST-1

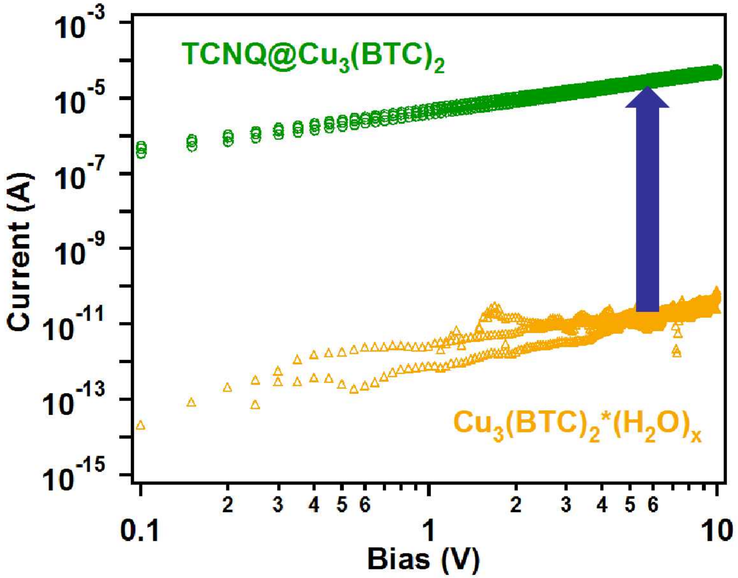


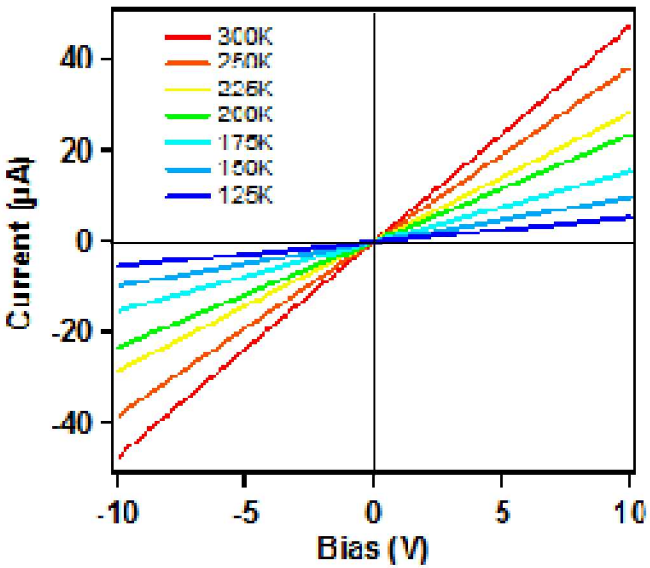




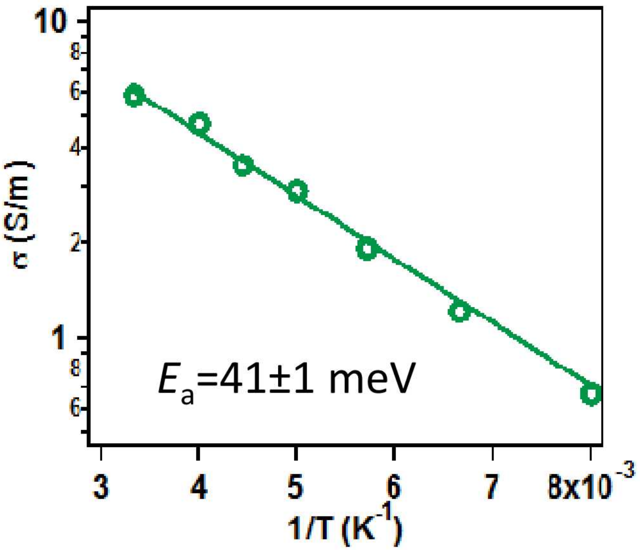
A. A. Talin, M. D. Allendorf, et al. *Science* 343, 66 (2014)

>10^7 increase in conductivity; hopping mechanism

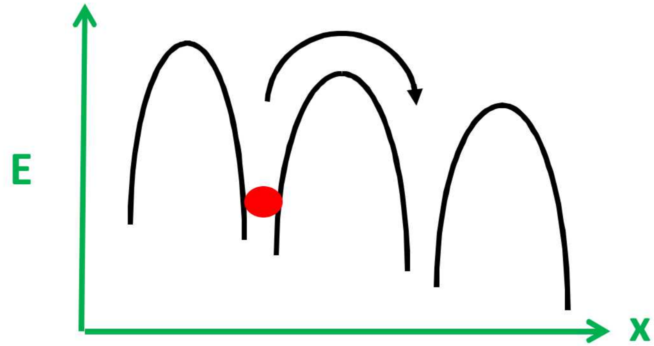




Ohmic conduction



Hopping conduction (not tunneling)

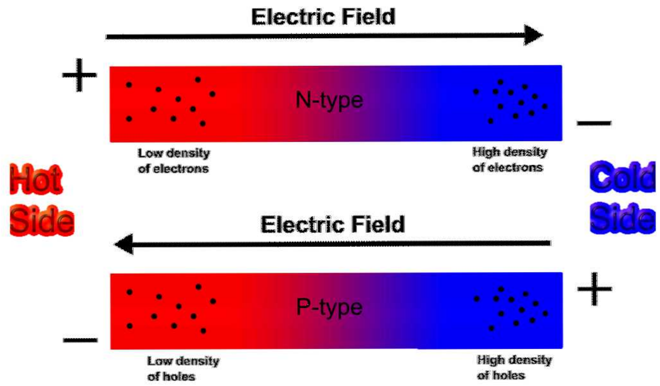


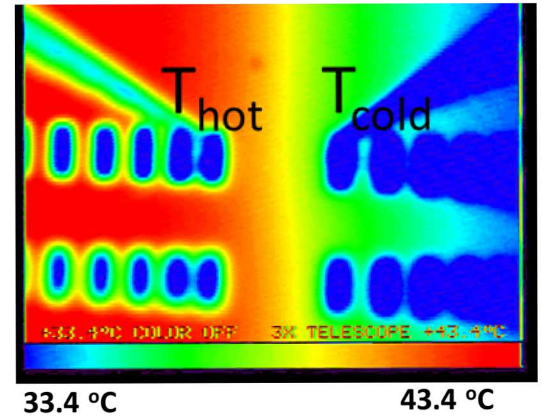
Seebeck coefficient measurements indicate that holes are the majority charge

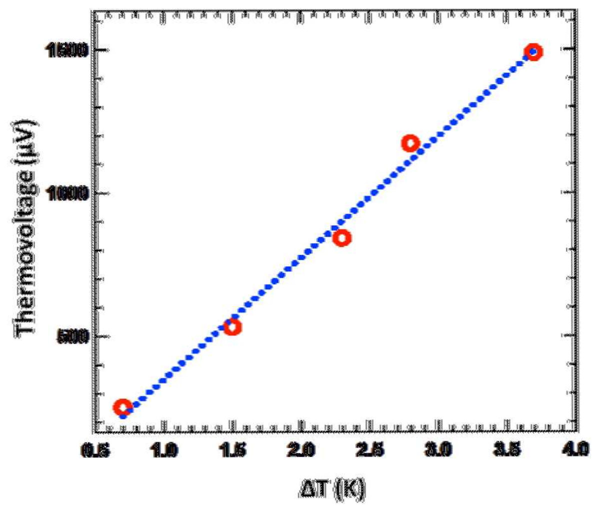
High positive Seebeck coefficient:

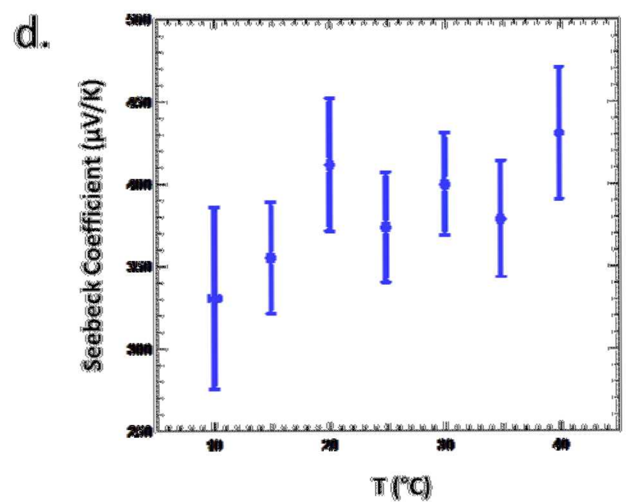
~400 µV/K vs.

170 µV/K for Bi_2Te_3



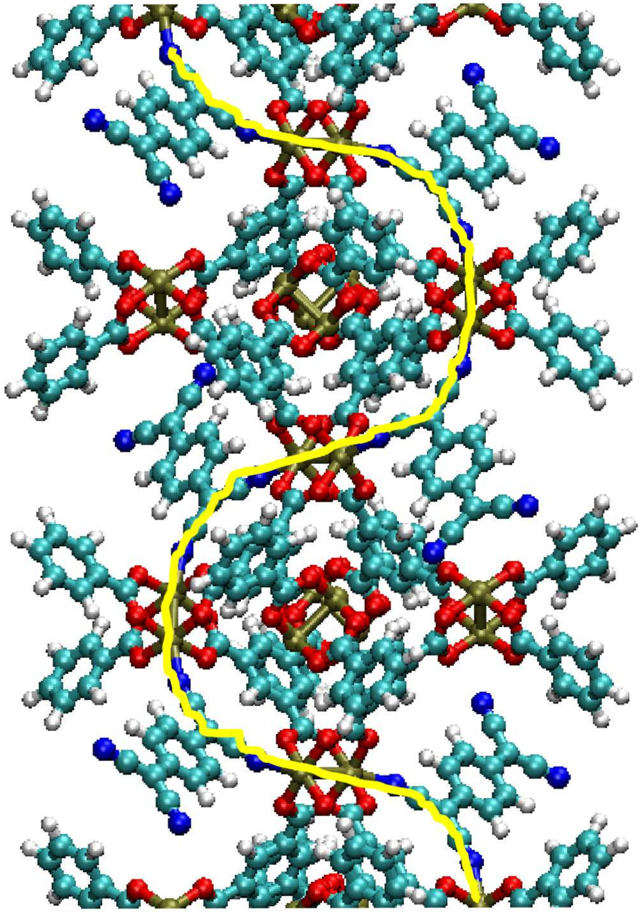


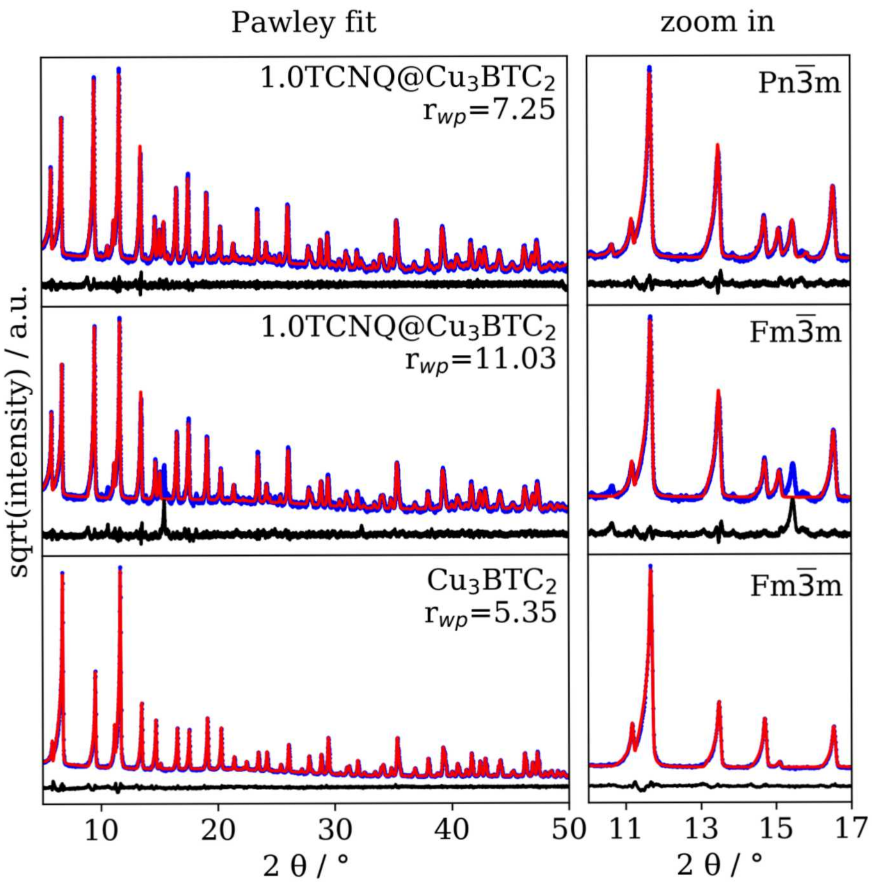




K. J. Erickson et al. *Advanced Materials* 27, 3453 2015

Conductivity mechanism: $Cu_2(btc)_4$ paddlewheels bridged by TCNQ molecules

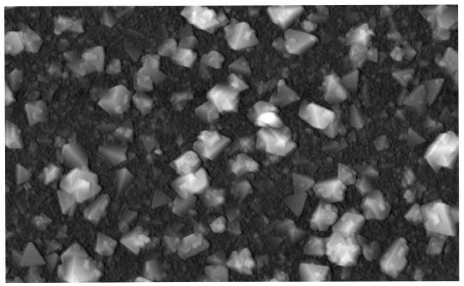


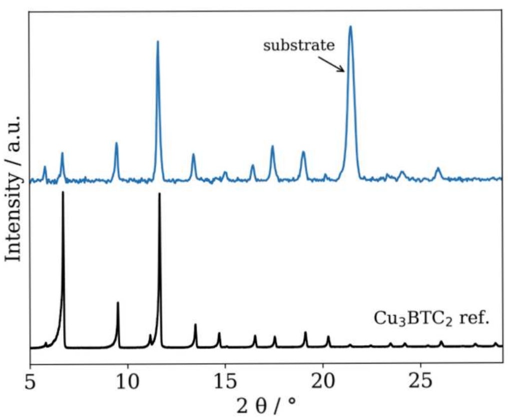


- **2 TCNQ will fit in each large pore (16 TCNQ/unit cell**

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

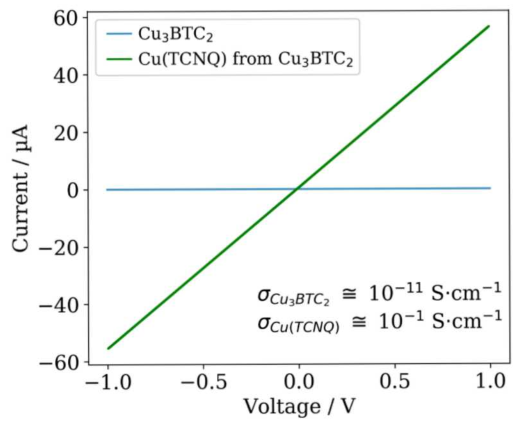
Transformation of Cu_3BTC_2 films in the presence of TCNQ

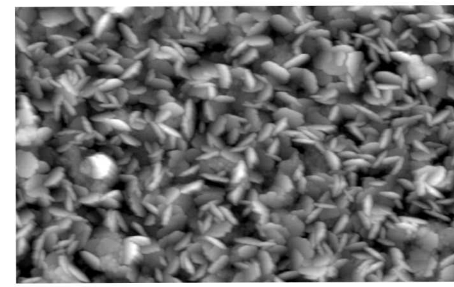


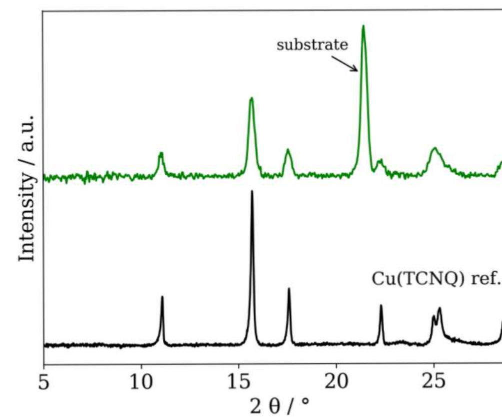


TCNQ (1mM) in MeOH

25 °C, overnight

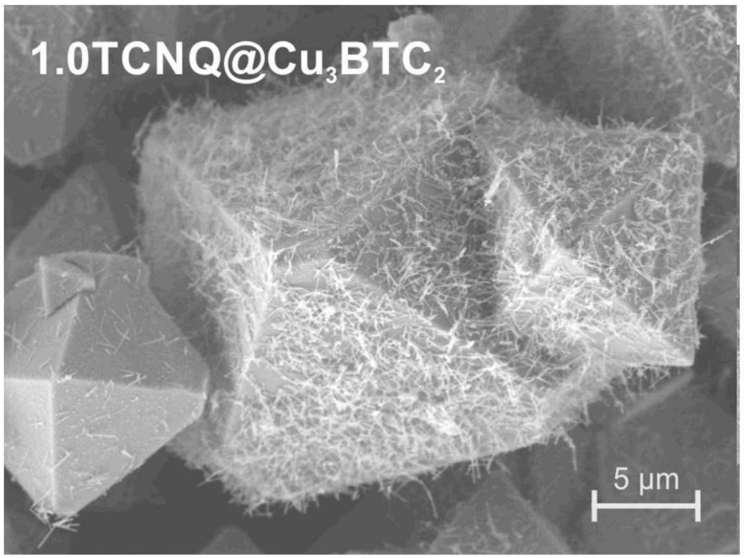


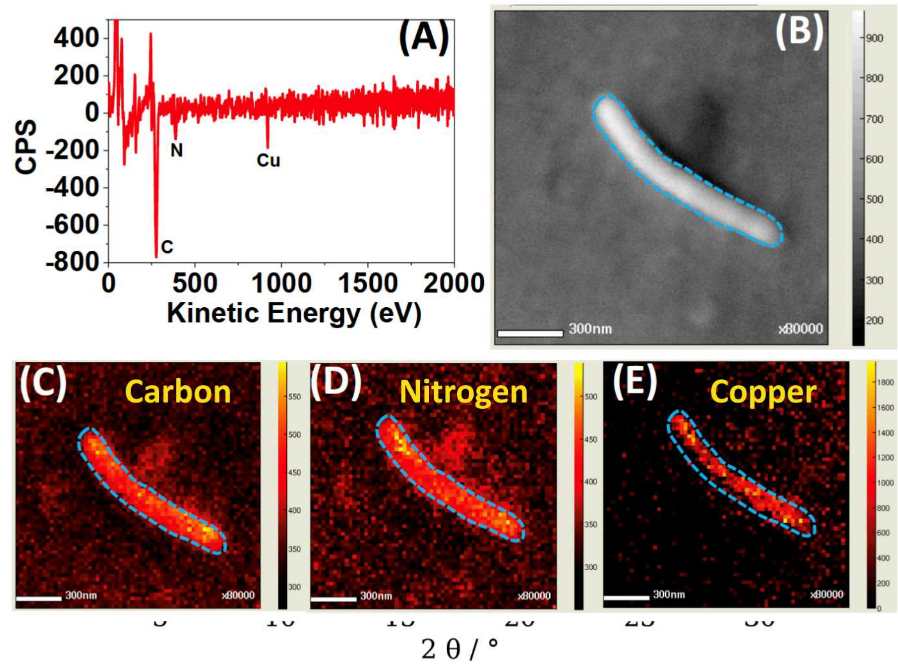




K. Thürmer, C. Schneider *et al., ACS Appl. Mater. Interfaces*, **2018**, *10* (45), 39400

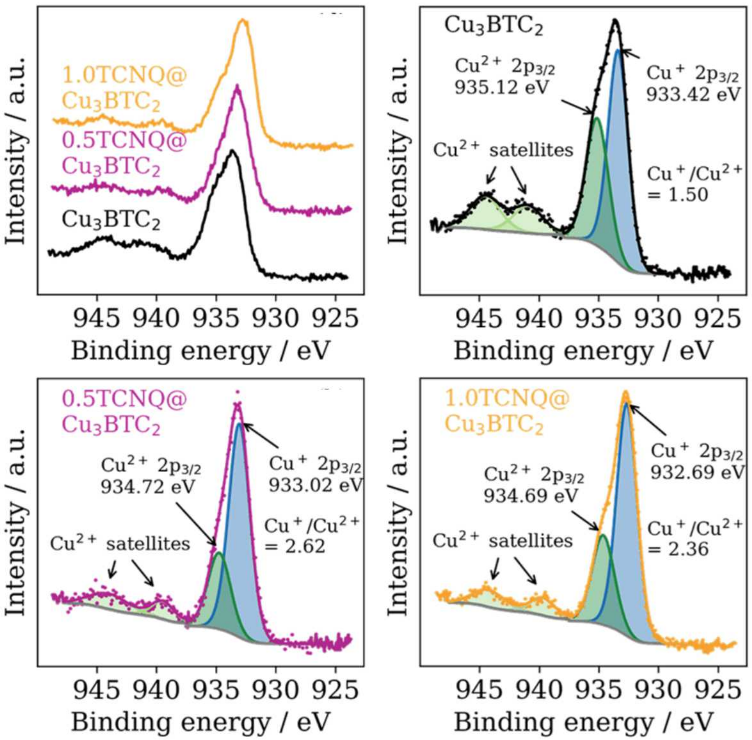
CuTCNQ nanowires form on crystallite surface during vapor-phase infiltration





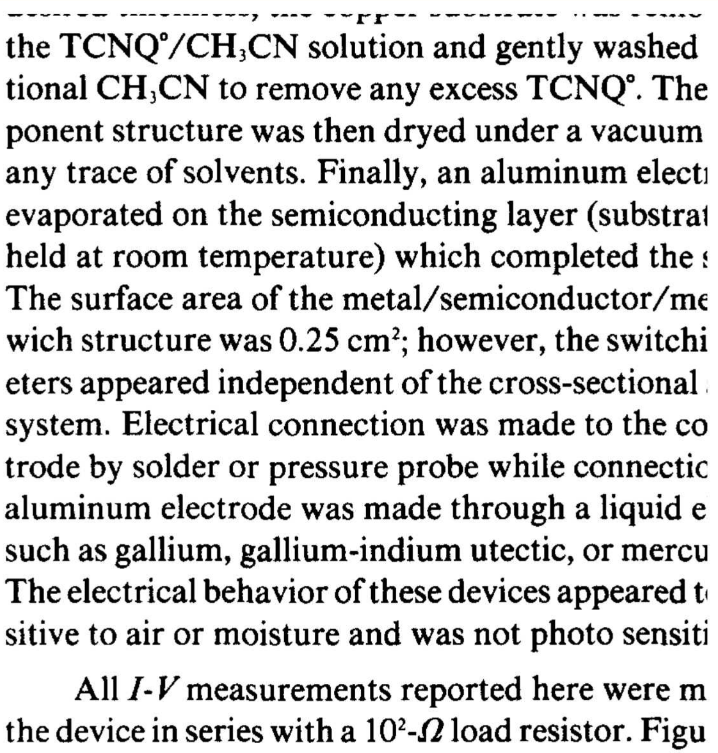
C. Schneider *et al., Chem. Sci.*, 2018, **9**, 7405-7412

XPS reveals a high concentration of Cu(I) species at the surface of HKUST-1 crystals both before and after TCNQ infiltration



Cu^{I} + $TCNQ^{0}$ → Cu^{II} + $TCNQ^{-I}$

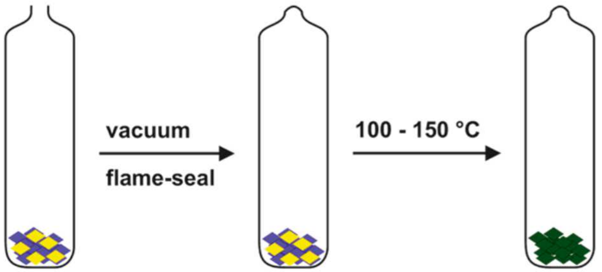
K. Thuermer, C. Schneider et al.
ACS Applied Materials & Interfaces **2018**, *10*, 39400


the TCNQ°/CH_3CN solution and gently washed
tional CH_3CN to remove any excess TCNQ°. The
ponent structure was then dryed under a vacuum
any trace of solvents. Finally, an aluminum electi
evaporated on the semiconducting layer (substrat
held at room temperature) which completed the s
The surface area of the metal/semiconductor/me
wich structure was 0.25 cm²; however, the switchi
eters appeared independent of the cross-sectional
system. Electrical connection was made to the co
trode by solder or pressure probe while connectic
aluminum electrode was made through a liquid e
such as gallium, gallium-indium utectic, or mercu
The electrical behavior of these devices appeared t
sitive to air or moisture and was not photo sensiti

All *I-V* measurements reported here were m
the device in series with a 10^2-Ω load resistor. Figu

Cu(TCNQ) displays electric-field-induced bistable switching behavior
→ *Suggests potential mechanism for conductivity modulation and resistive switching*
(e.g. see Potember et al. Appl.Phys.Lett. 1979, 34, 405

Conclusions



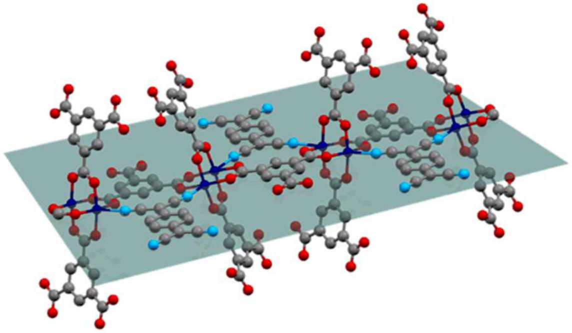
Vapor phase infiltration of MOFs provides well-defined materials

Cu_3BTC_2 → (DCM) → $TCNQ@Cu_3BTC_2$

Cu_3BTC_2 → (MeOH) → CuTCNQ

Cu_3BTC_2 → (VPI) → $TCNQ@Cu_3BTC_2$ (+ CuTCNQ)

Reaction conditions matter



TCNQ arranges preferentially in 111 lattice plane

$Cu^{I} + TCNQ^{0} \rightarrow Cu^{II} + TCNQ^{-I}$

TCNQ oxidizes Cu(I) species

- **Extent of reduction controllable by reaction stoichiometry**
- **Reversibility unknown at this stage**
- **Write-Once Read-Many (WORM) memory is possible device application**

Acknowledgements

- Dr. Christian Schneider, Prof. Roland Fischer (Tech. Univ. Munich)
- Mike Foster, Francois Leonard (Sandia)
- Andreas Centrone (NIST)
- Prof. Patrick Hopkins (Univ. Virginia)

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