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A roadmap for the integration of metal–organic frameworks with electronic devices and chemical sensors – Part 1

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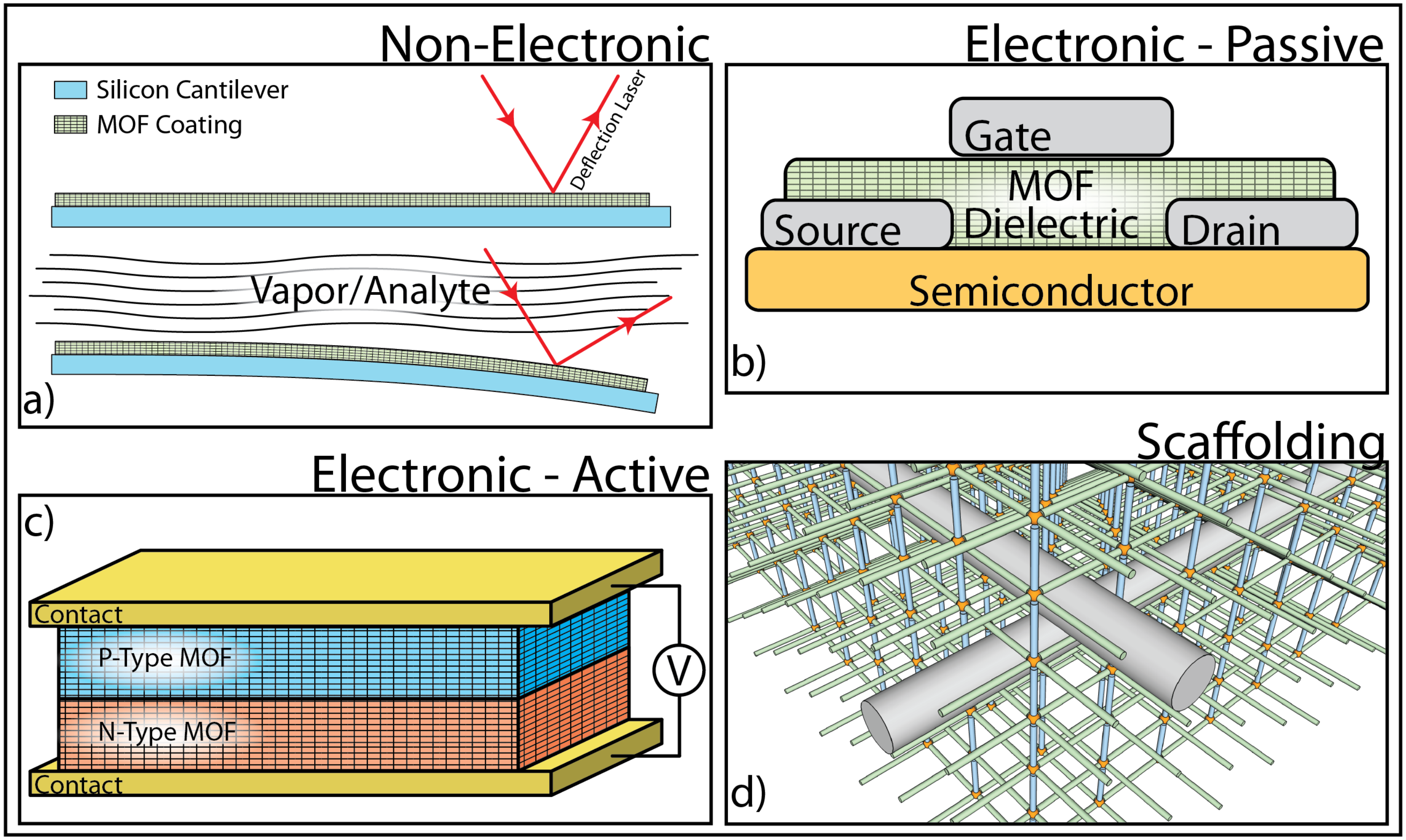
U.S. DEPARTMENT OF ENERGY

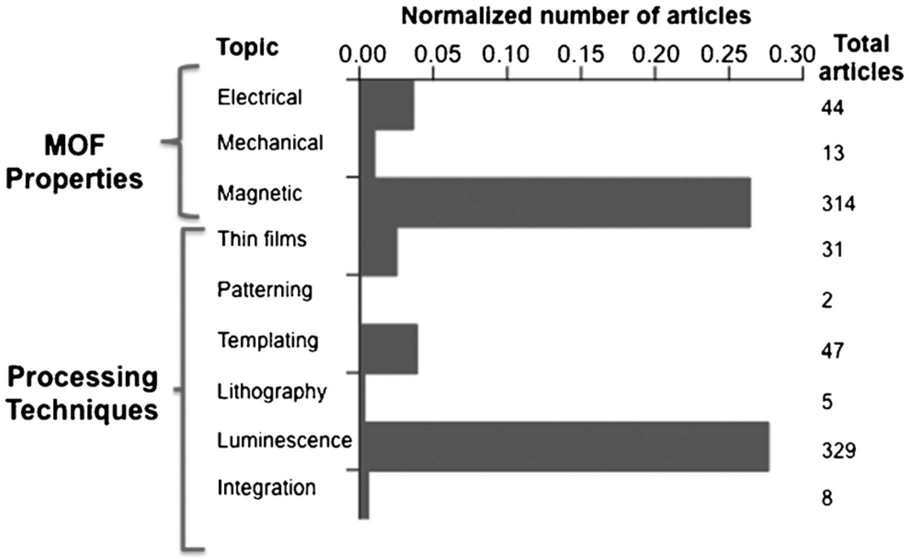
NNSA National Nuclear Security Administration

Potential functions of MOFs within electronic and microelectro-mechanical systems (MEMS)



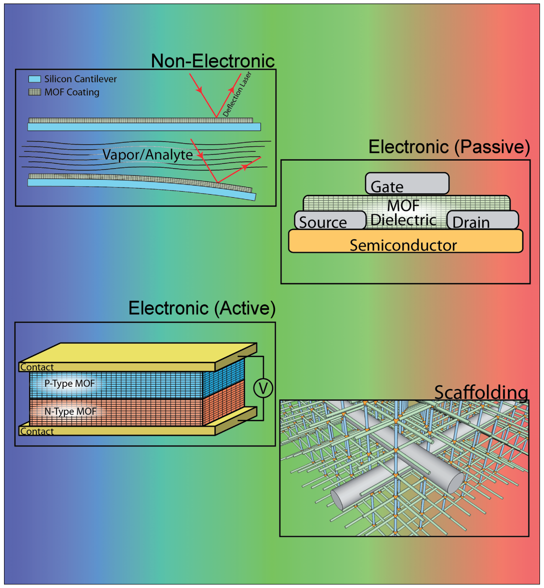
First “roadmap” for MOFs as electronic materials in 2011

- MOF research dominated by gas storage and separations
- Focus was on synthesizing new MOFs and determining their properties:
  - Magnetic
  - Luminescence
- Processing techniques very limited:
  - Thin films (31 papers)
  - Patterning (2 papers)
  - Integration (8 papers)



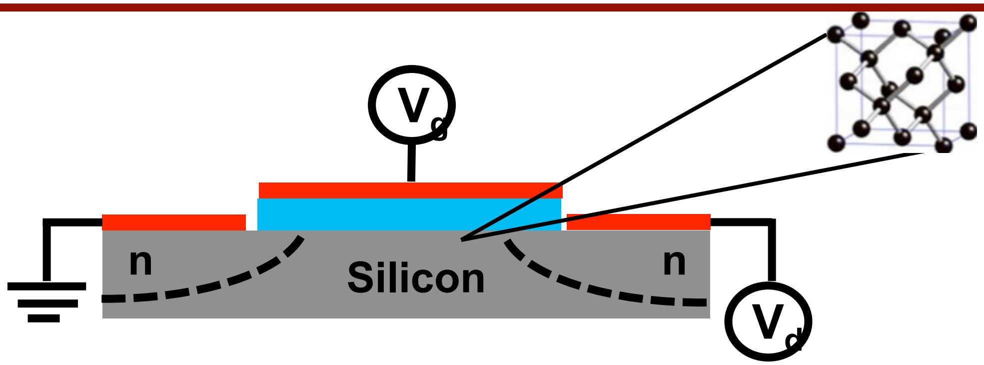
2011 Roadmap topics:

- Fundamental properties
- Thin-film growth and processing
- MOF hybrids and multilevel structures
- Device integration
- Manufacturing issues



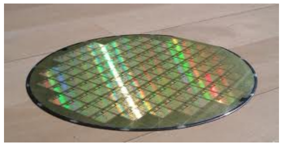
Allendorf, Schwartzberg, Stavila, Talin
Chem. Eur. J. 2011, **17**, 11372

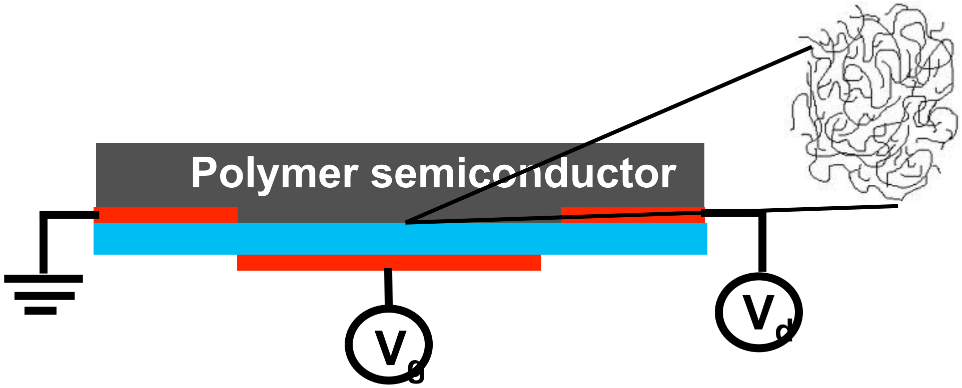
MOFs as electronic materials provide a new dimension for device design: nanoporosity



Crystalline inorganic conductor

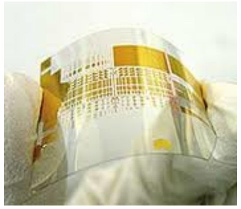
- High mobility
- Stability
- High cost
- Non-flexible
- Radiation damage

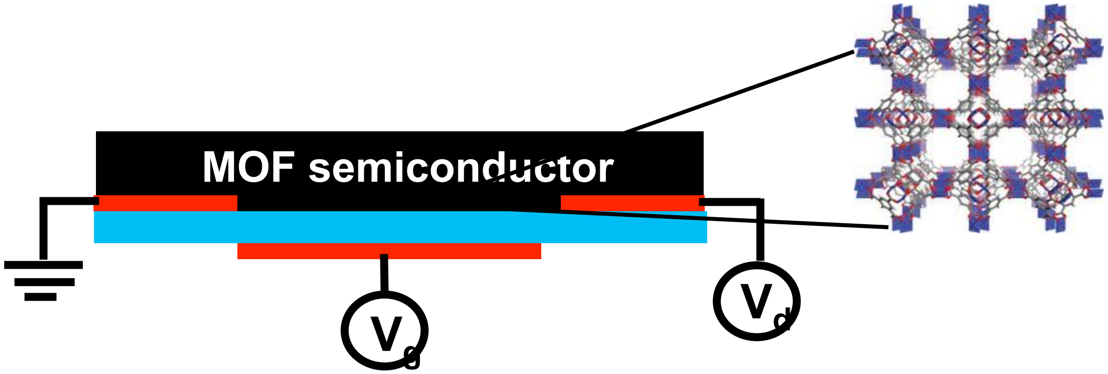




Disordered organic conductor

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



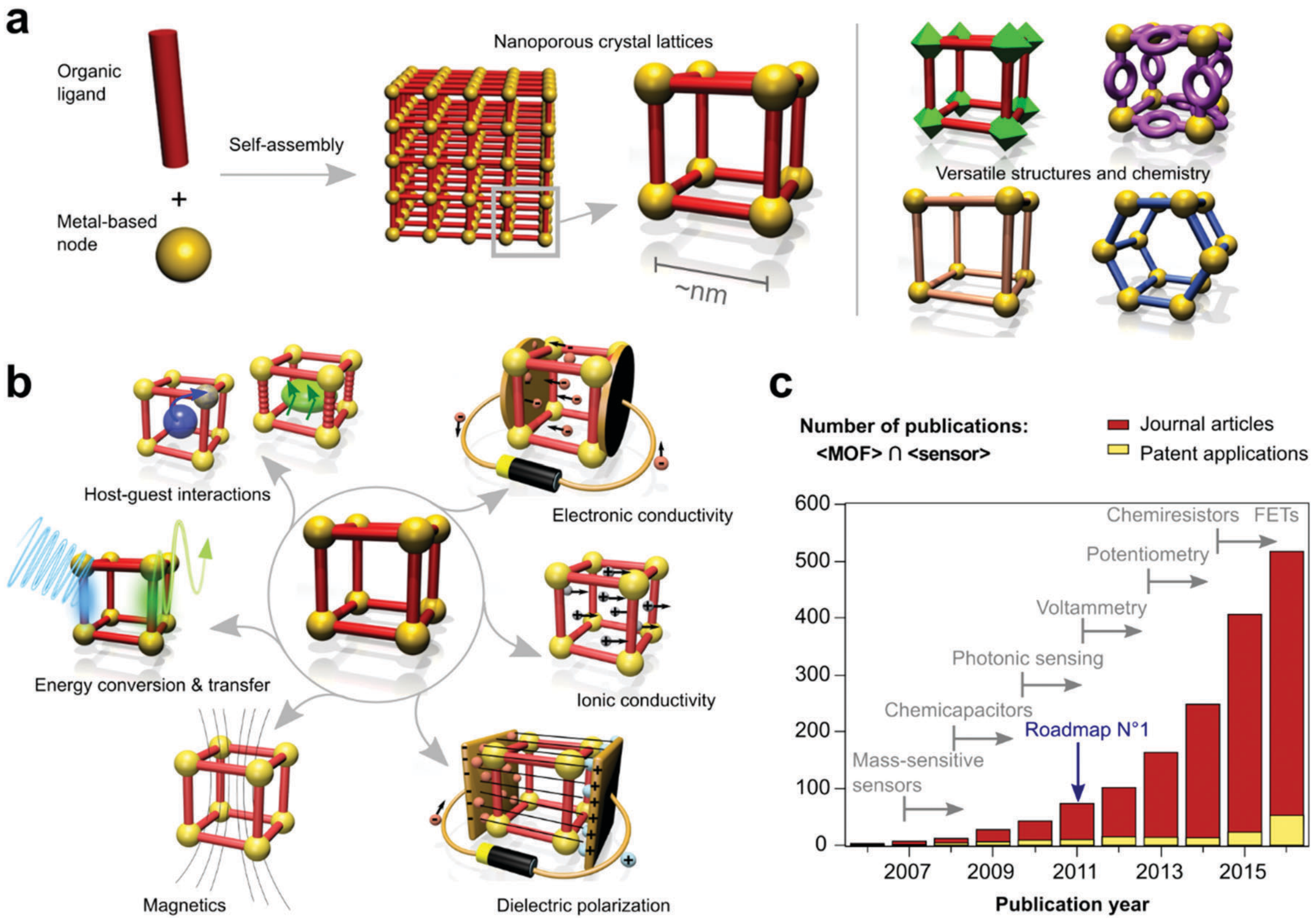


Crystalline MOF conductor

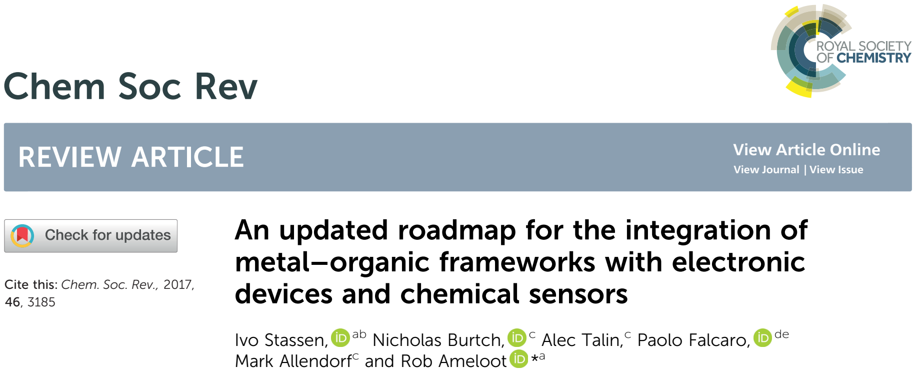
- Structurally flexible
- Tunable w/ chemistry
- Scalable to nanometers
- Low cost fabrication
- Reconfigurable electronics
- Rad-hard
- Novel electronic material

MOFs combine features of inorganic and organic materials

MOFs offer exceptional synthetic versatility for tuning not only pore size and chemistry, but also electronic structure



We updated the MOF Electronic Roadmap in 2017



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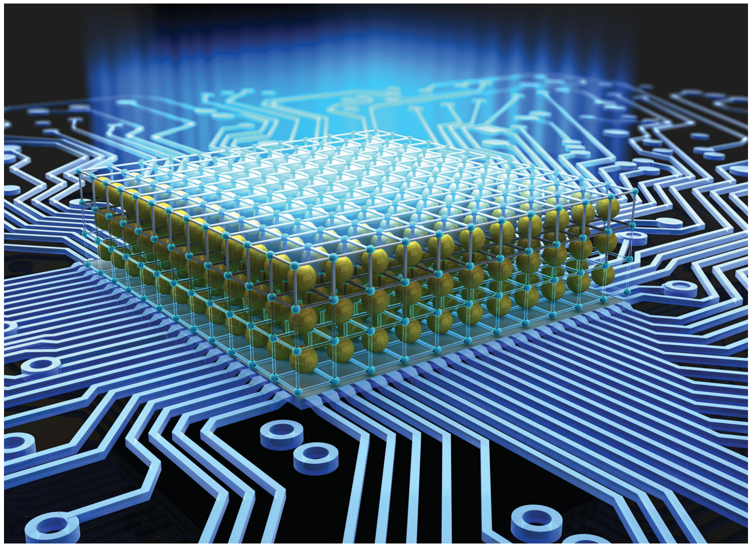
An updated roadmap for the integration of metal–organic frameworks with electronic devices and chemical sensors

Ivo Stassen,[ab] Nicholas Burtch,[c] Alec Talin,[c] Paolo Falcaro,[de] Mark Allendorf[c] and Rob Ameloot*[a]

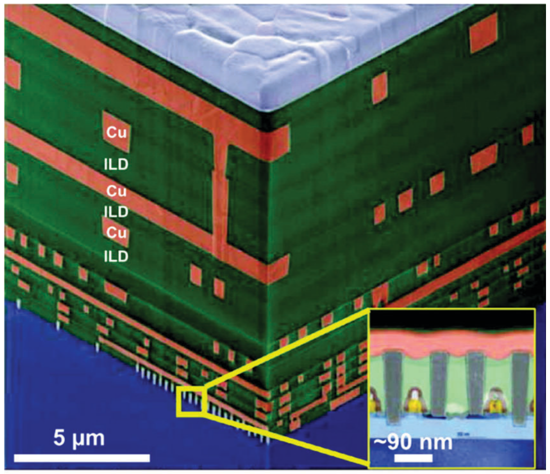
***Chem.Soc.Rev.*, 2017, 46, 3185**



- Highlights research aimed at implementing MOFs as an integral part of solid-state microelectronics and sensors
- Manufacturing these devices will critically depend on the compatibility of MOFs with existing fabrication protocols and predominant standards
- This implies a shift from the microcrystalline powder synthesis in chemistry labs, towards film deposition and processing in a cleanroom environment
- Critical directions for future research are proposed to stimulate the next steps towards MOF-based microelectronics within the community

Dielectrics: low-k and high-k

κ: the resistance of a material to formation of an internal electric field



- Density, porosity, and less-polarizable atoms decrease κ
- Low-κ dielectrics: $\kappa < 4$ (SiO_2)
  - Electrical insullator microelectronics
  - $\kappa = 2.3$ (0.1 MHz) ZIF-8
    - S. Eslava et al. *Chem. Mater.*, 2013, 25, 27
  - $\kappa = 2.4$ (0.1 MHz), 2D Sr(1,3-BDC) (pressed powder pellets)
    - M. Usman et al. *Mater. Chem. C,* 2014, 2, 3762

- High-κ dielectrics: $\kappa < 4$ (SiO_2)
  - Combined high-k, low electrical leakage and high breakdown voltage are needed in microelectronics to enable capacitive coupling
  - $\kappa = 19.5$ (106 Hz) interpenetrated Zn(dimethylammonium)(TBTC) framework, MOF-246.
    - W.-J. Li et al. *Nat. Commun.*, 2016, 7, 11830

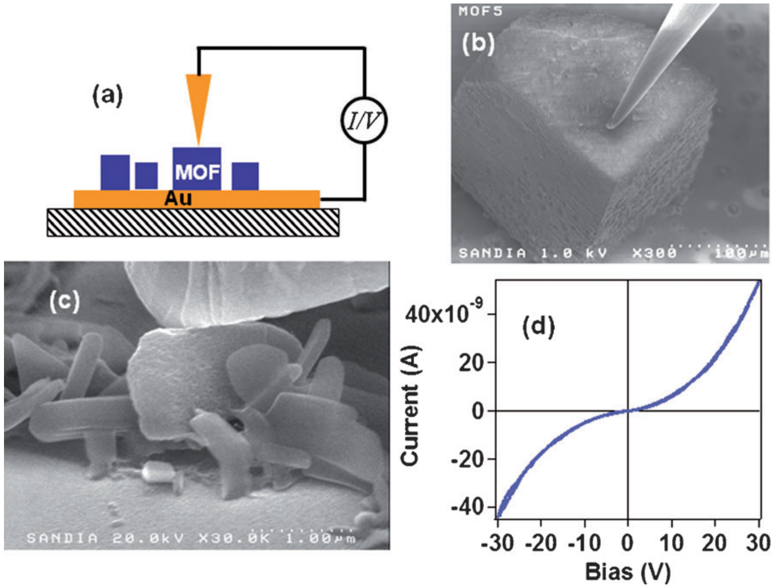
Electrical conductivity: one of the most critical MOF properties requiring improvements

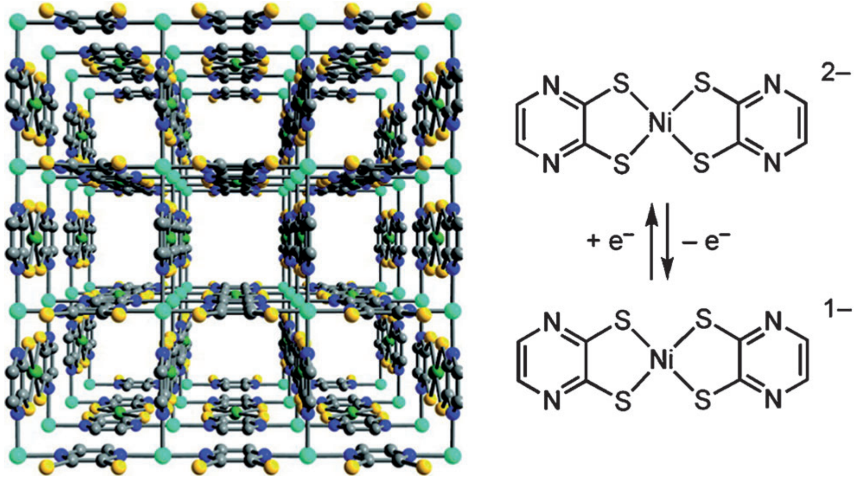
Situation 2011:

- **Conducting MOFs with permanent porosity: 1**
- **Insulating MOFs: thousands**

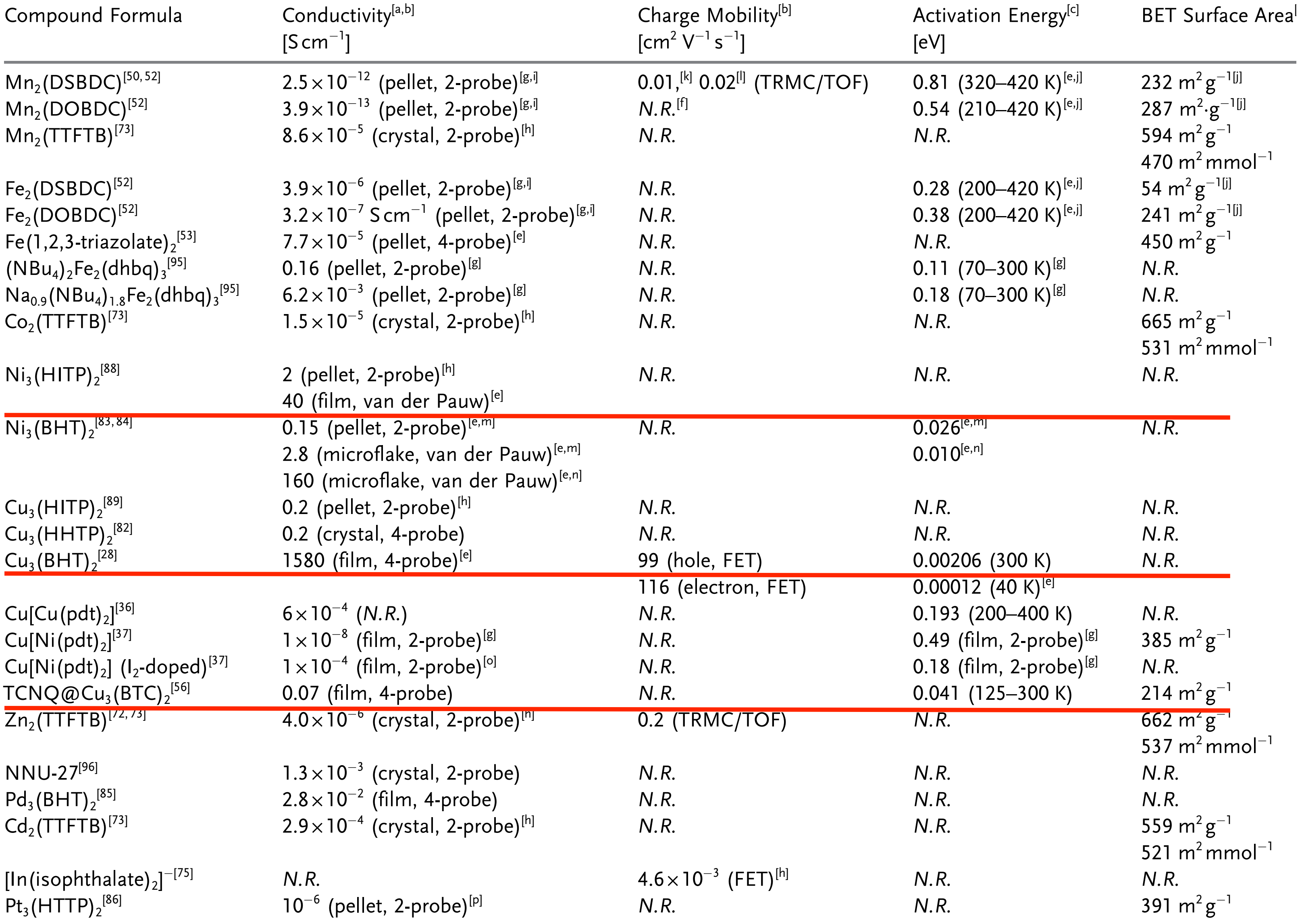
Allendorf, Schwartzberg, Stavila, Talin
Chem. Eur. J. 2011, **17**, 11372

Kobayashi, Jacobs, Allendorf, and Long
Chem. Mater. 2010, **22**, 4120





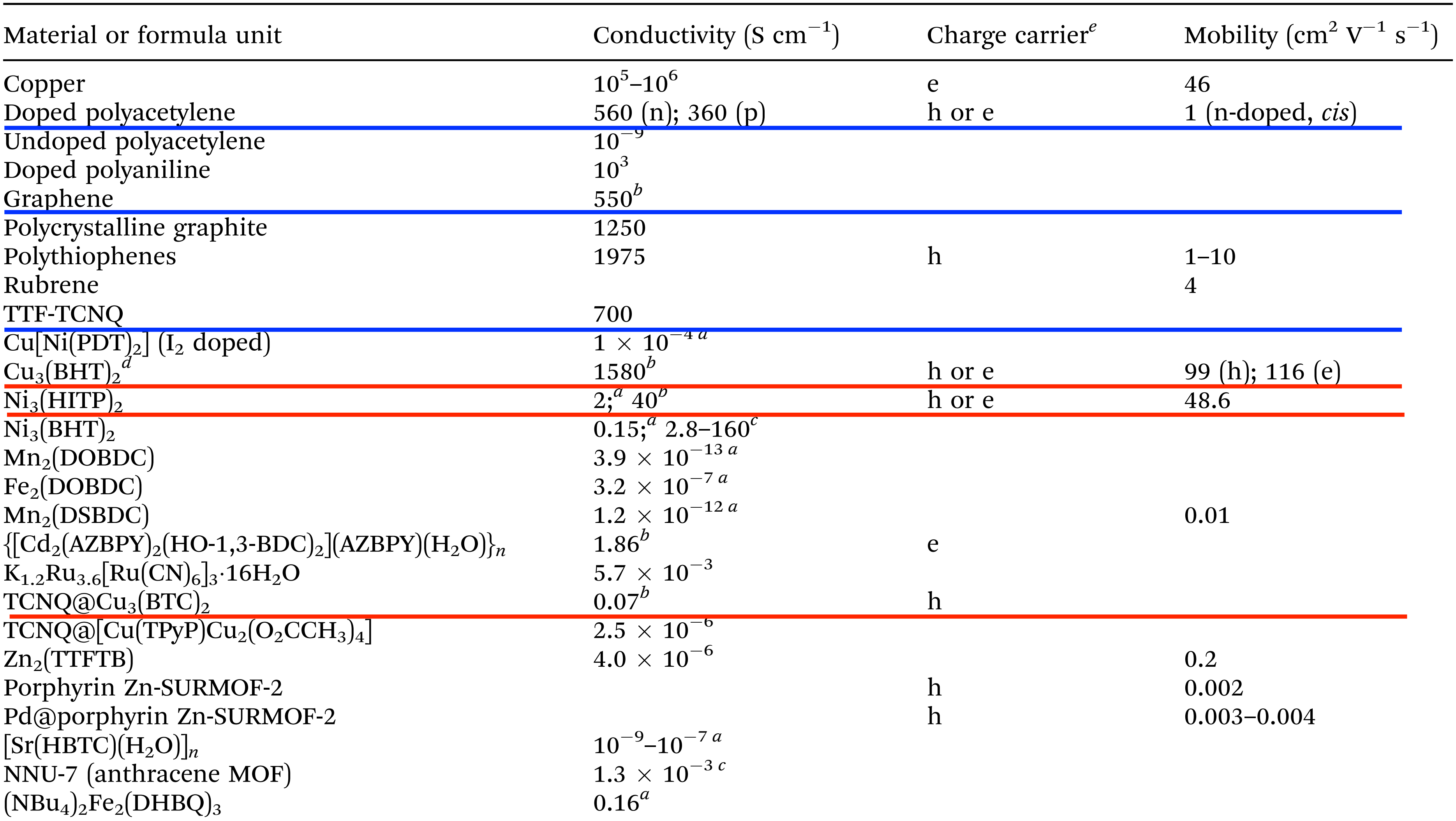
Situation in 2017: many more electrically conducting MOFs



Compound Formula	Conductivity[a,b] [S cm^{-1}]	Charge Mobility[b] [cm^2 V^{-1} s^{-1}]	Activation Energy[c] [eV]	BET Surface Area[
Mn$_2$(DSBDC)[50,52]	2.5×10^{-12} (pellet, 2-probe)[g,i]	0.01,[k] 0.02[l] (TRMC/TOF)	0.81 (320–420 K)[e,j]	232 m^2 g^{-1}[j]
Mn$_2$(DOBDC)[52]	3.9×10^{-13} (pellet, 2-probe)[g,i]	*N.R.*[f]	0.54 (210–420 K)[e,j]	287 m^2·g^{-1}[j]
Mn$_2$(TTFTB)[73]	8.6×10^{-5} (crystal, 2-probe)[h]	*N.R.*	*N.R.*	594 m^2 g^{-1} 470 m^2 mmol^{-1}
Fe$_2$(DSBDC)[52]	3.9×10^{-6} (pellet, 2-probe)[g,i]	*N.R.*	0.28 (200–420 K)[e,j]	54 m^2 g^{-1}[j]
Fe$_2$(DOBDC)[52]	3.2×10^{-7} S cm^{-1} (pellet, 2-probe)[g,i]	*N.R.*	0.38 (200–420 K)[e,j]	241 m^2 g^{-1}[j]
Fe(1,2,3-triazolate)$_2$[53]	7.7×10^{-5} (pellet, 4-probe)[e]	*N.R.*	*N.R.*	450 m^2 g^{-1}
(NBu$_4$)$_2$Fe$_2$(dhbq)$_3$[95]	0.16 (pellet, 2-probe)[g]	*N.R.*	0.11 (70–300 K)[g]	*N.R.*
Na$_{0.9}$(NBu$_4$)$_{1.8}$Fe$_2$(dhbq)$_3$[95]	6.2×10^{-3} (pellet, 2-probe)[g]	*N.R.*	0.18 (70–300 K)[g]	*N.R.*
Co$_2$(TTFTB)[73]	1.5×10^{-5} (crystal, 2-probe)[h]	*N.R.*	*N.R.*	665 m^2 g^{-1} 531 m^2 mmol^{-1}
Ni$_3$(HITP)$_2$[88]	2 (pellet, 2-probe)[h] 40 (film, van der Pauw)[e]	*N.R.*	*N.R.*	*N.R.*
Ni$_3$(BHT)$_2$[83,84]	0.15 (pellet, 2-probe)[e,m] 2.8 (microflake, van der Pauw)[e,m] 160 (microflake, van der Pauw)[e,n]	*N.R.*	0.026[e,m] 0.010[e,n]	*N.R.*
Cu$_3$(HITP)$_2$[89]	0.2 (pellet, 2-probe)[h]	*N.R.*	*N.R.*	*N.R.*
Cu$_3$(HHTP)$_2$[82]	0.2 (crystal, 4-probe)	*N.R.*	*N.R.*	*N.R.*
Cu$_3$(BHT)$_2$[28]	1580 (film, 4-probe)[e]	99 (hole, FET) 116 (electron, FET)	0.00206 (300 K) 0.00012 (40 K)[e]	*N.R.*
Cu[Cu(pdt)$_2$][36]	6×10^{-4} (*N.R.*)	*N.R.*	0.193 (200–400 K)	*N.R.*
Cu[Ni(pdt)$_2$][37]	1×10^{-8} (film, 2-probe)[g]	*N.R.*	0.49 (film, 2-probe)[g]	385 m^2 g^{-1}
Cu[Ni(pdt)$_2$] (I$_2$-doped)[37]	1×10^{-4} (film, 2-probe)[o]	*N.R.*	0.18 (film, 2-probe)[g]	*N.R.*
TCNQ@Cu$_3$(BTC)$_2$[56]	0.07 (film, 4-probe)	*N.R.*	0.041 (125–300 K)	214 m^2 g^{-1}
Zn$_2$(TTFTB)[72,73]	4.0×10^{-6} (crystal, 2-probe)[h]	0.2 (TRMC/TOF)	*N.R.*	662 m^2 g^{-1} 537 m^2 mmol^{-1}
NNU-27[96]	1.3×10^{-3} (crystal, 2-probe)	*N.R.*	*N.R.*	*N.R.*
Pd$_3$(BHT)$_2$[85]	2.8×10^{-2} (film, 4-probe)	*N.R.*	*N.R.*	*N.R.*
Cd$_2$(TTFTB)[73]	2.9×10^{-4} (crystal, 2-probe)[h]	*N.R.*	*N.R.*	559 m^2 g^{-1} 521 m^2 mmol^{-1}
[In(isophthalate)$_2$]$^-$[75]	*N.R.*	4.6×10^{-3} (FET)[h]	*N.R.*	*N.R.*
Pt$_3$(HTTP)$_2$[86]	10^{-6} (pellet, 2-probe)[p]	*N.R.*	*N.R.*	391 m^2 g^{-1}

Sun, Campbell, and Dinca *Angew. Chem. Int. Ed.* 2016, **55**

Charge transport properties of conducting MOFs are still relatively poor



Material or formula unit	Conductivity (S cm^{-1})	Charge carrier[e]	Mobility (cm^2 V^{-1} s^{-1})
Copper	10^5–10^6	e	46
Doped polyacetylene	560 (n); 360 (p)	h or e	1 (n-doped, *cis*)
Undoped polyacetylene	10^{-9}		
Doped polyaniline	10^3		
Graphene	550[b]		
Polycrystalline graphite	1250		
Polythiophenes	1975	h	1–10
Rubrene			4
TTF-TCNQ	700		
$Cu[Ni(PDT)_2]$ (I_2 doped)	1×10^{-4}[a]		
$Cu_3(BHT)_2$[d]	1580[b]	h or e	99 (h); 116 (e)
$Ni_3(HITP)_2$	2;[a] 40[b]	h or e	48.6
$Ni_3(BHT)_2$	0.15;[a] 2.8–160[c]		
$Mn_2(DOBDC)$	3.9×10^{-13}[a]		
$Fe_2(DOBDC)$	3.2×10^{-7}[a]		
$Mn_2(DSBDC)$	1.2×10^{-12}[a]		0.01
$\{[Cd_2(AZBPY)_2(HO\text{-}1,3\text{-}BDC)_2](AZBPY)(H_2O)\}_n$	1.86[b]	e	
$K_{1.2}Ru_{3.6}[Ru(CN)_6]_3 \cdot 16H_2O$	5.7×10^{-3}		
$TCNQ@Cu_3(BTC)_2$	0.07[b]	h	
$TCNQ@[Cu(TPyP)Cu_2(O_2CCH_3)_4]$	2.5×10^{-6}		
$Zn_2(TTFTB)$	4.0×10^{-6}		0.2
Porphyrin Zn-SURMOF-2		h	0.002
Pd@porphyrin Zn-SURMOF-2		h	0.003–0.004
$[Sr(HBTC)(H_2O)]_n$	10^{-9}–10^{-7}[a]		
NNU-7 (anthracene MOF)	1.3×10^{-3}[c]		
$(NBu_4)_2Fe_2(DHBQ)_3$	0.16[a]		

Ionic conductivity

Advantages of MOFs as solid-state electrolytes:

- Regular pores allow efficient transport
- Anhydrous transport is feasible
- Thermal stability allows operation > 100 °C

Proton transport [(a) in figure]

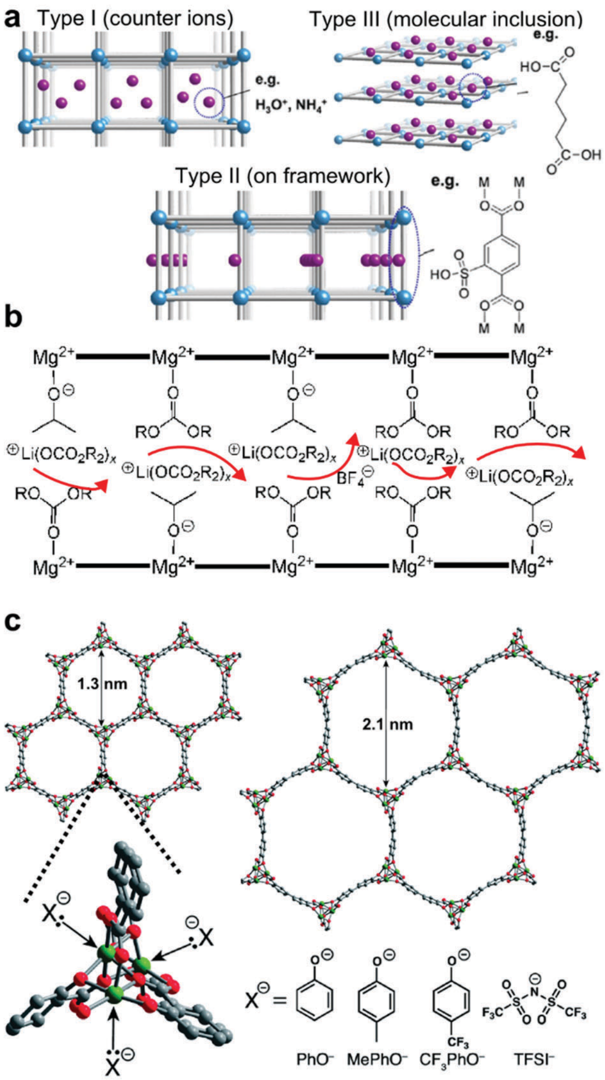
- Several strategies for introducing H$^+$:
  - Counterions as proton carriers
  - Acidic functional groups
  - Protonated guest molecules
- Triazole@sulfonated MOF: 5×10^{-4} S cm^{-1} at 150° C
  - J.A. Hurd et al. *Nat. Chem.* 2009

Li$^+$ transport [(b) in figure)

- Li-alkoxide grafting: MOF-74 0.012 mS cm^{-1}
  - B. M. Wiers et al. *JACS*, 2011, 133, 14522
- UiO-66 0.018 mS cm^{-1}
  - R. Ameloot et al. Chemistry, 2013, 19, 5533

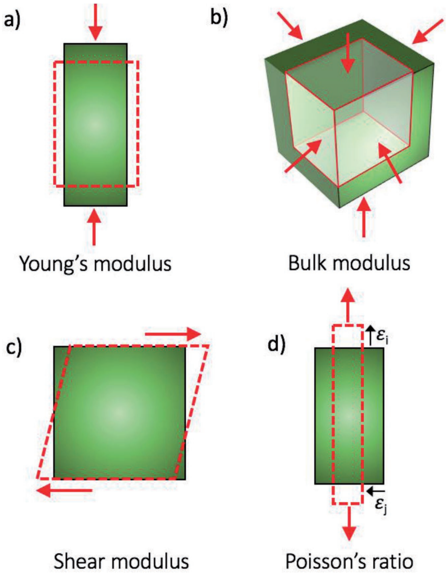
Mg^{2+} transport [(c) in figure]

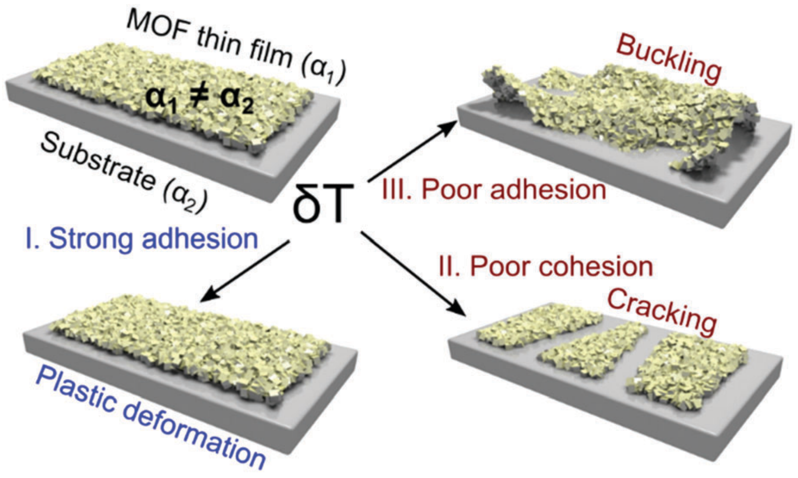
- 0.25 mS cm^{-1}
  - M.L. Aubrey *Energy Environ. Sci.*, 2014, 7, 667



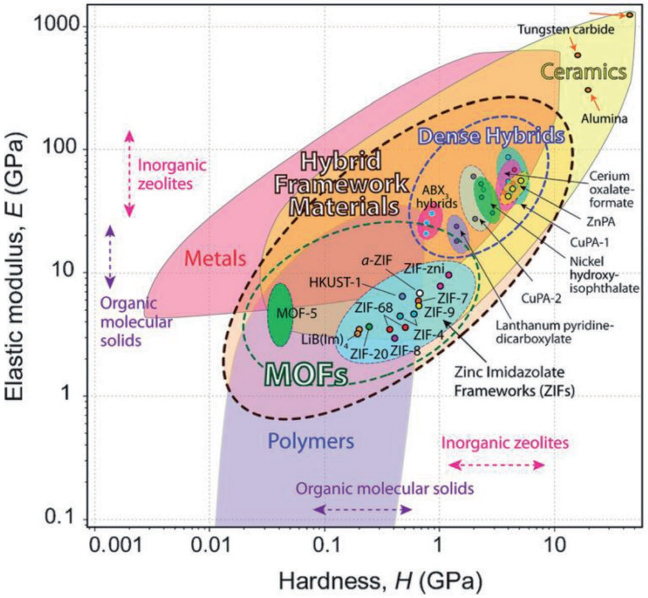
Mechanical and thermal properties

- MOFs are “soft” materials
- Thermal expansion is low
- Thermal conductivity
  - Negative thermal expansion common
  - TCE low compared with metals
- Anisotropy of bond strengths
- Structural flexibility leads to anomalous behaviors
- Structure-property relationships are being discovered





Thermal expansion mismatch



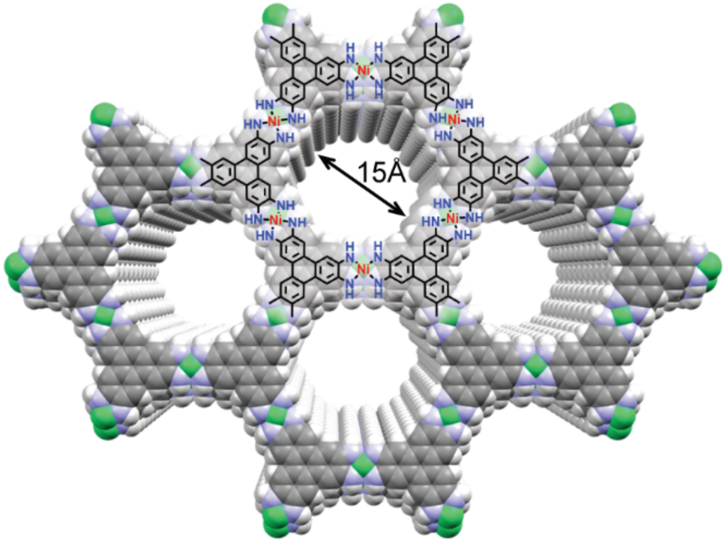
N.C. Burtch et al. *Adv. Mater.* **DOI: 10.1002/adma.201704124** Tan and A. K. Cheetham *Chem. Soc. Rev.* 2011, 40, 1059

MOF thermoelectric materials: two prototypes

$Ni_3(HITP)_2$

2D “Metal-Organic Graphene Analogue” (MOG)

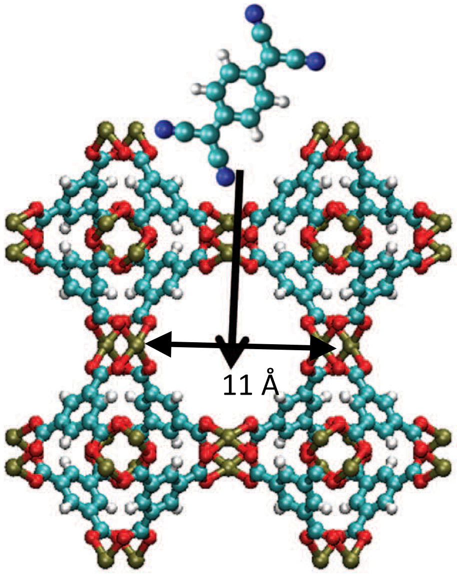
L. Sun et al. *Joule* 2017



$Cu_3(btc)_2$

3D Metal-Organic Framework

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



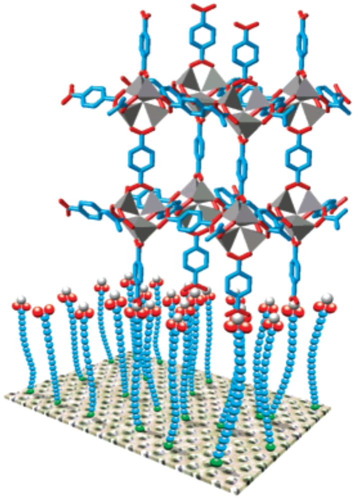
Material	Type	σ (S/m)	κ (W/m • K)	*S* (µV/K)	*PF* (µW/m • K²)	ZT (300K)
$TCNQ@Cu_3(BTC)_2$	*p*	0.45	0.25	+400	0.06	$0.7x10^{-4}$
$Ni_3(HITP)_2$	*n*	58.8	0.2	-11.9	0.01	$1.2x10^{-3}$

How can we improve the thermoelectric properties of MOFs?

Integration and assembly to create electronic devices

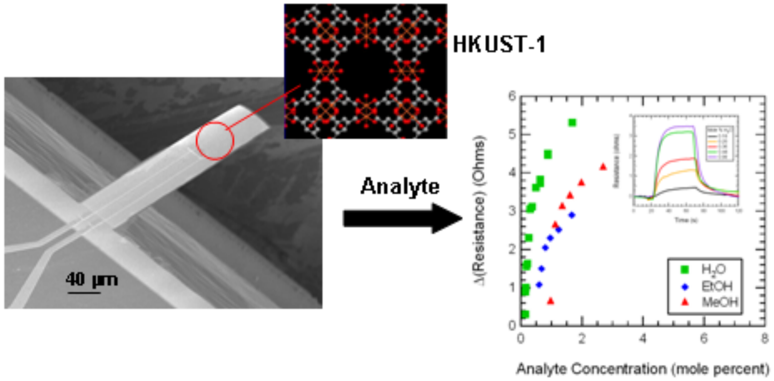
MOF growth on patterned substrate

S. Hermes et al.
***JACS* 2005**, 127, 13744



MOF-coated Microcantilever

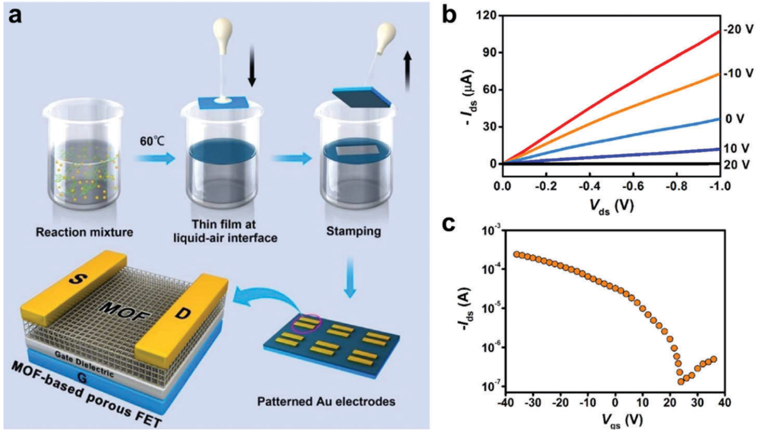
M. D. Allendorf et al.
***JACS* 2008**, *130*, 14404



FET

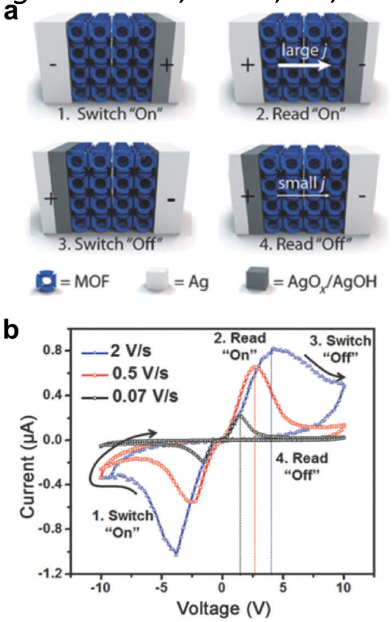
$Ni_3(HITP)_2$ MOG

G. Wu et al. *JACS*, 2017, 139, 1360



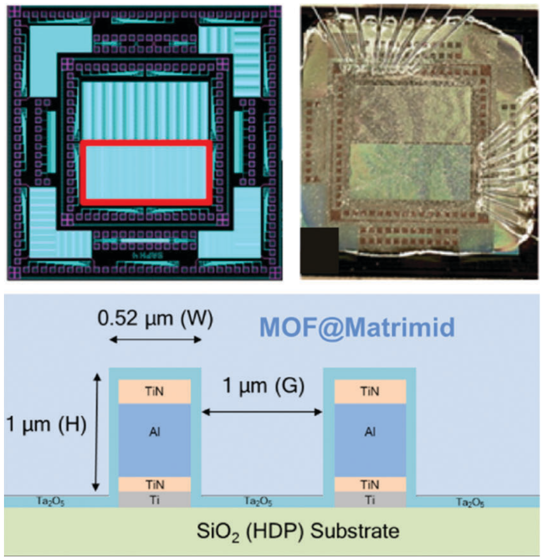
Memristor

S. M. Yoon et al.
Ang. Chem. IE, 2014, 53, 4437



Chemicapacitor

S. Sachdevaet al.
ACS Sens., 2016, 1, 1188



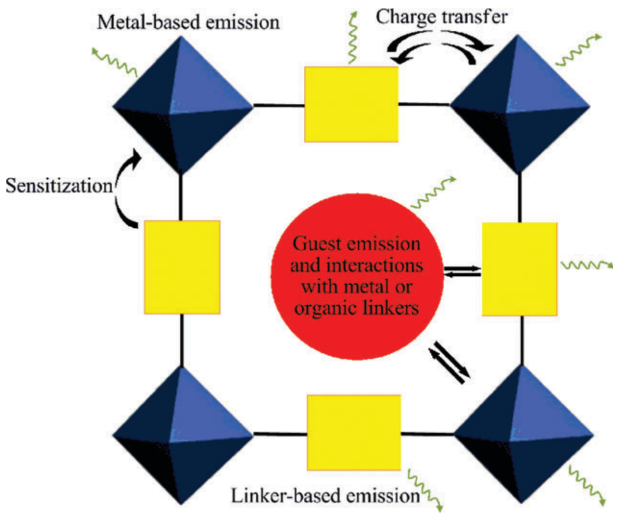
Luminescent frameworks are the largest subclass of electronically relevant MOFs

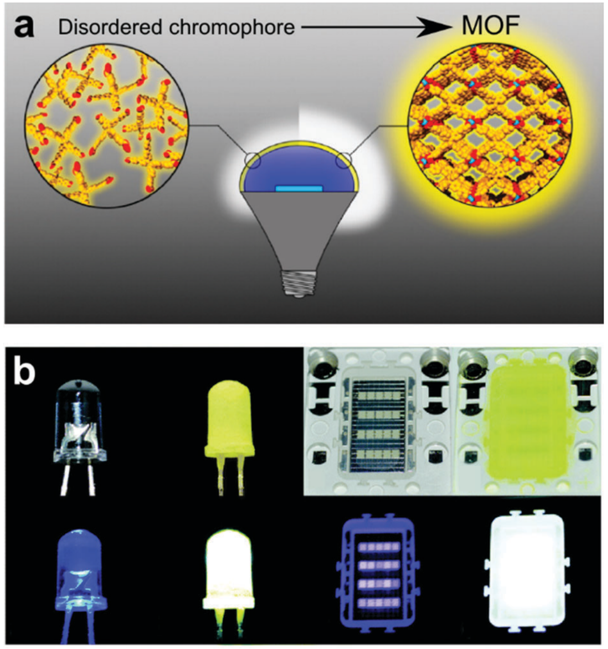
Many strategies

- **Linker**
- **Metal ion**
- **Guest**

Applications

- **Phosphors**
- **Chemical sensors**
- **Scintillators**
- **Thus far no semiconducting MOF as actual emitting layer**



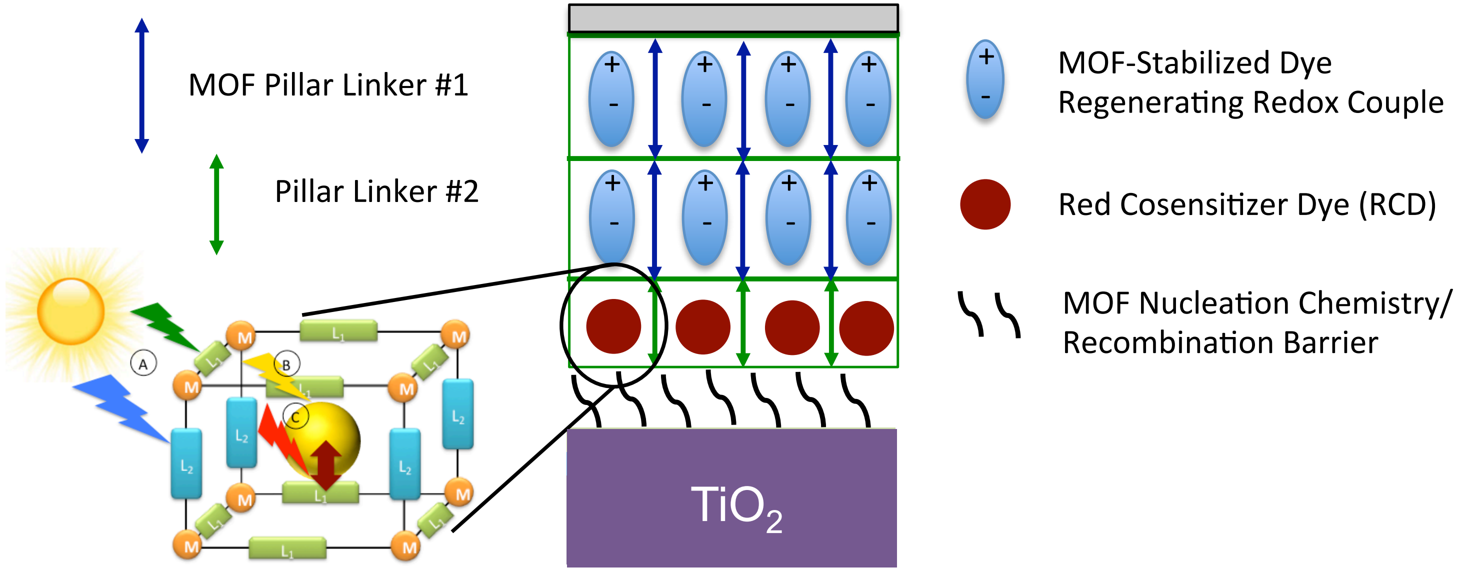


MOFs for light emitting devices. (a) Schematic illustration of the improvement in quantum yield of a yellow-emitting organic chromophore by incorporation in a rigid metal–organic framework. (W.P. Lustig et al. *Inorg. Chem.*, 2016, 55, 7250) (b) Blue LED bulb and plate coated with solution-processed Zn2(TCPBE) MOF phosphor as a demonstration of application in white LEDs (Z. Hu et al. *Chem. Commun.*, 2015, 51, 3045).

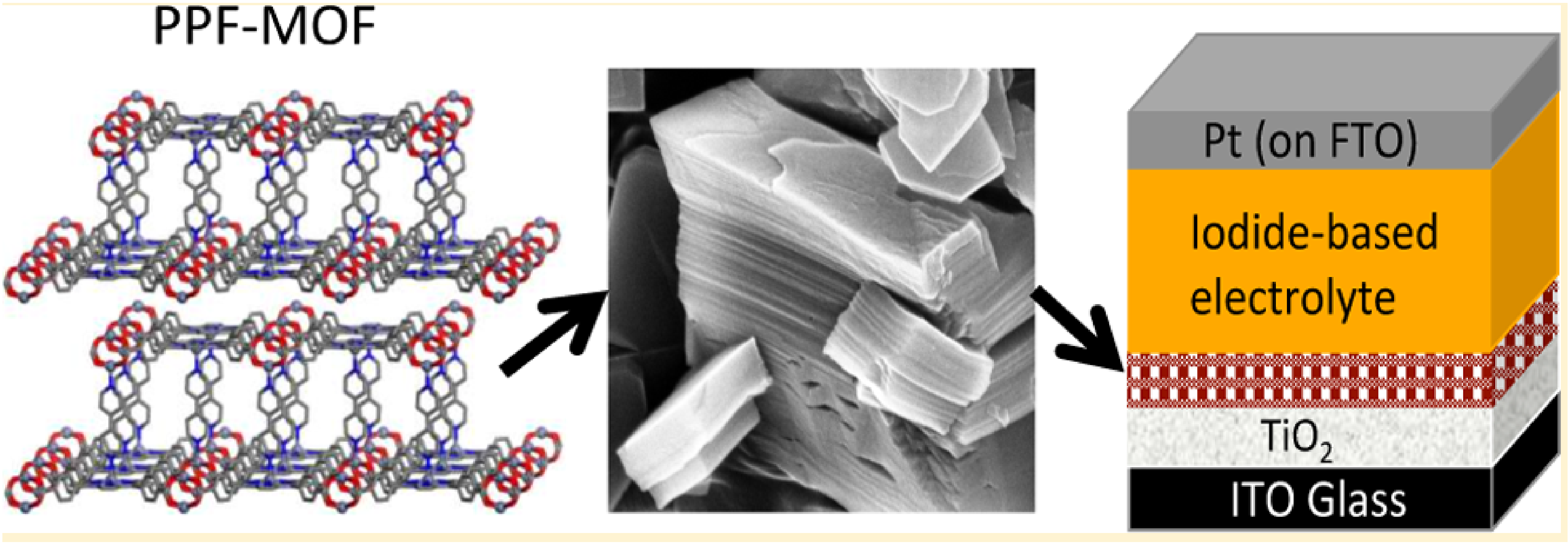
Can Metal-Organic Frameworks (MOFs) address the challenges facing DSSC?

Roles and advantages of MOFs in DSSCs

Challenge	MOF role
Light harvesting	Multiple linkers + guest molecules for broad solar coverage
Dye aggregation	Crystalline structure, confined guests prevent aggregation
Band offsets	Tunable linker and guest electronic structure
Stability/reliability	Rigidified, isolated linkers; confined electrolyte



Integrating MOFs in DSSC devices



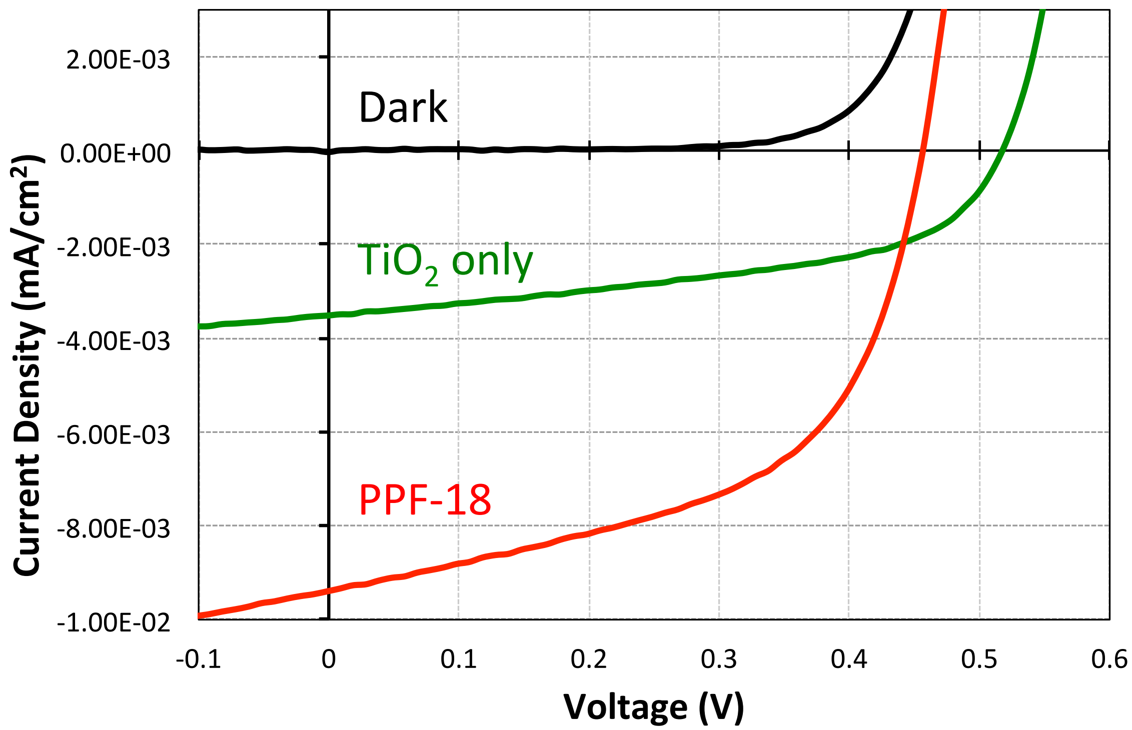
E. Spoerke et al. J. Phys. Chem. C 2017, 121, 4816

<u>Challenges</u>:

- **How do we incorporate MOFs into DSSCs as active layer materials?**
- **How do we know that the MOF is doing something?**

DSSC sensitized by MOF nanocrystals

Reduced photocurrent in the absence of PPF-18



AM 1.5 illumination

Averaged metrics:

Voc (V) = 0.537 ± 0.023

Jsc (mA/cm^2) = 0.00410 ± 0.00090

FF = 0.486 ± 0.014

η (%) = 0.00107 ± 0.000233

Voc (V) = 0.425 ± 0.029

Jsc (mA/cm^2) = 0.00797 ± 0.0012

FF = 0.548 ± 0.014

η (%) = 0.00186 ± 0.000338

E. Spoerke et al. *J. Phys. Chem. C* 2017, 121, 4816

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