Conducting 2D and 3D MOFs: Measurements, mechanisms and types

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Modulating
Multifunctional
Molecular
Materials

ESAM2023
1st European School on Advanced Materials

Outline

1. Introduction. Conducting MOFs
2. Conductivity measurements
3. Electronic states, conductivity mechanisms and pathways
4. Types of conducting MOFs
   1. Intrinsically conducting MOFs
   2. Extrinsically conducting MOFs
5. Conclusions

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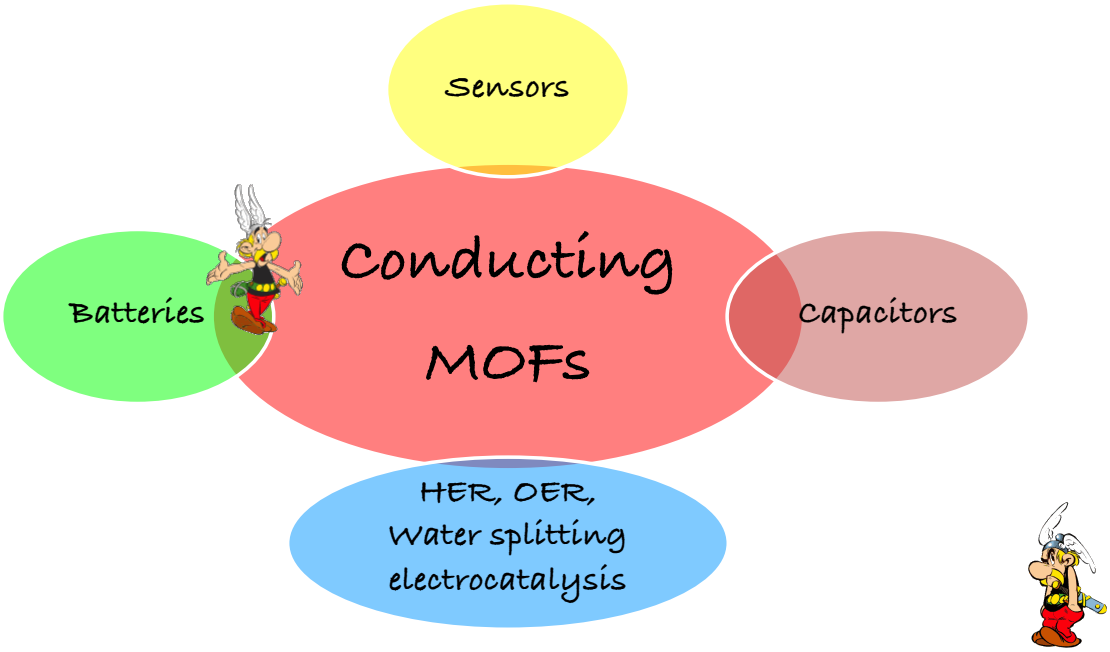
Introduction. Conducting MOFs



...but electrical conductivities are still very low...

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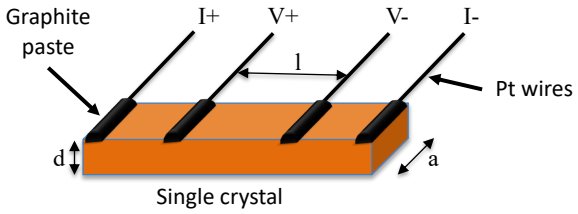
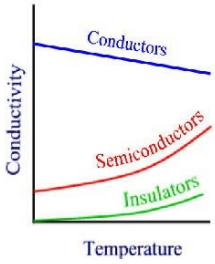
Conductivity measurements

$\sigma = ne\mu$

σ = electrical conductivity
n = concentration of charge carriers
e = electronic charge
μ = mobility of the charge carriers

$$R = \frac{V}{I} \rightarrow \rho(\Omega.cm) = R(\Omega)\frac{S(cm^2)}{l(cm)} \rightarrow \sigma = \frac{1}{\rho}$$





Conductivity measurements

irregular

square

Van der Pauw

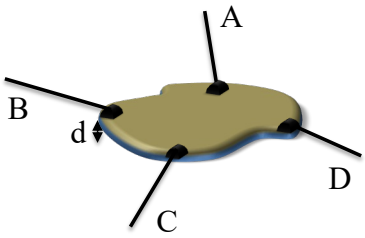
$$R_{CD} = \frac{V_{CD}}{I_{AB}} \qquad R_{DA} = \frac{V_{DA}}{I_{CB}}$$

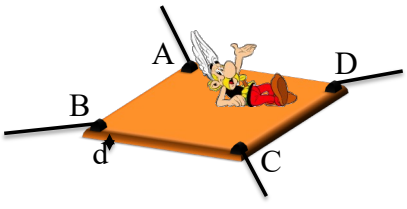
$$R_a = \frac{V_{AB}}{I_{CD}} \qquad R_b = \frac{V_{AD}}{I_{BD}}$$

$$\exp\left(\frac{-\pi R_{CD} d}{\rho}\right) + \exp\left(\frac{-\pi R_{DA} d}{\rho}\right) = 1$$

$$\rho = \frac{\pi d}{\ln 2}\frac{R_a + R_b}{2} f(R_a/R_b)$$

f is a sigmoidal function

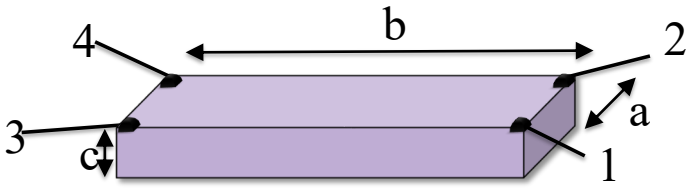




Conductivity measurements

Other geometries

Montgomery



$$\sqrt{\rho_a \rho_b} = \frac{a}{b} f(R_a/R_b)$$

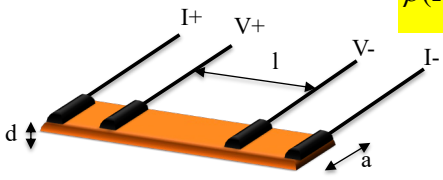
$$\sqrt{\rho_a \rho_b} = c R_a f'(b/a)$$

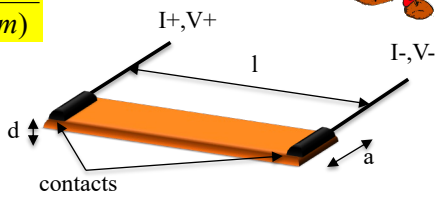
$$R_a = \frac{V_{34}}{I_{12}} \qquad R_b = \frac{V_{13}}{I_{24}}$$

f and f' are exponential functions

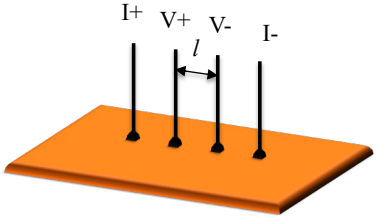
Two- or four contacts method ?

$$\rho(\Omega.cm) = R(\Omega)\frac{S(cm^2)}{l(cm)}$$

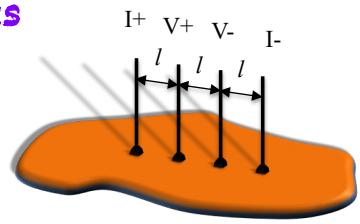




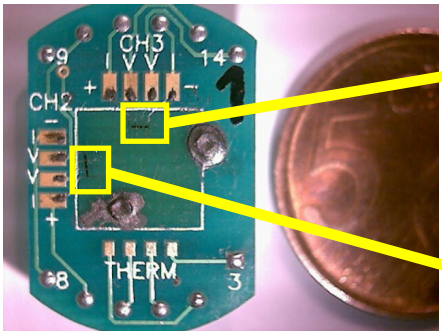
Four points

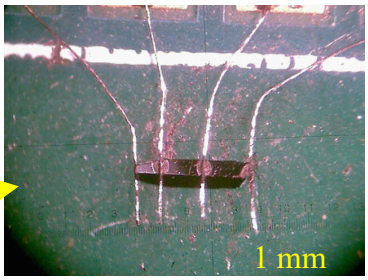


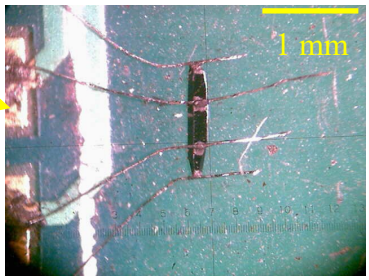
$$\rho = 2\pi l \frac{V}{I}$$



Some examples







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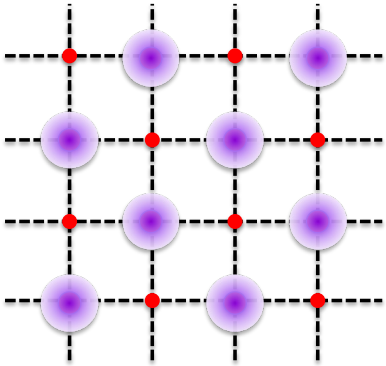
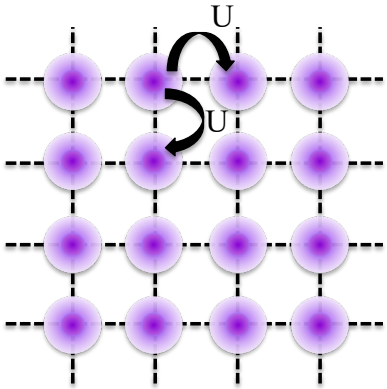
Electronic states

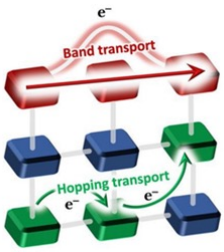




Charge Dispropotionation (CD)
or Charge Ordering (CO)
(non-uniform charge distribution
due to structural or polarising effects)

Mott insulator (MI)
(non degenerated half-filled
systems with U > W). No Mixed-Valence
U = on-side coulomb repulsion
W = bandwidth ≈ kinetic energy of e-

Conductivity mechanisms



Conductivity mechanisms

Band transport

S. Arrhenius

Classic (Arrhenius)

$$\sigma = \sigma_0 exp\left[-\frac{E_a}{kT}\right]$$

$$E_a = \frac{E_g}{2}$$

E_g > 3 eV → insulator

E_g < 3 eV → insulator

Hopping Model (disorder)

$$\sigma = \sigma_0 exp\left[-\left(\frac{T_0}{T}\right)^d\right]$$

d = 1/2 Variable Range (1D-VRH)

d = 1/3 (2D)

d = 1/4 (3D)

N. F. Mott

$$k_B T_0 = \frac{16}{L * N(E_F)}$$

L = correlation lenght

d = 1/(n+1)
n = dimensionality

Conductivity pathways

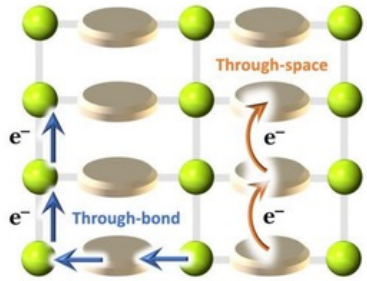
Conductivity pathways

- Through bond → $(-M-X-)_n$ lattices
- Through layer → Graphene-like lattices
- Through space → π–π, S···S, M···M interactions
- Redox hopping → Mixed-valence ligand or metals

Intrinsically conducting

- Through guest → Conducting guests

Extrinsically conducting



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Intrinsically conducting MOFs

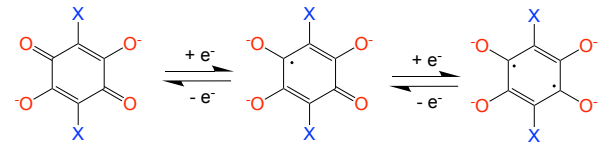
Charge transport occurs only through the metal-ligand backbone of the framework

1. Redox active ligands

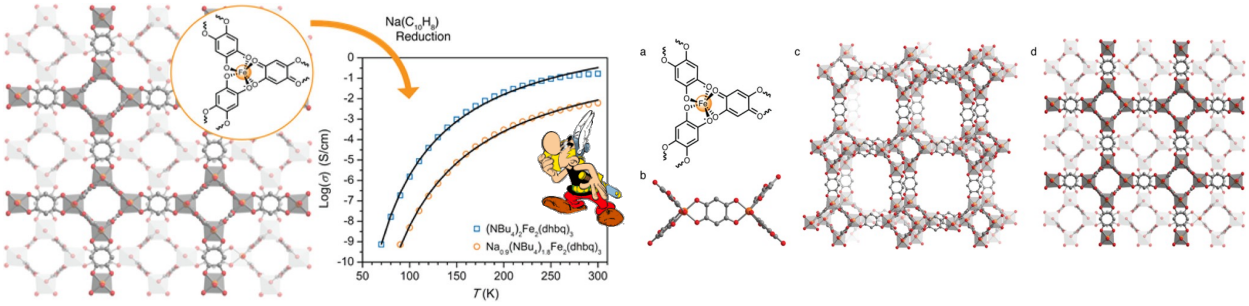
3D-$(NBu_4)_2[Fe^{III}_2(dhbq^{2-/3-})_3]$

$\sigma_{300\,K}$ = 0.16 S cm^{-1} E_a = 110 meV (oxidized)

$\sigma_{300\,K}$ = 0.0062 S cm^{-1} E_a = 180 meV (reduced)



benzoquinone semiquinone cathecolate



Long, J. R. et al. *J. Am. Chem. Soc.*, **2015**, *137*, 15703

Intrinsically conducting MOFs

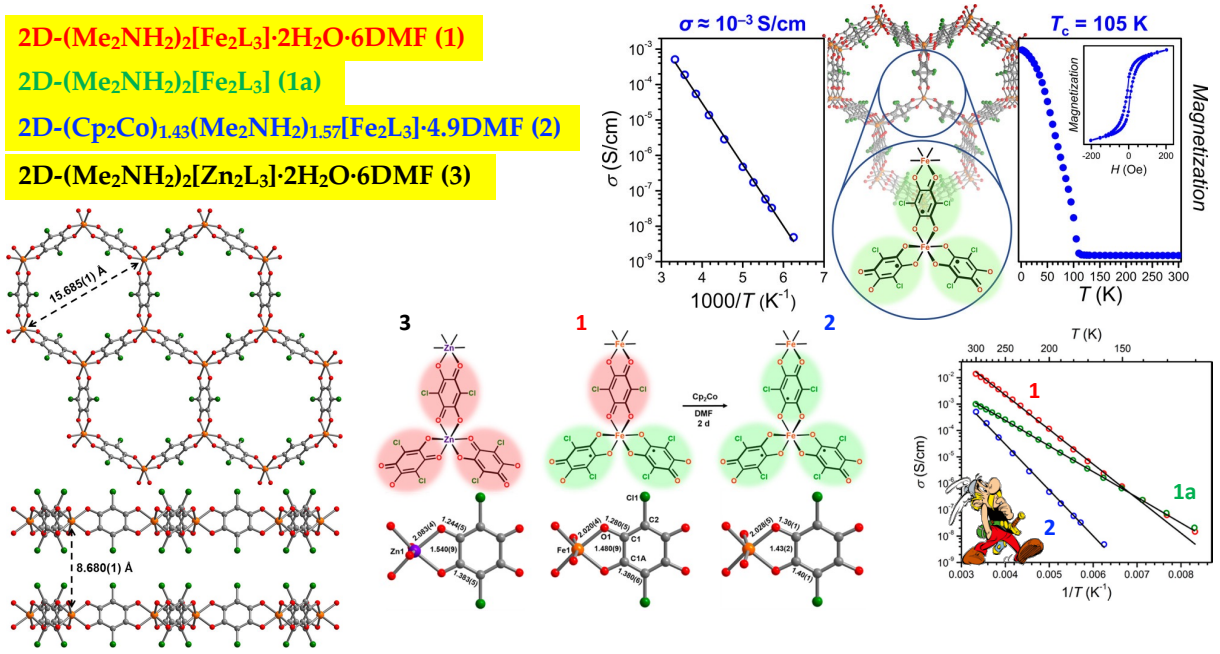
1. Redox active ligands

2D-$(Me_2NH_2)_2[Fe_2L_3]\cdot 2H_2O\cdot 6DMF$ (1)

2D-$(Me_2NH_2)_2[Fe_2L_3]$ (1a)

2D-$(Cp_2Co)_{1.43}(Me_2NH_2)_{1.57}[Fe_2L_3]\cdot 4.9DMF$ (2)

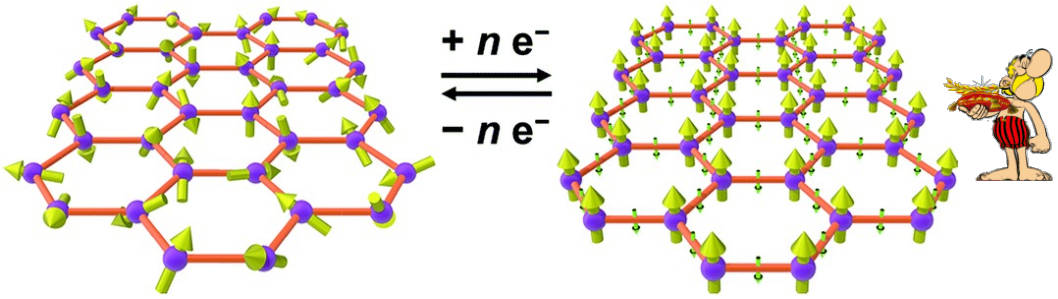
2D-$(Me_2NH_2)_2[Zn_2L_3]\cdot 2H_2O\cdot 6DMF$ (3)



Harris, T. D. et al. *J. Am. Chem. Soc.* **2017**, *139*, 4175

Intrinsically conducting MOFs

1. Redox active ligands



$(Me_4N)_2[Mn^{II}_2(C_6O_4Cl_2^{2-})_3]$

Paramagnetic

$\sigma_{300\,K} = 10^{-13}$ S cm^{-1}

$Na_3(Me_4N)_2[Mn^{II}_2(C_6O_4Cl_2^{3-})_3]$

Permanent magnet

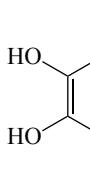
$\sigma_{300\,K} = 10^{-8}$ S cm^{-1}

Harris, D. T. et al. *Chem. Sci.* **2019**, *10*, 4652

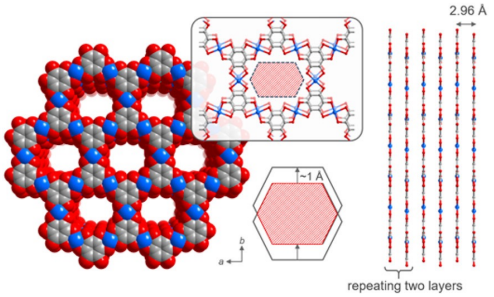
Intrinsically conducting MOFs

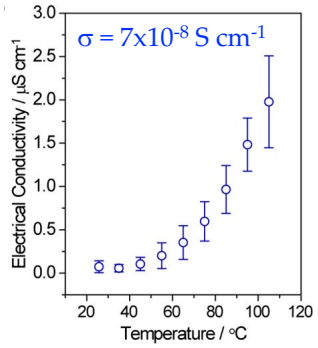
2. Extended conjugated organic ligands

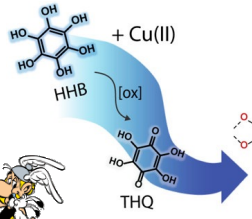
$Cu_3(HHB)_2$

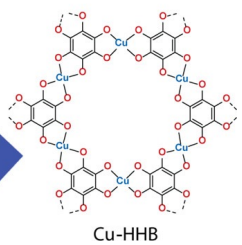


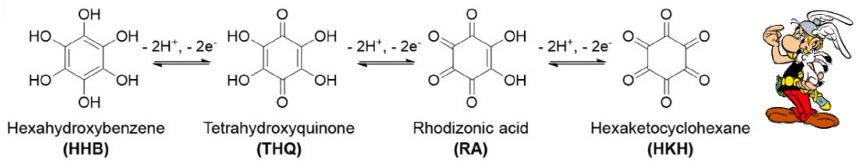
Hexahydroxybenzene
H_6HHB









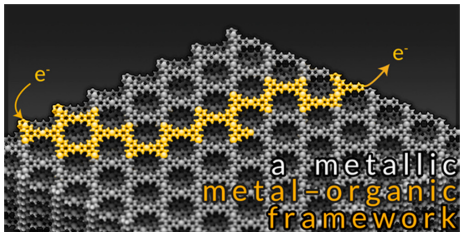


Hexahydroxybenzene **(HHB)** — Tetrahydroxyquinone **(THQ)** — Rhodizonic acid **(RA)** — Hexaketocyclohexane **(HKH)**

Bao, Z. et al. *J. Am. Chem. Soc.* **2018**, *140*, 14533

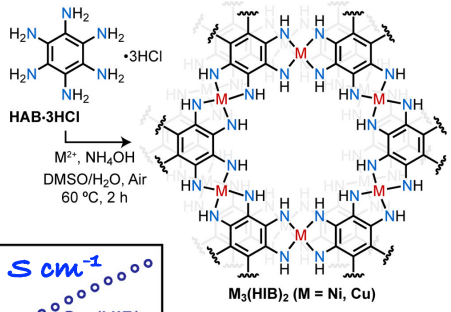
Intrinsically conducting MOFs

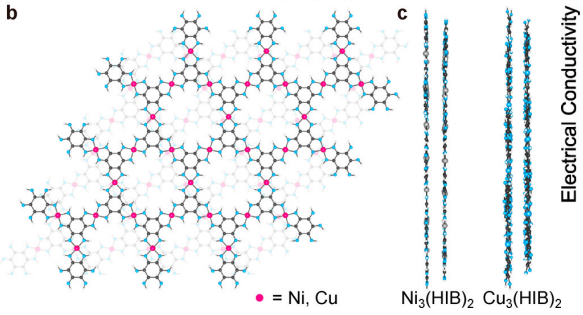
2. Extended conjugated organic ligands

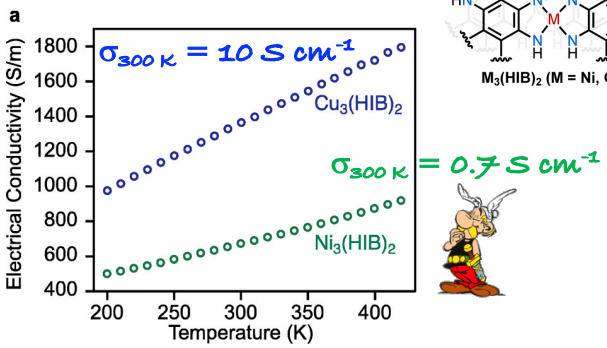


$Ni_3(HIB)_2$

$Cu_3(HIB)_2$







Carlos J. Gómez-García. Universidad de Valencia. ESMA-Gandía-18/10/23

Dincă, M. *J. Am. Chem. Soc.* **2017**, *139*, 13608

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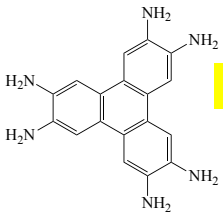
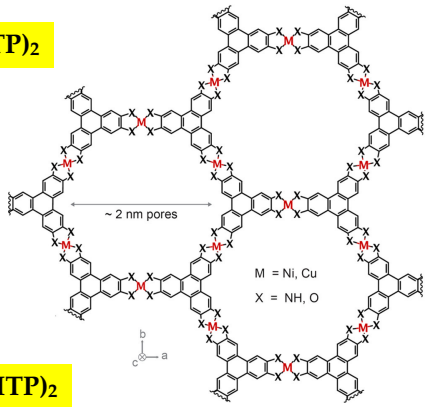
Intrinsically conducting MOFs

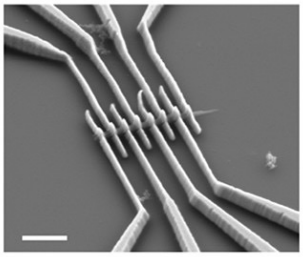
2. Extended conjugated organic ligands

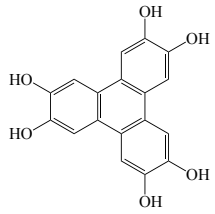


Hexaaminoterphenylene
(H_6HITP)

$Ni_3(HITP)_2$





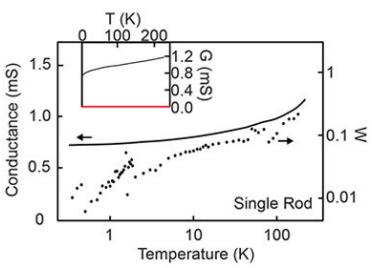


Hexahydroxyterphenylene
(H_6HHTP)

$Cu_3(HHTP)_2$

$\sigma_{300\,K}$ = 10-150 S cm^{-1} (M = Ni)

$\sigma_{300\,K}$ = 8x10^{-4} S cm^{-1} (M = Cu)



Dinca, M. *Nat. Mater.* **2017**, *16*, 220

Kim, P. *ACS Cent. Sci.* **2019**, *5*, 1959

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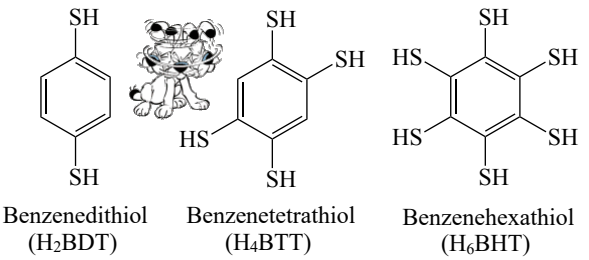
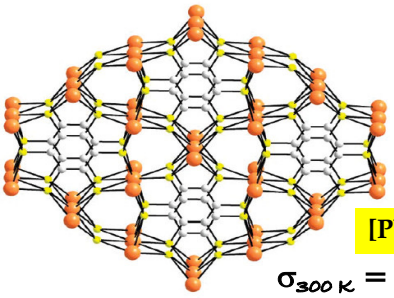
Intrinsically conducting MOFs

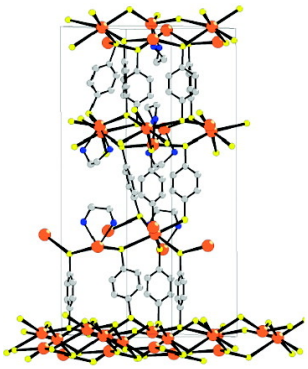
3. S-containing ligands





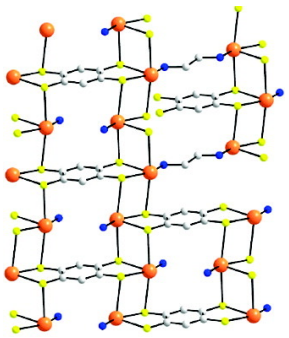
[Pb3(BHT)]

$\sigma_{300\,K} = 2 \times 10^{-6}$ S cm^{-1}



[Pb3(BDT)3(en)2]

$\sigma_{300\,K} = 10^{-12}$ S cm^{-1}



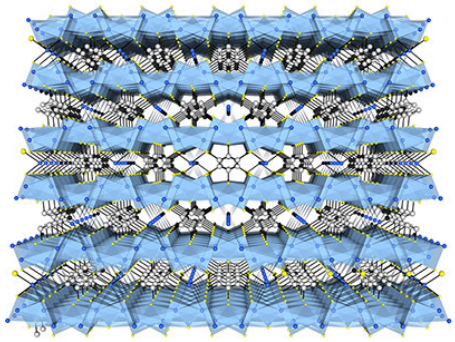
[Pb2(BTT)(en)]

$\sigma_{300\,K} = 10^{-12}$ S cm^{-1}

Rheingold, A. L. et al. *J. Am. Chem. Soc.* **2008**, 130, 14

Intrinsically conducting MOFs

3. S-containing ligands



$[Ag_5(C_6S_6)]_n$, Ag-BHT

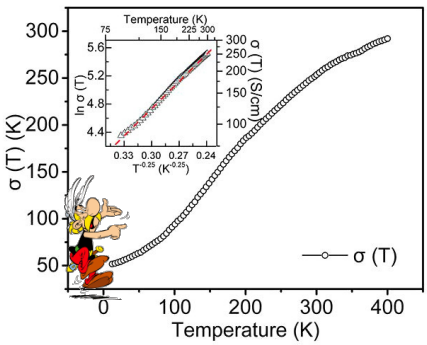
Ag5(BHT)

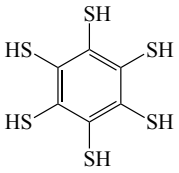
Metallic Ag-BHT
σ_{RT} = 250 S·cm^{-1}

Reduction

Semiconducting Ag-BHT
$\sigma_{RT} = 7.3 \times 10^{-2}$ S·cm^{-1}

$\sigma_{300\,K} = 250$ S cm^{-1}





Benzenehexathiol
(H6BHT)

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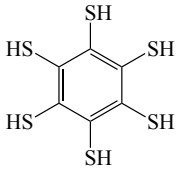
Sun, J. et al. *J. Am. Chem. Soc.* **2018**, *140*, 15153

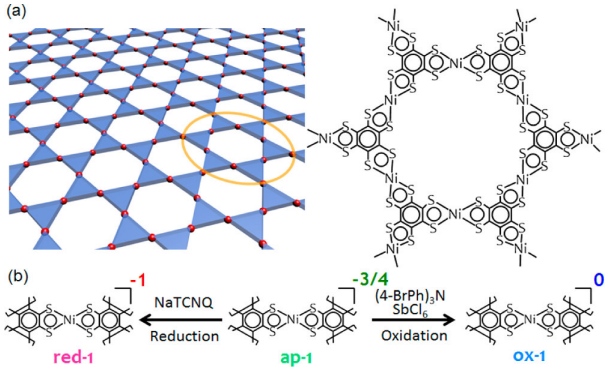
Intrinsically conducting MOFs

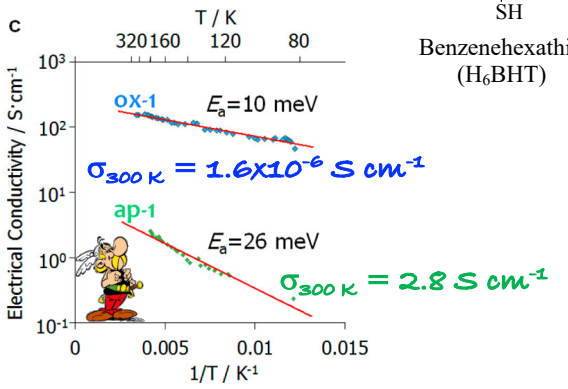
3. S-containing ligands

$Ni_3(H_3BHT)_2$



Benzenehexathiol
(H_6BHT)





Su, W. F. et al. *Langmuir* **2018**, *34*,15754

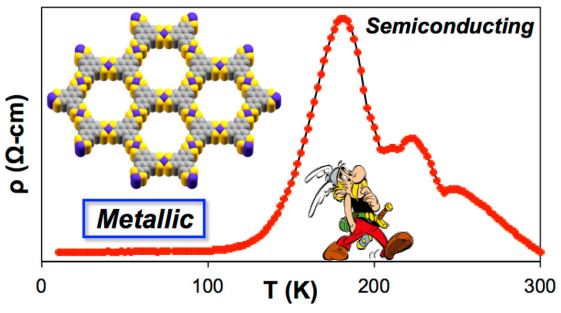
Takata, M. et al. *J. Am. Chem. Soc.* **2013**, *135*, 2462

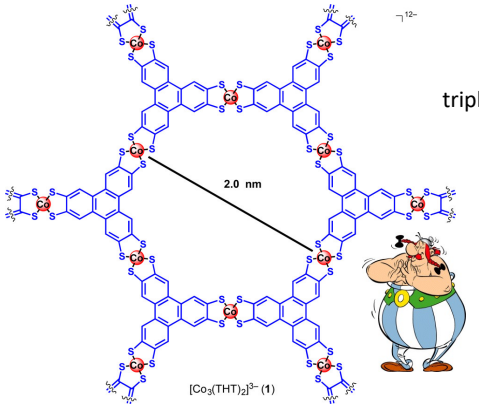
Ishizaka, K. et al. *J. Am. Chem. Soc.* **2014**, *136*, 14357

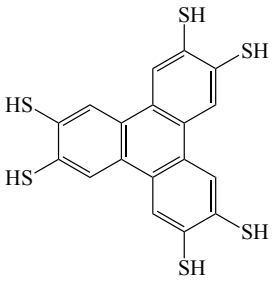
Intrinsically conducting MOFs

3. S-containing ligands

$Co_3(H_3TPHT)_2$





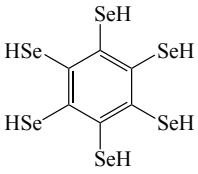


triphenylenehexathiolate
(H_6TPHT)

Marinescu, S. C. et al. *J. Am. Chem. Soc.* **2017**, *139*, 10863

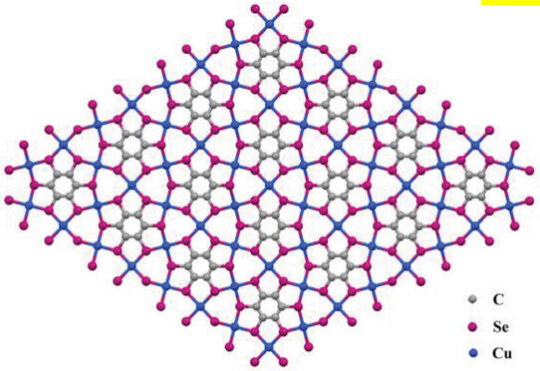
Intrinsically conducting MOFs

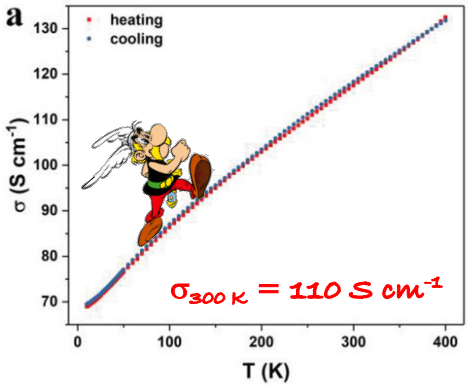
3. S-containing ligands



Benzenehexaselenolate
(H_6BHSe)

$Cu_3(BHSe)_2$

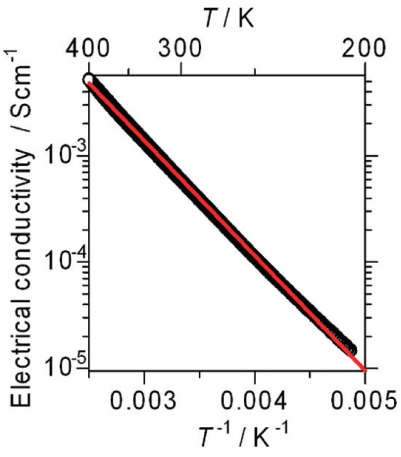




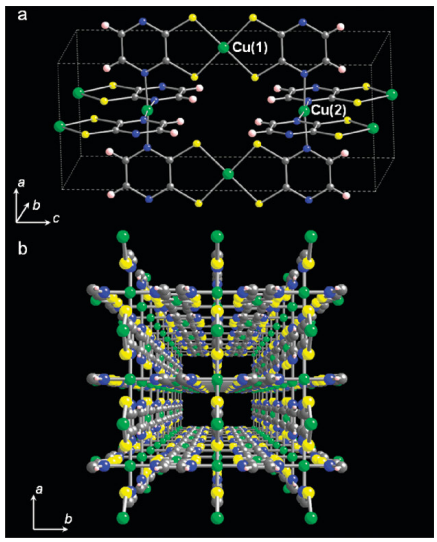
Zhu, D. et al. *Adv. Sci.* **2019**, *6*, 1802235

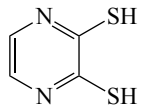
Intrinsically conducting MOFs

4. Mixed-valence metal ions



$\sigma_{300\,K} = 6X10^{-4}$ S cm^{-1}





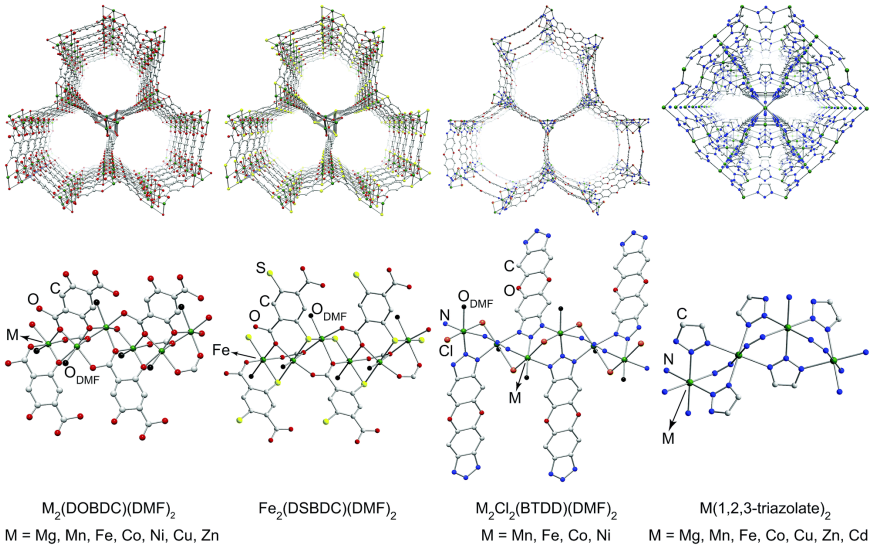
2,3-pyrazinedithiolate
(pdt)

$Cu^{I}[Cu^{III}(pdt)_2]$

Kitagawa, H. et al. *Inorg. Chem.* **2009**, *48*, 9048

Intrinsically conducting MOFs

4. Mixed-valence metal ions

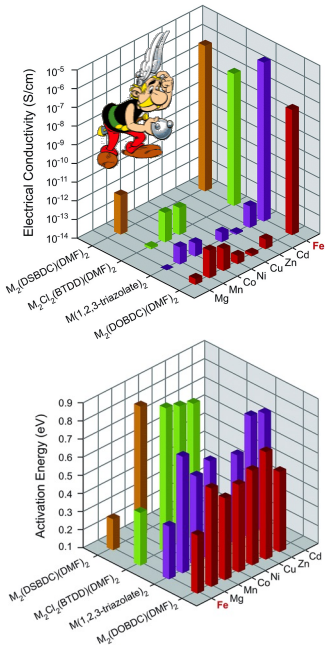


$M_2(DOBDC)(DMF)_2$
M = Mg, Mn, Fe, Co, Ni, Cu, Zn

$Fe_2(DSBDC)(DMF)_2$

$M_2Cl_2(BTDD)(DMF)_2$
M = Mn, Fe, Co, Ni

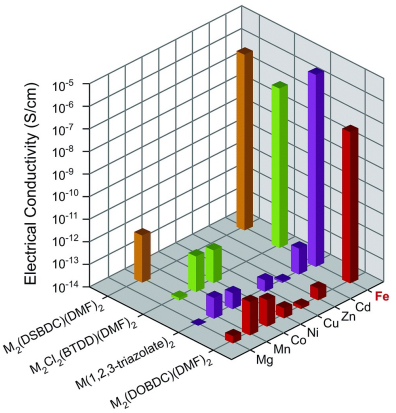
$M(1,2,3\text{-triazolate})_2$
M = Mg, Mn, Fe, Co, Cu, Zn, Cd

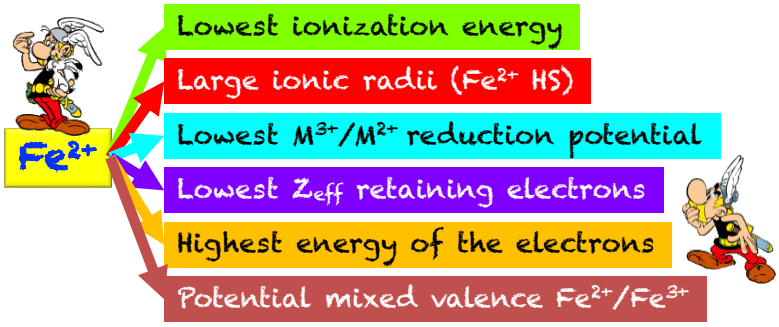


Dinca, M. et al. *Chem. Sci.* **2017**, *8*, 4450

Intrinsically conducting MOFs

4. Mixed-valence metal ions



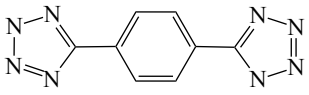


Dinca, M. et al. *Chem. Sci.* **2017**, *8*, 4450

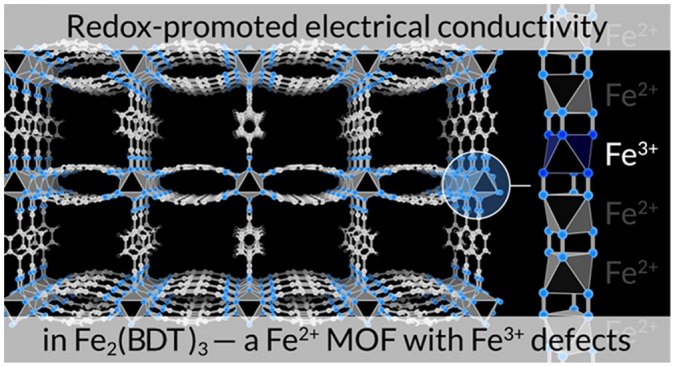
Intrinsically conducting MOFs

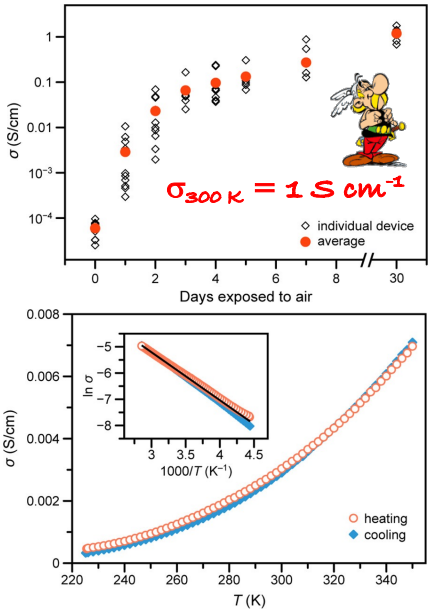
4. Mixed-valence metal ions

$[Fe_2(H_{0.67}BDT)_3]\cdot xH_2O$



(5,5′-(1,4-phenylene)bis(1*H*-tetrazole))
(H_2BDT)



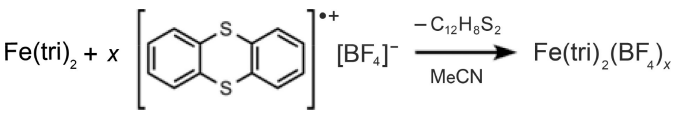


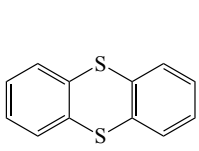
Li, D. et al *Chem. Commun.* **2012**, *48*, 3960

Dinca M. et al *J. Am. Chem. Soc.* **2018**, *140*, 7411

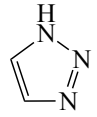
Intrinsically conducting MOFs

4. Mixed-valence metal ions

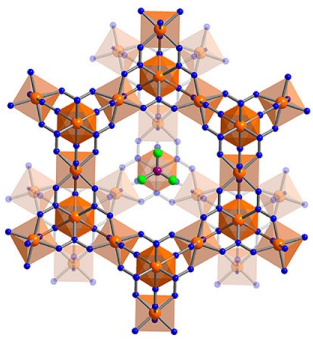




triantrene



1,2,3-triazole
(Htri)

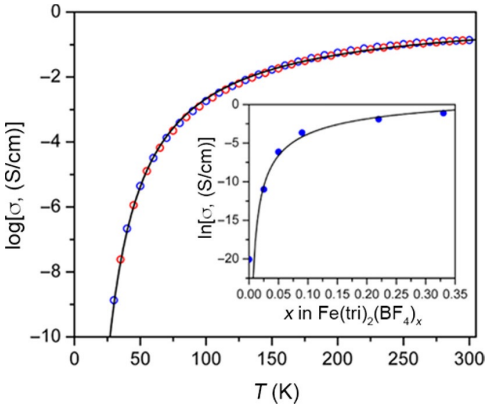


$Fe(tri)_2(BF_4)_x$ $0 \le x \le 0.33$

Low-Spin Fe^{2+}
$\sigma \approx 10^{-9}$ S/cm

Oxidation

Mixed-Valence
Low-Spin $Fe^{2+/3+}$
$\sigma \approx 10^{-1}$ S/cm

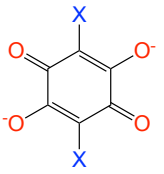


Long, J. R. et al *J. Am. Chem. Soc.* **2018**, *140*, 8526

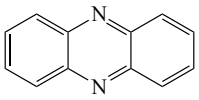
Intrinsically conducting MOFs

4. Mixed-valence metal ions

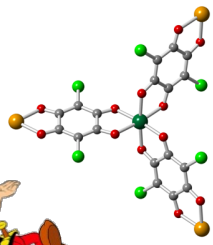
$[(H_3O)(H_2O)(phz)_3][Fe^{II}Fe^{III}(C_6O_4X_2)_3]\cdot 12H_2O$

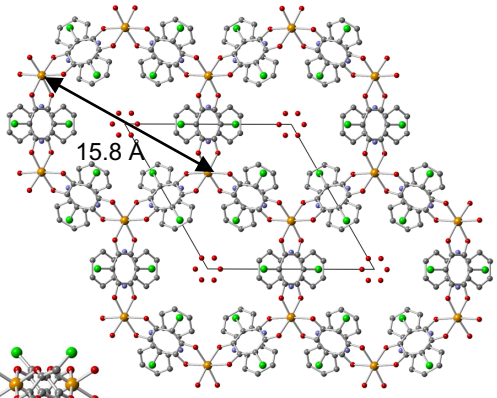


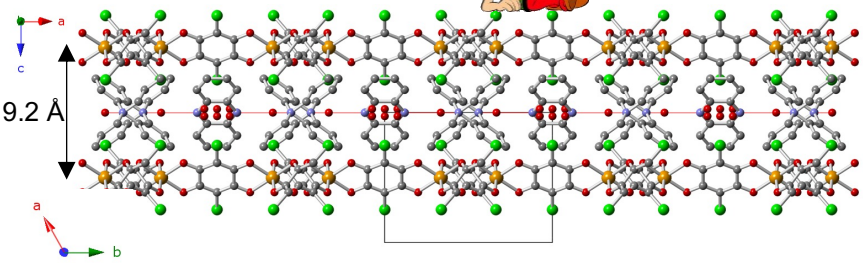
X = Cl and Br



Phenazine (phz)







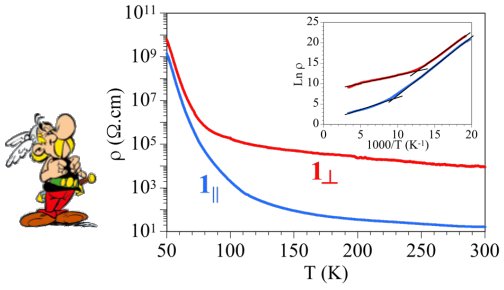
Gómez-García, C. J. et al. *ACS Appl. Mater. Interfaces* **2017**, *9*, 26210

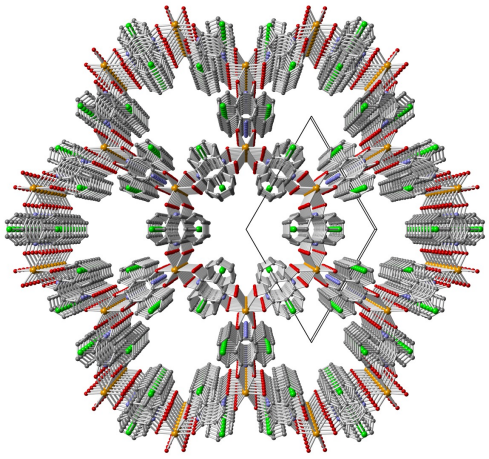
Intrinsically conducting MOFs

4. Mixed-valence metal ions

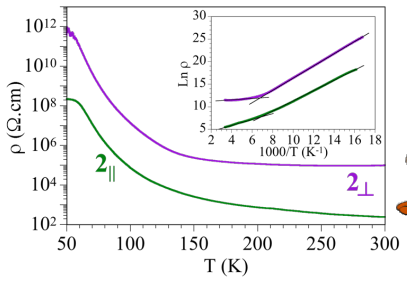
$[(H_3O)(H_2O)(phz)_3][Fe^{II}Fe^{III}(C_6O_4X_2)_3]\cdot 12H_2O$

$\sigma_{300\,K} = 3\times10^{-2}$ S cm^{-1} (X = Cl)





$\sigma_{300\,K} = 3\times10^{-3}$ S cm^{-1} (X = Br)



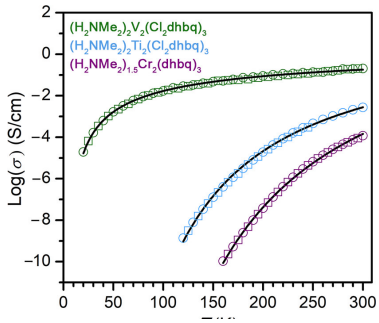
Carlos J. Gómez-García. Universidad de Valencia. ESMA-Gandía-18/10/23

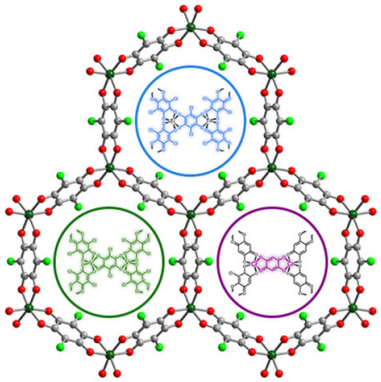
Gómez-García, C. J. et al. *ACS Appl. Mater. Interfaces* **2017**, *9*, 26210

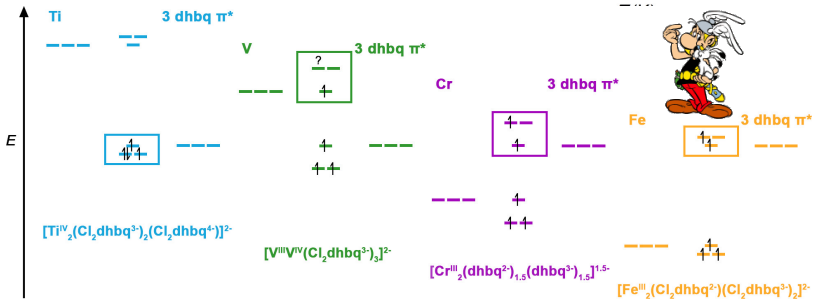
Intrinsically conducting MOFs

5. Electronic structure of the metal ions

Compound	σ_{300K} (S cm^{-1})	Mechanism
$(H_2NMe_2)_2[Ti_2(C_6O_4Cl_2)_3]$	2.7×10^{-3}	Redox hopping
$(H_2NMe_2)_2[V_2(C_6O_4Cl_2)_3]$	0.45	VRH
$(H_2NMe_2)_{1.5}[Cr_2(C_6O_4Cl_2)_3]$	1.2×10^{-4}	Redox hopping



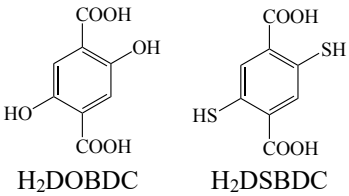


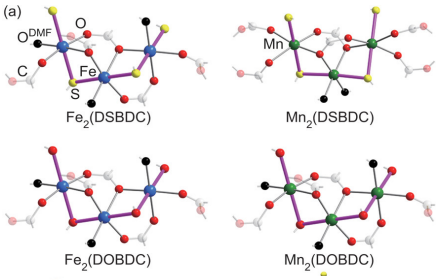


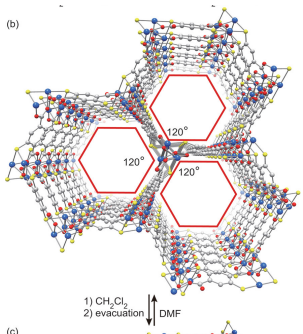
Long, J. R. et al. *J. Am. Chem. Soc.* **2018**, *140*, 3040

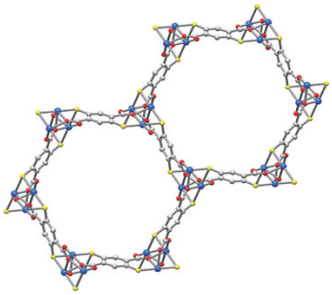
Intrinsically conducting MOFs

5. Electronic structure of the metal ions









M_2(DEBDC) **E** = S, O

M = Fe^{2+}, σ ≈10^{-6} S/cm

10^6 Electrical Conductivity Enhancement

M = Mn^{2+}, σ ≈10^{-12} S/cm

Mn_2(DOBCD)

Mn_2(DSBCD)

Fe_2(DOBCD)

Fe_2(DSBCD)

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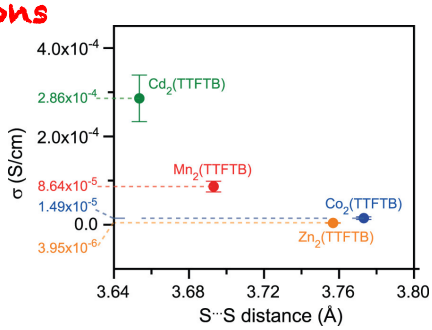
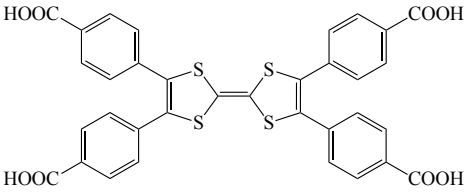
Dincă, M. et al *J. Am. Chem. Soc.* **2015**, *137*, 6164

Intrinsically conducting MOFs

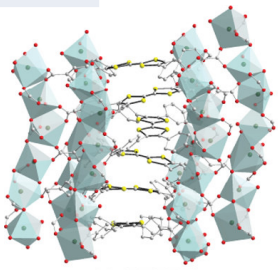
6. Size of the metal ions

Compound	radius (pm)	S···S (Å)	σ_{300K} (S cm^{-1})
Co_2TTFTB	88.5	3.7732(26)	1.49×10^{-5}
Zn_2TTFTB	88.0	3.7568(13)	3.95×10^{-6}
Mn_2TTFTB	97.0	3.6929(6)	8.64×10^{-5}
Cd_2TTFTB	109.0	3.6538(23)	2.86×10^{-4}

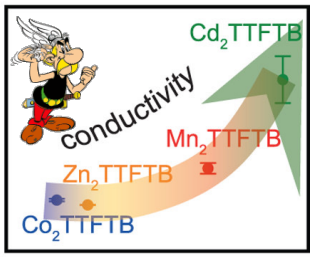




Tetrathiafulvalene tetrabenzoate
(H_4TTFTB)



M_2(TTFTB)
● = Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}



decreasing S···S distance

Dincă, M. et al. *J. Am. Chem. Soc.* **2015**, *137*, 1774

Outline

1. Introduction. Conducting MOFs
2. Conductivity measurements
3. Electronic states, conductivity mechanisms and pathways
4. Types of conducting MOFs
   1. Intrinsically conducting MOFs
   2. Extrinsically conducting MOFs
5. Conclusions

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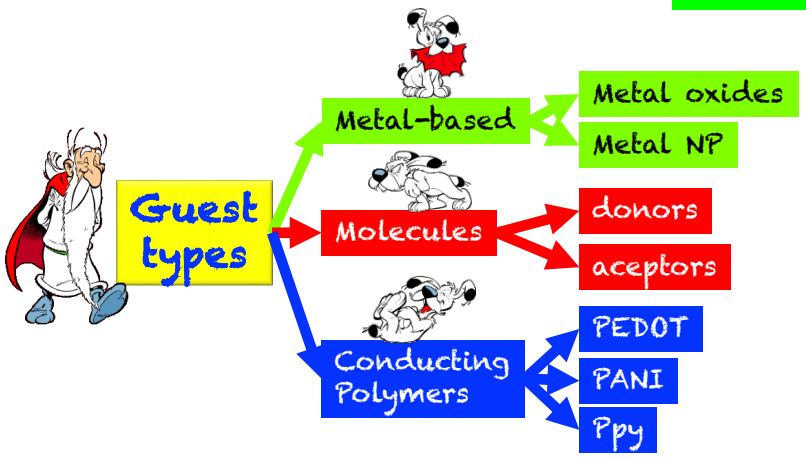
Extrinsically conducting MOFs

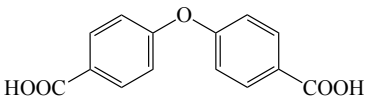
Charge transport occurs through the guest species within the host framework → Charge transport strongly depends on the guest (that may interact with the framework



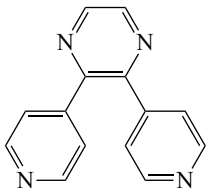
Extrinsically conducting MOFs

1. Metal-based guests

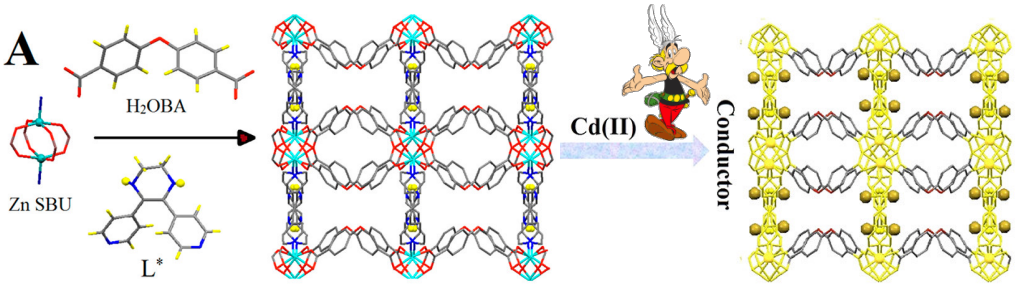
[Zn(OBA)(DPTHD)]·DMF



4,4′-oxybis(benzoic acid) (H_2OBA)



5,6-di(pyridin-4-yl)-1,2,3,4-tetrahydropyrazine (DPTHD)



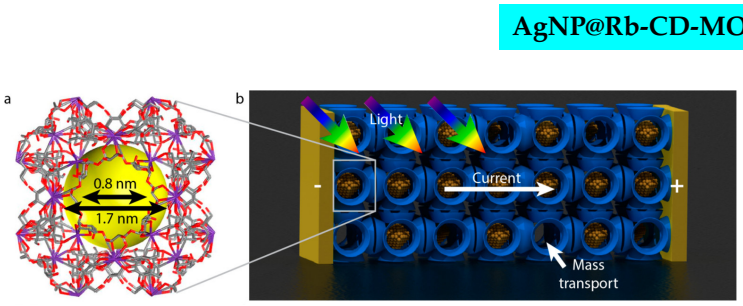
$\sigma = 5.8 \times 10^{-6}$ S cm^{-1} → $\sigma = 1.8 \times 10^{-2}$ S cm^{-1}

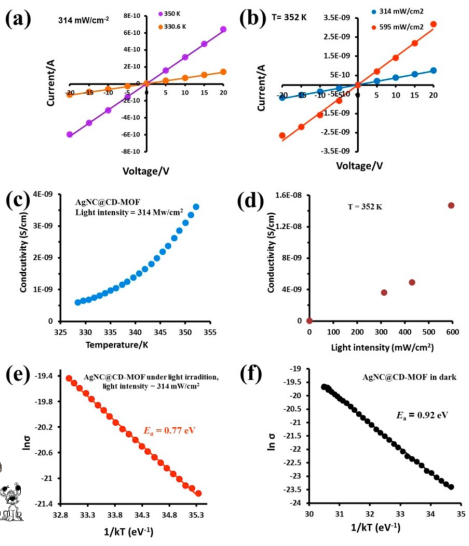
Morsali, A. et al. *J. Am. Chem. Soc.* **2019**, *141*, 11173

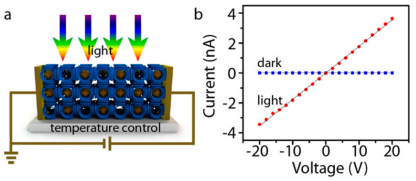
Extrinsically conducting MOFs

1. Metal-NP-based guests

AgNP@Rb-CD-MOF

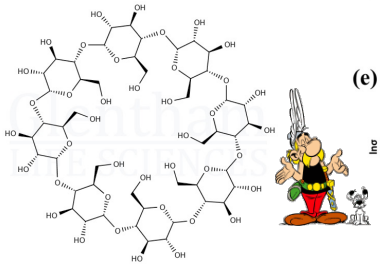






σ_{352K} (off)= 6.8×10^{-10} S cm^{-1}

σ_{352K} (on) = 1.47×10^{-8} S cm^{-1}



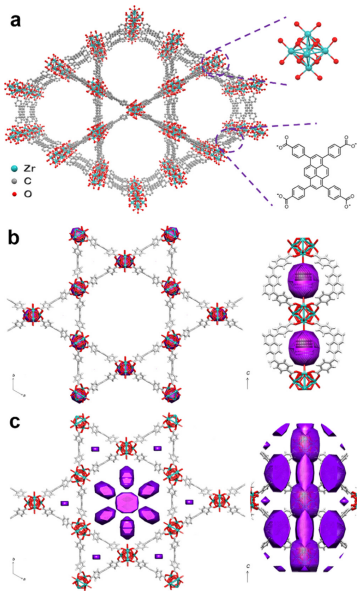
γ-cyclodextrin (CD)

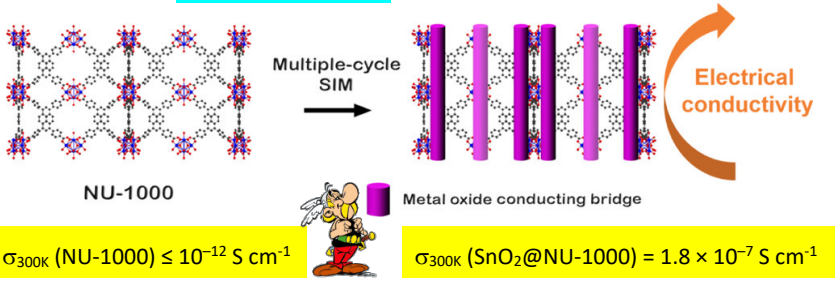
Grzybowski, B. A. et al. *J. Am. Chem. Soc.* **2015**, *137*, 8169

Extrinsically conducting MOFs

1. Metal oxide-based guests

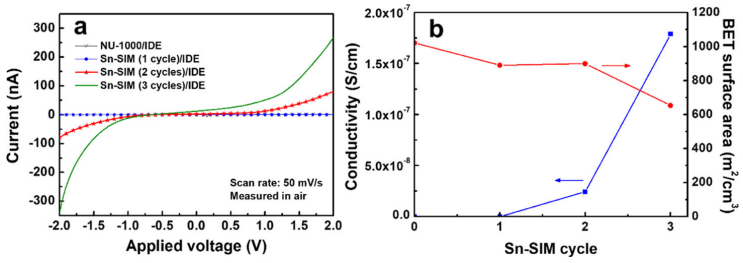
SnO_2@NU-1000





σ_{300K} (NU-1000) ≤ 10^{-12} S cm^{-1}

σ_{300K} (SnO_2@NU-1000) = 1.8×10^{-7} S cm^{-1}



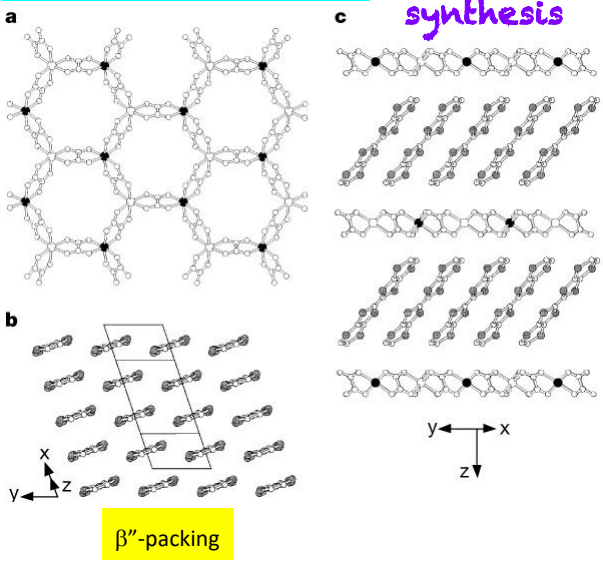
Hupp, J. T. et al. *ACS Appl. Mater. Interfaces* **2018**, *10*, 30532

Extrinsically conducting MOFs

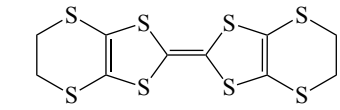
2. Molecular guests (donors)

$(BEDT\text{-}TTF)_3[MnCr(C_2O_4)_3]$

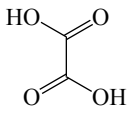
in-situ synthesis



β”-packing

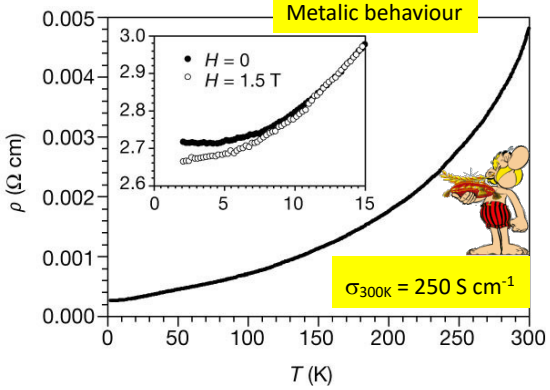


bis(ethylenedithio)tetrathiafulvalene
(BEDT-TTF)



Oxalic acid
($H_2C_2O_4$)

Metalic behaviour



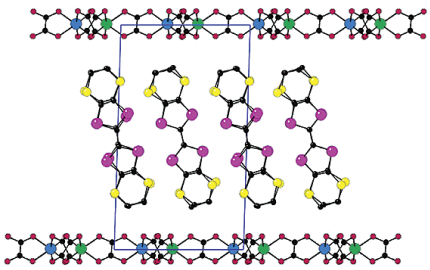
σ_{300K} = 250 S cm^{-1}

Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447

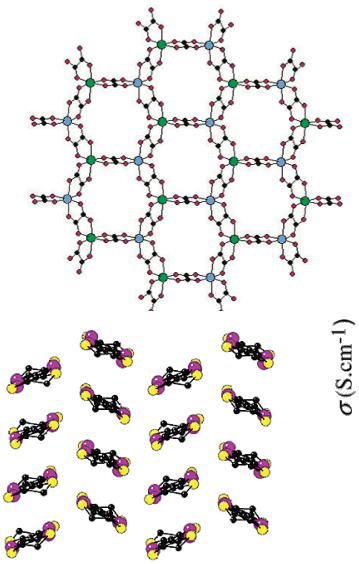
Extrinsically conducting MOFs

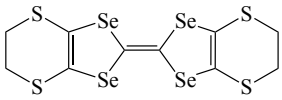
2. Molecular guests (donors)

$(BEDT\text{-}TSF)_x[MnCr(C_2O_4)_3]$

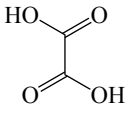


α-packing

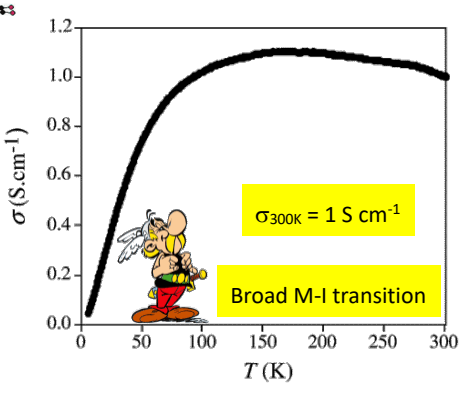




bis(ethylenedithio)
tetraselenafulvalene
(BEDT-TTF)



Oxalic acid
($H_2C_2O_4$)



σ_{300K} = 1 S cm^{-1}

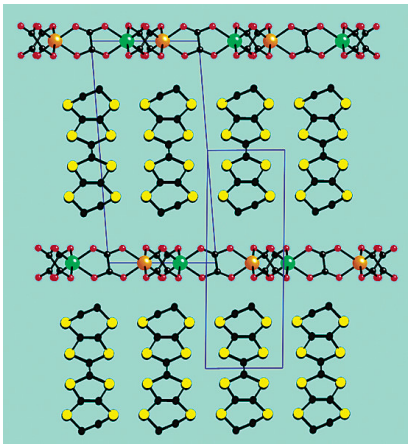
Broad M-I transition

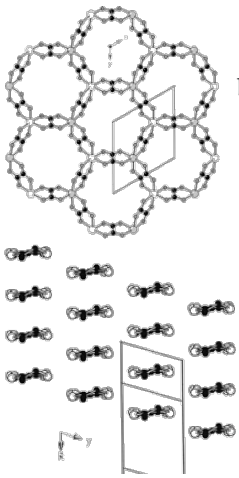
Coroando, E.; Galán-Mascarós, J. R.; Gómez-García, C. J. et al. *J. Am. Chem. Soc.* **2003**, *125*, 10774

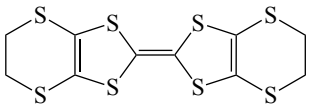
Extrinsically conducting MOFs

2. Molecular guests (donors)

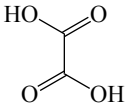
$(BEDT\text{-}TTF)_3[MnRh(C_2O_4)_3]$



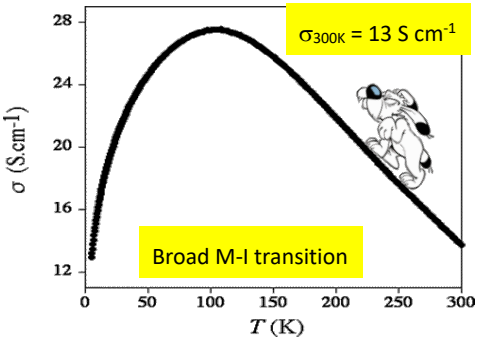




bis(ethylenedithio)tetrathiafulvalene
(BEDT-TTF)



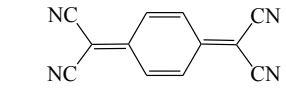
Oxalic acid
($H_2C_2O_4$)



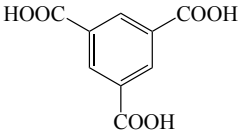
Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J. et al. *Inorg. Chem.* **2004**, *43*, 4808

Extrinsically conducting MOFs

2. Molecular guests (aceptors)

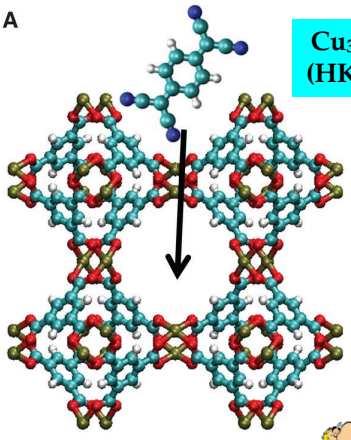


7,7,8,8-tetracyanoquinododimethane
(TCNQ)

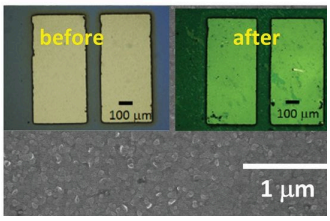


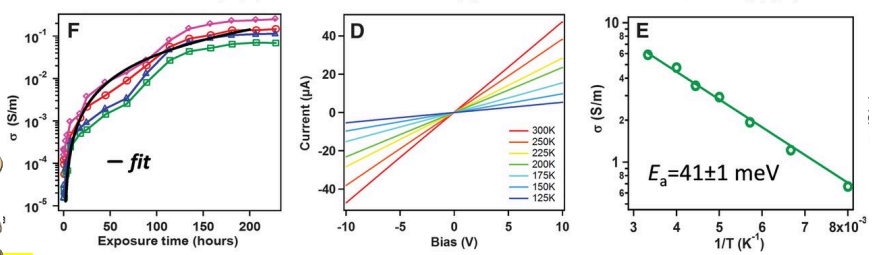
benzene-1,3,5-tricarboxylic acid
(BTC)

A



$Cu_3(BTC)_2$ (HKUST-1)





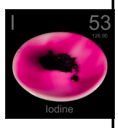
σ_{300K} (HKUST) ≈ 10^{-8} S cm^{-1}

σ_{300K} (TCNQ@HKUST) = $7x10^{-2}$ S cm^{-1}

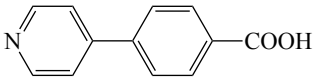
Allendorf, M. D. et al. *Science* **2014**, *343*, 66

Extrinsically conducting MOFs

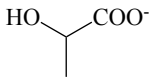
2. Molecular guests (aceptors)



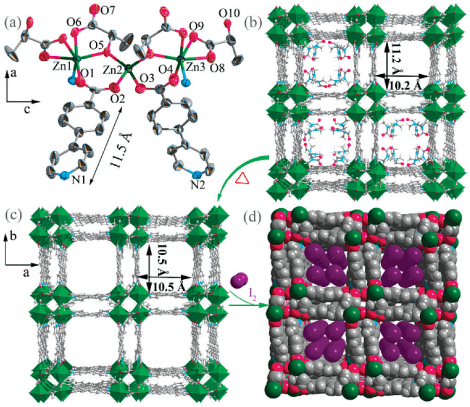
$[M_3(DL\text{-}lac)_2(pybz)_2].nDMF$ M = Zn^{2+}, Co^{2+}

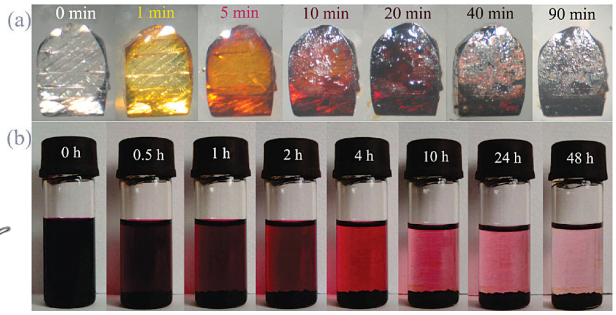


4-pyridine benzoate (pybz)



D,L-Lactate (DL-lac)





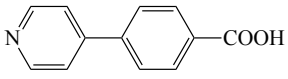
σ_{300K} (MOF) ≈ $7x10^{-6}$ S cm^{-1}

σ_{300K} (I_2@MOF) = $3.4x10^{-3}$ S cm^{-1}

Kurmoo, M. et al. *J. Am. Chem. Soc.* **2010**, *132*, 2561

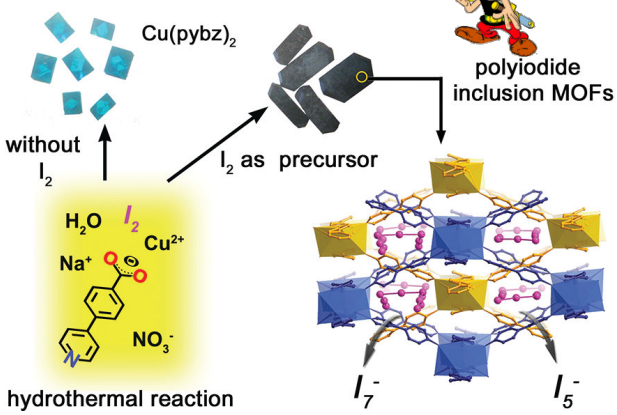
Extrinsically conducting MOFs

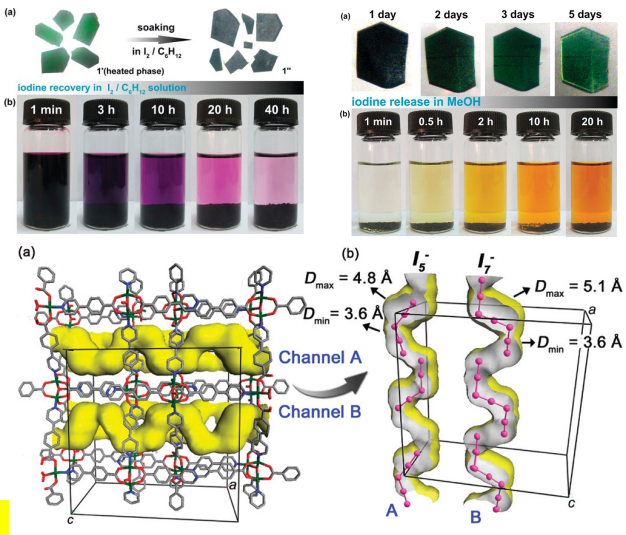
2. Molecular guests (aceptors)



4-pyridine benzoate (pybz)

$[Cu_6(pybz)_8(OH)_2]\cdot(I_5)\cdot(I_7)$





σ_{300K} (MOF) < 10^{-12} S cm^{-1}

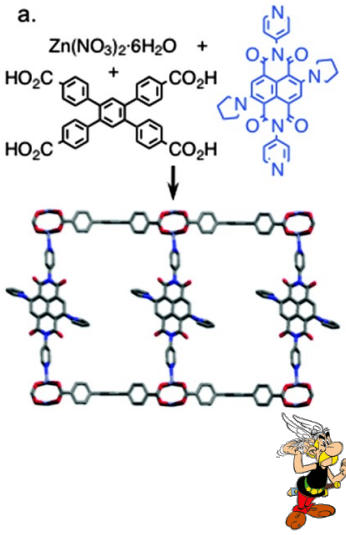
σ_{300K} (I_7+I_5@MOF) = $8x10^{-7}$ S cm^{-1}

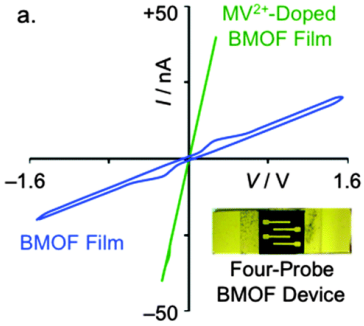
Zeng, M.-H. et al. *J. Am. Chem. Soc.* **2012**, *134*, 4857

Extrinsically conducting MOFs

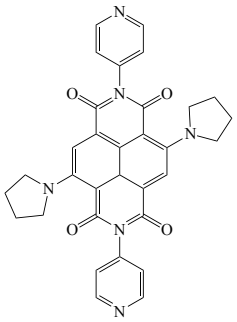
2. Molecular guests (aceptors)

[Zn_2(TCPB)(BPDPNDI)]

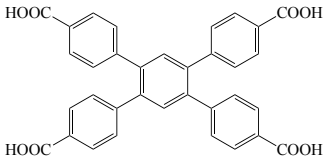




Guest	σ_{MOF} (S cm^{-1})	$\sigma_{Guest@MO}$ (S cm^{-1})
MV^{2+}	6 x 10^{-7}	2.3x10^{-5}
DFDNB	6 x 10^{-7}	3.5x10^{-6}
DNT	6 x 10^{-7}	1.5x10^{-6}
C_{60}	6 x 10^{-7}	4x10^{-7}



N,N′-bis(4-pyridyl)-2,6-dipyrrolidyl naphthalenediimide (BPDPNDI)

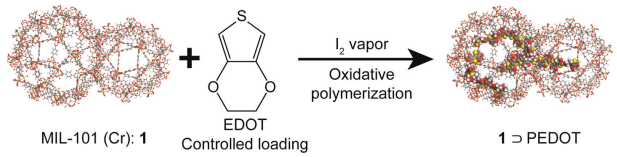


1,2,4,5-tetrakis-(4-carboxyphenyl)benzene (TCPB)

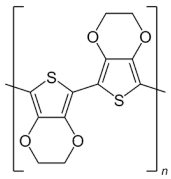
Saha, S. et al. *J. Mater. Chem. C* **2016**, *4*, 894

Extrinsically conducting MOFs

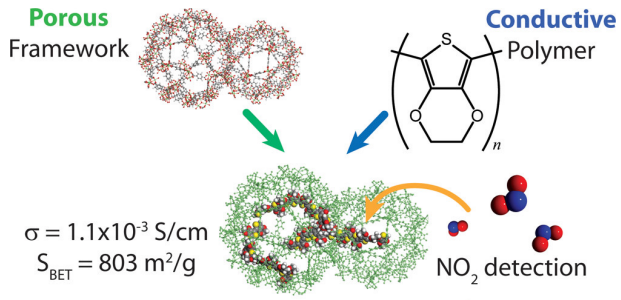
3. Conducting polymers



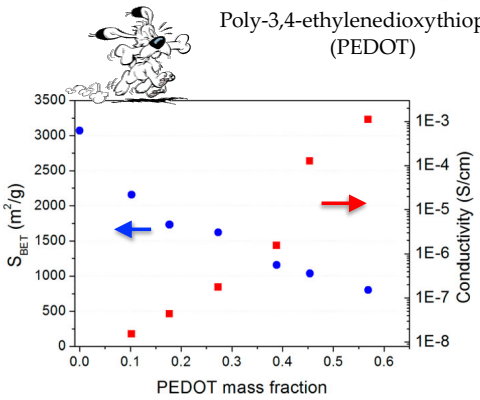
Cr-MIL-101



Poly-3,4-ethylenedioxythiophene (PEDOT)



Highly porous and conductive composite



σ_{300K} (MIL-101) ≈ 10^{-11} S cm^{-1}

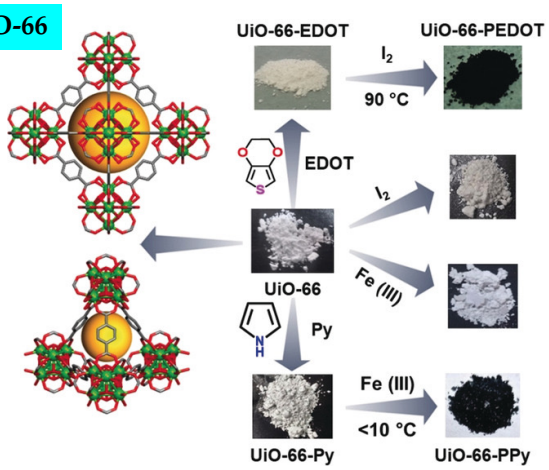
σ_{300K} (PEDOT@MIL-101) = 1.1x10^{-7} S cm^{-1}

Uemura, T. at al. *J. Am. Chem. Soc.* **2016**, *138*, 10088

Extrinsically conducting MOFs

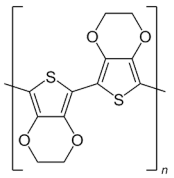
3. Conducting polymers

UiO-66

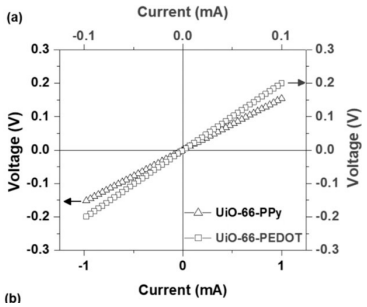


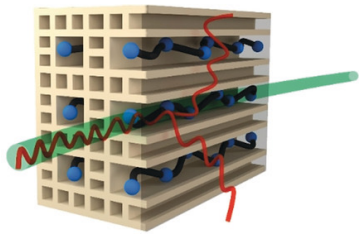
MOF	Guest	σ_{MOF} (S cm^{-1})	$\sigma_{Guest@MOF}$ (S cm^{-1})
UiO-66	PEDOT	Insulator	10^{-3}
UiO-66	PPy	Insulator	$2x10^{-2}$

Poly-pyrrole (Ppy)



Poly-3,4-ethylene dioxythiophene (PEDOT)



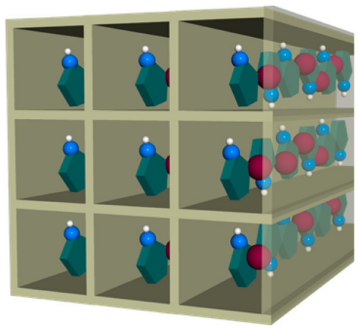


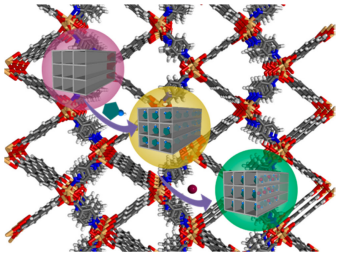
Ballav, N. et al. *Angew. Chem. Int. Ed.* **2019**, *59*, 2215

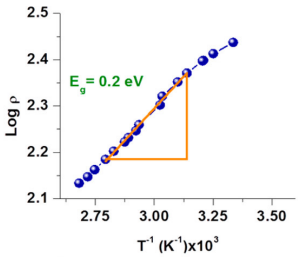
Extrinsically conducting MOFs

3. Conducting polymers

[Cd(NDC)$_{0.5}$(PCA)].G$_x$

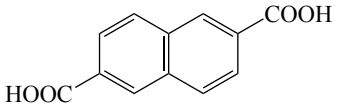




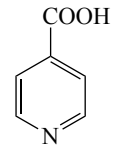


σ_{300K} (MOF) < 10^{-12} S cm^{-1}

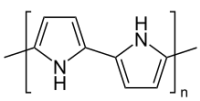
σ_{300K} (PPy@Cd-MOF) = 10^{-3} S cm^{-1}



2,6-napthalenedicarboxylic acid (H_2NDC)



4-pyridinecarboxylic acid (HPCA)

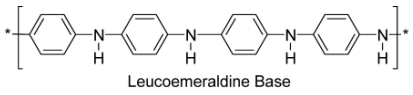


Poly-pyrrole (Ppy)

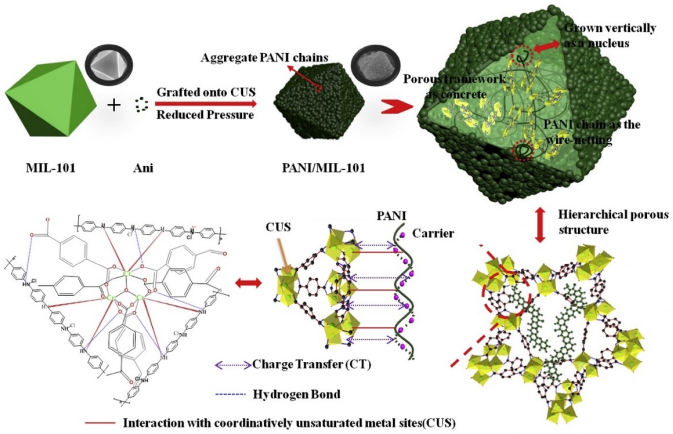
Ballav, N. et al. *J. Phys. Chem. Lett.* **2016**, *7*, 2945

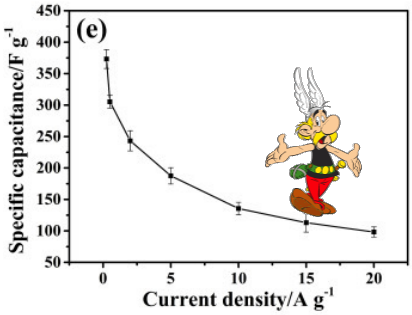
Extrinsically conducting MOFs

3. Conducting polymers



MIL-101





σ_{300K} (PANI) = 0.16 S cm^{-1}

σ_{300K} (MIL-101-Cr) ≈ 10^{-11} S cm^{-1}

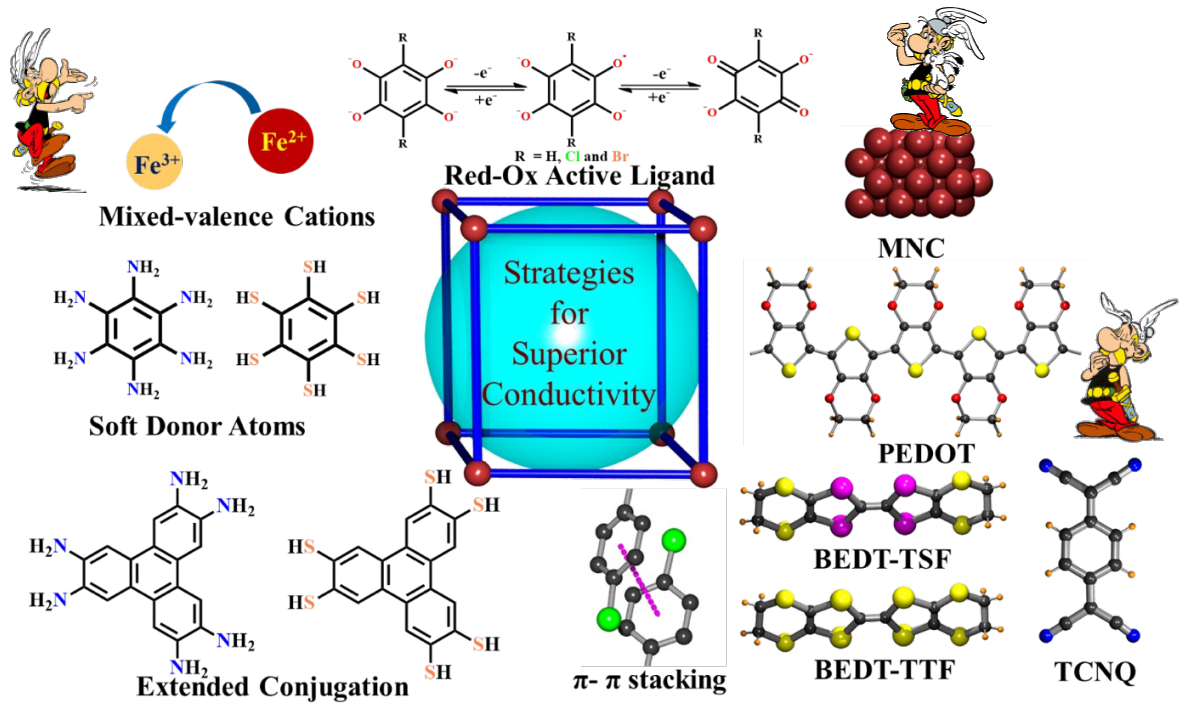
σ_{300K} (PANI@MIL-101-Cr) = 0.43 S cm^{-1}

Wang, C. et al. *Electrochim. Acta* **2018**, *281*, 582

Outline

1. Introduction. Conducting MOFs
2. Conductivity measurements
3. Electronic states, conductivity mechanisms and pathways
4. Types of conducting MOFs
   1. Intrinsically conducting MOFs
   2. Extrinsically conducting MOFs
5. Conclusions

Conclusions



Acknowledgments

Modulating Multifunctional Molecular Materials

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