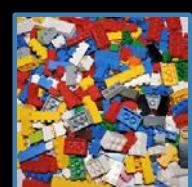


# Metal-Organic Frameworks: When the whole is more than the sum of its parts.

*Dr. Dr. Danny E. P. Vanpoucke*

Belgian Physical Society Meeting, Ghent  
May 18<sup>th</sup> 2016



# Metal-Organic Frameworks



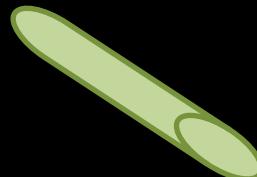
Inorganic  
node



# Metal-Organic Frameworks



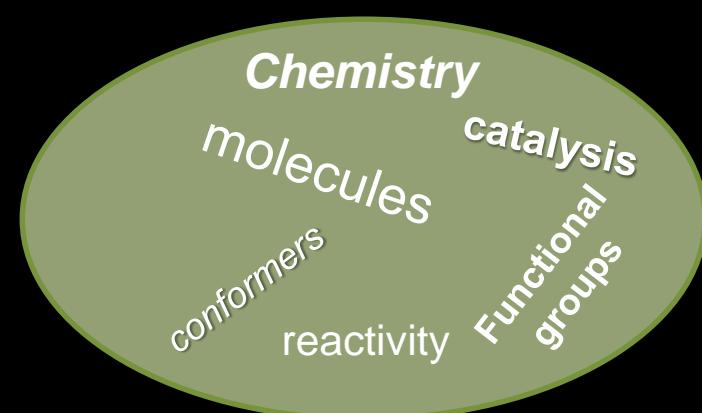
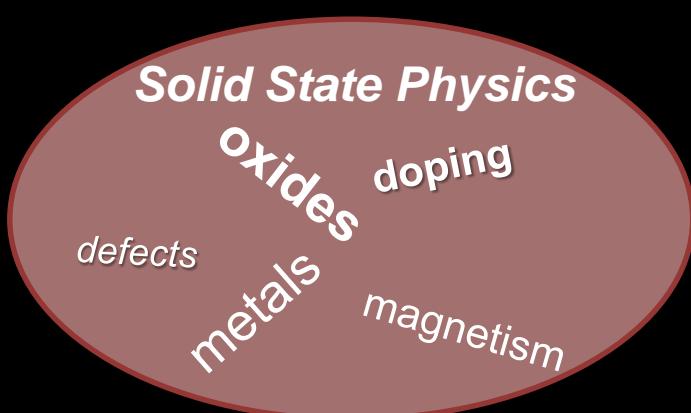
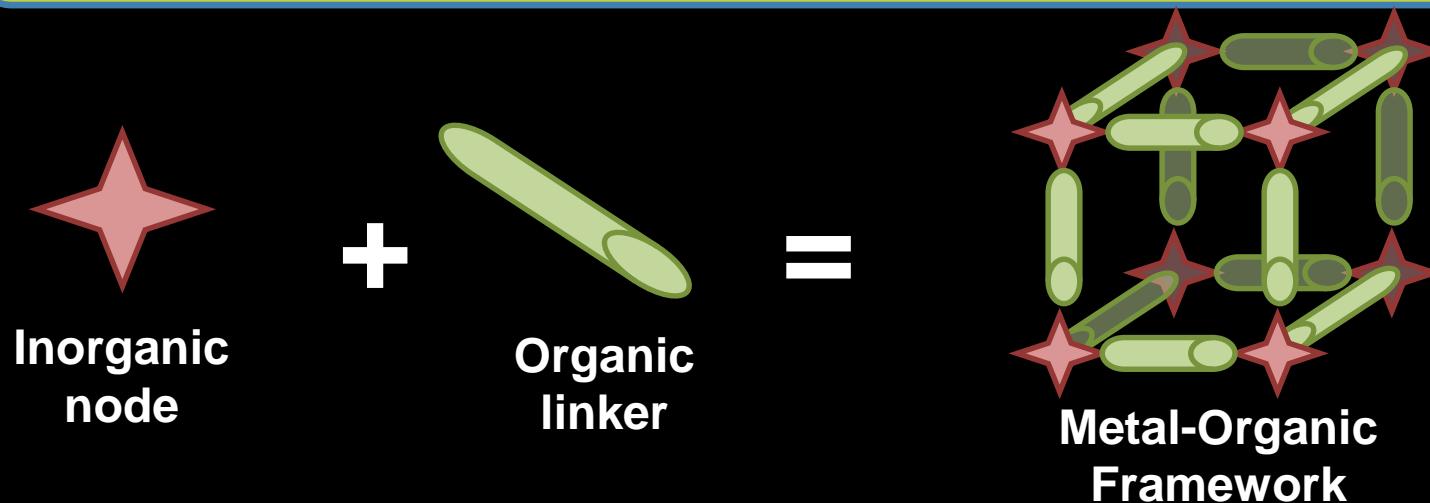
Inorganic  
node



Organic  
linker

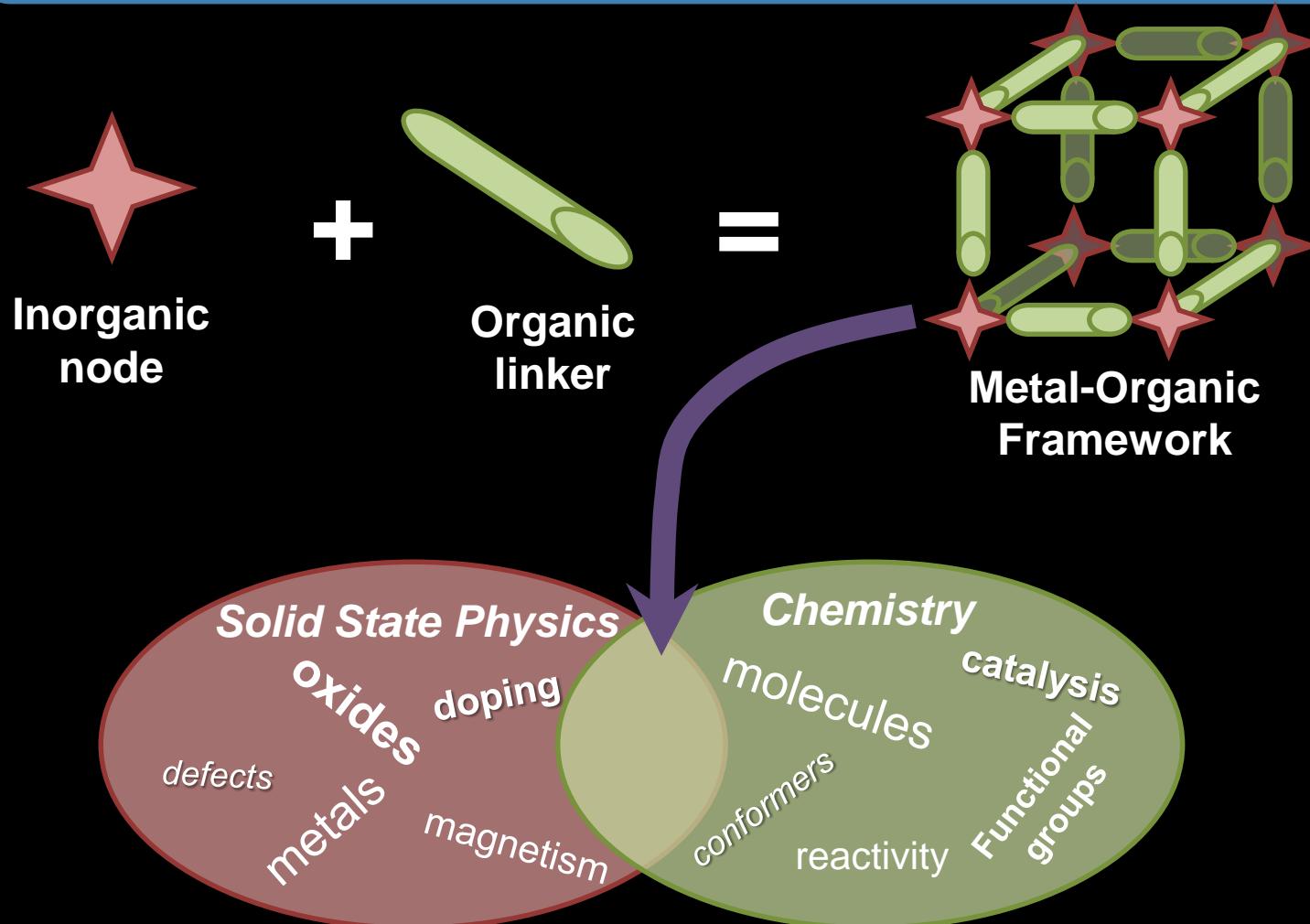


# Metal-Organic Frameworks





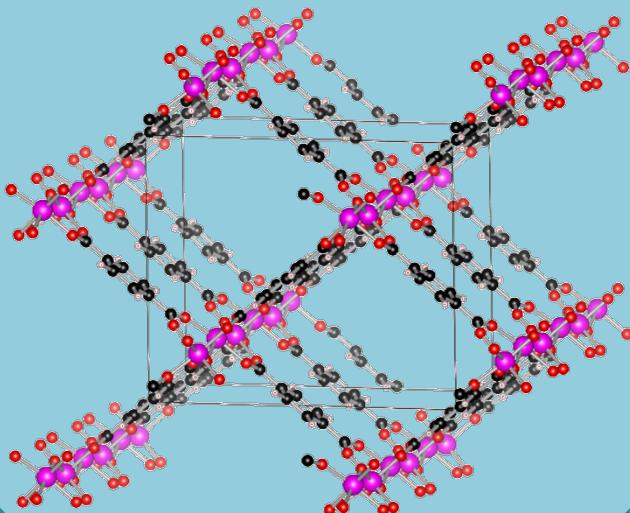
# Metal-Organic Frameworks



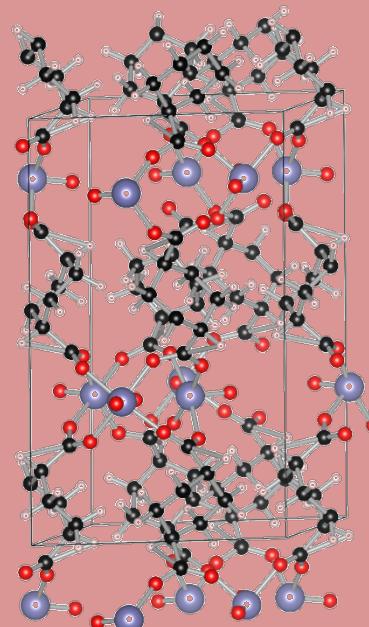


# Metal-Organic Frameworks

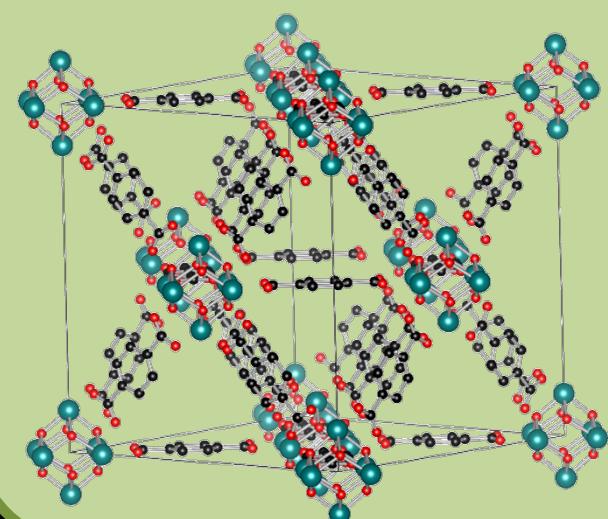
MIL-47(V)



COK-69(Ti)



UiO-66(Zr)

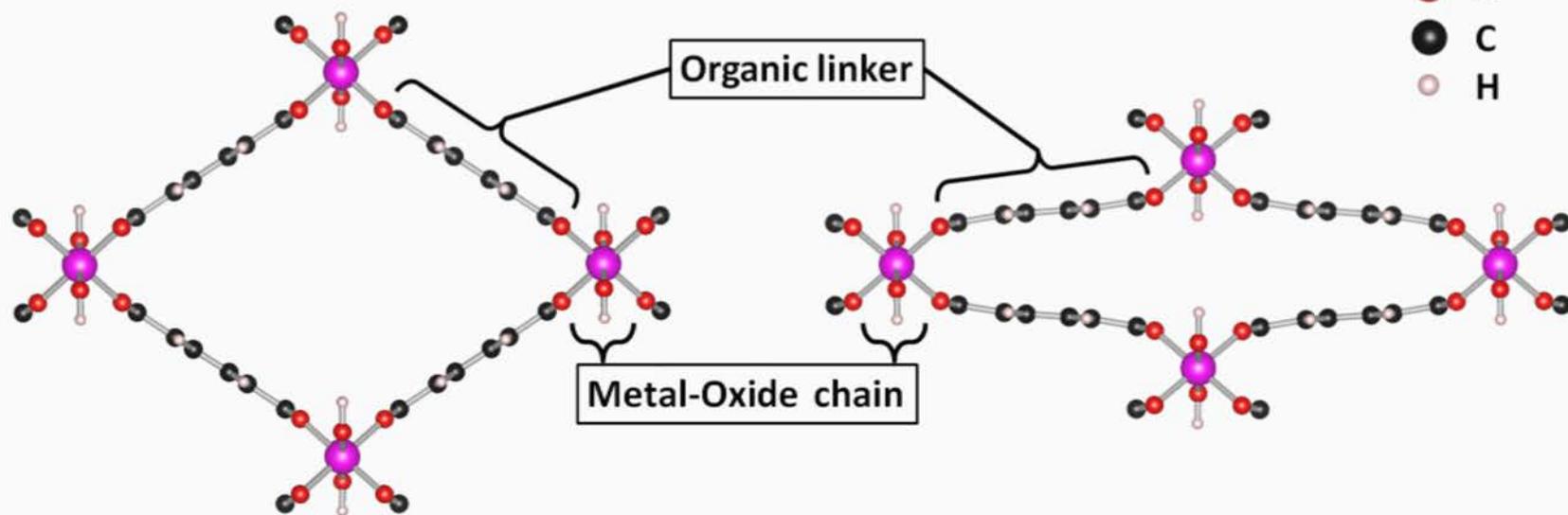
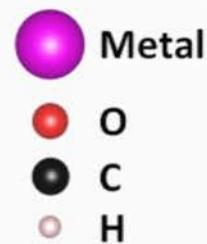


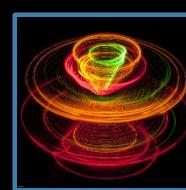


# Flexible MIL-47(V)

## MIL-53(M) series topology

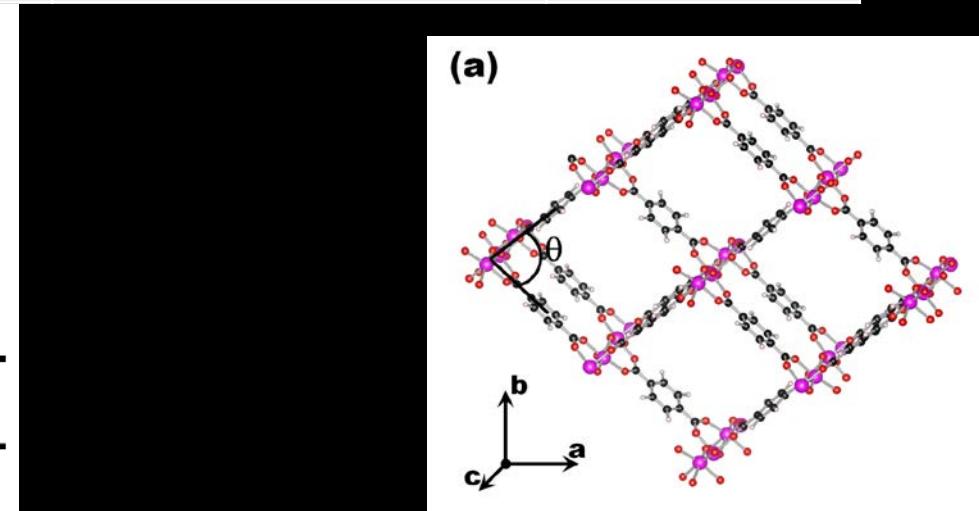
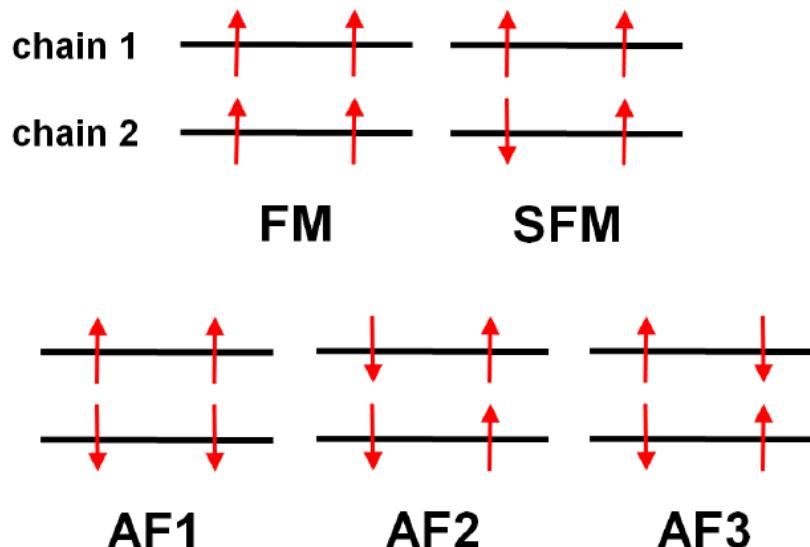
M(OH)(BDC) with M=Transition Metal



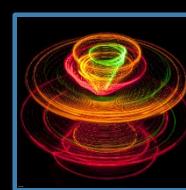


# The role of spin-configurations

	Large Pore		Narrow Pore	
	$E_0$ [meV]	$B_0$ [GPa]	$E_0$ [meV]	$B_0$ [GPa]
FM	0	5.95	0 (+13 vs LP)	2.84
AF1	-16	6.14	-10	2.83
SFM	-144	7.17	-77	2.64
AF2	-279	8.13	-168	2.37
AF3	-278	8.12	-167	2.46

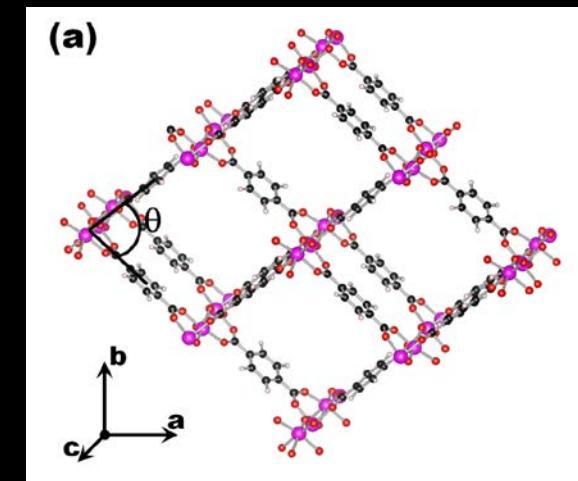
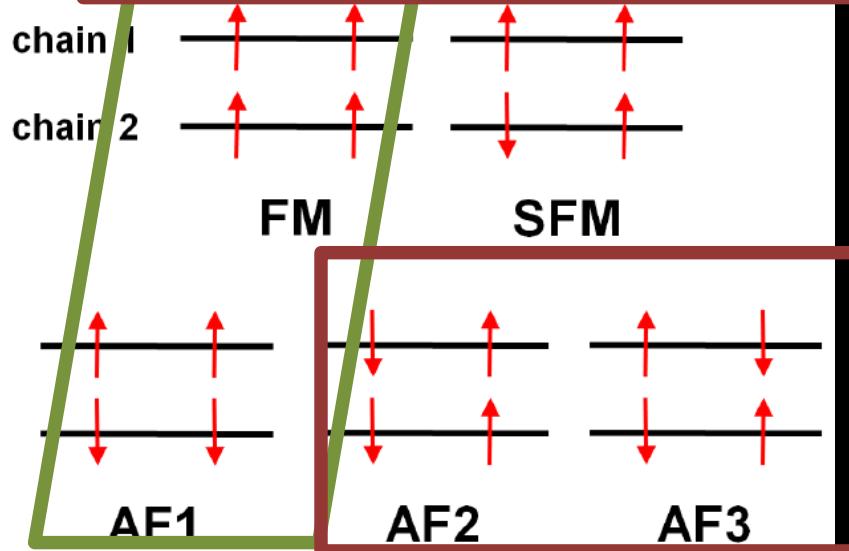


Beilstein J. Nanotechnol. 5, 1738-1748 (2014)



# The role of spin-configurations

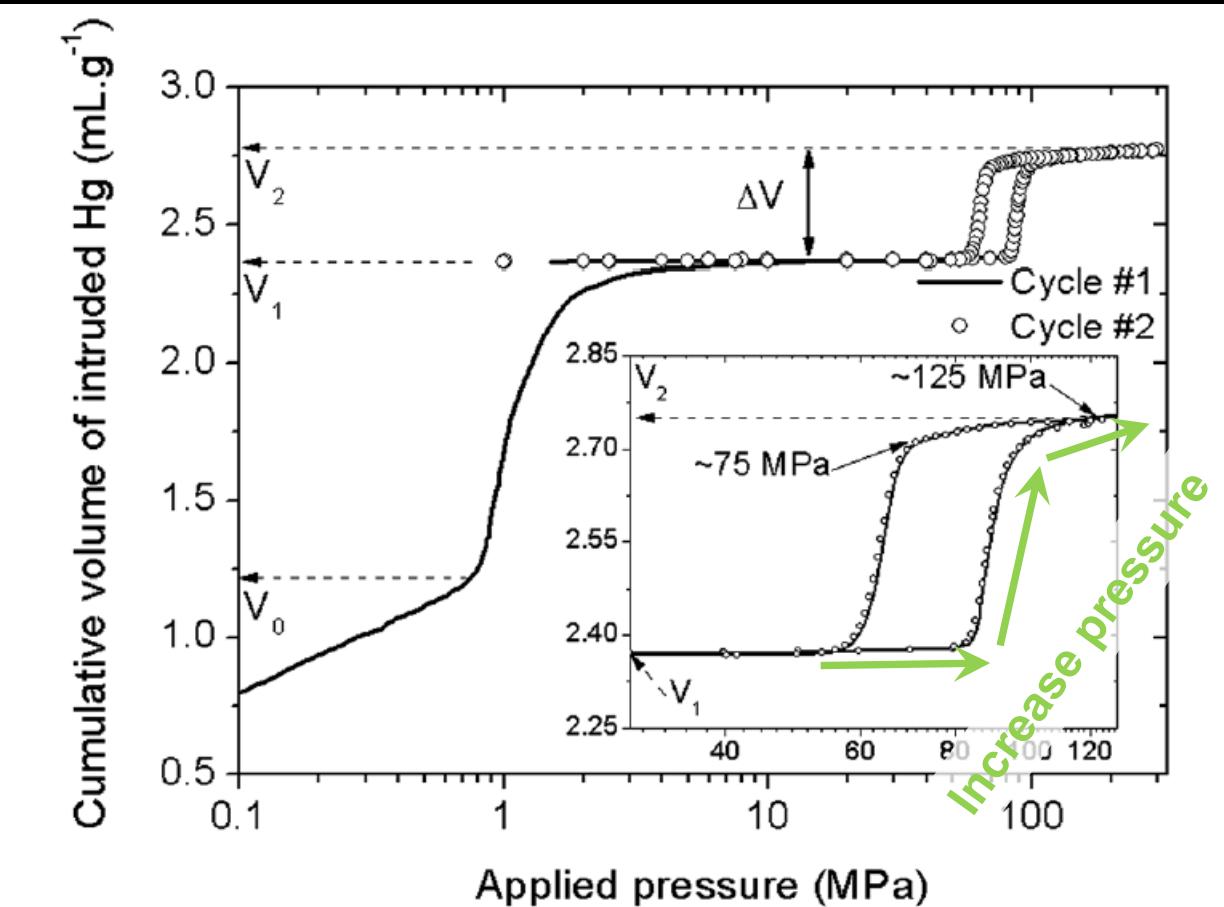
	Large Pore		Narrow Pore	
	$E_0$ [meV]	$B_0$ [GPa]	$E_0$ [meV]	$B_0$ [GPa]
FM	0	5.95	0 (+13 vs LP)	2.84
AF1	-16	6.14	-10	2.83
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AF3	-278	8.12	-167	2.46



Beilstein J. Nanotechnol. 5, 1738-1748 (2014)

mm

# MIL-47(V) under pressure

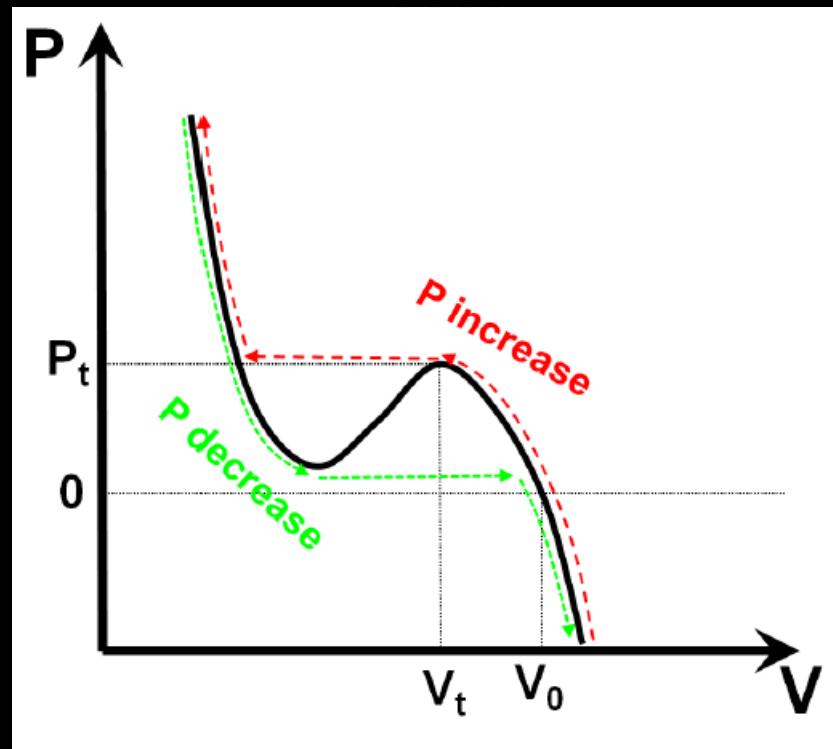


**Fig. 1** Cumulative volume of intruded mercury in a two cycles intrusion-extrusion as a function of the applied pressure obtained for the MIL-47(V<sup>IV</sup>) sample.

Yot et al., Chem. Sci. 3, 1100-1104 (2012)

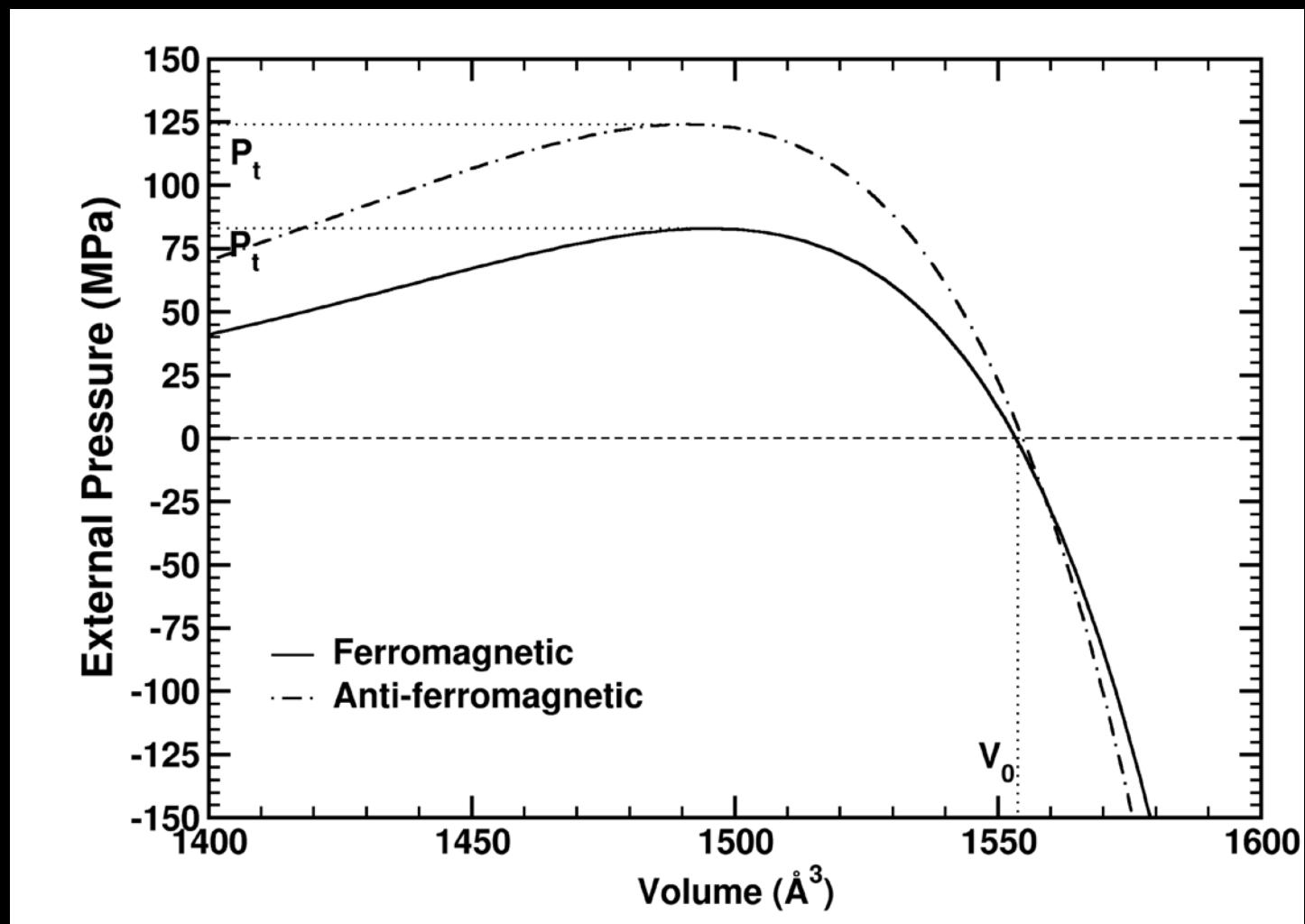


# Spin configurations vs. the world





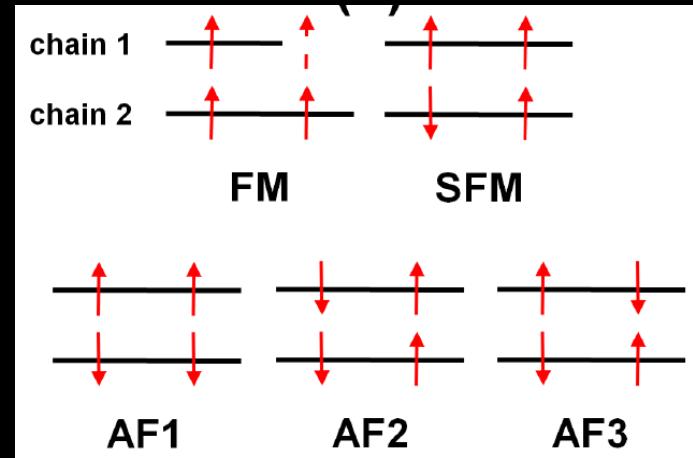
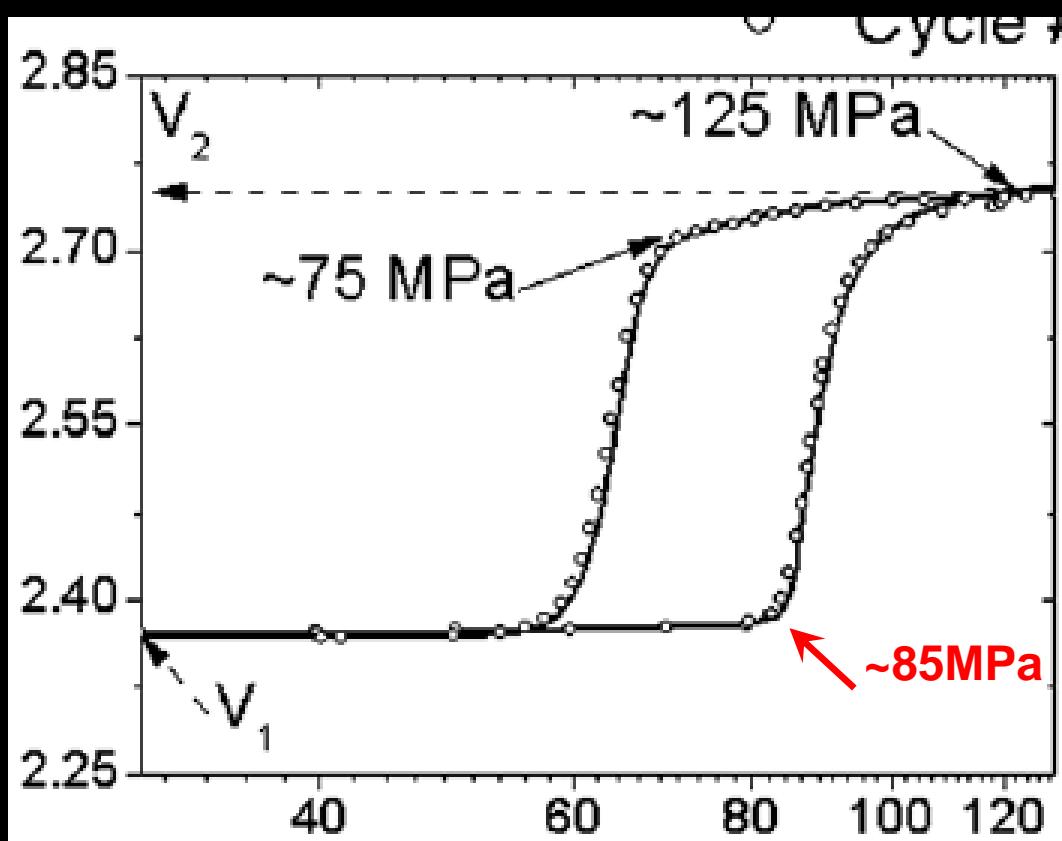
# Spin configurations vs. the world



Beilstein J. Nanotechnol. 5, 1738-1748 (2014)



# Spin configurations vs. the world

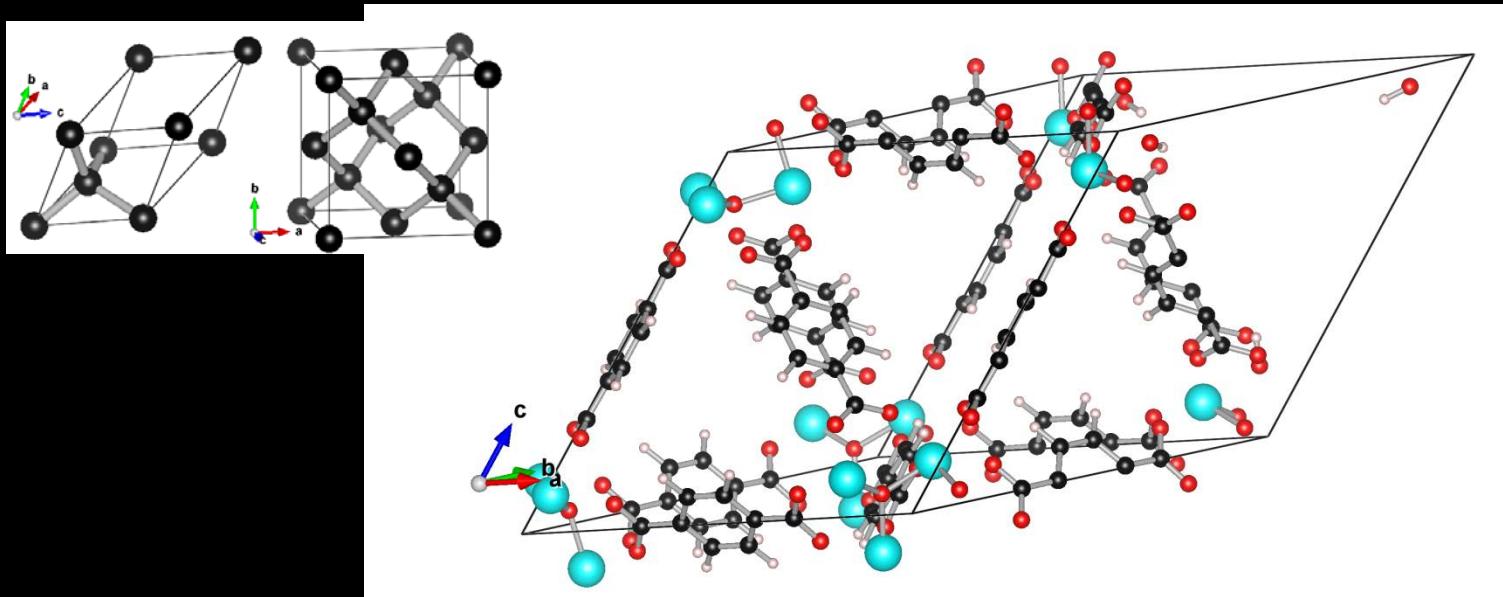


	$P_t$ [MPa]	$V_t$ [A <sup>3</sup> ]
FM	83	1495.3
AF1	82	1498.5
SFM	102	1495.5
AF2	124	1490.7
AF3	124	1490.7

→ Spin visible in experiments

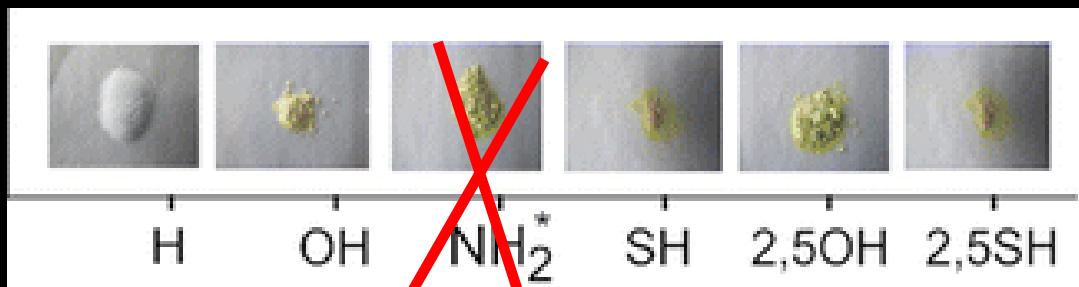


# UiO-66(Zr): BG-tuning for luminescence



Primitive unit cell: 1 cluster + 6 linkers  
(~120 atoms =  $\frac{1}{4}$  conventional cell)

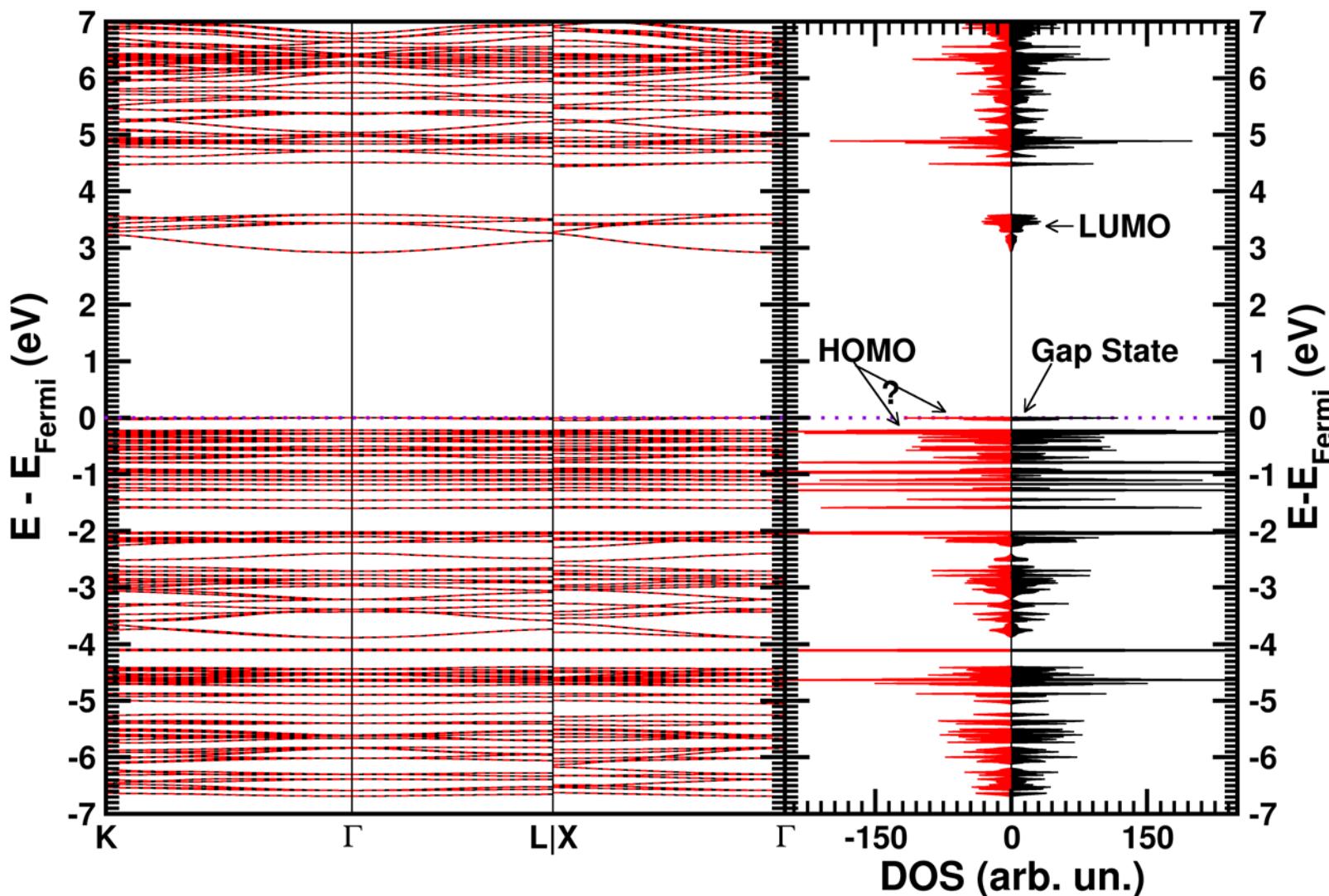
Functionalization:



Inorg. Chem. 54(22), 10701-10710 (2015)



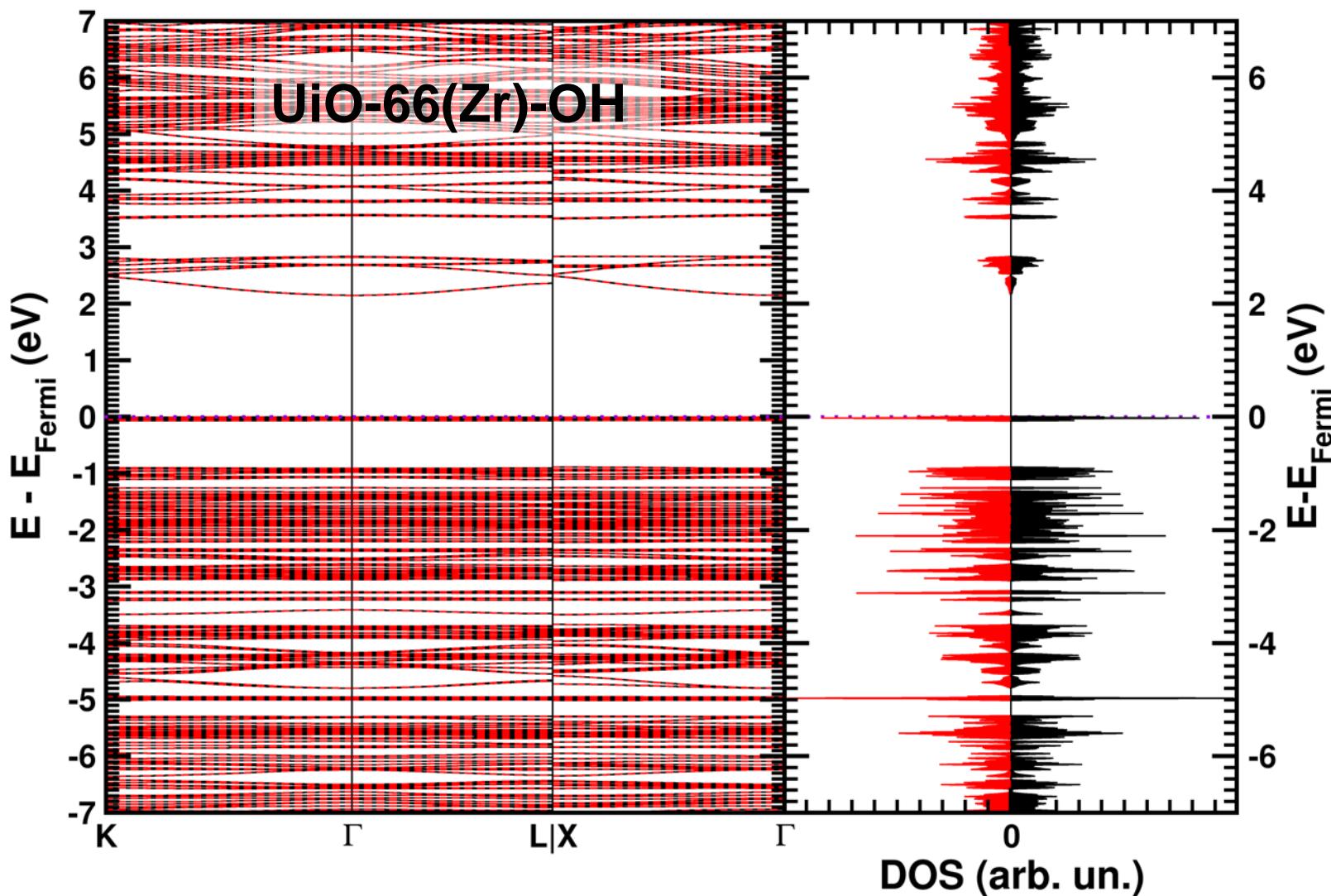
# .... Eppur si muove



Inorg. Chem. 54(22), 10701-10710 (2015)



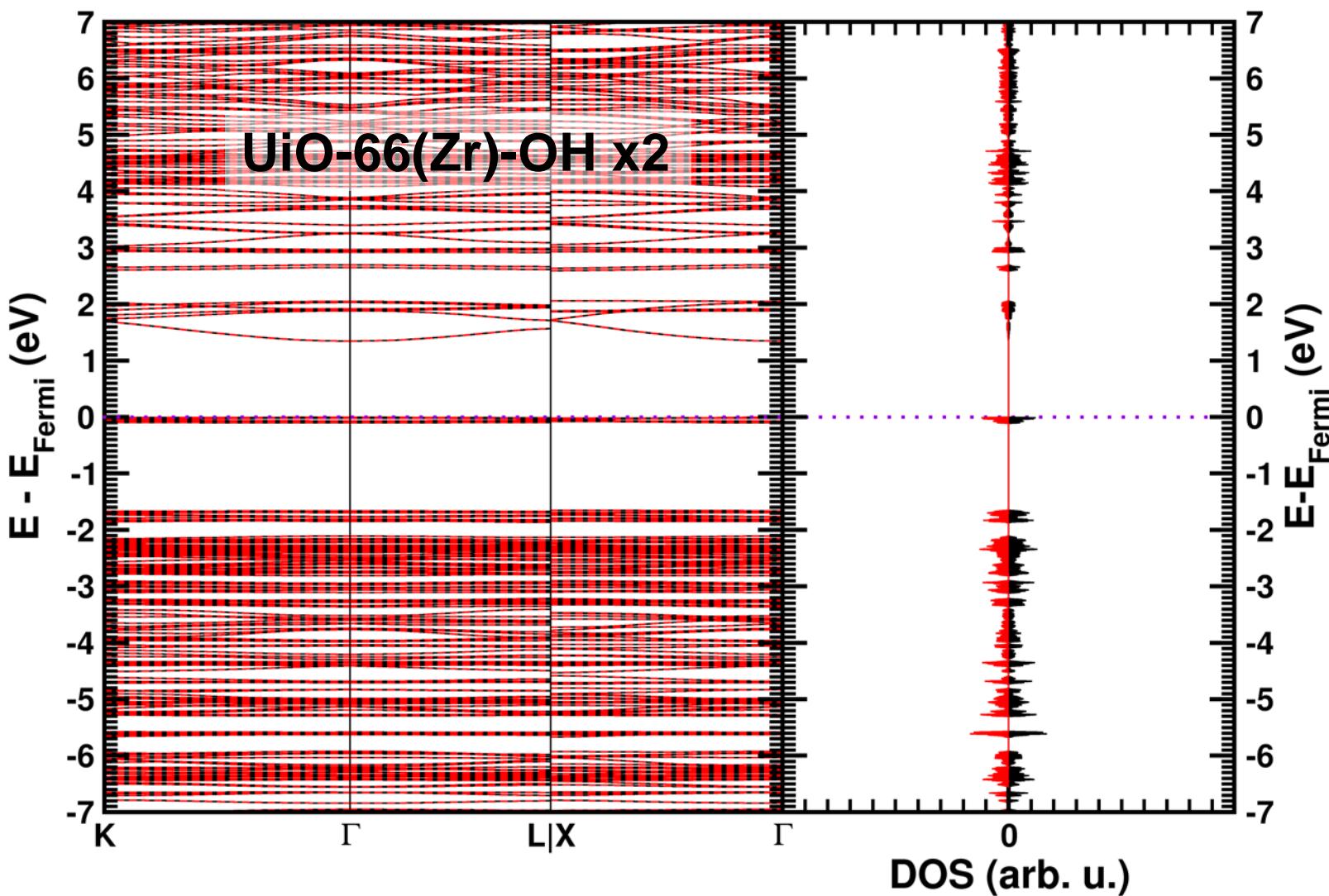
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Inorg. Chem. 54(22), 10701-10710 (2015)



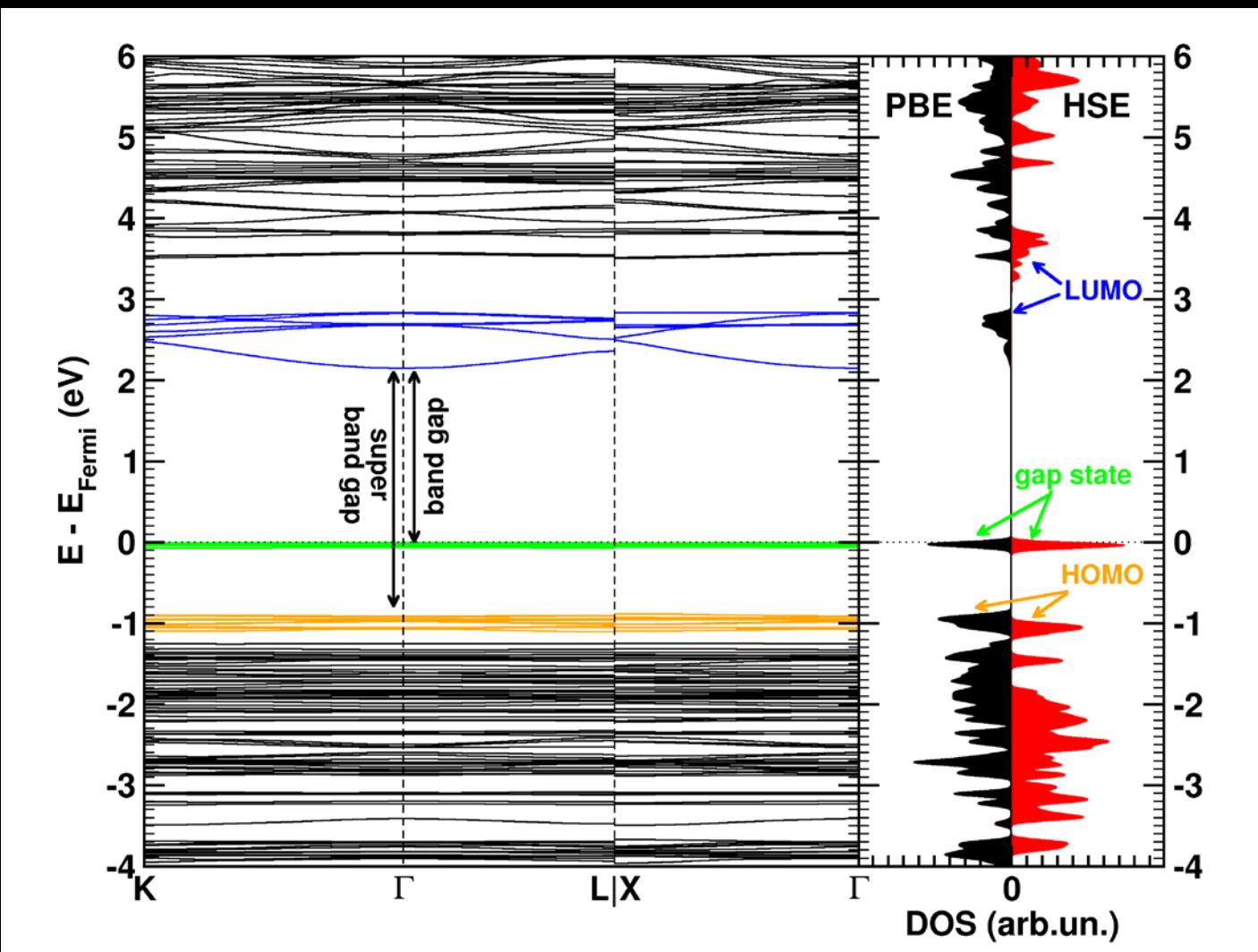
# ... Eppur si muove



Inorg. Chem. 54(22), 10701-10710 (2015)



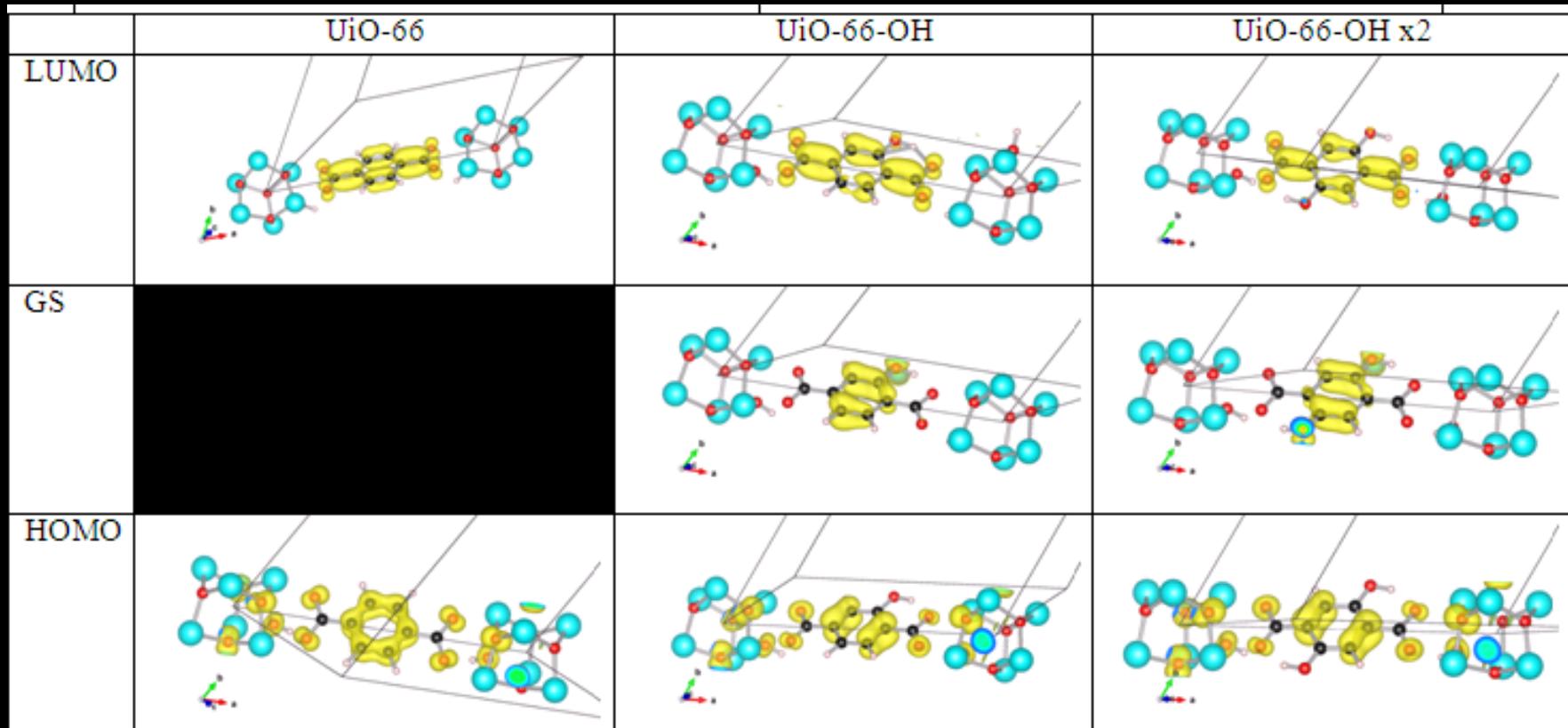
# Valence & Conduction bands



Inorg. Chem. 54(22), 10701-10710 (2015)



# Valence & Conduction bands



Inorg. Chem. 54(22), 10701-10710 (2015)



# BG tuning...and experiment

	PBE		HSE06		Exp.
	Band gap (eV)	Gap State width	Band gap (eV)	Gap State width	Band gap (eV)
UiO-66	2.920	0.040	4.030	0.100	3.97
UiO-66-OH	2.150	0.070	3.010	0.200	3.21
UiO-66- OHx2	1.350	0.100	2.150	0.220	2.54
UiO-66-SH	1.850	0.220	2.661	0.350	2.63
UiO-66- SHx2	1.331	0.230 & 0.220	2.101	0.360 & 0.350	-

Inorg. Chem. 54(22), 10701-10710 (2015)



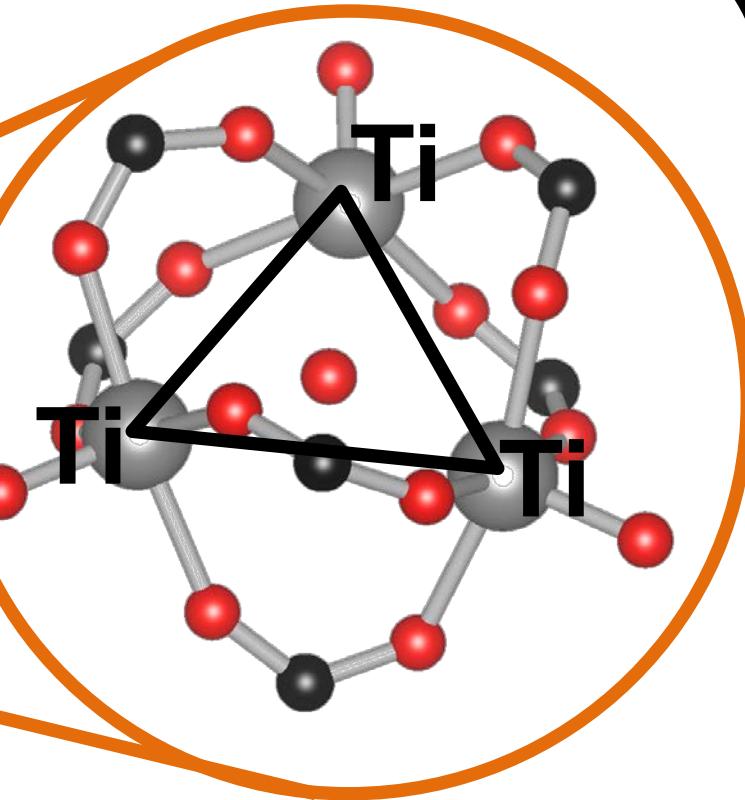
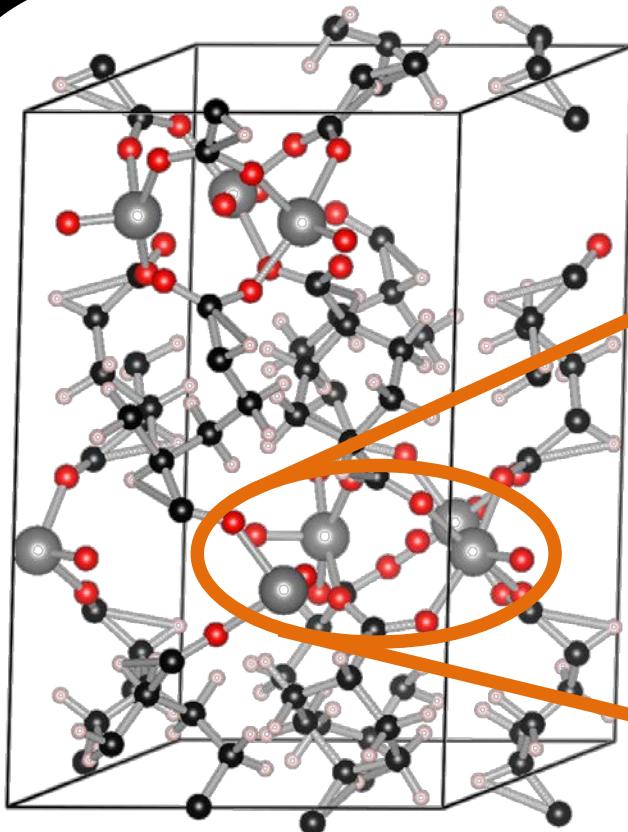
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UiO-66- SHx2	1.331	0.230 & 0.220	2.101	0.360 & 0.350	-

Inorg. Chem. 54(22), 10701-10710 (2015)



# COK-69: Ti<sup>3+</sup> luminescence



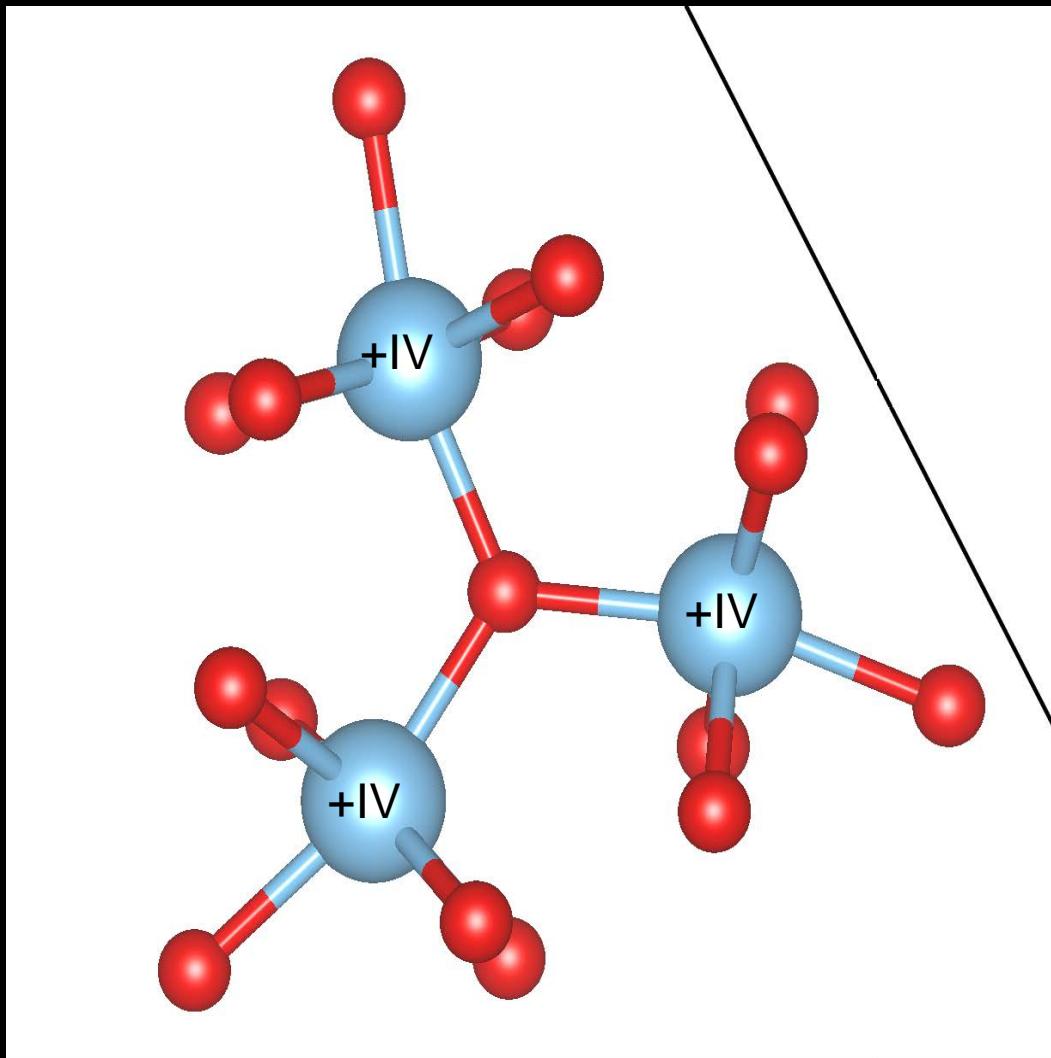
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Angew. Chem. Int. Ed 54, 13912-13917 (2015)

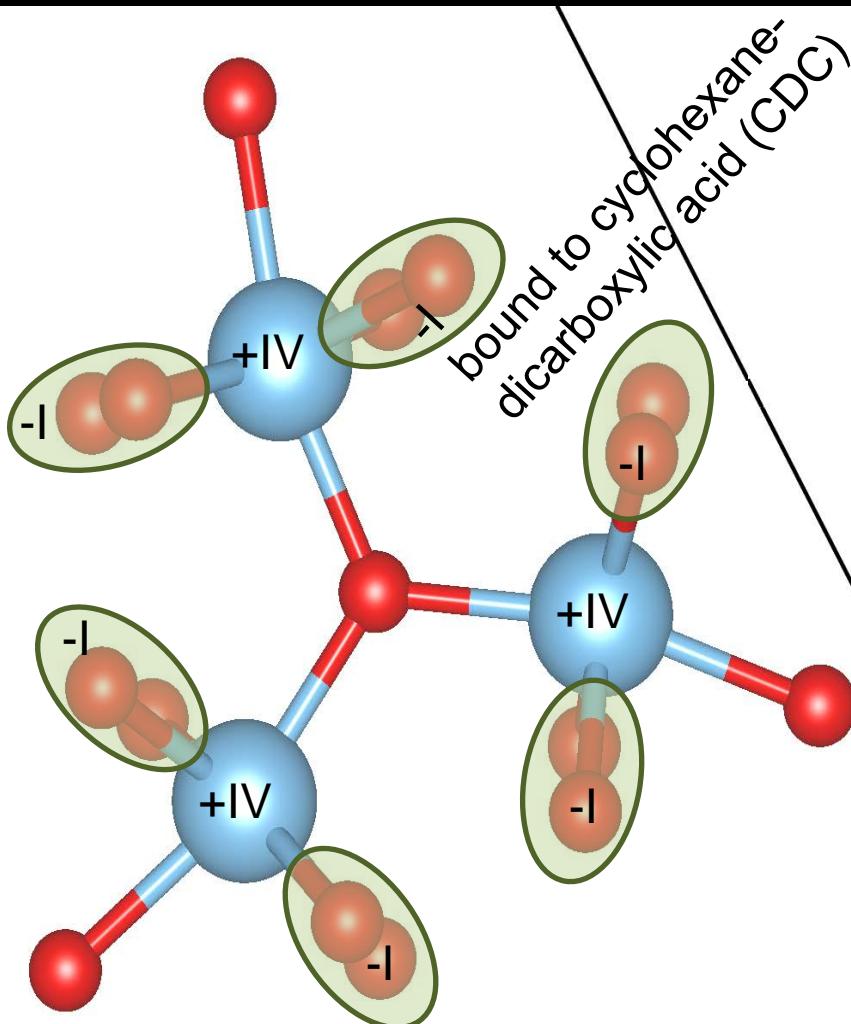


# Where's Hydrogen: COK-69



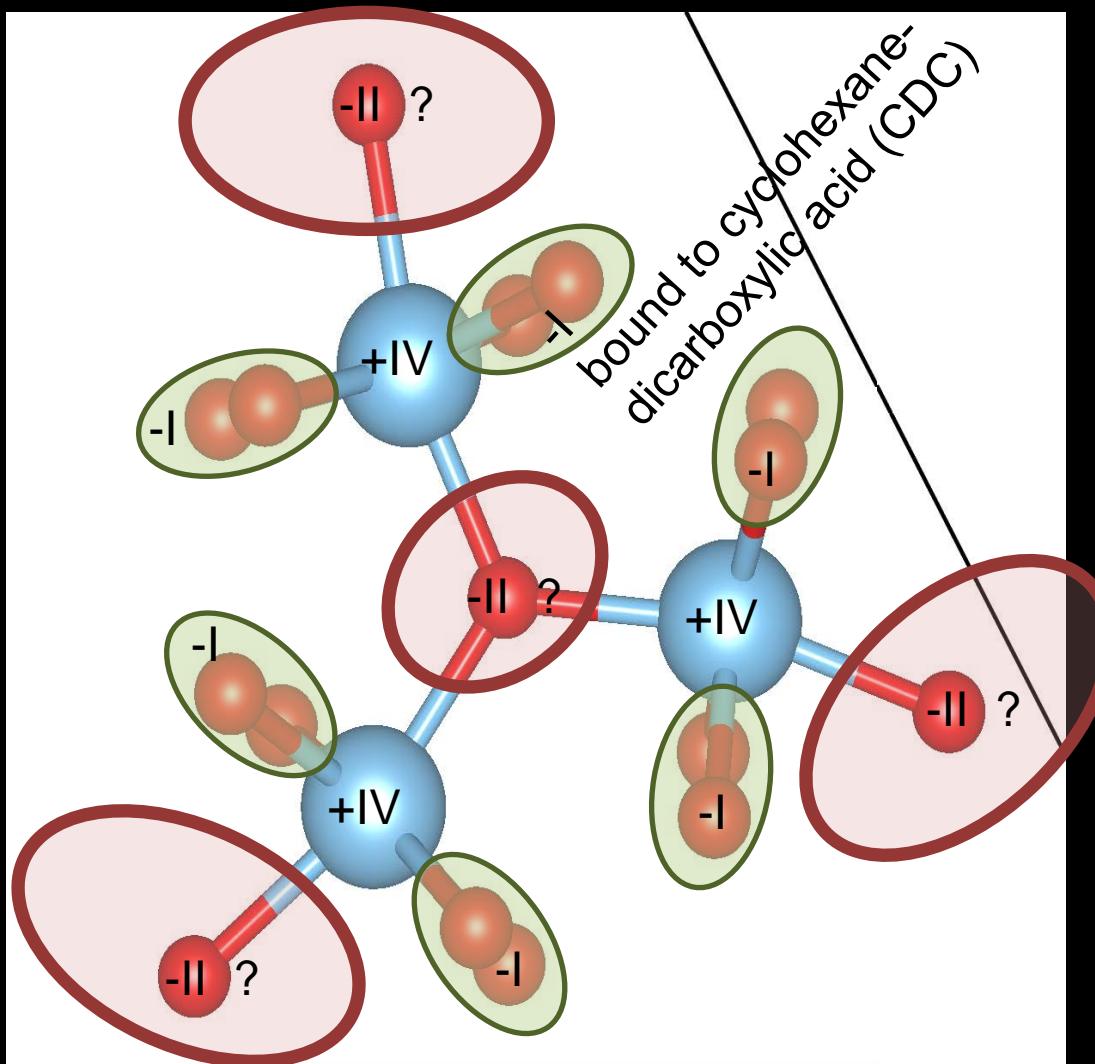


# Where's Hydrogen: COK-69





# Where's Hydrogen: COK-69

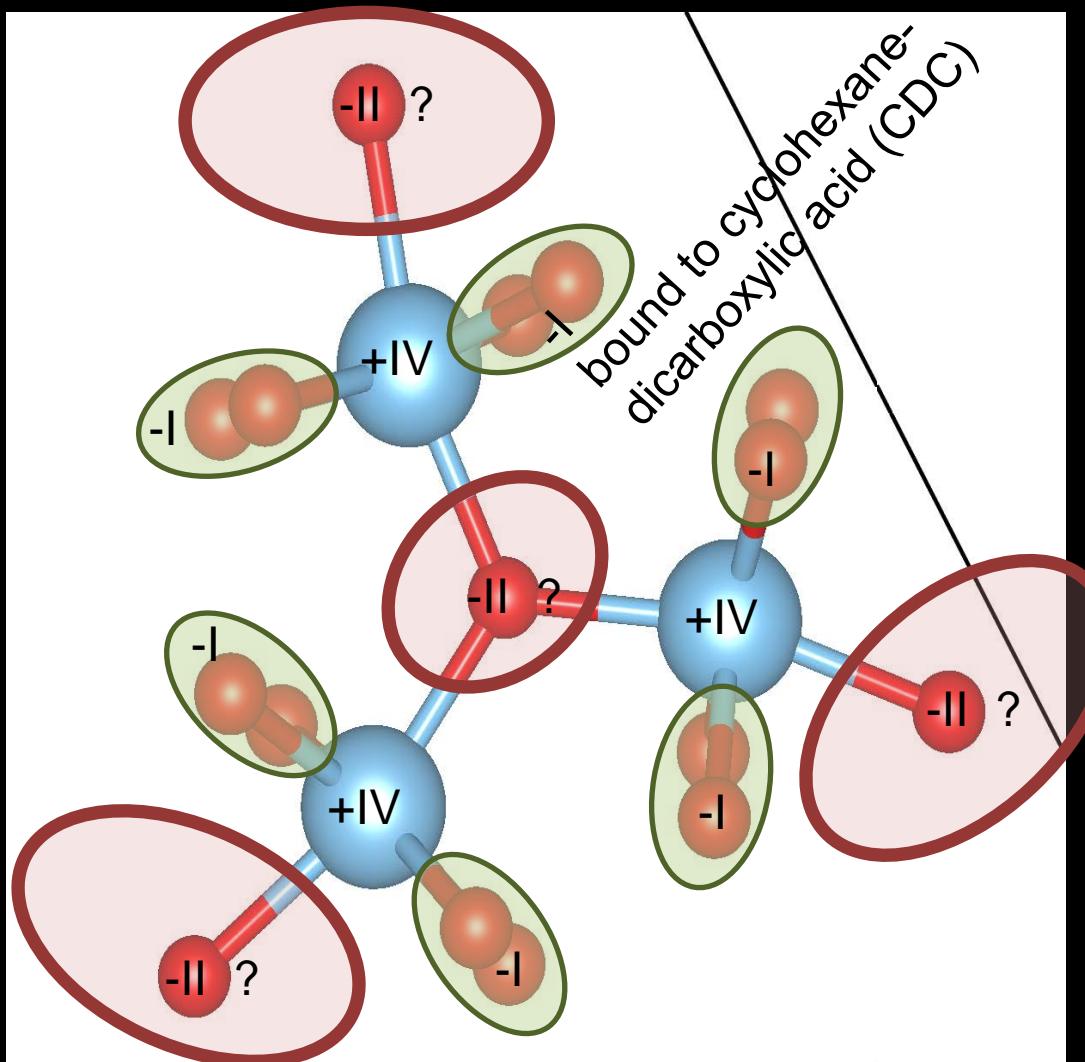


**Ti-O cluster**

**Formal Charge: -II**



# Where's Hydrogen: COK-69



## Ti-O cluster

Formal Charge: -II

→ Add 2x H

→ 2x OH or 1x H<sub>2</sub>O

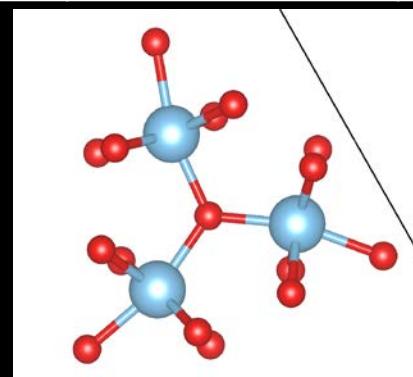
-----OR-----

→ Remove 1x O



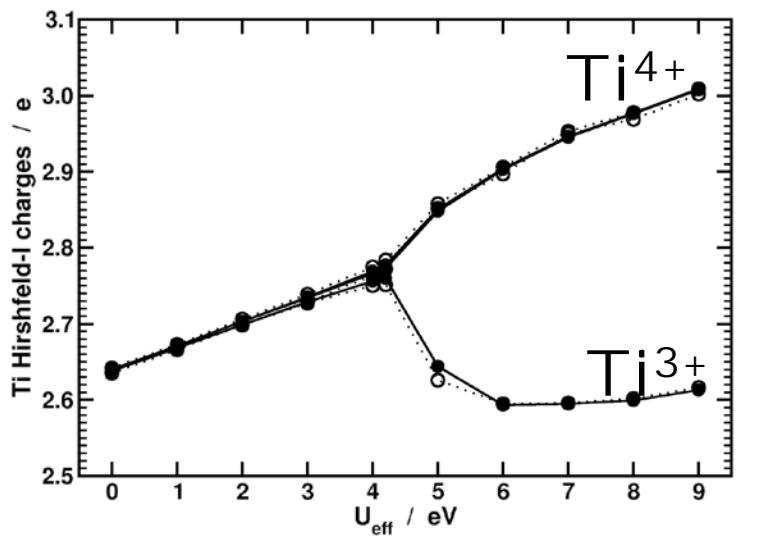
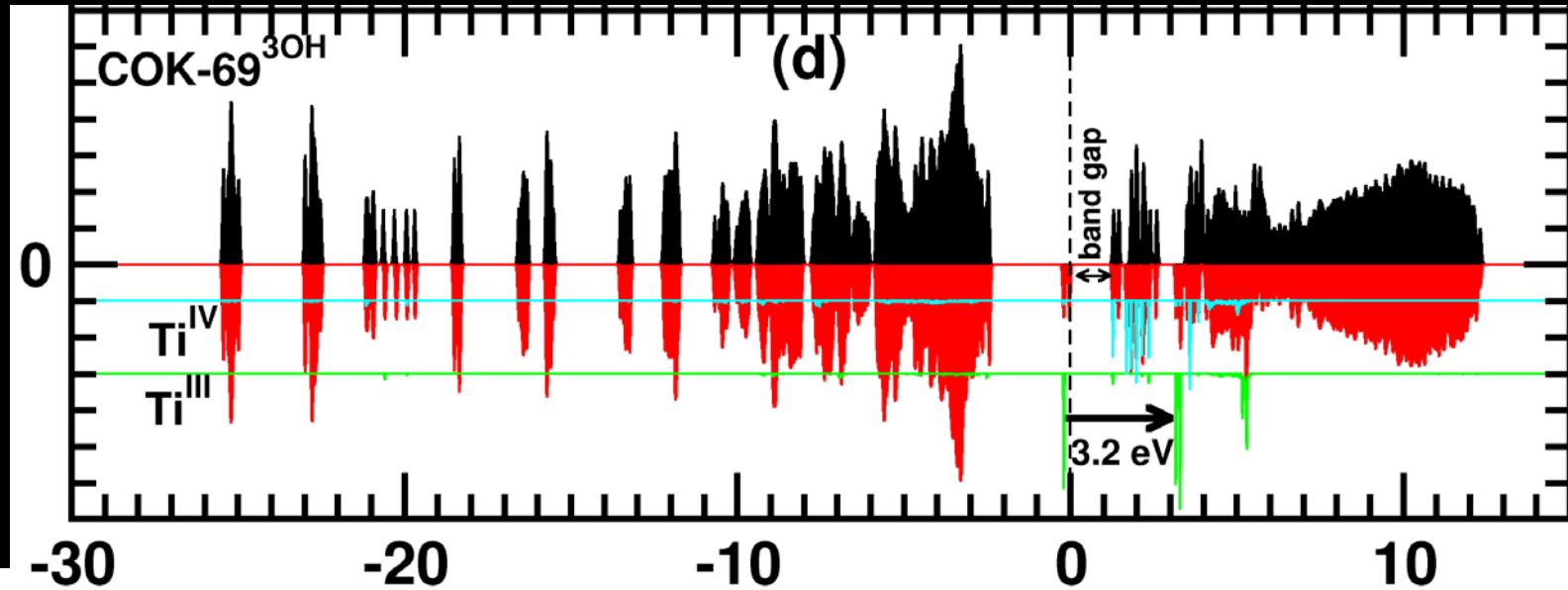
# Where's Hydrogen: COK-69

	$E_f$ (PBE)	BG (PBE)	$E_f$ (PBE+U)	BG (PBE+U)
COK-69(Ti)	0.000	0.00	0.000	0.01
- O (side)	-2.739	2.31		
- O ( $\mu_3$ )	-3.110	3.01		
+ H <sub>2</sub> O (side)	-6.054	2.43	-5.975	2.79
+ H <sub>2</sub> O ( $\mu_3$ )	-4.792	2.69		
+ 2x OH	-5.821	2.22	-6.307	2.60
+ 3x OH	-6.430	0.60	-7.499	1.78





# Atoms in MOF's: Ti<sup>3+</sup> luminescence



$E - E_{\text{Fermi}}$  (eV)

Calculated Hirshfeld-I charges show only differentiation of Ti<sup>3+</sup> and Ti<sup>4+</sup> at high (DFT+)U value.

Angew. Chem. Int. Ed 54, 13912-13917 (2015)

J. Comput. Chem. 34(5), 405-417 (2013)



# Acknowledgements

## CMM

- Stijn De Baerdemacker
- Jan Jaeken
- Veronique Van Speybroeck

## COK

- Bart Bueken
- Dirk De Vos

## COMOC

- Kevin Hendrickx
- Pascal Van Der Voort

Financial support and technical support:



Research Foundation  
Flanders  
Opening new horizons



That's all Folks!  
Any Question?

# More ...



## Condensed Matter Science in Porous Frameworks: On Zeolites, Metal- and Covalent-Organic Frameworks

Metal-Organic Frameworks, Covalent-Organic Frameworks and Zeolites are three classes of highly porous materials which have received an exponentially growing interest over the last decade. While the first two consist of molecular linkers connected through metal(oxide) or non-metal nodes, the later consists of silicon-oxide based clusters and have a uniform well defined framework. Due to their modular nature, they are highly tuneable allowing for the active design of materials having specific catalytic properties, luminescent or magnetic behaviour. The presence of mechanical properties (such as breathing) is another interesting aspect of some of these materials, while the combination of different properties makes them of interest for sensor-applications. In addition, fine tuning the porosity allows for the use of these materials in sorption and separation processes.

Developments in computational methods and the evolution of computational resources have made these materials also accessible for theoretical approaches, leading to new insights in these materials and the ability to guide the experimental design towards new porous frameworks.

### Call for abstracts

We invite both experimental and theoretical researchers studying porous frameworks to submit abstracts for both oral and poster contributions to this colloquium at the CMD26 conference. We invite experimental researchers to present their newly synthesized porous frameworks and investigations of the tuneability of porous frameworks. Theoretical researchers are invited to present their work leading to new and deeper understanding of porous frameworks at the level of their underlying physics and chemistry, but also their predictions of new porous frameworks with interesting physical properties. The colloquium will consist of three sessions focussing on MOFs, COFs and Zeolites respectively, and aims for equal contributions from theoretical and experimental researchers.

### Time and Place

The colloquium is part of the CMD26 – Condensed Matter Conference, taking place in the MartinPlaza Conference Centre in **Groningen, The Netherlands** on September 4<sup>th</sup>-9<sup>th</sup>, 2016.

### Best Poster Prize

The best poster prize will recognize the high quality of the research presented in poster format, and will be awarded to the presenting author. All posters presented within the symposium are eligible.

### More information

- CMD26: <http://cmd26.eu>
- Registration: <http://cmd26.eu/registration/>
- Abstract Submission: <http://cmd26.eu/abstract-submission/>
- CMD26 Colloquia: <http://cmd26.eu/scientific-programme/>

### Colloquium sponsors



← Colloquium on Porous Frameworks  
@ CMD26, September 4<sup>th</sup> – 9<sup>th</sup>  
Groningen, The Netherlands.  
(Early bird registration June 20<sup>th</sup>)

→ Indeterminism in Newtonian physics:  
a quest for probabilities

Sylvia Wenmackers @16h30  
(Statistical & Mathematical Physics)