CHEMICAL MODELING TO DESIGN A SUSTAINABLE ENERGY FUTURE

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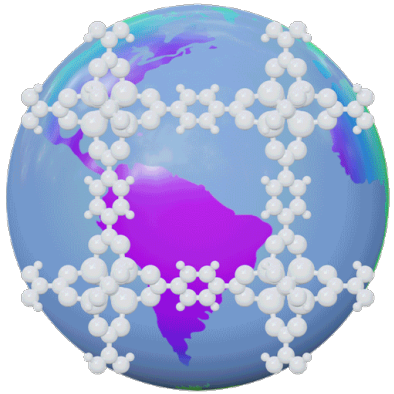


Accademia dei Lincei

November 12, 2021

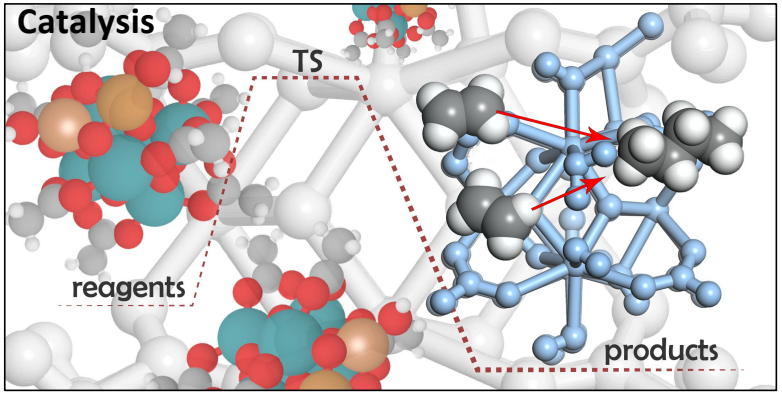
My Career Path

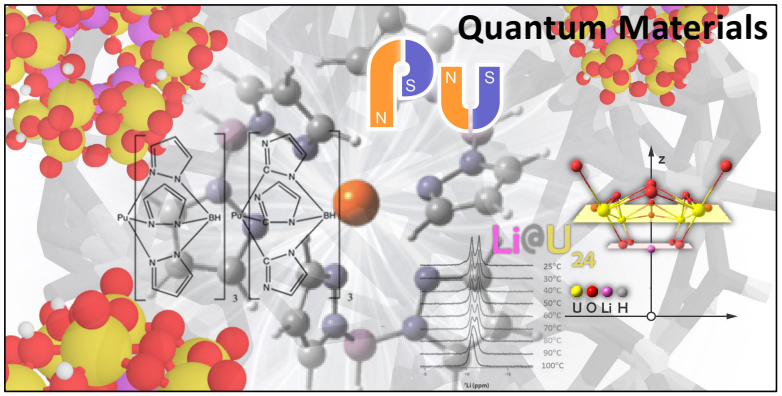
- Undergraduate and graduate studies University of Bologna

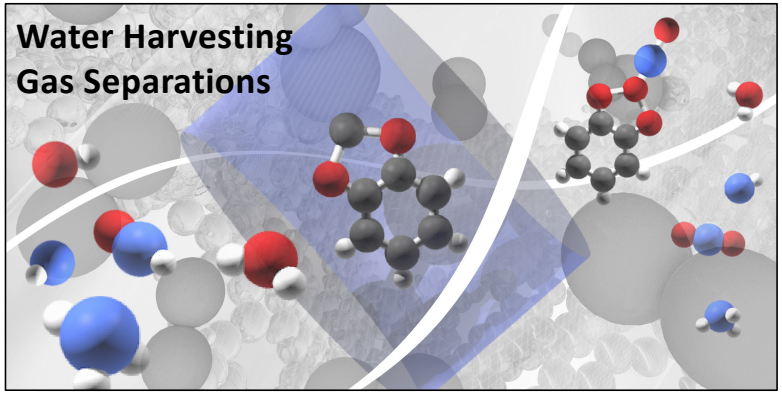
  PhD in theoretical chemistry 1993-1997 (Gian Luigi Bendazzoli and Paolo Palmieri)

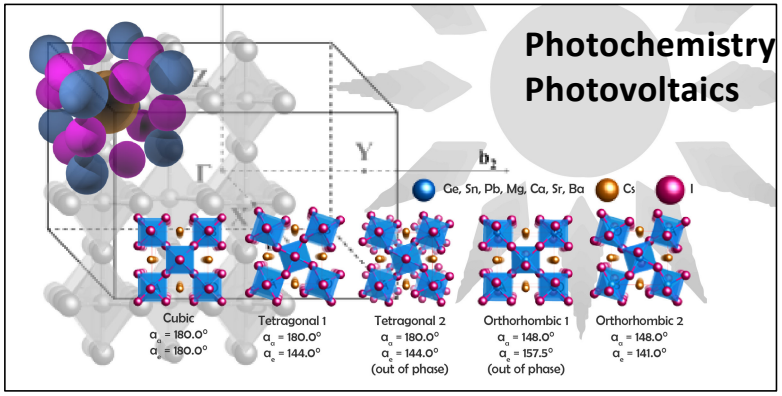
- Postdoctoral associate Cambridge UK 1998-1999 (Nicholas Handy)
- Ricercatore Palermo 2000-2005
- Associate professor Geneva Switzerland 2005-2008
- 2009-2020: Professor University of Minnesota
- 2020-present: Professor University of Chicago

Develop **Novel Quantum Chemical Methods** and Study Phenomena Related to **Sustainable Energies**

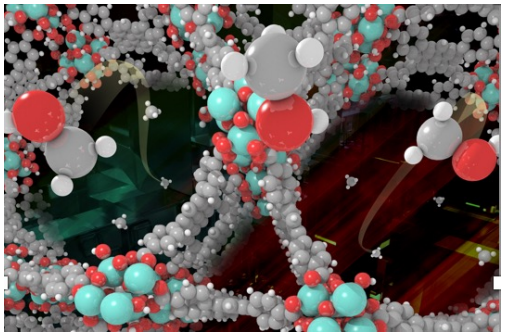


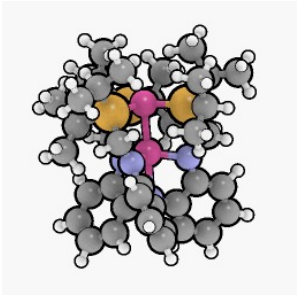






Near-Degeneracy Electron Correlation Effects in Extended Systems





A balanced quantum mechanical treatment of systems with near degeneracies of electronic states requires a multiconfiguration wave function.

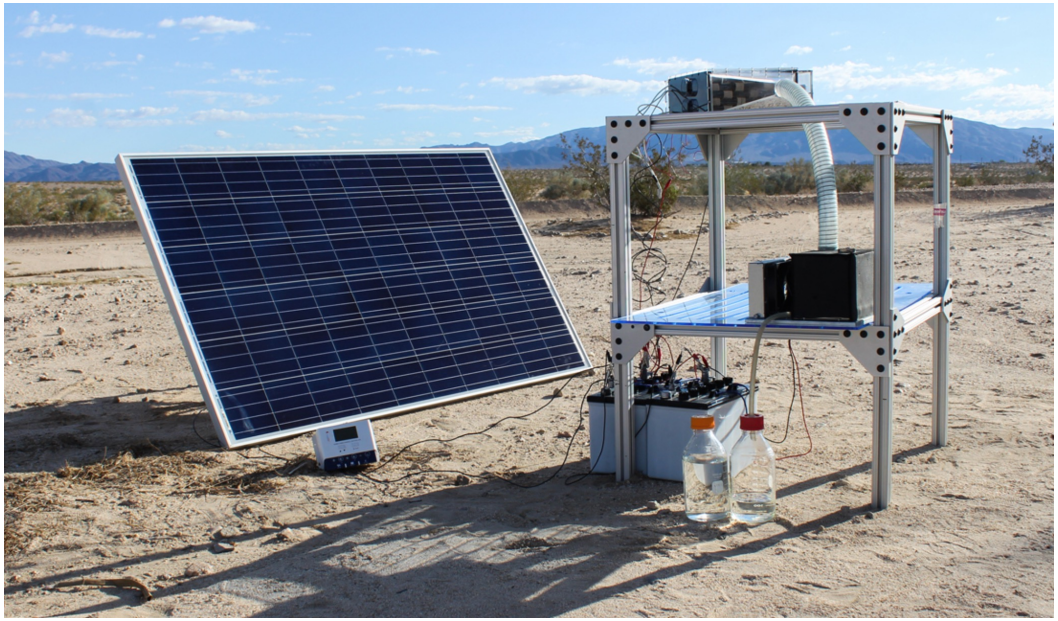
Conventional methods for such wave functions are not well suited for extended systems.

Long-term Goal: ***develop new methodologies for strongly correlated, extended systems.***

Combine them with data science.

Develop theories and algorithms for quantum computers.

Metal-Organic Frameworks for Atmospheric Water Harvesting

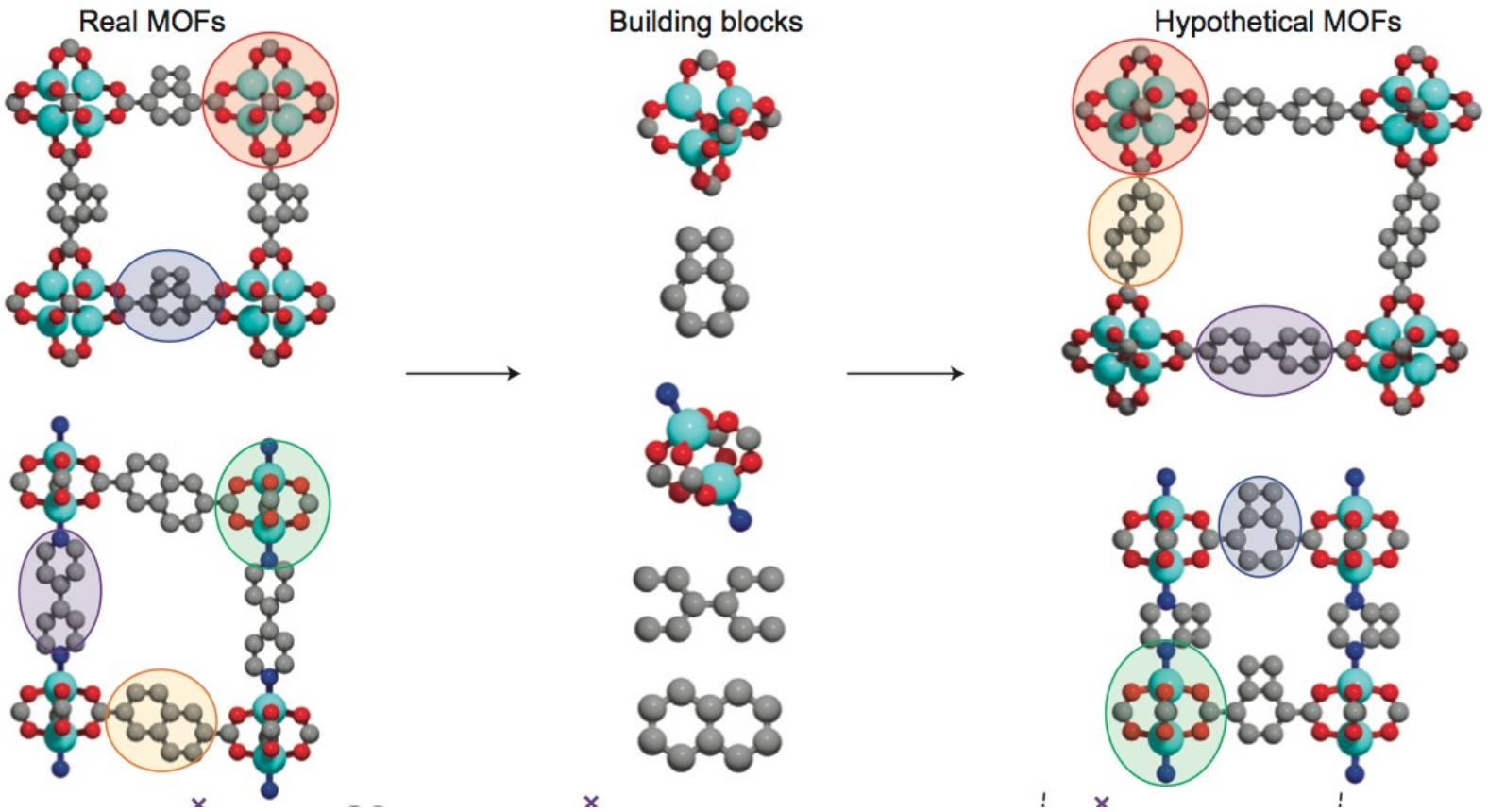


- Metalorganic frameworks (MOFs) can extract atmospheric water in the desert to produce potable water
- How do such MOFs “pluck out” water from arid air and easily release it, on the molecular level?

https://www.science.org/content/article/crystalline-nets-harvest-water-desert-air-turn-carbon-dioxide-liquid-fuel

In collaboration with Omar Yaghi, Joachim Sauer and GE (DARPA)

Why Do Theorists Love MOFs?



137,000 Hypothetical Structures

Wilmer et al. *Nature Chem.* 4 (2), 83-89, 164, (2012)

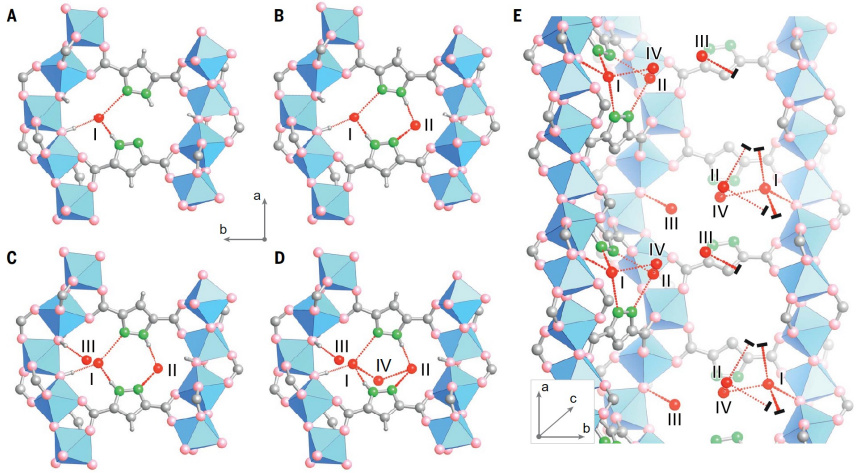
Evolution of Water Structures in MOFs

The mechanism of how water-binding sites are populated is hard to decipher.

It requires high quality data and the ability to collect these data at each loading increment.

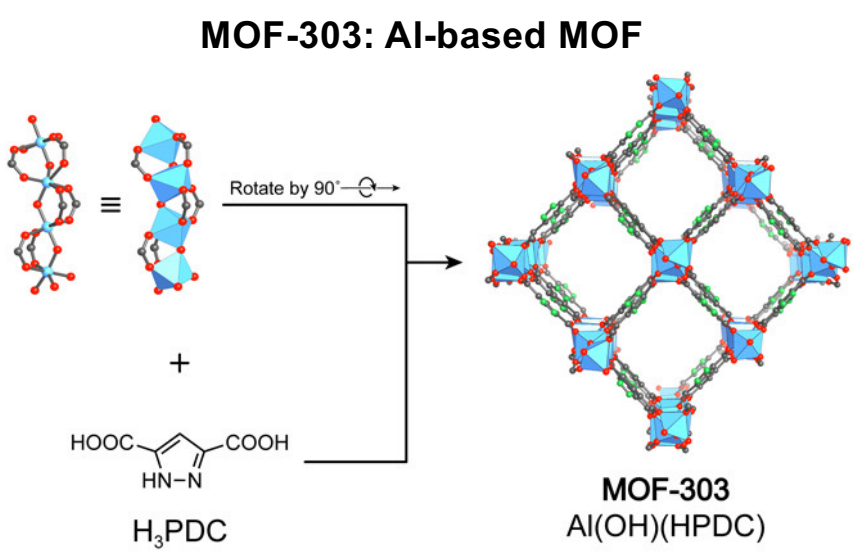
Knowledge of the mechanism for water behavior in MOFs should enable the design of water-harvesting systems that can operate with greater energy efficiency and productivity.

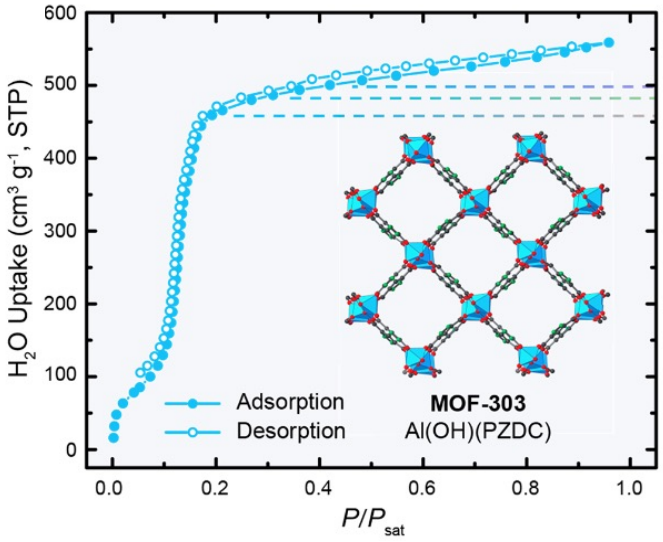
Theory can help understanding how water binds and predict new systems!



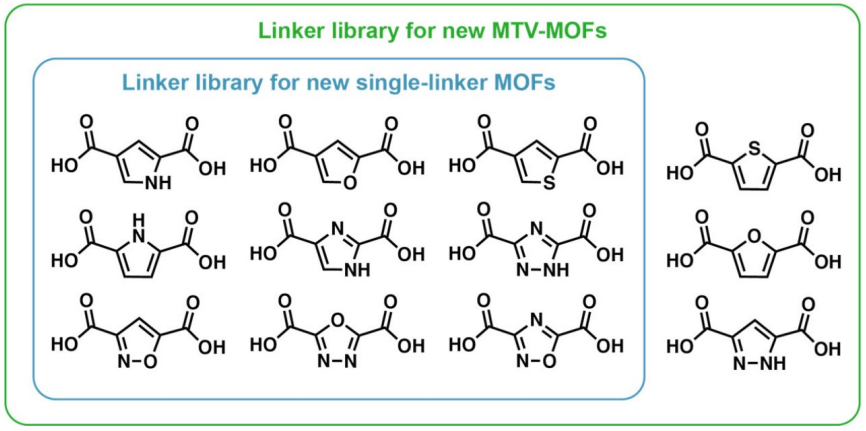
In collaboration with Omar Yaghi, Joachim Sauer and GE (DARPA)

Enhancing the Water Uptake in MOF-303 Architecture





- Rod-like Al(OH)(-$COO)_2$ units + 1H-pyrazole-3,5-dicarboxylate linker
- Hydrophilic 1D pores with 6 Å diameter and 0.54 cm^3/g free pore volume
- Max. water capture capacity of 0.48 g/g



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Hanikel N., …, Yaghi O., ACS Cent. Sci. 2019, 5, 10, 1699–1

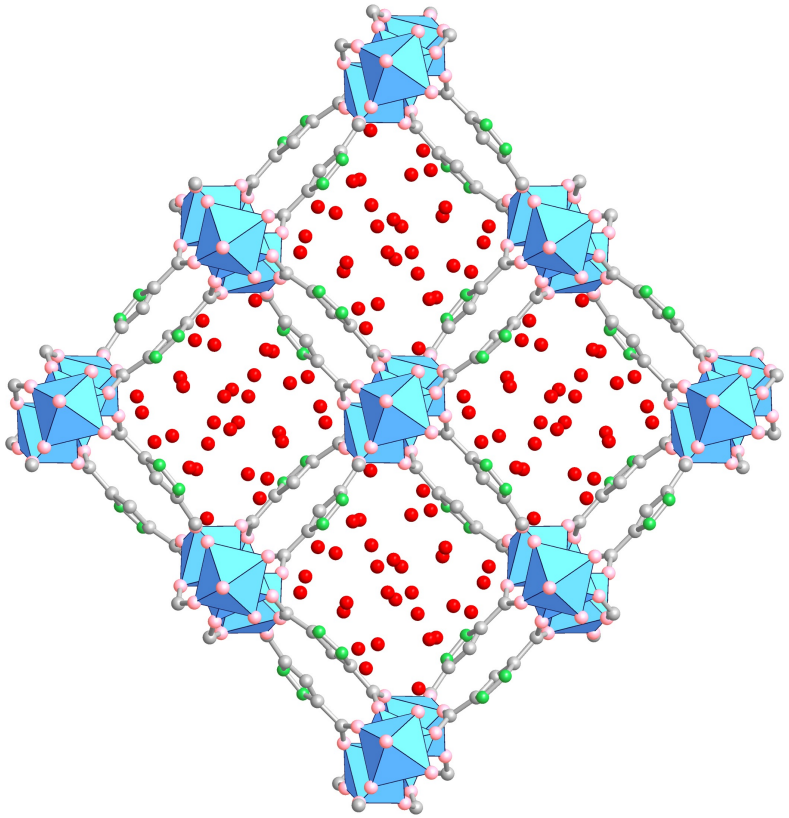
Understanding the Water Uptake Mechanism in MOF-303

All water molecules were located in the pores using single-crystal x-ray diffraction (SXRD) and computations independently.

The molecule-by-molecule sequence of filling these locations was identified.

Organic linkers play a primary role as adsorptive sites in MOF-303.

They are aligned to create hydrophilic pockets into which the first water molecules bind strongly and seed further uptake.



Hanikel et al., LG Science 374, 454–459 (2021)

Computational Modeling of the Water Uptake in MOF-303

- **First layer** water adsorption sites in MOF-303 (*trans linkers*): Water molecules adsorb in unique sites through H-bonds with node hydroxy and linker pyrazole groups

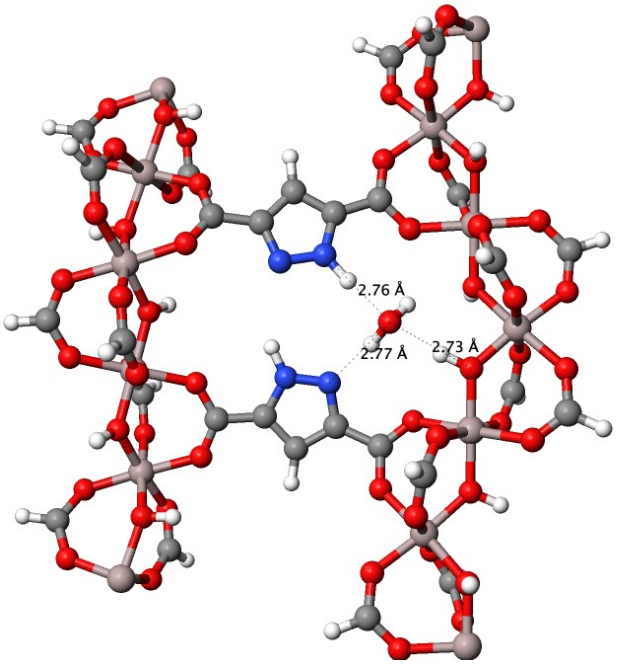
1st site

$\Delta E = -81.8\ kJ/mol$

3 contacts:

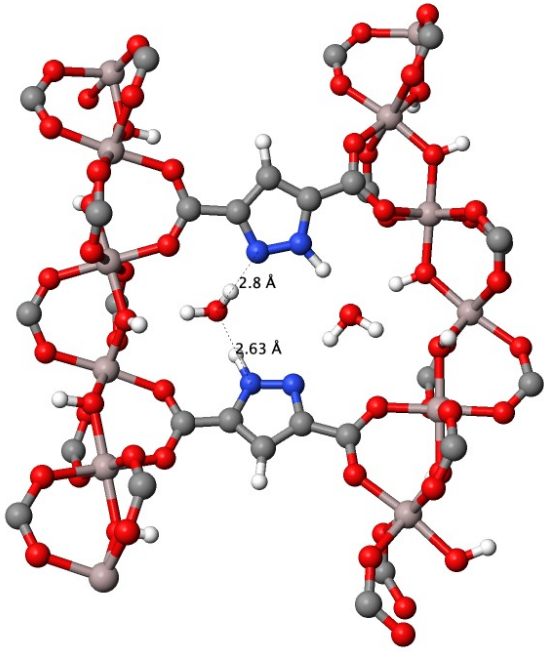
- ❑ (Al)OH(don) – 1
- ❑ NH_{linker}(don) – 1
- ❑ N_{linker}(acc) – 1

*don: donor
*acc: acceptor



1 water/per 2 Al

2nd site



2 water/per 2 Al

$\Delta E_{avg} = -80.2\ kJ/mol$

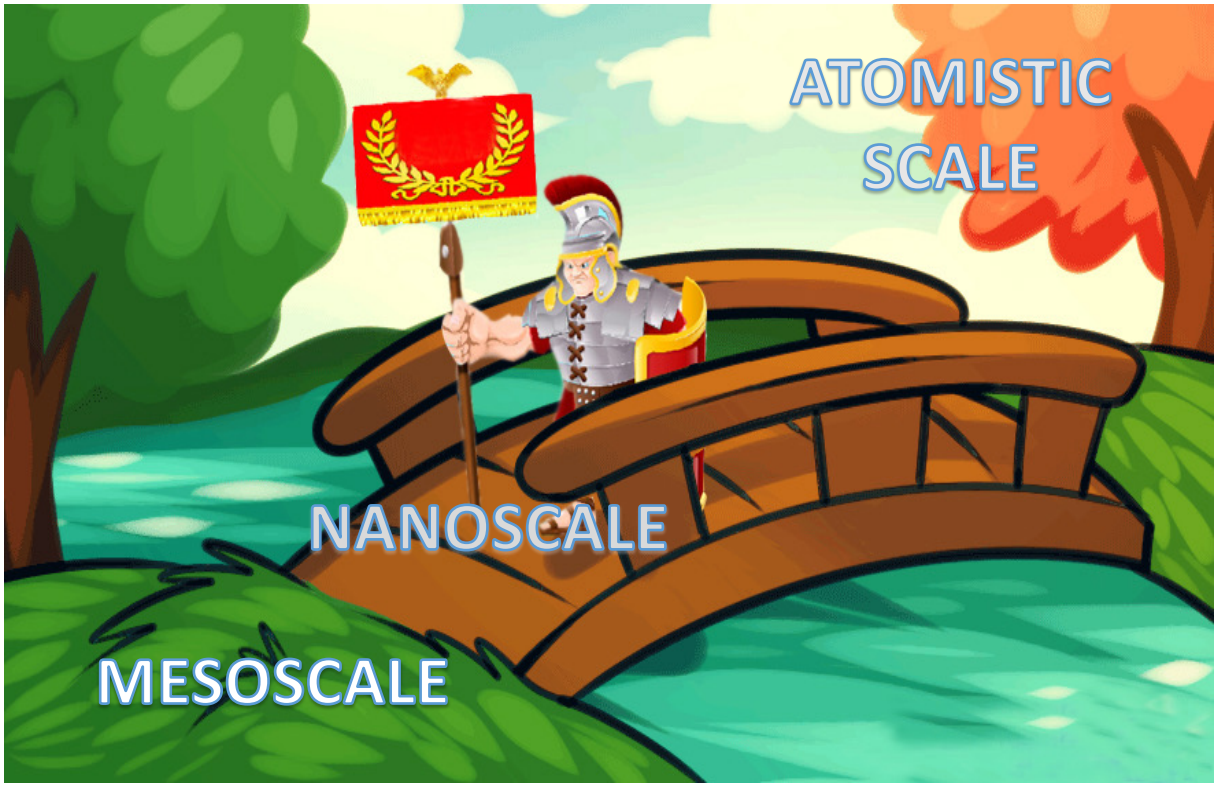
2 contacts:

- ❑ NH_{linker}(don) – 1
- ❑ N_{linker}(acc) – 1

*don: donor
*acc: acceptor

Hanikel et al., LG Science 374, 454–459 (2021)

Quo Vadis?



Courtesy of Jenny Vitillo

Take Home Messages

- To deal with complexity, it is necessary to **establish consistency between frameworks**.
- Better methods for accounting for **multi-reference effects and entanglement in molecules and solids**.
- **Better algorithms** for all of these problems and algorithms that work on computers of tomorrow.
- Develop a closed loop wholistic architecture that utilizes both **high throughput experiment and high throughput computation**.
- Enhance the **speed and fluidity of the experiment-computation collaboration**

Acknowledgments

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Omar Yaghi
UC Berkeley

Thanks to the Italian academic system.

The education that we receive in this country is outstanding!

DARPA

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