Water intrusion mechanism into ZIF-8: on the trail of water percolation through nanocages

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Granada

5th European Conference on Metal Organic Frameworks and Porous Polymers
EUROMOF
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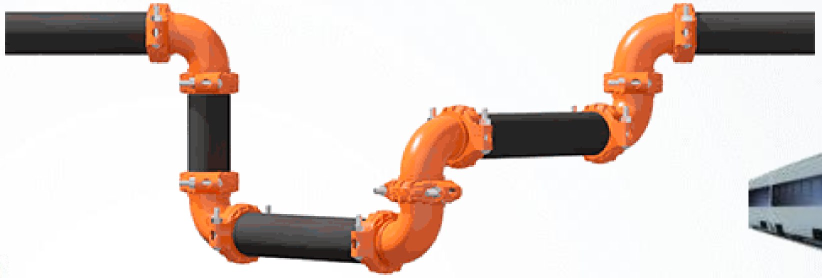
Index

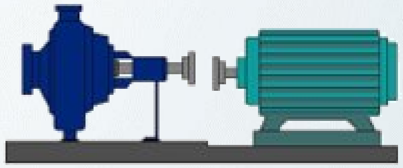
ELECTRO INTRUSION

1. Introduction

Mechanical energy dissipation, storage and conversion

Source: The bridge tank



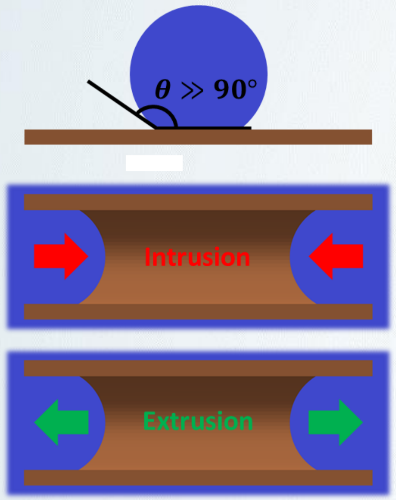


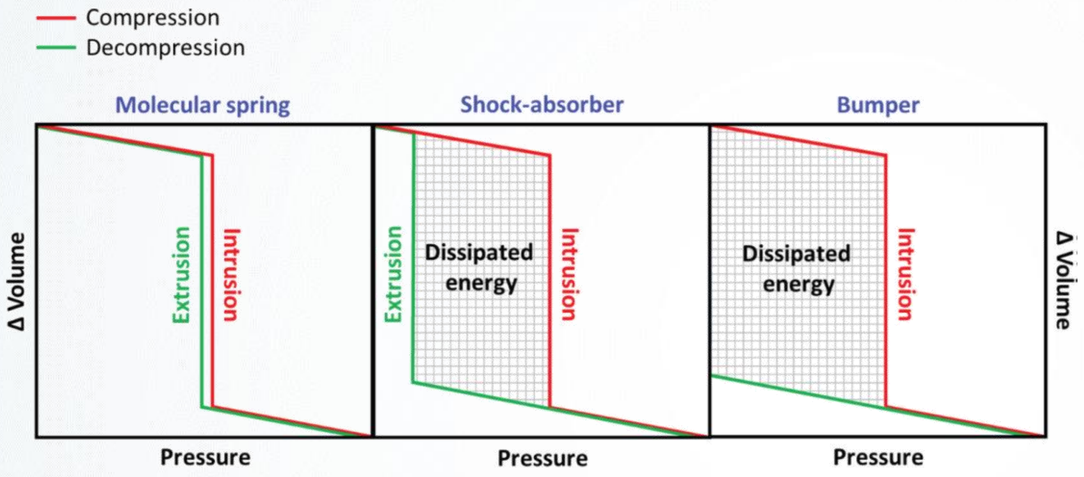
✓ Mechanical energy is wasted every day. Let’s use it as an energetic resource

ELECTRO INTRUSION

1. Introduction

MOFs for energy dissipation



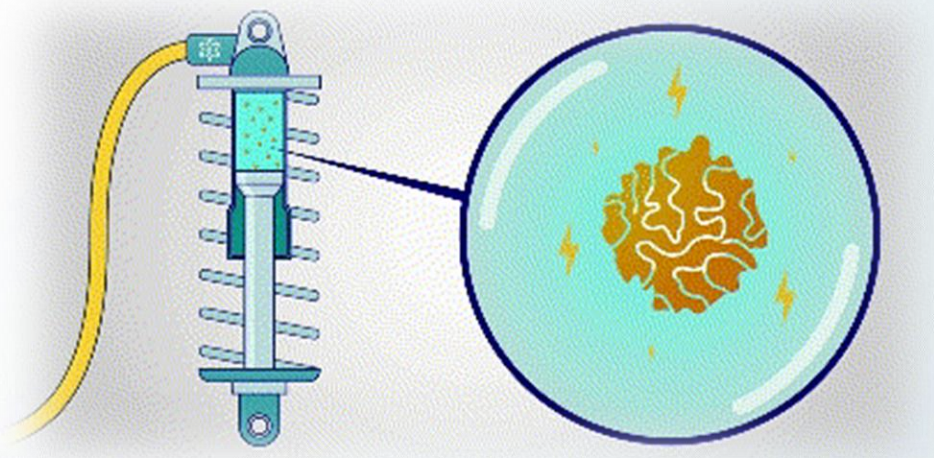


A. Le Donne et al., *Advances in Physics: X*, **2022**, 7:1, 2052353

- ✓ (Super)hydrophobic materials: Contact angle >90º to enhance the Int-ext pressure
- ✓ Porous materials: Accessible pores for water intrusion and high surface areas to enhance the surface on int-ext takes place.
- ✓ Tunable structure: Different chemistry, topology… → performance optimization

Electro-Intrusion: materials for converting vibrations into electricity.

Building triboelectric nanogenerators

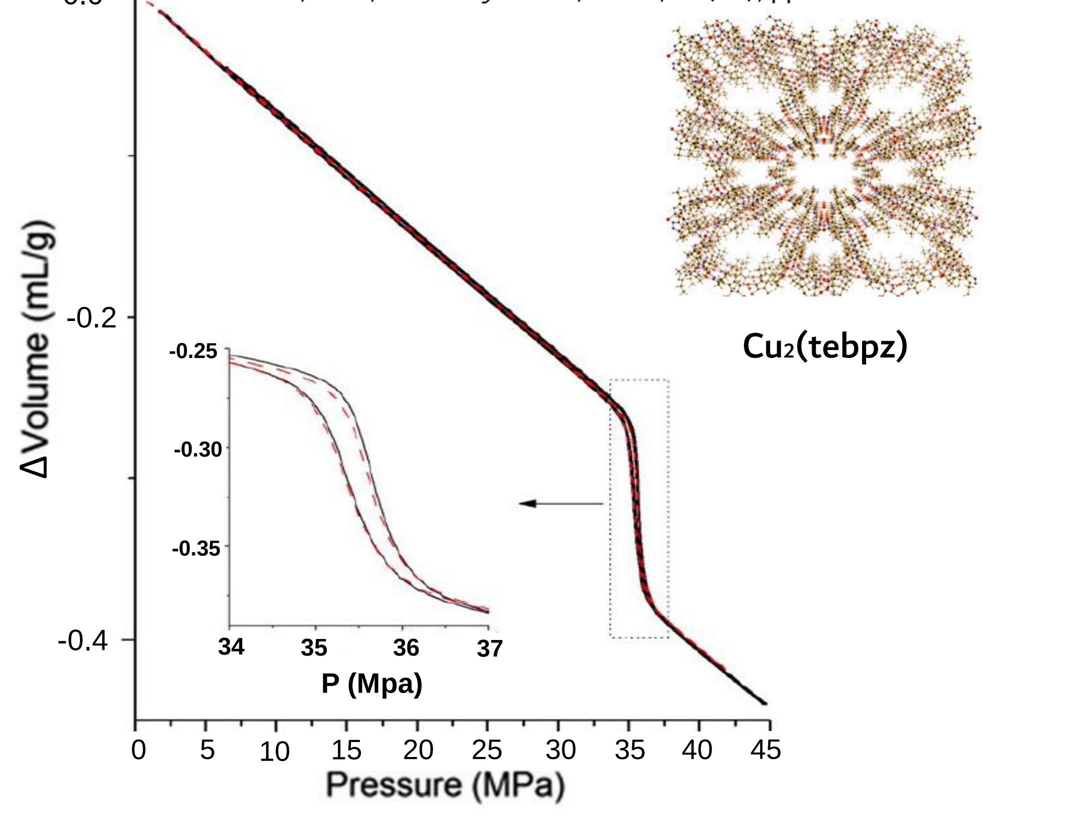


Project webpage: www.electro-intrusion.eu

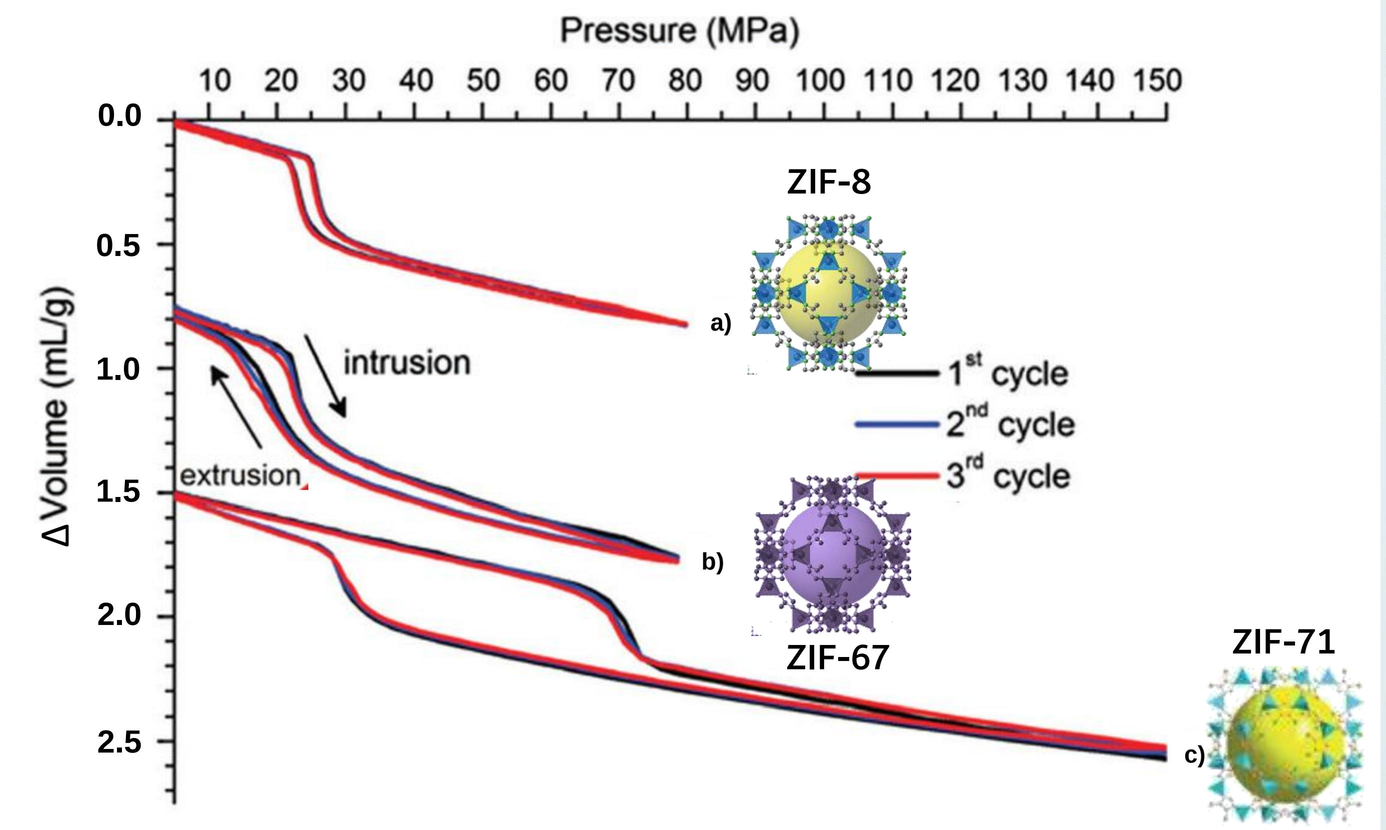
1. Introduction

MOFs for energy dissipation

Y. Grosu, et al., *ChemPhysChem*, **2016**, *17*(21), pp.3359-3364



Few MOFs reported so far exhibiting water int-ext



I. Khay et al., *Dalton Trans.*, **2016**, 45, 4392-4400

Cu_2(tebpz) & several Zeolitic Imidazole Frameworks (ZIFs) have demonstrated promising performances

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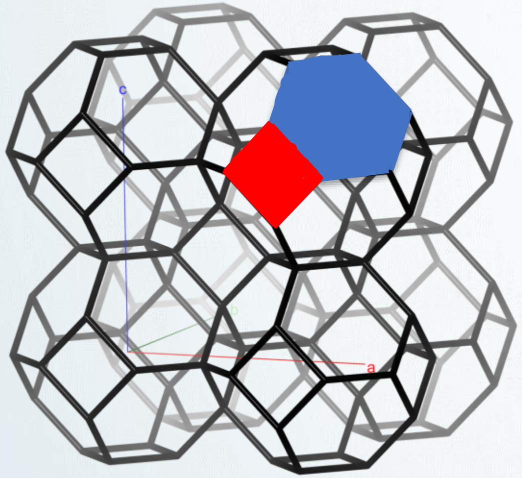
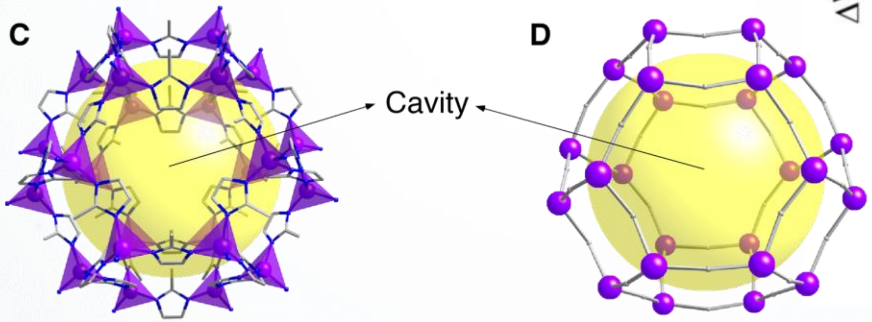
1. Introduction

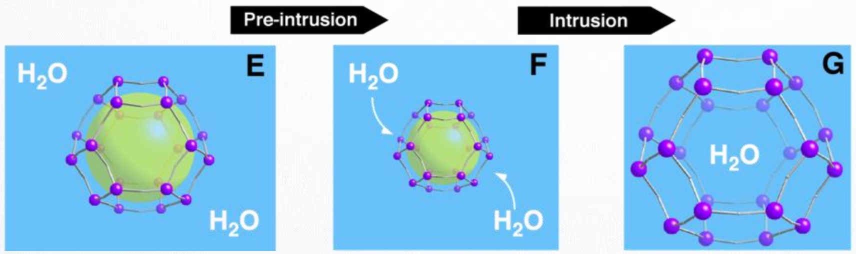
ZIF-8 as reference material

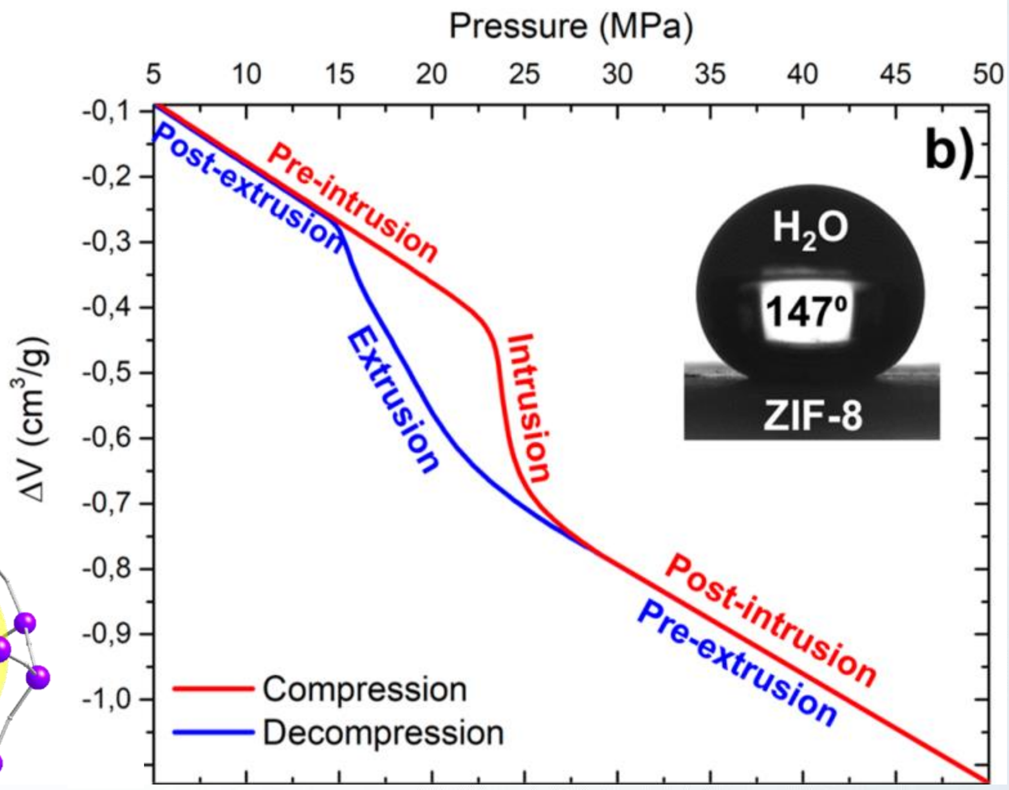
- ZIF-8 arised as one of the microporous reference materials in the field

- Pore size
- Topology
- Surface area
- Hydrophobicity
- Flexibility → Gate opening effect of imidazolates
- Negative compressibility under hydrostatic pressure









M. Tortora et al., *Nano Lett.* **2021**, 21, 2848–2853

Reported negative compressibility of ZIF-8

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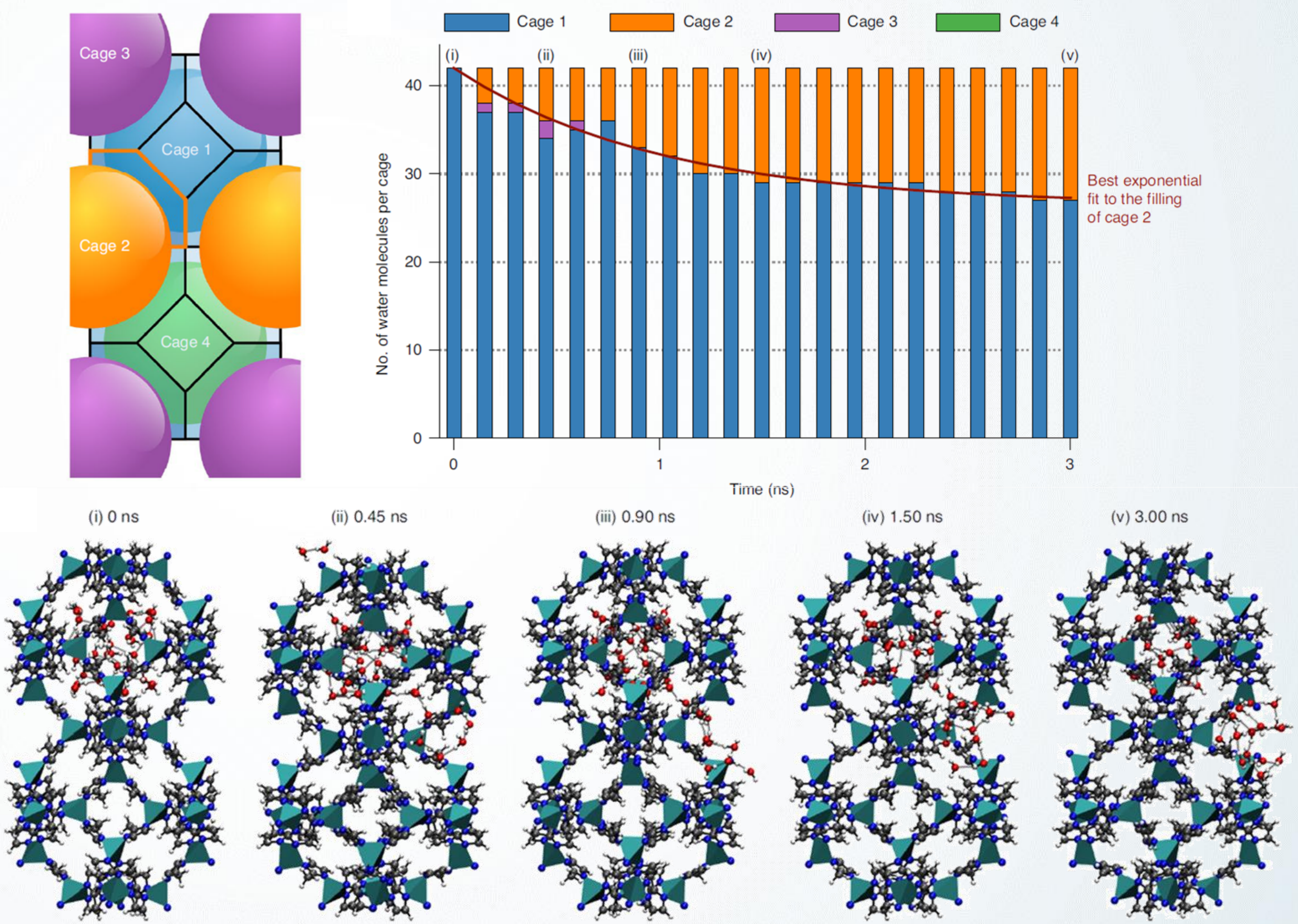
1. Introduction

H_2O intrusion mechanism into ZIF-8



- ✓ 1st proposal of H_2O intrusion mechanism into ZIF-8: process governed by water vapor condensation inside the cages.

Sun et al., *Nature Materials* **2021**, 20, 1015–1023.

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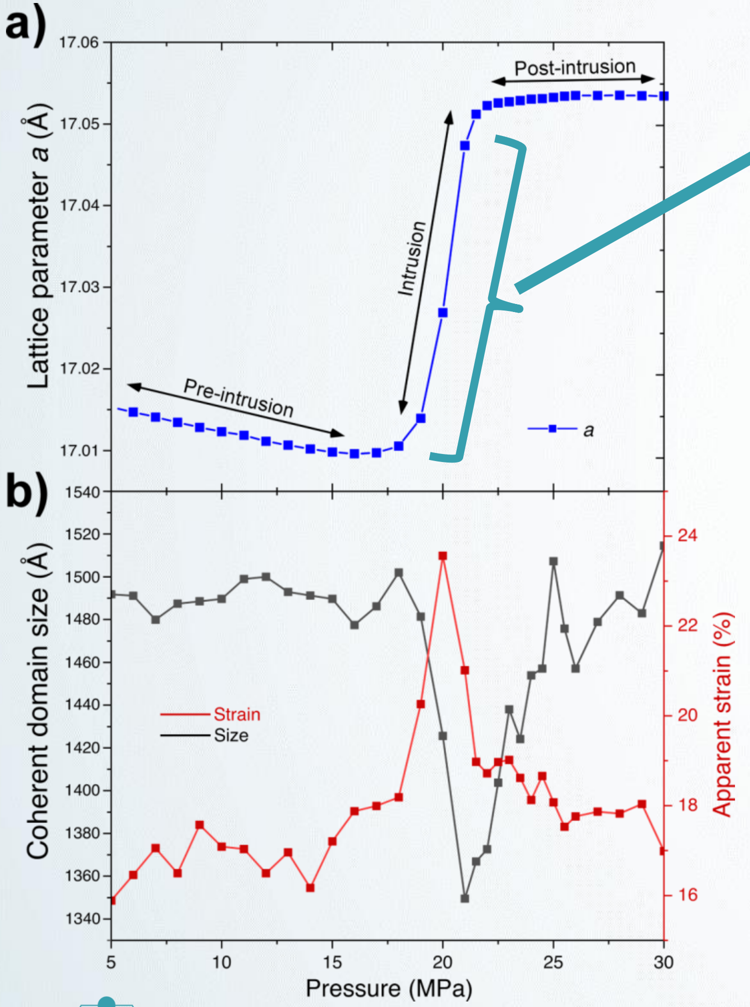
2. Experimental approach

Intrusion porosimtrey and *in operando* synchrotron radiation



Reported negative compressibility of ZIF-8

M. Tortora et al., *Nano Lett.* **2021**, 21, 2848–2853

- ✓ Wet cavities are larger than dry ones. Formation of domains of fully wet and completely dry cages can be detected by synchrotron radiation

- ✓ ZIF-8 is intruded by water following a cascade mechanism by progressive filling of connected cages, which account for the observed shrinkage and growth of coherent domains

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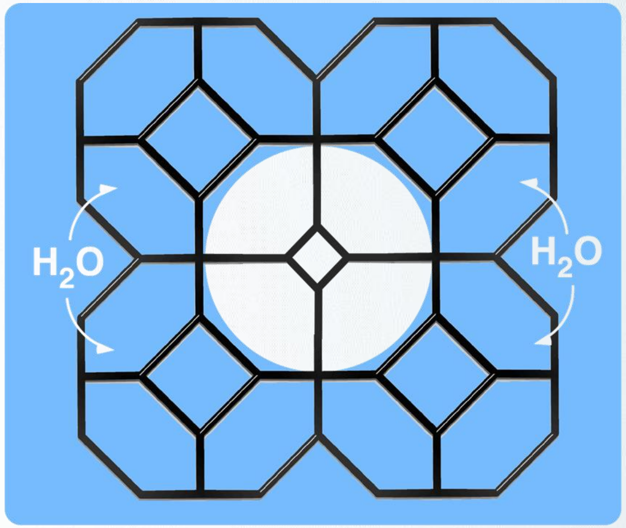

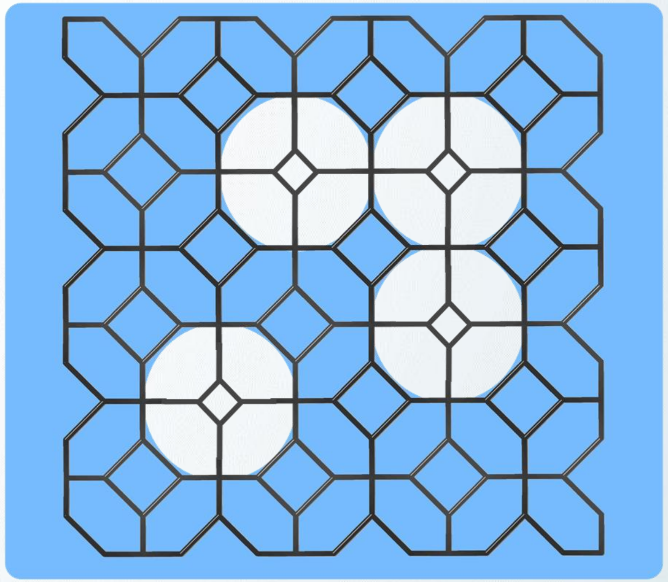

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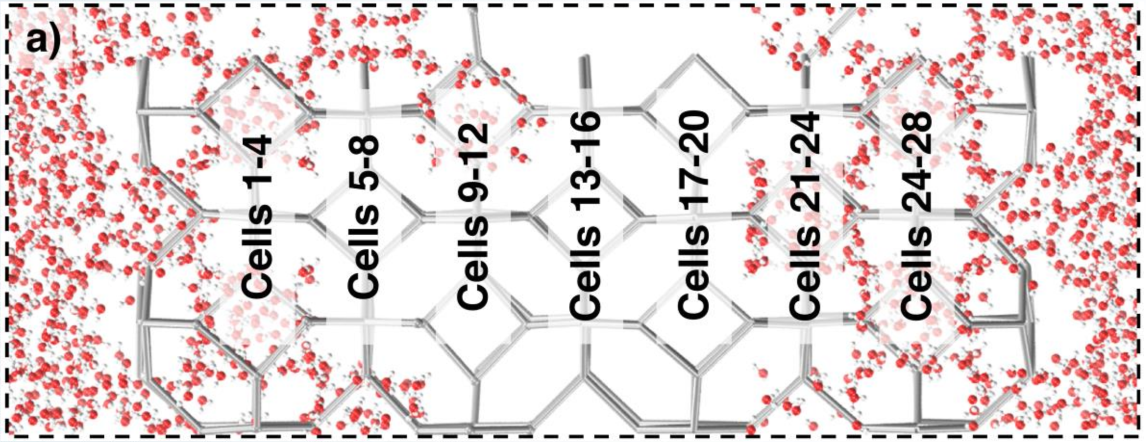
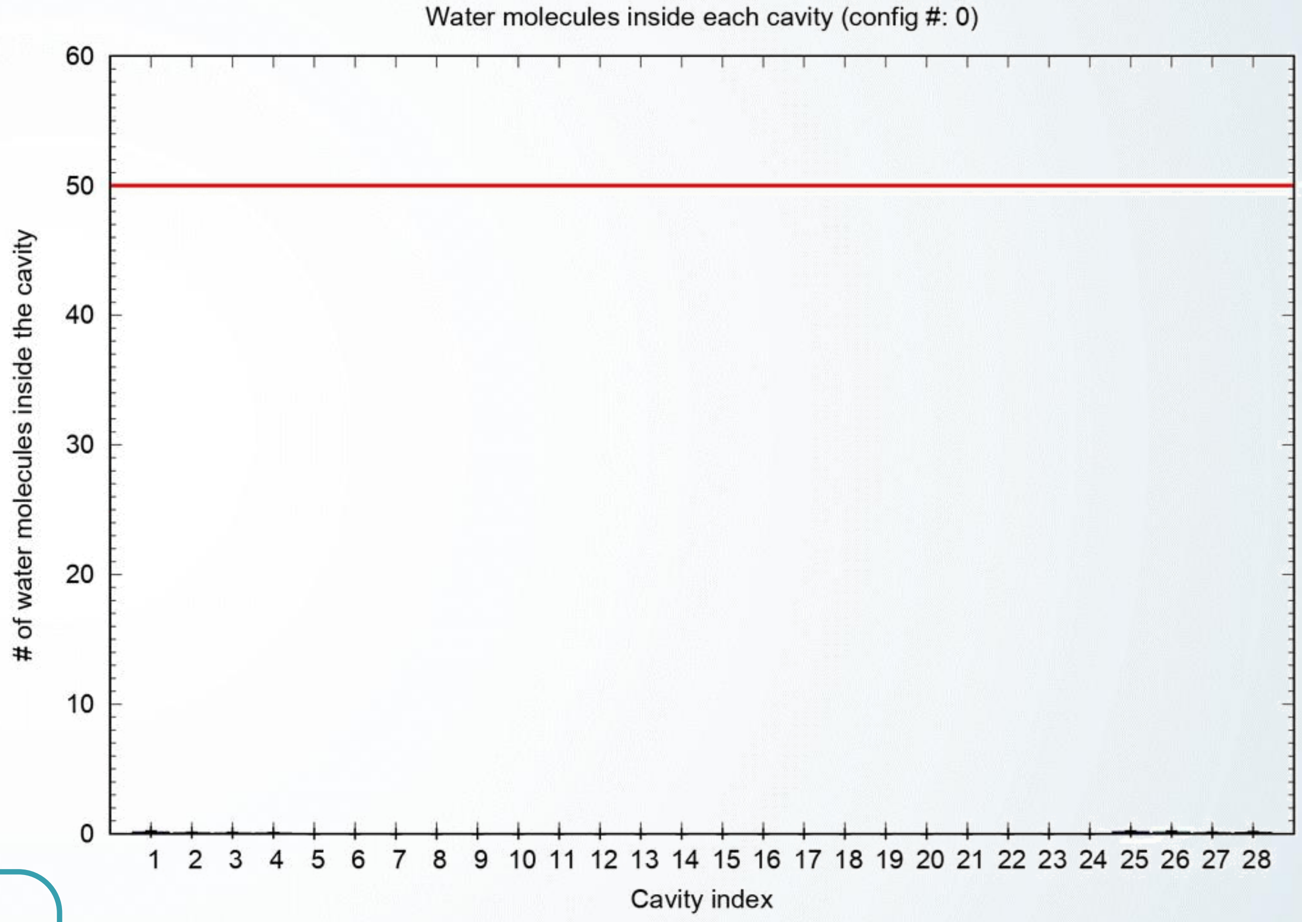
3. Theoretical approach

Atomistic simulations



- ✓ The wetting of the computed slab starts by the complete filling of specific cages belonging to the outermost layers.
- ✓ Waterfront proceeds by filling cages connected to the wet ones through hexagonal apertures



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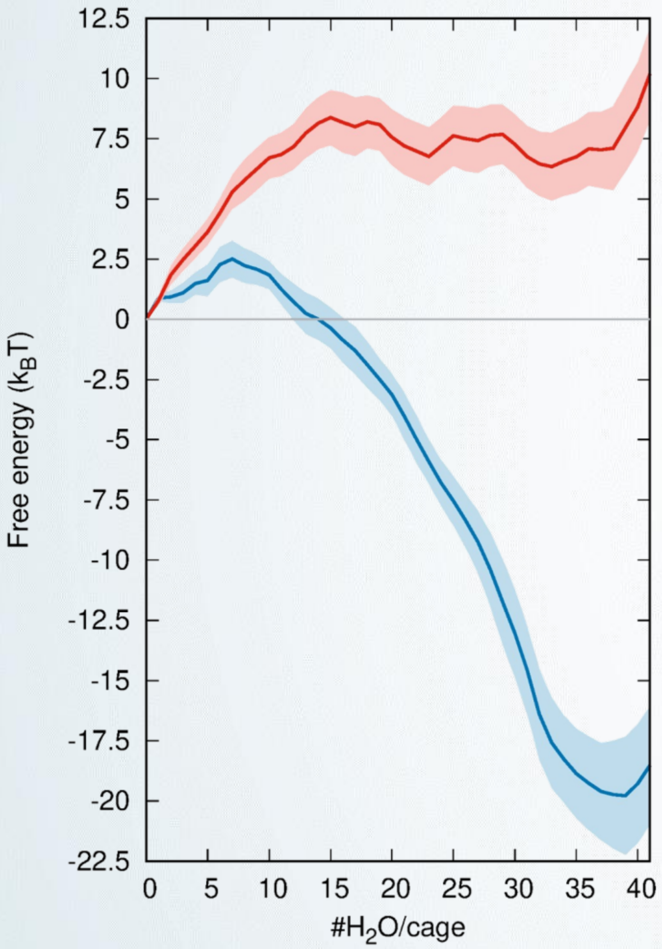
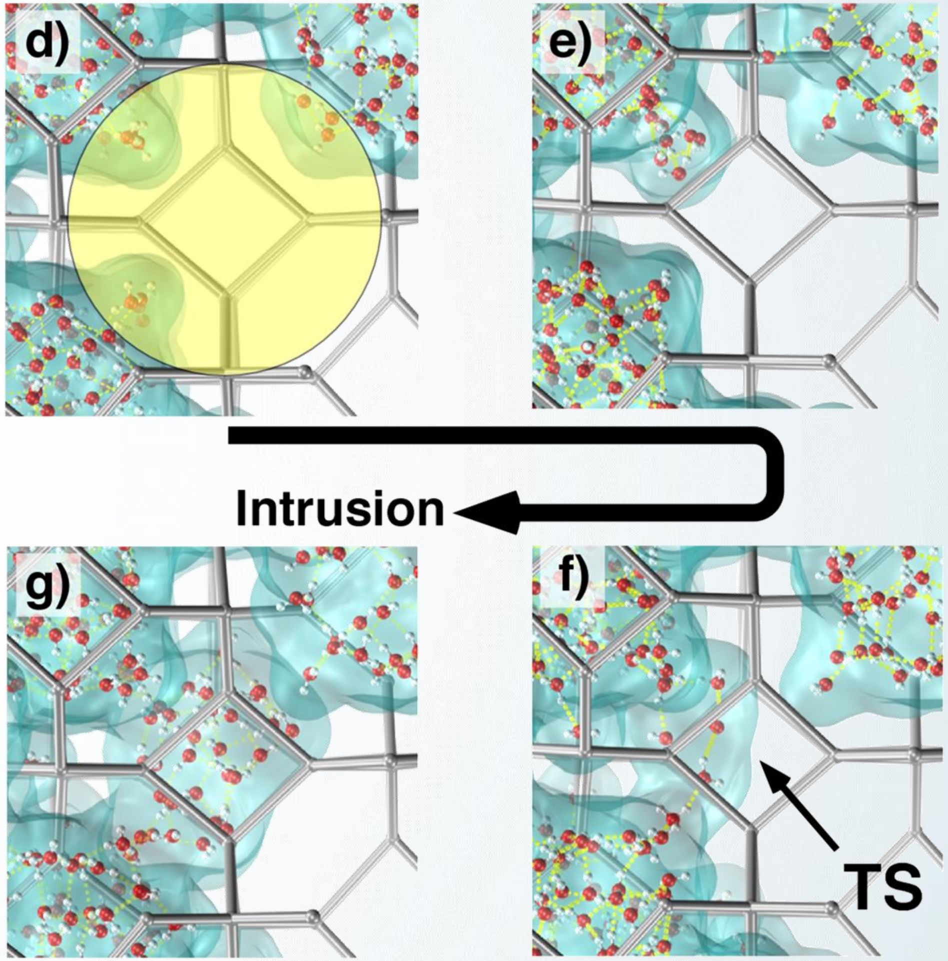
3. Theoretical approach

Atomistic simulations



- ✓ It is energetically more convenient to form a water bridge across several 6MR apertures with already filled ZIF-8 cavities → contrary to condensation mechanism
- ✓ The transition state is determined by the formation of a hydrogen bond bridge between water molecules penetrating from neighboring wet cages.



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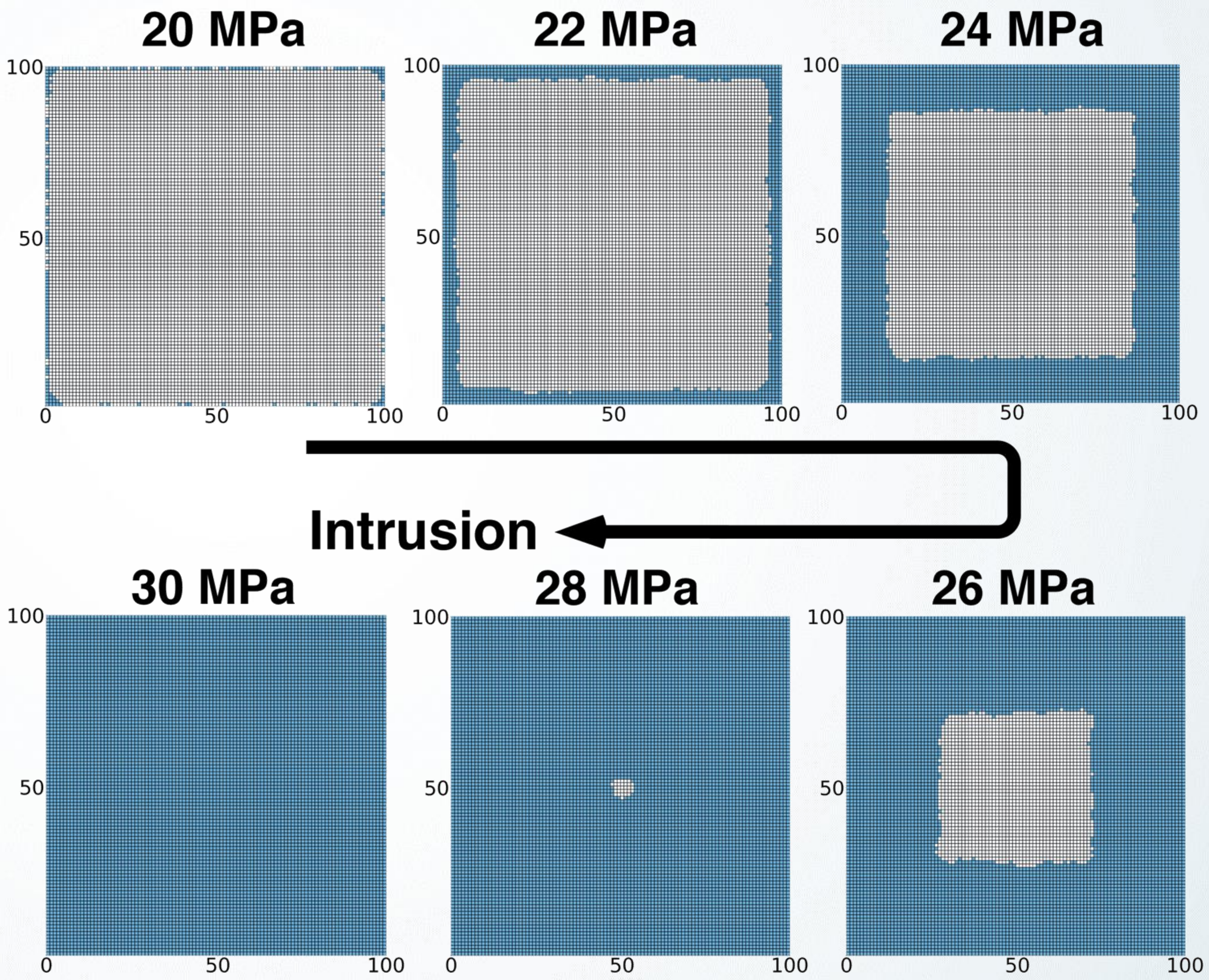
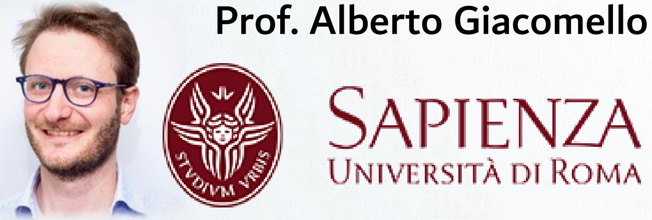
3. Theoretical approach

Stochastic model

- ✓ Stochastic model in which cages undergo wetting or drying with a probability depending on the number of wet neighbors.
- ✓ Stabilization provided by hydrogen bonding across hexagonal apertures results in the formation of one large coherent domain while the random filling of cages by condensation is negligible.



Prof. Alberto Giacomello



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5. Conclusions

CONCLUSIONS

- Via a combination of experimental and theoretical approaches we have clarified the intrusion mechanism of ZIF-8 under hydrostatic pressure, which proceeds by cascade filling of neighboring cages.
- In operando synchrotron radiation tracked the evolution of domains of wet/dry cages during intrusion, indicating the formation coherent domains of wet cages which grow during the process.
- RMD simulations gave microscopic evidence of the formation of coherent domains due to penetration of water in connected ZIF-8 cages, rather than water condensation in individual ones, as previously proposed.
- The detailed wetting mechanism of a single cage shows that the kinetic bottleneck of the process is the formation of hydrogen bonds bridging water molecules across neighboring apertures.
- A stochastic model informed by MD simulations confirms the prevalence of cascade penetration in coherent domains as opposed to a condensation scenario. Thus, the shape of the domains of wet cages seems compatible with the classical capillarity concept of surface energy because they tend to minimize the surface area.

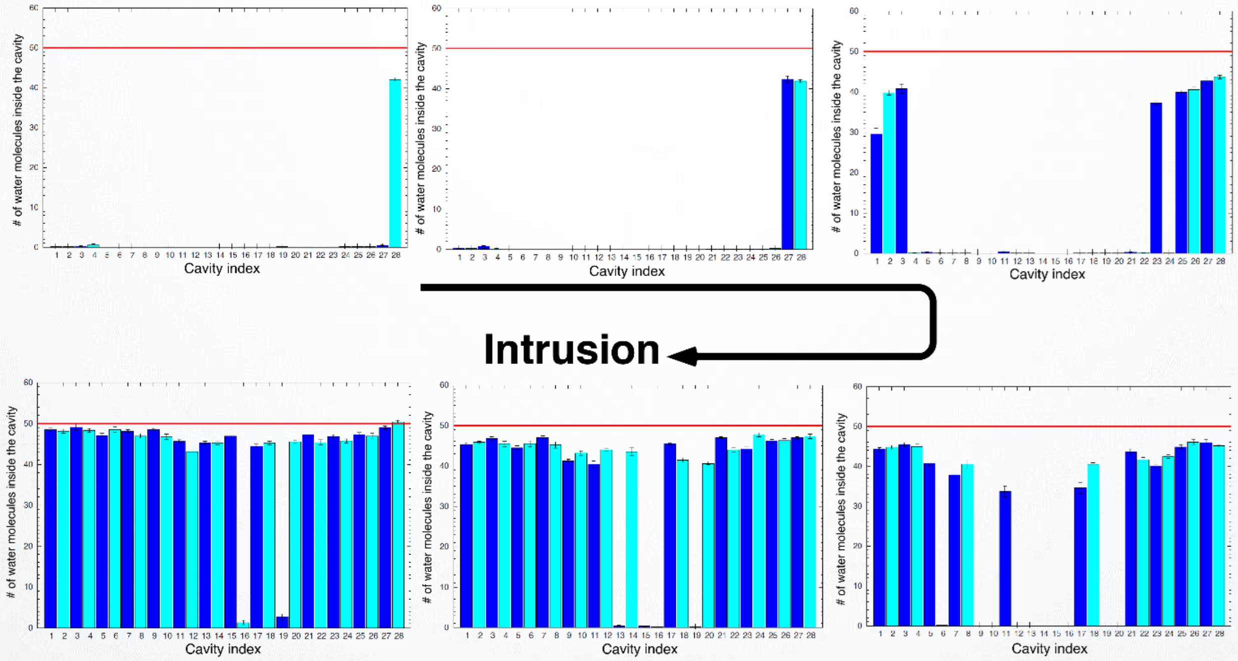
6. Keep diving into other MOFs

Open questions

- As critical characteristics responsible for the water intrusion mechanism if ZIF-8 is the presence of interconnected cages we expect a similar mechanism to hold also for other ZIF MOFs.

- For example, for ZIF-67, which is an isomorph to ZIF-8, simulations show cage-by-cage intrusion.

- Other ZIFs, e.g., ZIF-12, with different morphologies and cage and aperture sizes, might show some differences with respect to the mechanism discussed today.



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EURO mof 2023

Thanks for your attention!

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