Effect of flexibility on the water intrusion/extrusion pressure of ZIF-8_Cm for energy conversion applications

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19th September 2022, European Research Society 2022 Fall Meeting, *Warsaw*

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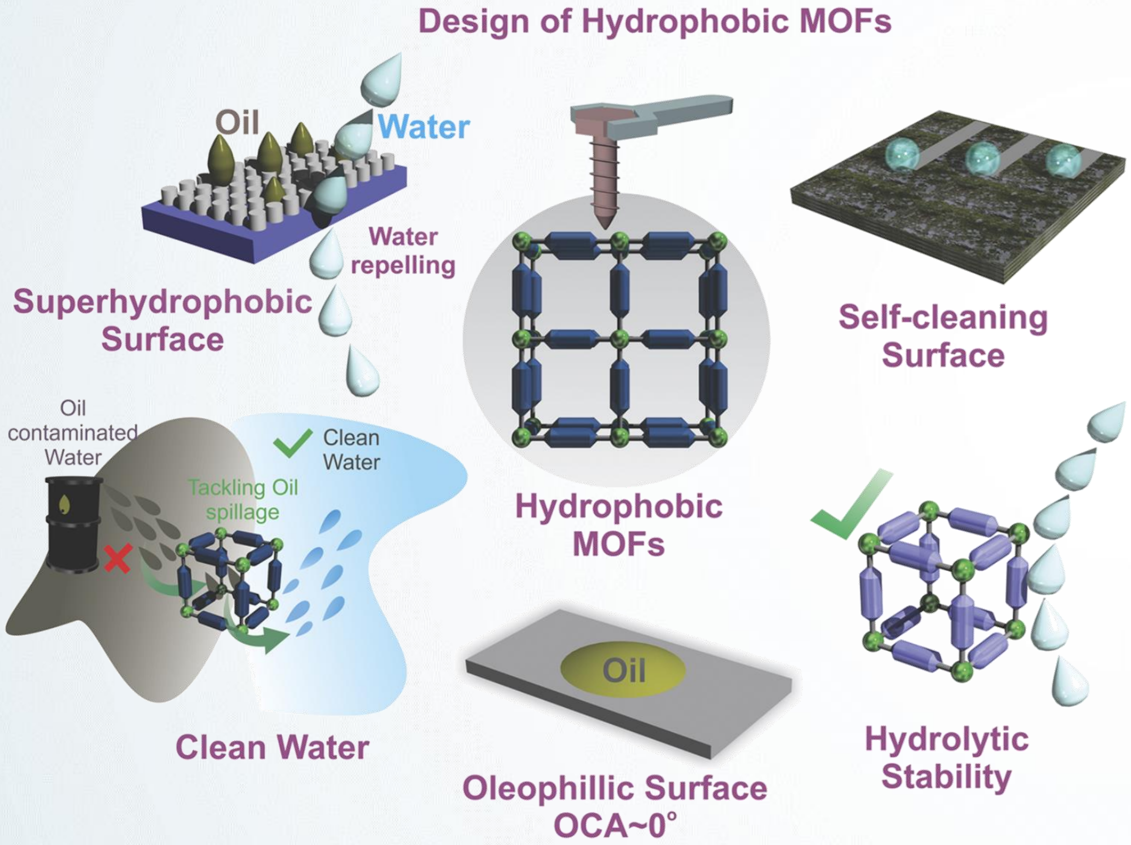
ELECTRO INTRUSION

1. Introduction

Hydrophobic MOFs

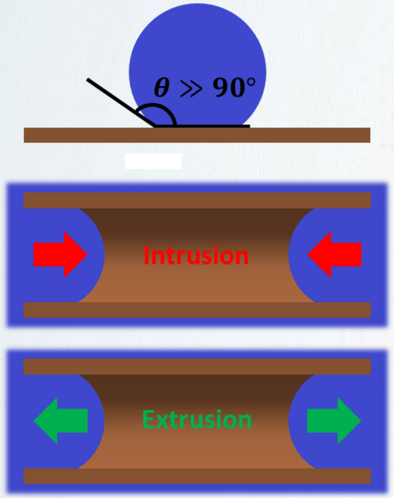


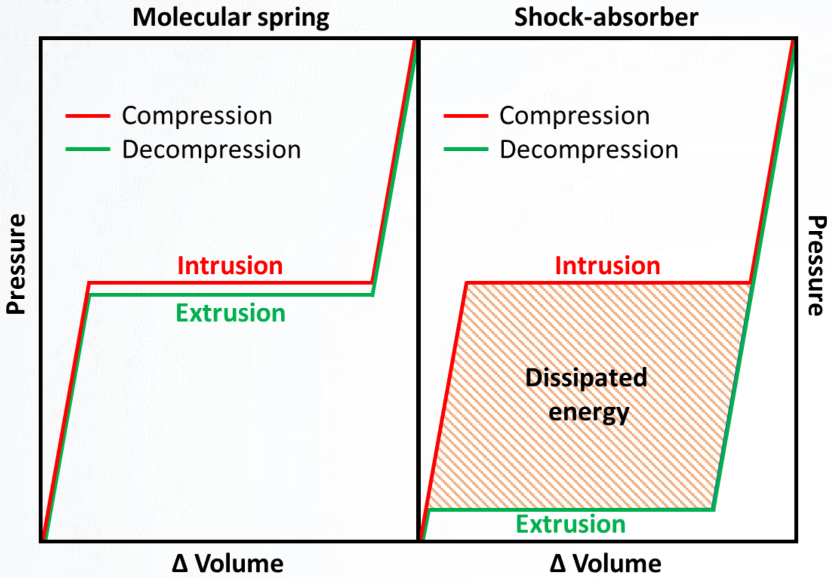
S. Mukherjee et al., *APL Mater.*, **2019**, 7, 050701

- ✓ Among well known metal-organic frameworks, hydrophobic MOFs arise as great candidates in many fields
- ✓ Superhydrophobic MOFs (WCA > 90º) arise as emergent materials for energy dissipation applications

1. Introduction

MOFs for energy dissipation



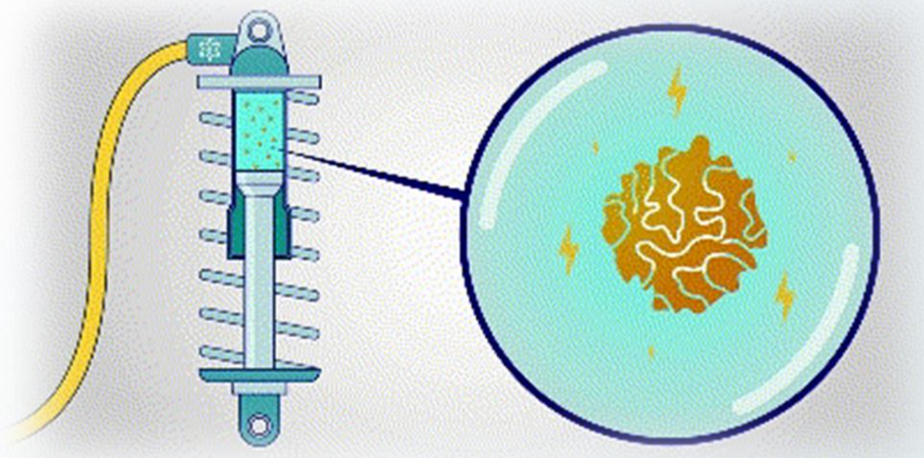


- P. Zajdel et al., *ACS Appl. Mater. Interfaces* **2022**, 14, 23, 26699–26713

✓ (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

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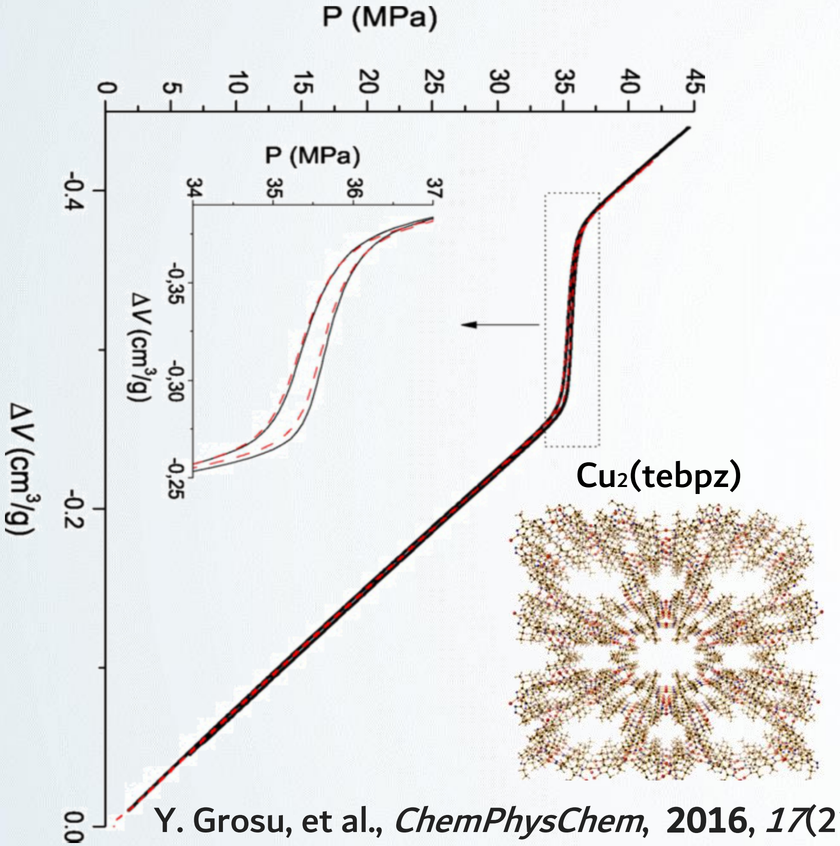
MOFs for energy dissipation

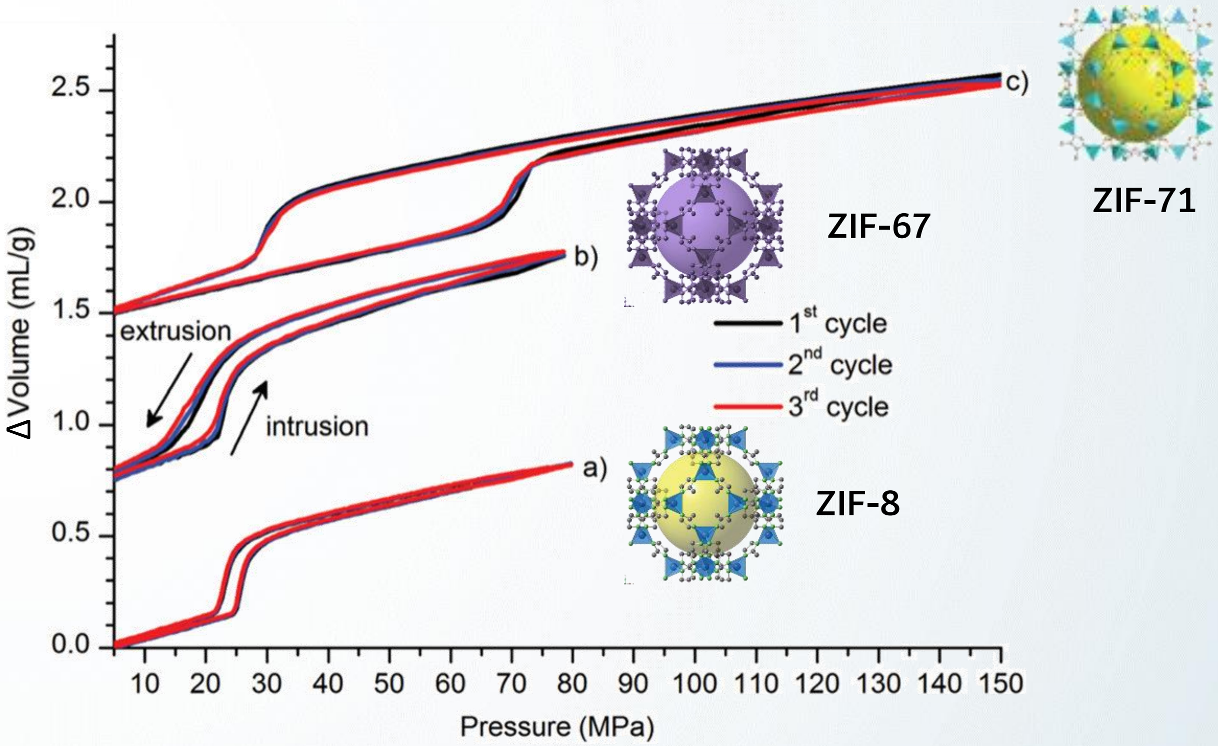


Cu₂(tebpz)

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

Hydrophobic Zeolitic Imidazole Frameworks (ZIFs) have demonstrated promising performances

Few MOFs reported so far exhibiting water int-ext



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

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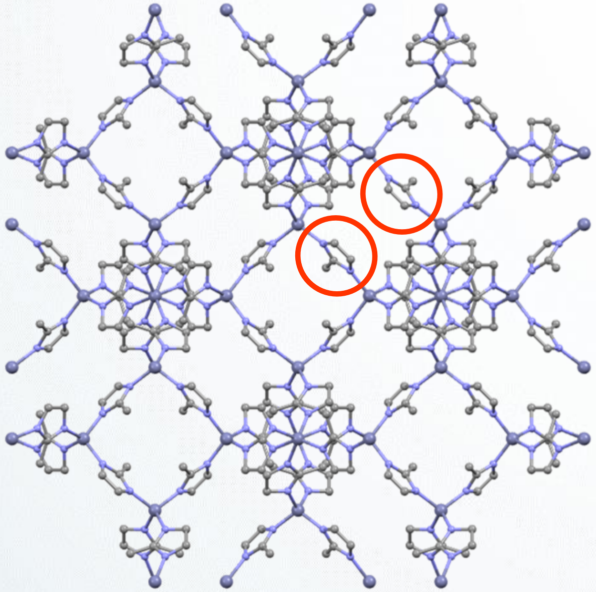
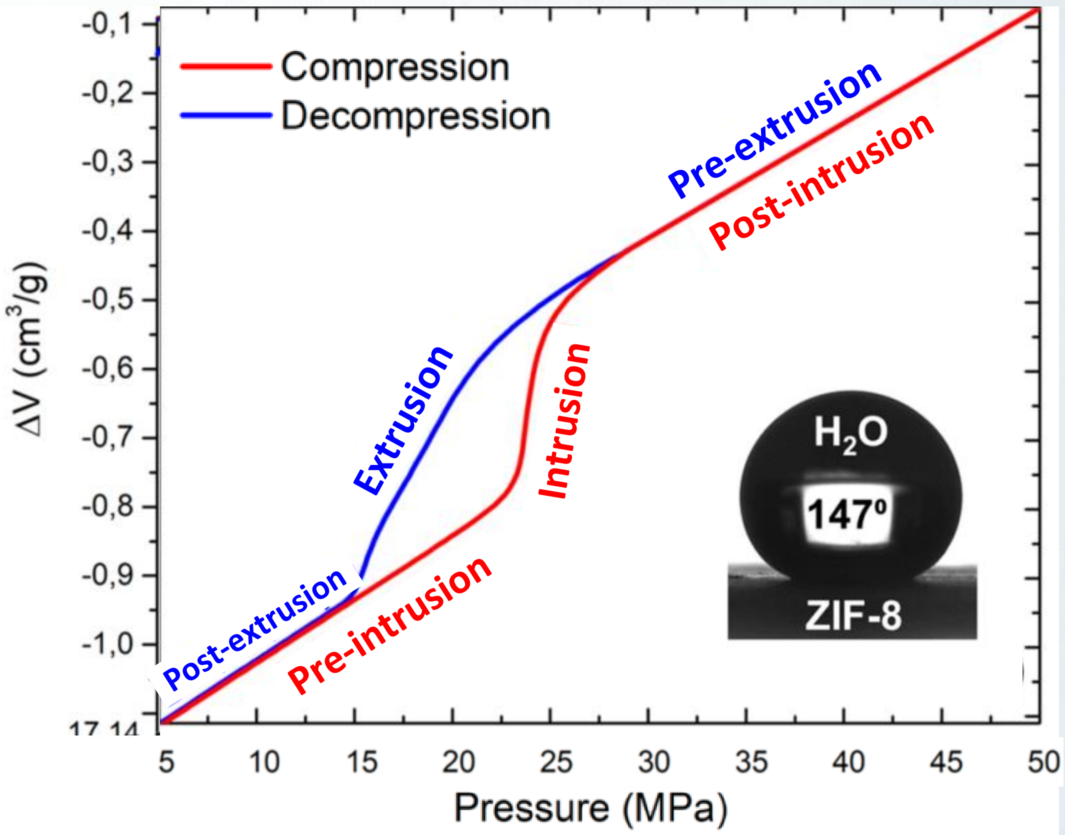
1. Introduction

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





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

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2. Material

Stiffened ZIF-8

- ✓ Stiff…
- ✓ Stiffene… _Cm phase as

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2. Material

Synthesis and structural characterization of stiffened ZIF-8

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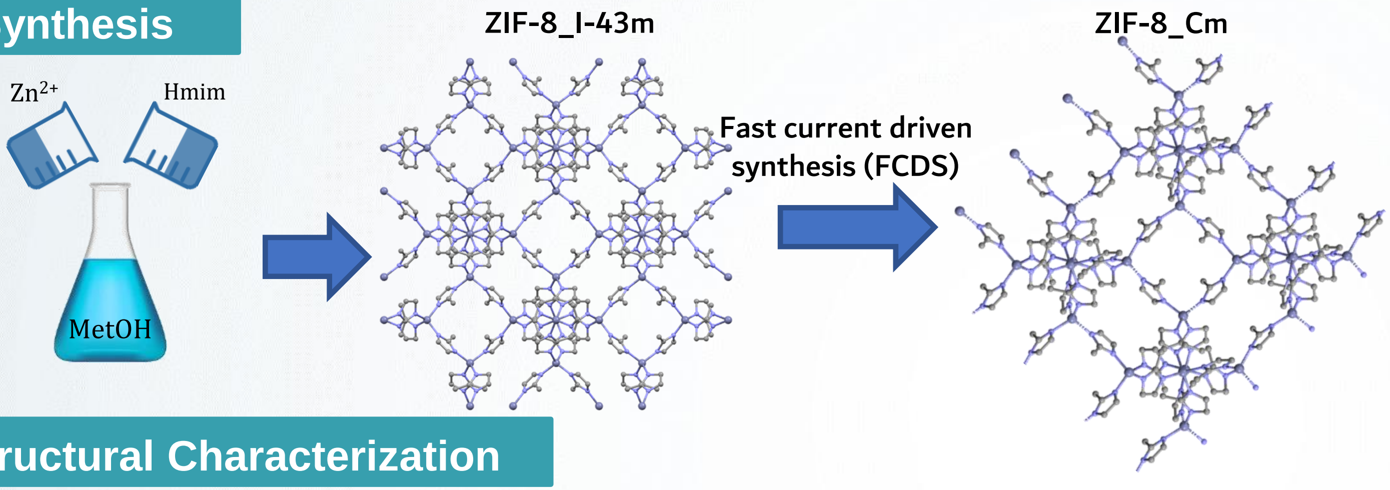
Synthesis



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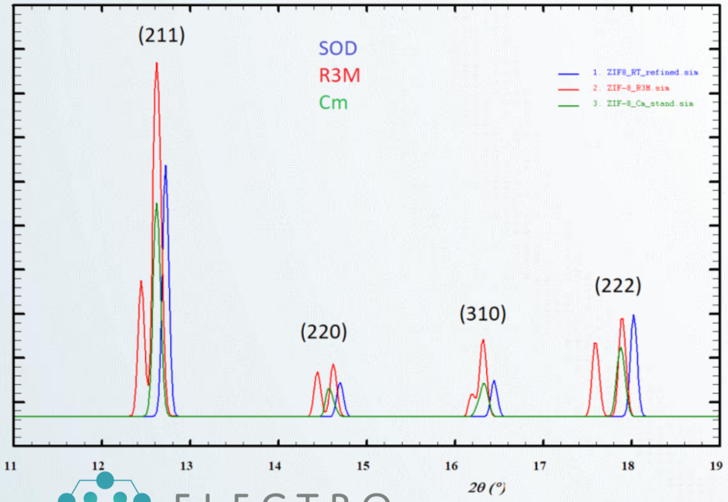
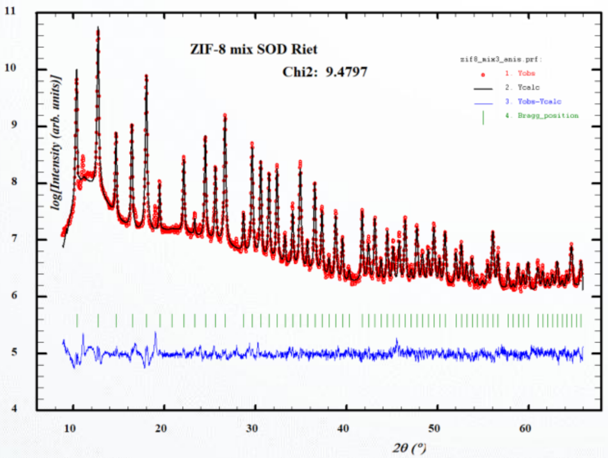
- ✓ *E* field to stiffen cubic ZIF-8 and create different phases ZIF-8 in the sample
- ✓ Inconsistencies in differentiation of phases

Structural Characterization

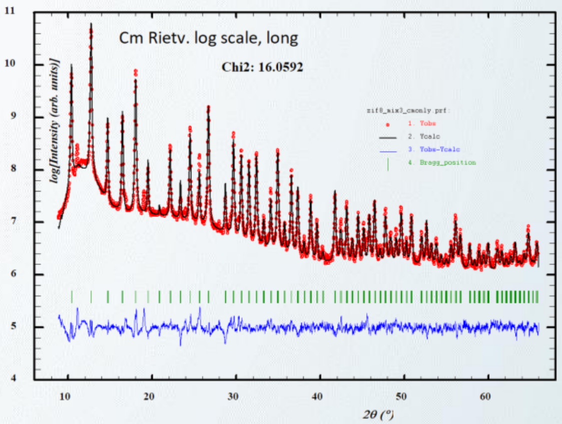


Rietveld ZIF-8_I-43m



	ZIF-8_I-43m	ZIF-8_Cm
Rp	14,8	19,4
Rwp	15,6	20,2
Rexp	5,06	5,04
Chi2	9,48	16,1
Bragg R	4,79	8,33
Rf	3,4	4,67
Vol	4937,4	4924,9
a	17,0281 Å	17,0424 Å
b		24,038 Å
c		14,734 Å
β		125,319º

Rietveld ZIF-8_Cm



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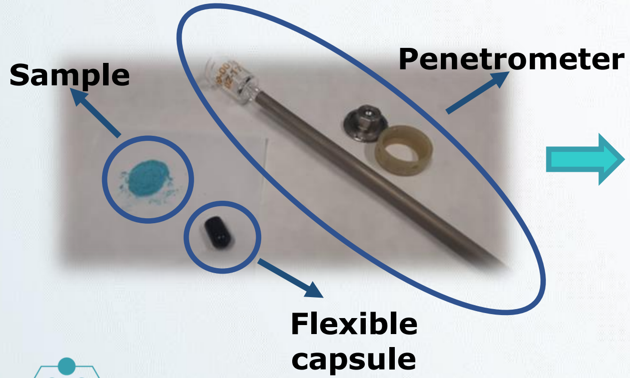
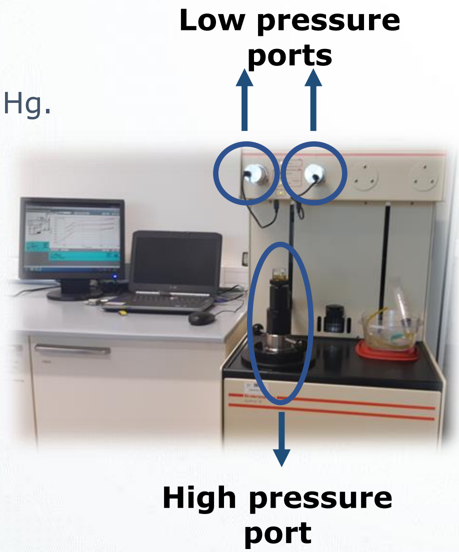
3. Characterization

Water porosimetry

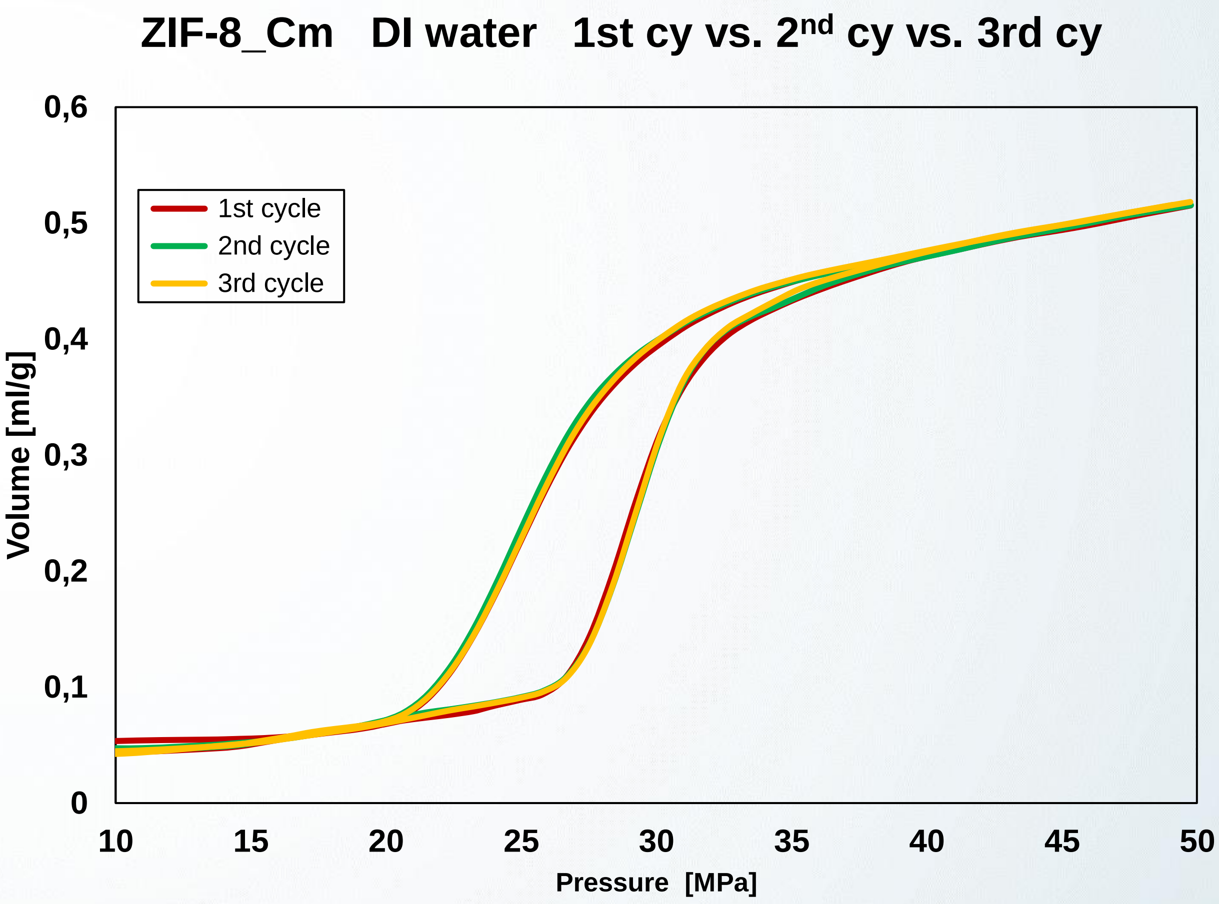
H_2O intrusion-extrusion tests

- Water intrusion-extrusion into-from porous material with ΔP
  - Pressure applied by Hg
  - Possibility to apply different P rates
  - Possibility to test different non-wetting liquids
- Non-destructive technique
- Low sample mass needed for each test
- Easy sample preparation. Not waste of Hg.





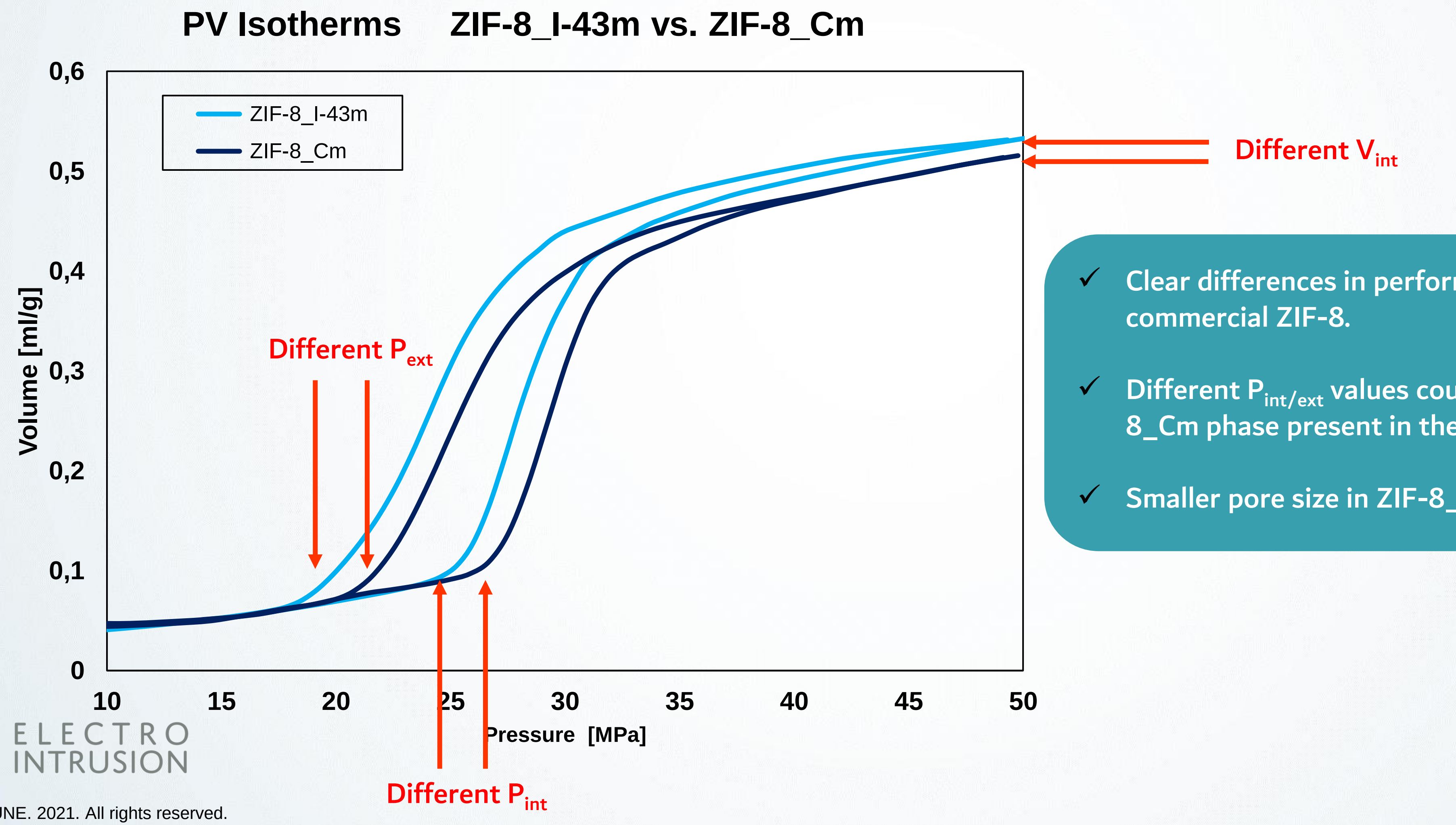
PV isotherms



4. Results & Discussion

ZIF-8_I4-3m vs. ZIF-8_Cm

Performances in H_2O int-ext



- Clear differences in performances compared to commercial ZIF-8.
- Different $P_{int/ext}$ values could lie on the rigidity of ZIF-8_Cm phase present in the sample.
- Smaller pore size in ZIF-8_Cm also affects V_{int}.

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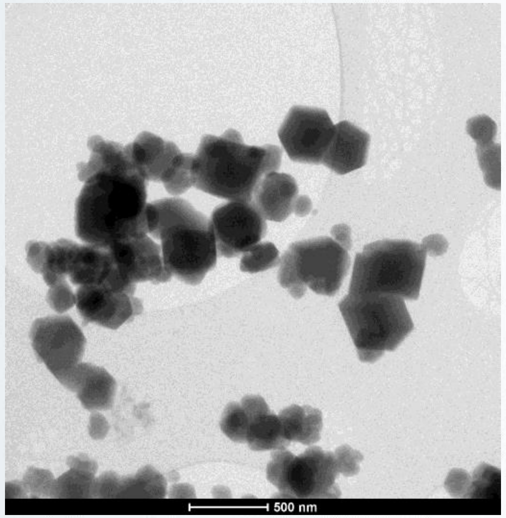
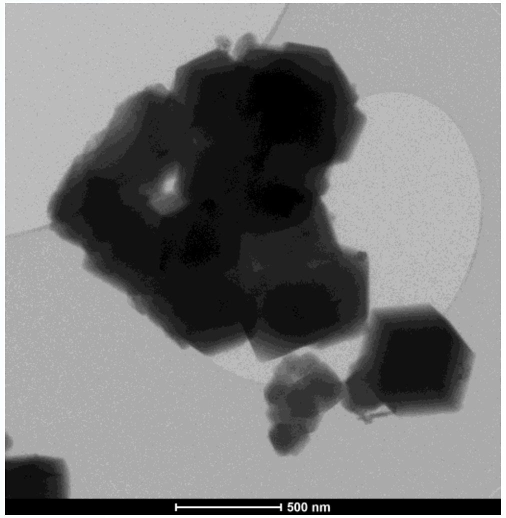
4. Results and Discussion

Crystal size and shape

ZIF-8_Cm	ZIF-8_I4-3m

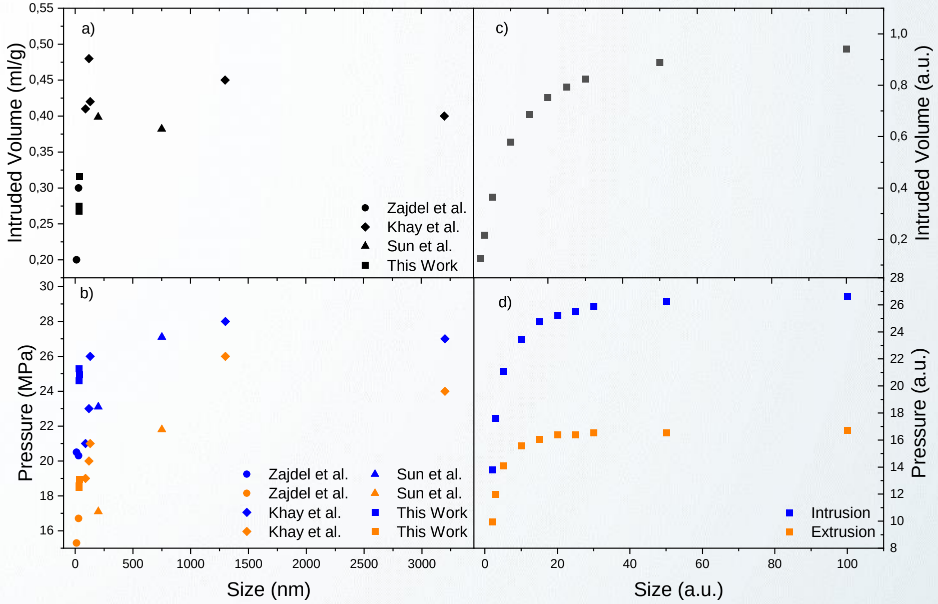




	Morphology	Mean crystal size
ZIF-8_I4-3m	dodecahedra	340 nm
ZIF-8_Cm	dodecahedra	230 nm

- I. Khay et al., *RSC Adv.*, **2015**, 5, 31514-31518

- ✓ Crystal morphology fit with commercial ZIF-8 and crystal size are in the same range.
- ✓ As previously explored (crystal size and morphology could change int-ext performances. However, this doesn't seem to play the main role in this case.



- L. Johnson et al., *Tuning the Threshold Pressure of Wettability for Hydrophobic Microporous Materials by Crystal Size for Energy Storage/Conversion Applications*, **2022**, In preparation.

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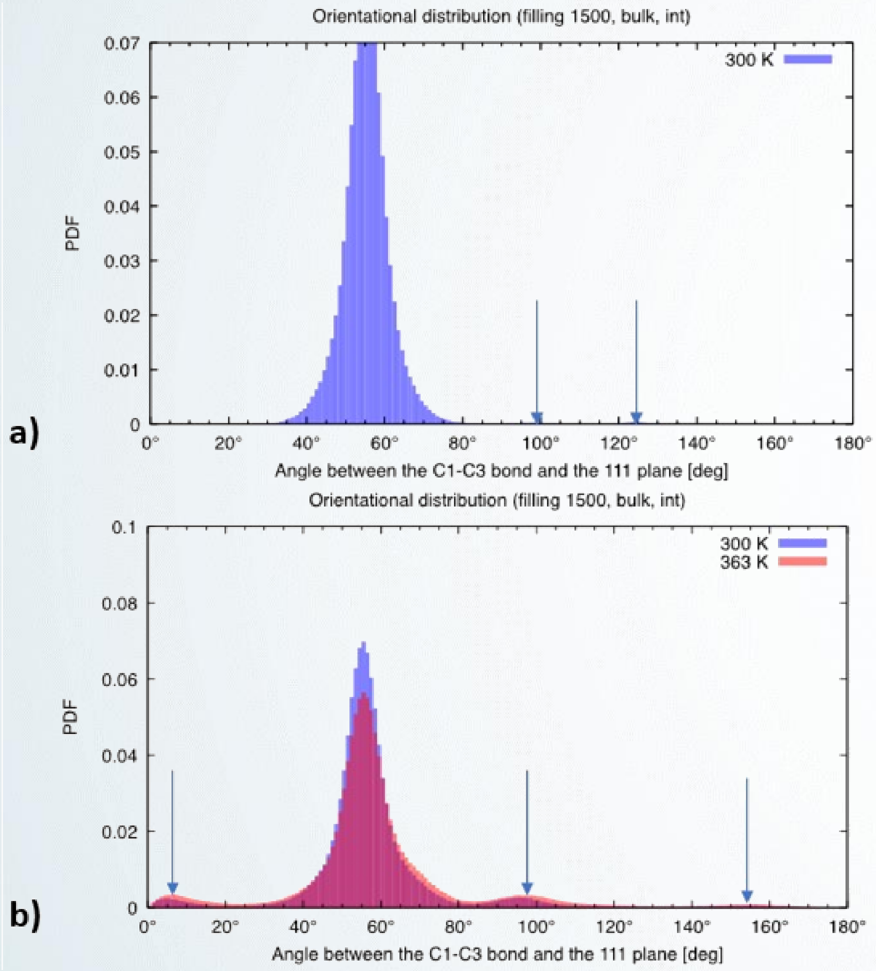
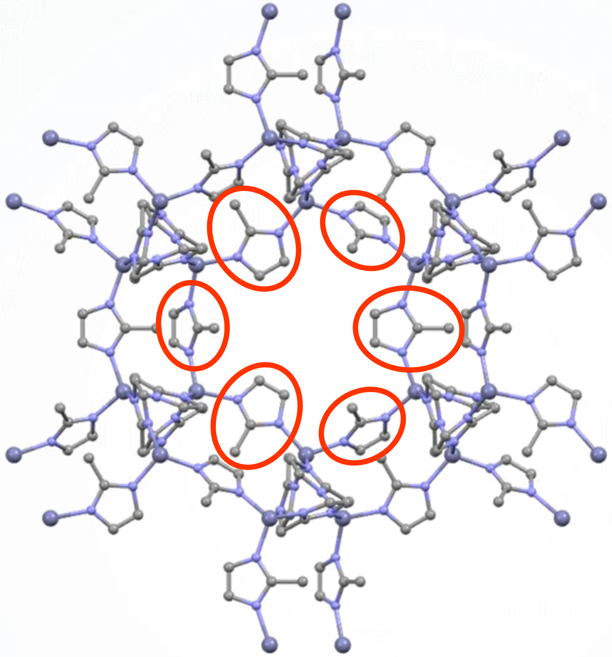
4. Results & discussion

Simulations





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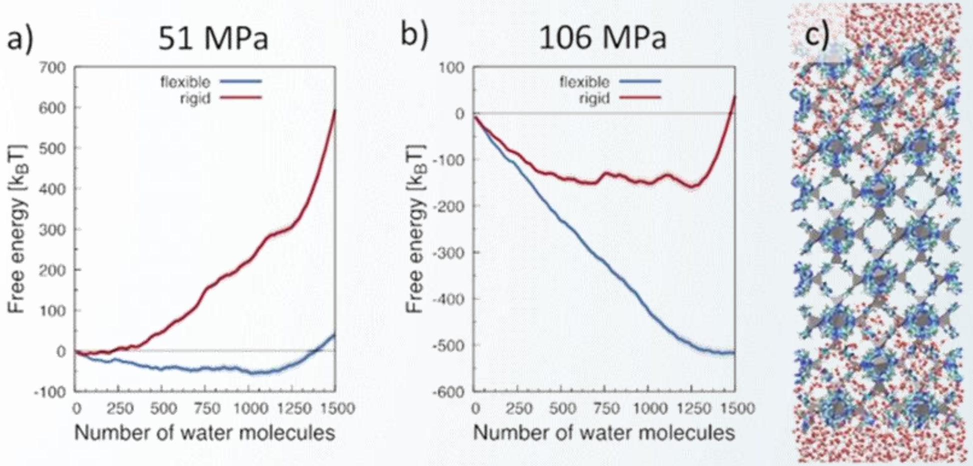

✓ Probability distribution function angle the Imidazolate linker makes with the 111-direction for ZIF-8 with fixed lateral dimensions and that free to expand for the most extreme filling case (120% filling level)

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5. Conclusions

CONCLUSIONS

- ZIF-8 synthesized using FCDS exhibit a clear increase in Pint and Vint related with the rigidity of its structure.

- Structural characterization of the sample does not offer clear evidence in the differentiation or quantification of the different phases present in the sample, proposed in previous publications.

- As proposed by atomistic simulations, the restriction of movement of the imidazolates in [111] hinders intrusion as the pore windows cannot swing open when water molecules enter the cavity windows, thus raising the free-energy associated with intrusión.

Open questions

- Method to differentiate the ZIF-8_I-43m from ZIF-8_Cm and proper characterization and quantification of the three different phases coexisting in the sample

- Reach different percentages of stiffened ZIF-8 up to 100% of that phase in the sample in order to tune the P_{int}.

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Thanks for your attention!

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