



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

**Eder Amayuelas, Josh David Littlefair, Luis Bartolomé, Sandeep Kumar Sharma, Jaideep Mor, Pranav Utpalla, Paweł Zajdel, Yaroslav Grosu**

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*Warsaw*



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## **1. Introduction**

## **2. Materials**

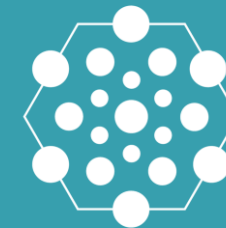
## **3. Characterization**

## **4. Results and Discussion**

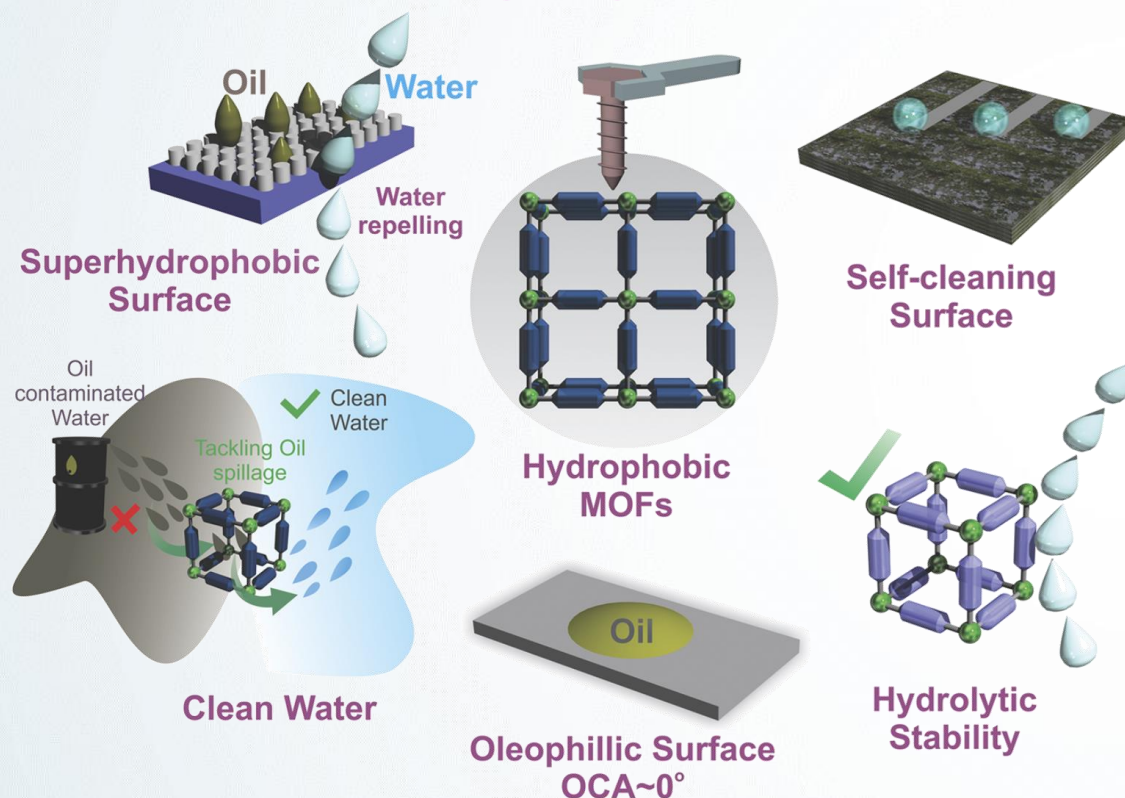
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# 1. Introduction

## Hydrophobic MOFs



### Design of Hydrophobic MOFs

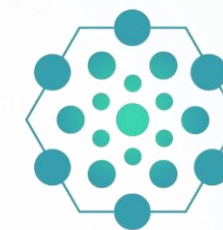
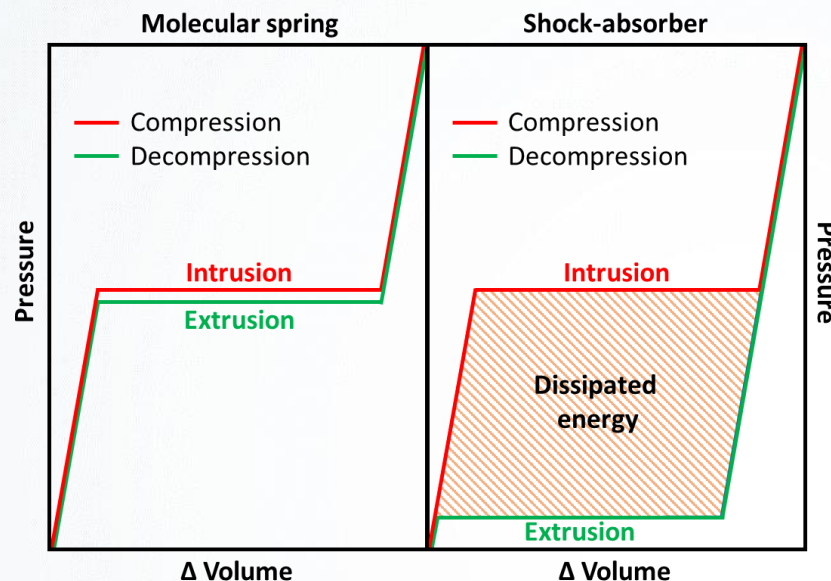
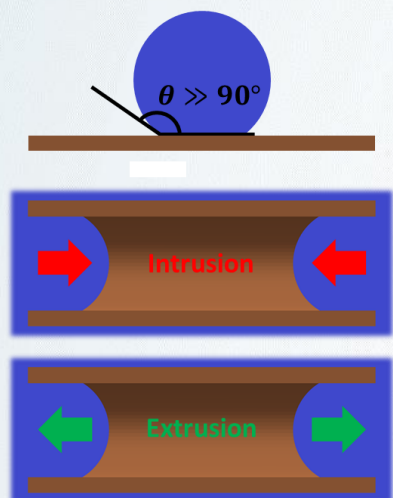
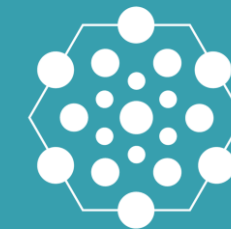


S. Mukherjee et al., *APL Mater.*, **2019**, 7, 050701

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

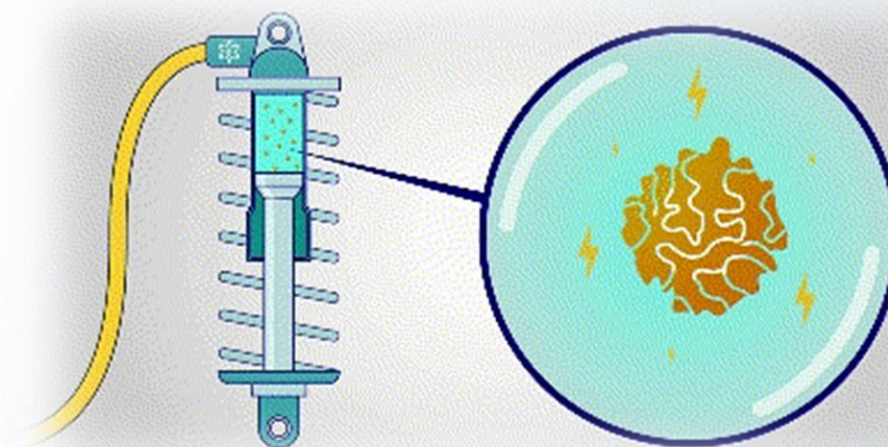
# 1. Introduction

## MOFs for energy dissipation



Electro-Intrusion: materials for converting vibrations into electricity.

Building triboelectric nanogenerators



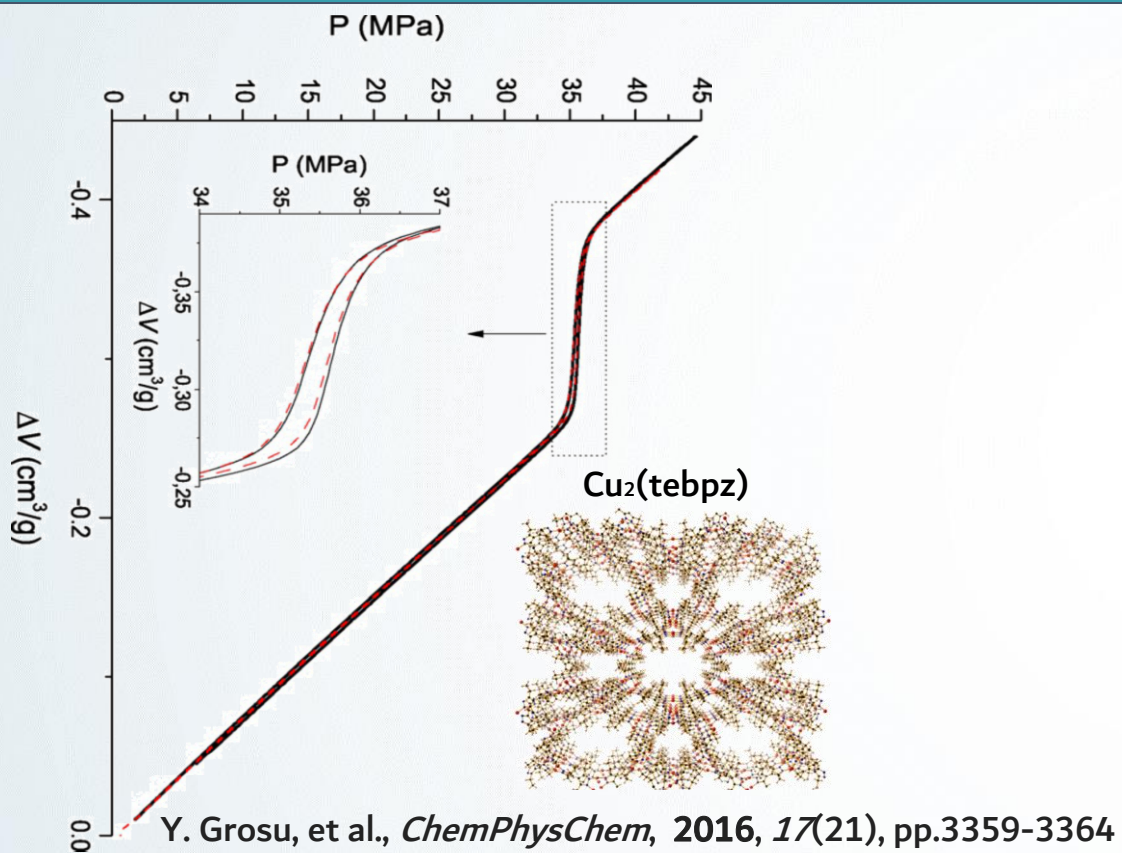
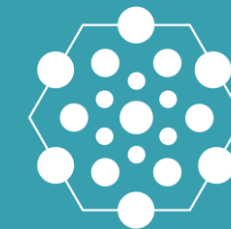
Project webpage: [www.electro-intrusion.eu](http://www.electro-intrusion.eu)

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

- ✓ (Super)hydrophobic materials: Contact angle  $>90^\circ$  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...  $\rightarrow$  performance optimization

# 1. Introduction

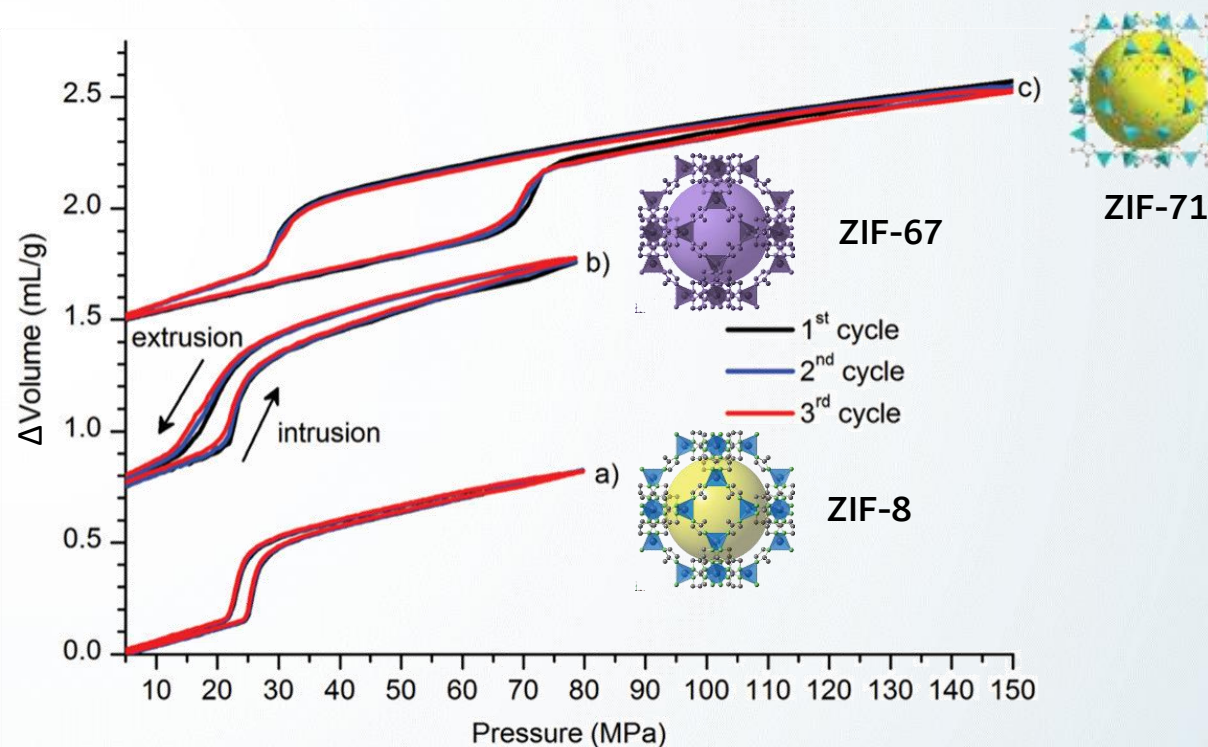
## MOFs for energy dissipation



Hydrophobic Zeolitic Imidazole Frameworks (ZIFs) have demonstrated promising performances

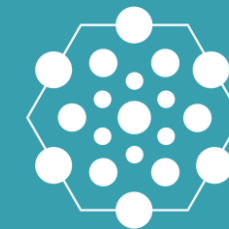


Few MOFs reported so far exhibiting water int-ext

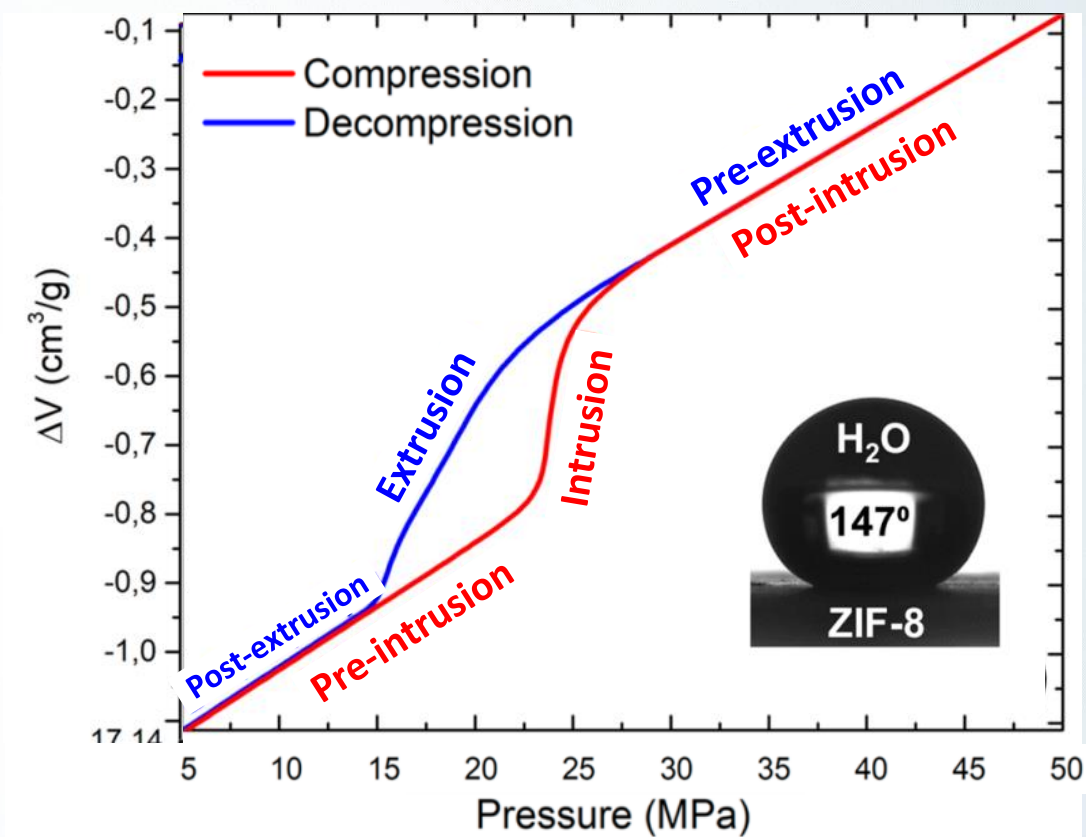
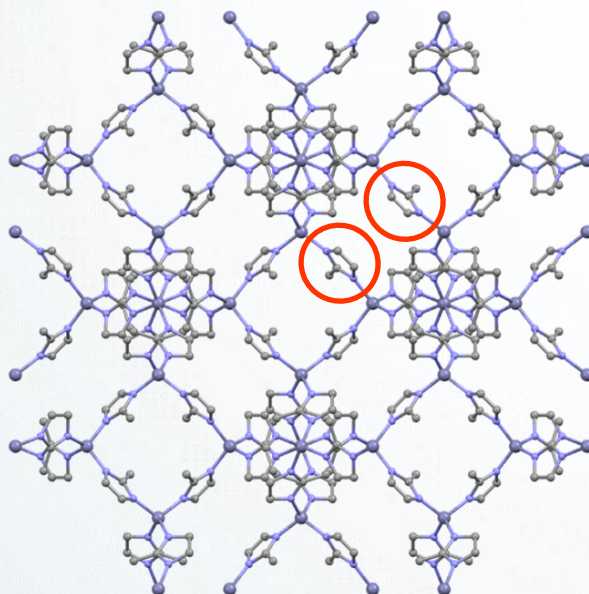


# 1. Introduction

## ZIF-8 as reference material



- ✓ ZIF-8 arises 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

# 2. Material

## Stiffened ZIF-8



### Restricting Lattice Flexibility in Polycrystalline Metal-Organic Framework Membranes for Carbon Capture

Deepu J. Babu, Guangwei He, Jian Hao, Mohammad Tohidi Vahdat, Pascal Alexander Schouwink, Mounir Mensi, and Kumar Varoon Agrawal\*

Although polycrystalline metal-organic framework (MOF) membranes offer several advantages over other nanoporous membranes, thus far they have not yielded good CO<sub>2</sub> separation performance, crucial for energy-efficient carbon capture. ZIF-8, one of the most popular MOFs, has a crystallographically determined pore aperture of 0.34 nm, ideal for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation; however, its flexible lattice restricts the corresponding separation selectivities to below 5. A novel postsynthetic rapid heat treatment (RHT) implemented in a few seconds at 360 °C, which drastically improves carbon capture performance of the ZIF-8 membranes, is reported. Stiffening is confirmed by the appearance of a temperature-activated port, attributed to a stronger interaction of gas molecules with the framework, with activation energy increasing with the molecular size (H<sub>2</sub>, Unprecedented CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, and H<sub>2</sub>/CH<sub>4</sub> selectivity of 30, 30, and 175, respectively, and complete blockage of C<sub>3</sub>H<sub>6</sub> are incorporated in the ZIF-8 lattice, increasing the lattice rigidity. RHT treatment is a facile and versatile technique that can improve gas-separation performance of the MOF membranes.



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these properties by postsynthetic treatment (6,7) and defect engineering (8,9) has been a powerful tool to engineer membranes, mainly to improve the separation performance (14)

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### Fine tuning of pore architecture and morphology of stiffened Zeolitic Imidazolate Frameworks synthesized using fast current driven method and mixed ligand strategy

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<sup>b</sup> Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India  
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#### ARTICLE INFO

**Keywords:**  
 Zeolitic imidazolate frameworks  
 Pore architecture  
 Fast current driven synthesis  
 Mixed ligand strategy

#### ABSTRACT

Zeolitic Imidazolate Frameworks (ZIFs) show great promise in molecular separation as well as recognition owing to their crystalline morphology consisting of a well designed pore architecture. However, the sieving performance of ZIFs remains limited due to their fixed pore sizes and framework flexibility. In the present study, fast current driven synthesis (FCDS) has been used to prepare the stiffened phase of mixed ligands (2-methylimidazole and benzimidazole) based ZIFs having tunable pore sizes and morphologies. X-ray diffraction has been used to determine the crystal structure of the frameworks, which were observed to be crystalline through a wide range of ligand ratio (benzimidazole fraction: ~0.206–0.972). The random distribution of both the ligands in the frameworks has been established through complementary methods viz. Raman spectroscopy, Fourier transform infrared and scanning electron microscopy. Morphology of the frameworks was observed to vary from micrometer size individual crystals to spherical aggregates of inter-grown nanocrystals to individual nanocrystals. Pore sizes determined using positronium lifetime measurements were observed to be consistent with the literature for pure phase of ZIF-7 and stiffened ZIF-8. The pore sizes were observed to vary with the benzimidazole ligand fraction confirming that mixed ligand strategy can be used to efficiently tune the pore sizes of the frameworks. Positronium diffusion investigation confirms that pore interconnectivity is inferior as compared to stiffened ZIF-8 but superior than ZIF-7 in these mixed ligand frameworks.

substrates and even polymer hollow fibers to demonstrate the production scalability.

COMMUNICATION  
**Ultra-Tuning of the Aperture Size in Stiffened ZIF-8<sub>cm</sub> Frameworks with Mixed-Linker Strategy for Enhanced CO<sub>2</sub>/CH<sub>4</sub> Separation**  
 Qianqian Hou<sup>[a]</sup>, Ying Wu<sup>[a]</sup>, Sheng Zhou<sup>[a]</sup>, Yanying Wei<sup>[a,7]</sup>, Jürgen Caro<sup>[a,b,1]</sup> and Haihui Wang<sup>[a,1]</sup>

**Abstract:** ZIF-8 membrane has the potential for CO<sub>2</sub>/CH<sub>4</sub> separation based on size exclusion. But if traditionally prepared by solvothermal method, it shows only negligible selectivity due to the linker mobility. Here, ~500 nm-thin hybrid ZIF-7,8 membranes are prepared by a current-driven synthesis (FCDS) with suppressed linker mobility and narrowed window aperture as well as the parent skeleton and the mixed-linker strategy significantly sharpened the aperture size simultaneously. The separation factor above 25, with exceptional molecular selectivity shows separation performance with separation temperature separation

obtained by the ZIF-8 membranes<sup>[7]</sup>, due to the linker mobility that permits much larger molecules (i.e. CH<sub>4</sub>) to pass through the ZIF-8 apertures<sup>[10]</sup>. Previously, the linker mobility was described as a "swinging saloon door"<sup>[10]</sup>. Hence, suppressing this swing motion is important to further improve the molecular sieving capability. Recently it was reported<sup>[8]</sup> that an external electric field (E-field) can cause the lattice distortion of ZIF-8, and a stiffer polymorph (ZIF-8<sub>cm</sub>) with suppressed linker mobility can be obtained. The stiffened structure can improve the molecular sieving capability, especially for larger molecule pairs (such as propane/propane). In a previous work, the inborn stiffened ZIF-8<sub>cm</sub> membrane is prepared by a fast current-driven synthesis (FCDS). It should be noted that the ZIF-8<sub>cm</sub> phase still shows the linker mobility to some extent, which allows the big molecules of propane passing through but the flexibility has been

ain size is limited. The much higher than that for ment at a relatively higher



Article

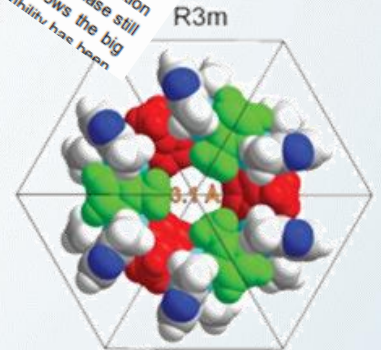
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Stiffened ZIF-8<sub>cm</sub> Frameworks with Mixed-Linker Strategy for Enhanced CO<sub>2</sub>/CH<sub>4</sub> Separation

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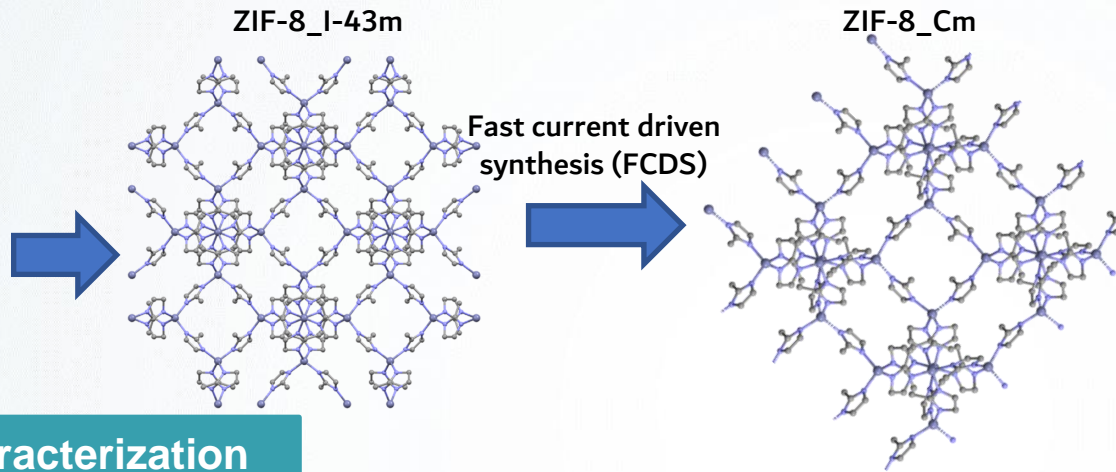
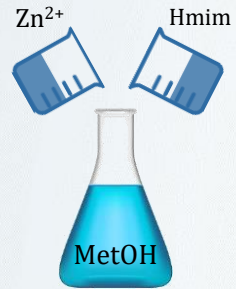


# 2. Material

## Synthesis and structural characterization of stiffened ZIF-8



### Synthesis



Dr. Pranav Utpalla



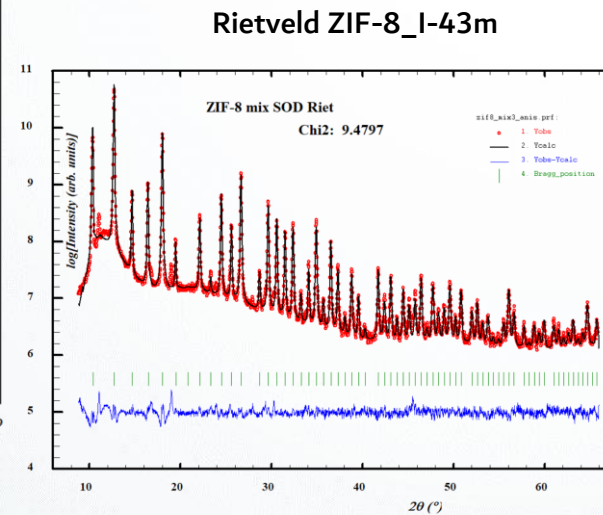
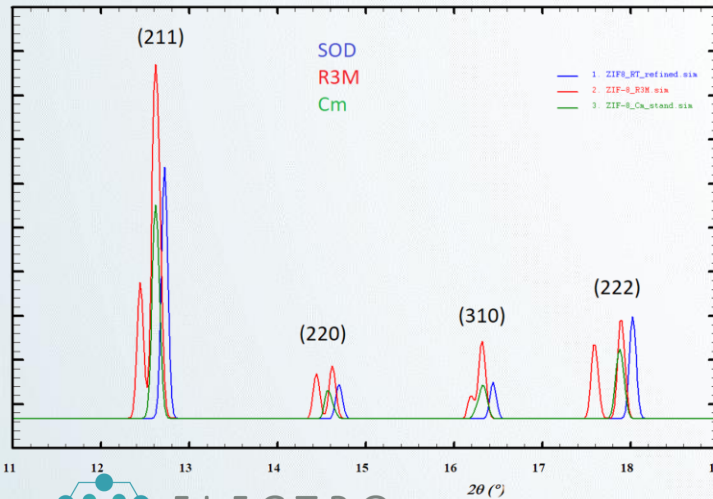
Prof. Pawel Zajdel



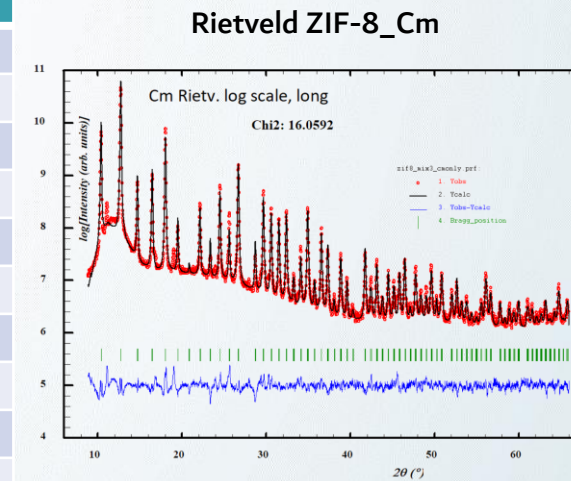
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### Structural Characterization

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



	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		125,319°





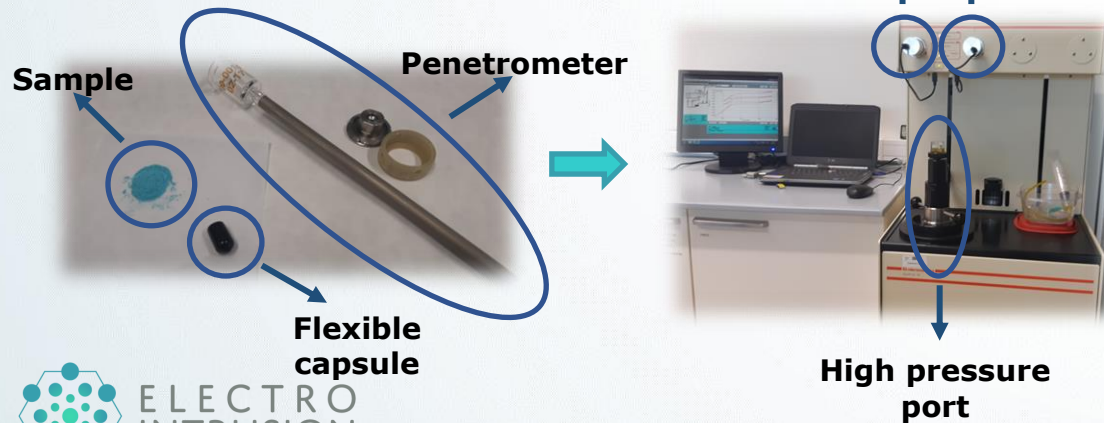
# 3. Characterization



## Water porosimetry

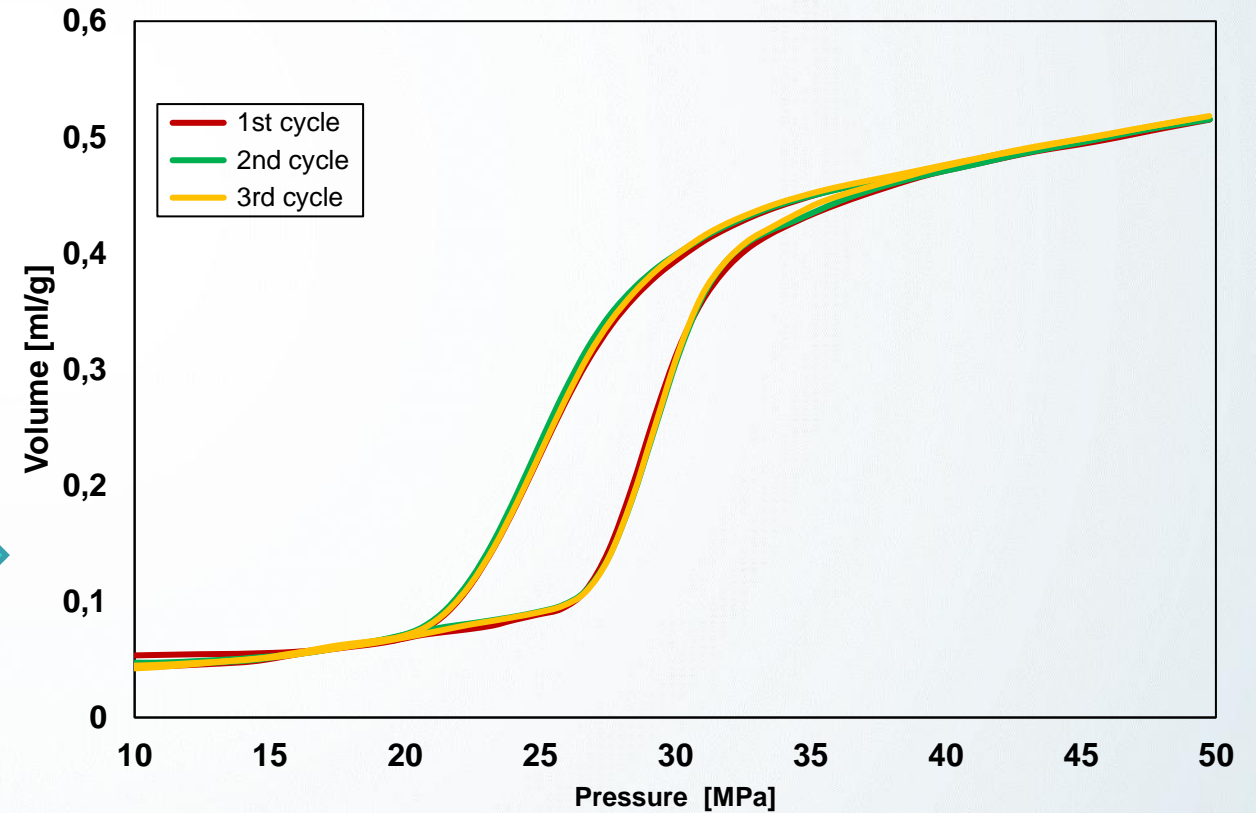
### H<sub>2</sub>O intrusion-extrusion tests

- Water intrusion-extrusion into-from porous material with  $\Delta P$ 
  - 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

ZIF-8\_Cm DI water 1st cy vs. 2<sup>nd</sup> cy vs. 3rd cy



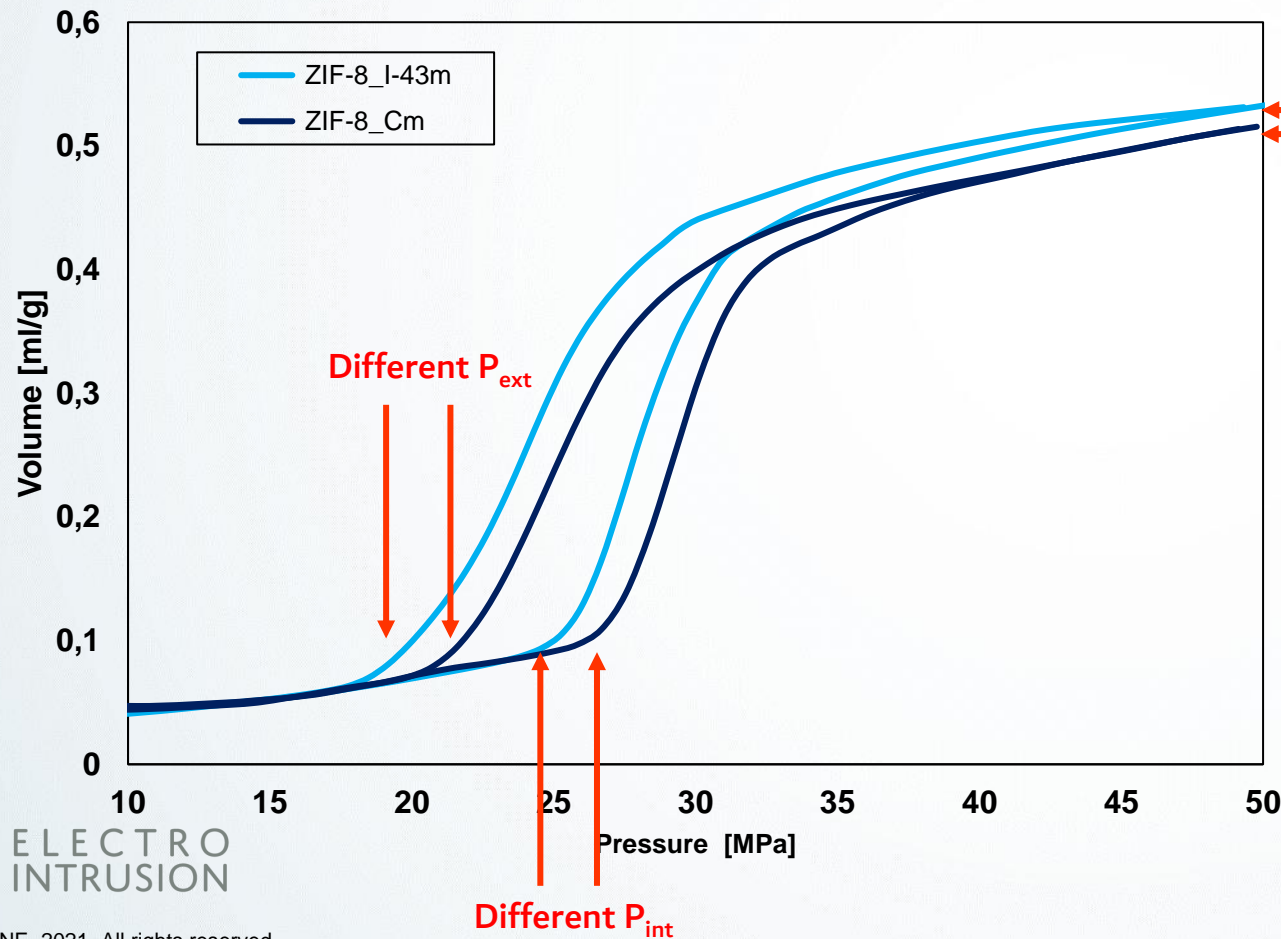
# 4. Results & Discussion

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



## Performances in H<sub>2</sub>O int-ext

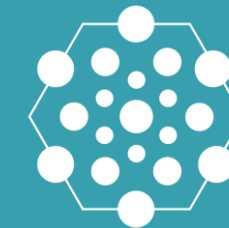
### PV Isotherms ZIF-8\_I-43m vs. ZIF-8\_Cm



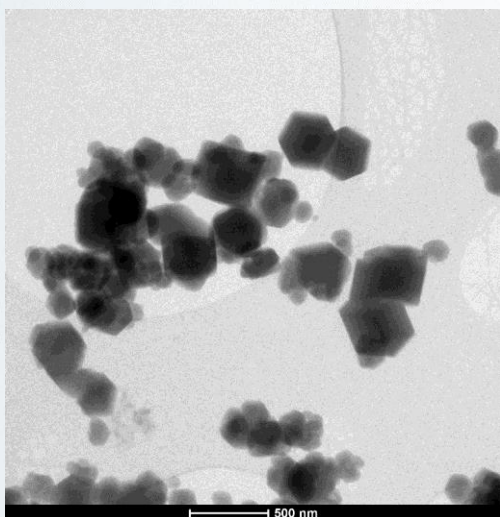
- ✓ Clear differences in performances compared to commercial ZIF-8.
- ✓ Different  $P_{int/ext}$  values could lie on the rigidity of ZIF-8\_Cm phase present in the sample.
- ✓ Smaller pore size in ZIF-8\_Cm also affects  $V_{int}$ .

# 4. Results and Discussion

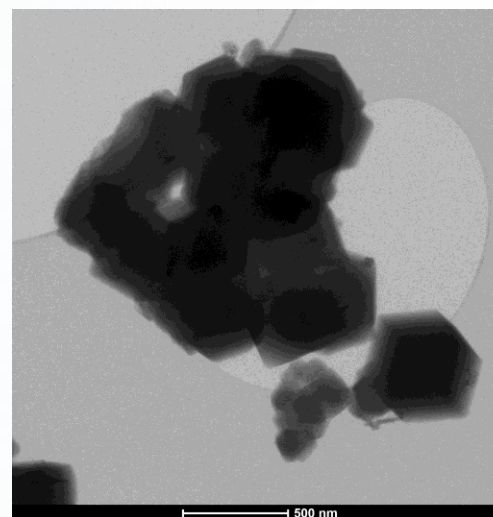
## Crystal size and shape



ZIF-8\_Cm

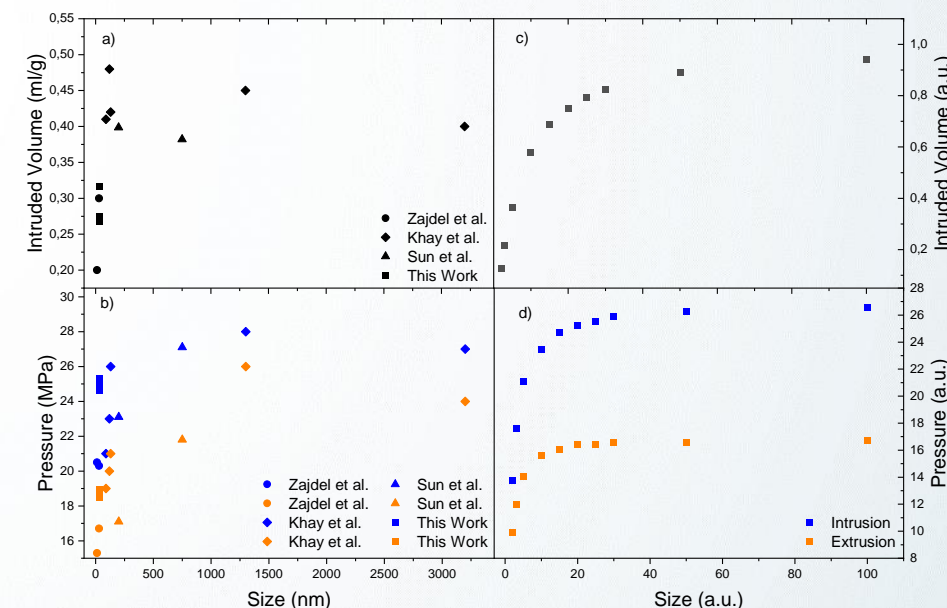


ZIF-8\_I4-3m



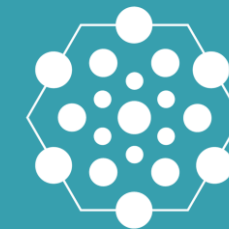
	Morphology	Mean crystal size
ZIF-8_I4-3m	dodecahedra	340 nm
ZIF-8_Cm	dodecahedra	230 nm

- ✓ 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.



# 4. Results & discussion

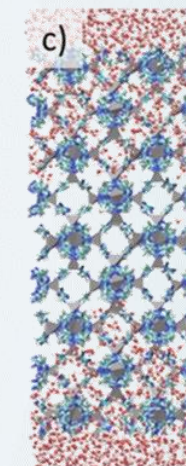
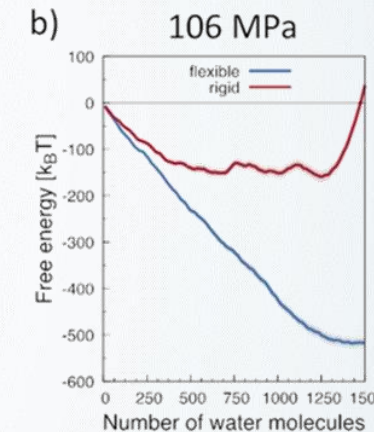
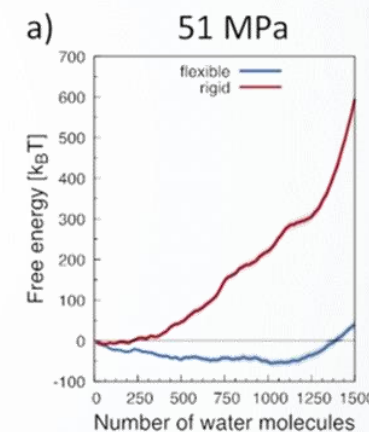
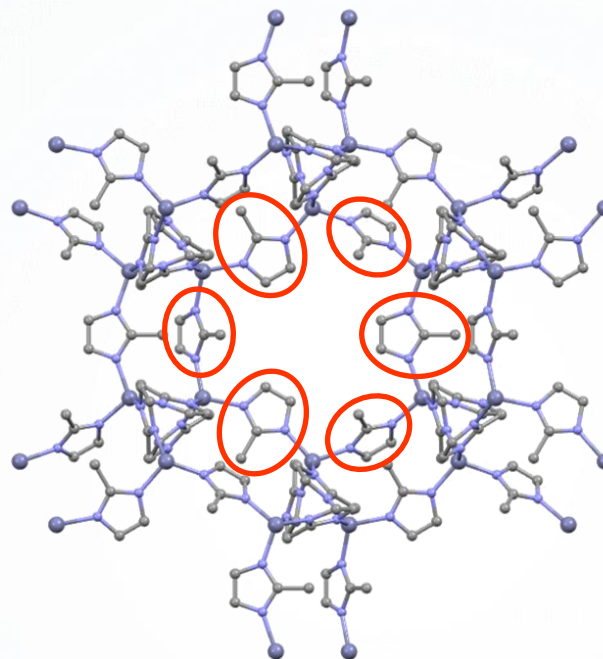
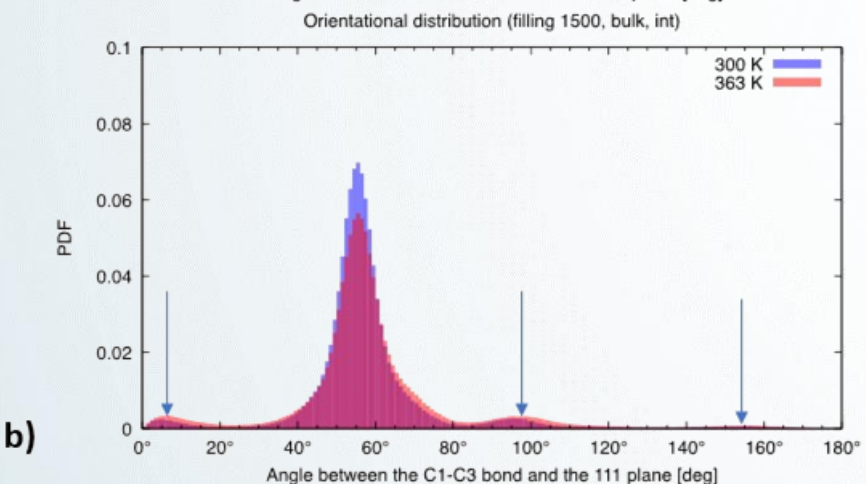
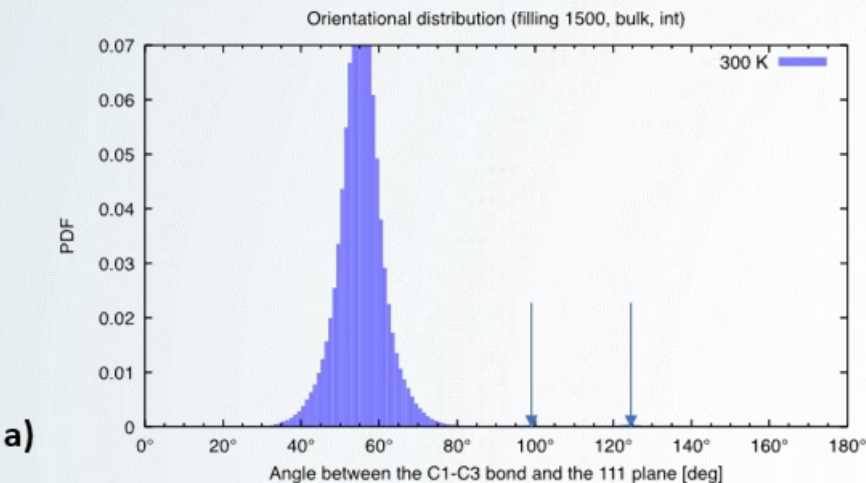
## Simulations



Dr. Josh David Littlefair



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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)

# 5. Conclusions



## CONCLUSIONS

- ZIF-8 synthesized using FCDS exhibit a clear increase in  $P_{int}$  and  $V_{int}$  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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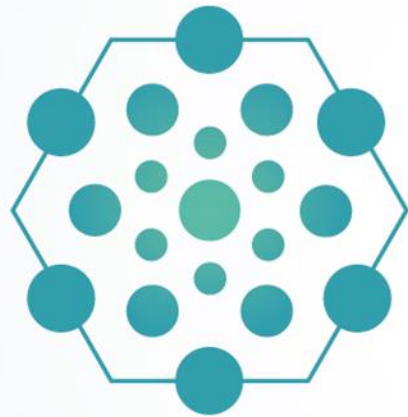


# Thanks for your attention!



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# ELECTRO INTRUSION