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In-situ parametric study of D_2O intrusion into large cage hydrophobic MOF

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Rozpraszanie neutronów i metody komplementarne w badaniach materii

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Introduction

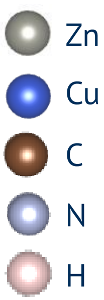
Background
Increasing renewable energy production exceeds consumption during peak periods.

Problem
Need for new energy storage and conversion methods to prevent waste.

Solution
Use of lyophobic porous materials with non-wetting liquids for energy storage.

Relevance
Wetting-dewetting of nanoporous materials is crucial for applications in separation, chromatography etc.

Metal-Organic Frameworks (MOFs)



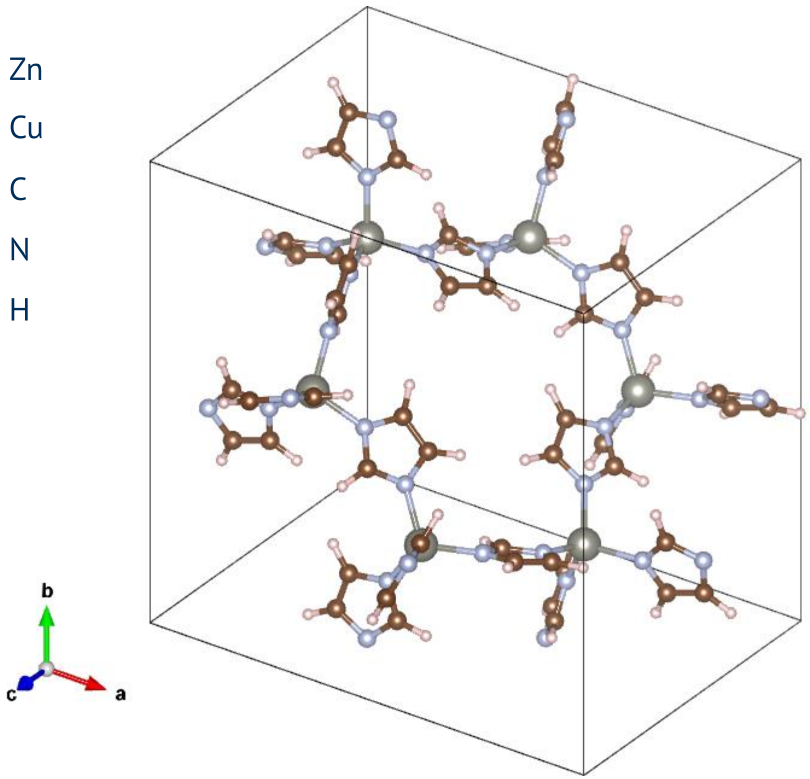


Fig. 1 ZIF-8 unit cell

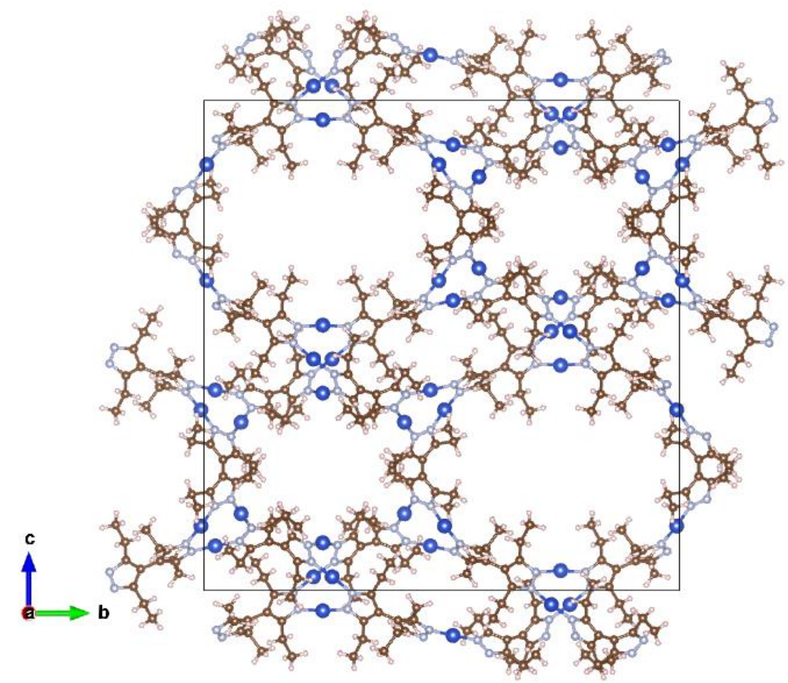


Fig. 2 Cu_2L structure

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Energy Storage/Conversion Mechanism

- **Concept**: Energy storage via pressure-volume work ($p\Delta V$).
- **Components**: Pressure (p) and volume of pores filled by liquid (ΔV).
- **Materials used**: Metal-Organic Frameworks (MOFs)

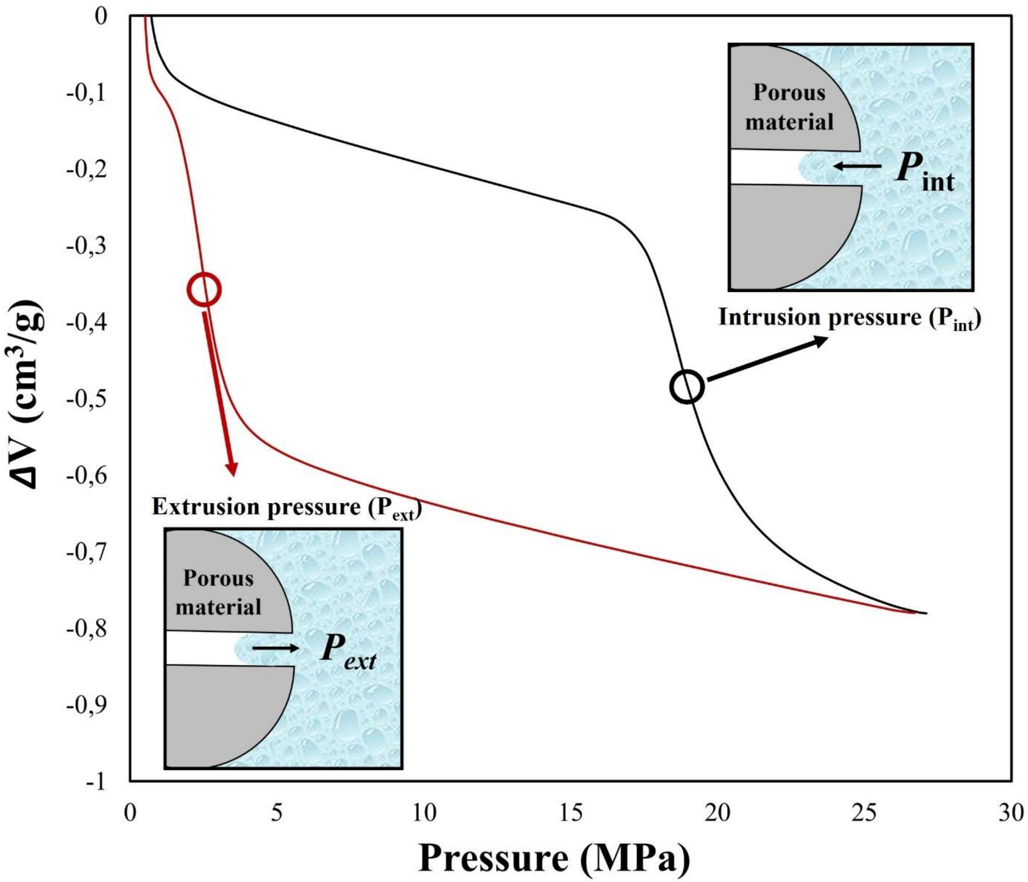


Fig. 3 Scheme of liquid intrusion/extrusion into/from porous material [E. Amayuelas, S. Kumar Sharma, J. Mor, L. Bartolomé, L. J. W. Johnson, D. Caporale, A. Le Donne, G. Sigolo, L. Scheller, V. Cristiglio, P. Zajdel, S. Meloni, Y. Grosu**.** *Submitted*.]

Unit cell change and *p*Δ*V*

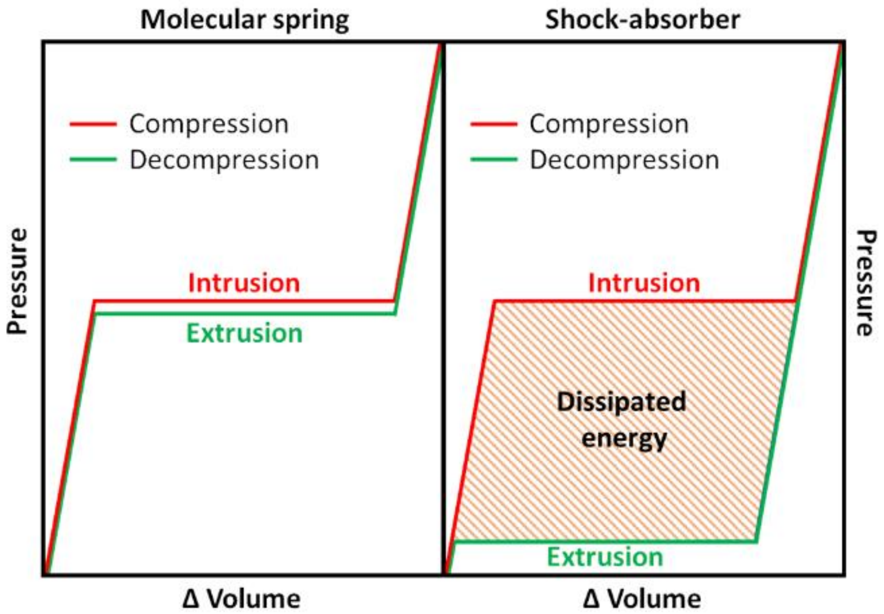


Fig. 4 Diagram illustrating changes in the volume of a unit cell as a function of pressure and transformation pathway

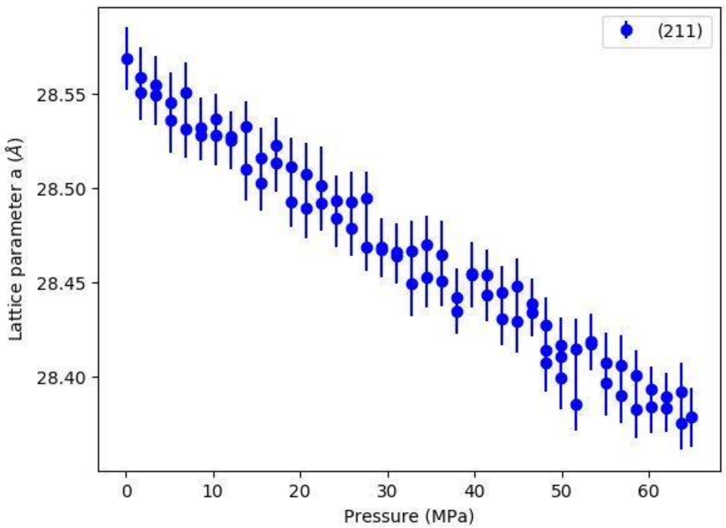


Fig. 5 Preliminary results showing the change in lattice parameters as a function of pressure (15 min/point) for the D2O+ZIF-71 system. Data obtained on the VSANS instrument at NCNR. Intrusion was not achieved due to the pressure limit of the apparatus.

Research Goal

- **Goal**: Determine mechanisms linking macroscopic parameters to atomic-scale phenomena during intrusion/extrusion processes in MOFs.

- **Method**: Analyze structural responses using in-operando neutron scattering.

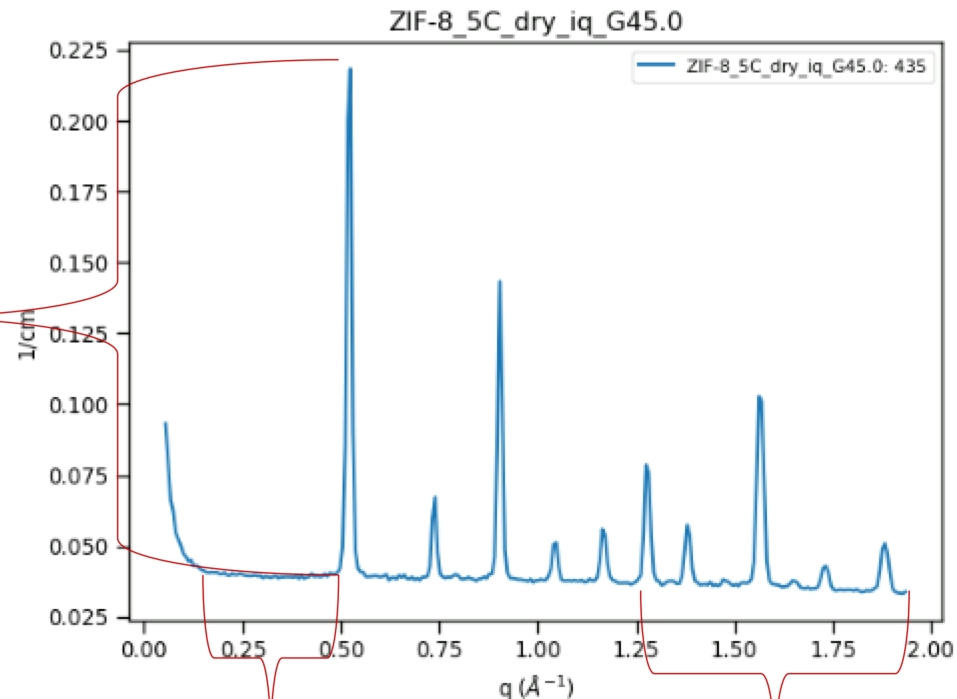
Materials and Methods

- **MOFs Studied**: ZIF-8, ZIF-7, and hybrid mixed-linker ZIF-7-8.
- **Non-Wetting Liquid**: Heavy water (D2O).
- **Techniques Used**:
  - High-pressure intrusion-extrusion experiments
  - Neutron diffraction structural analysis
  - MD simulations
- **Conditions**: High pressures up to 100 MPa.

in-operando Neutron Scattering

- Allows observation of material structure changes during intrusion/extrusion

Bragg Peak Intensity
Amount of D2O confined in hydrophobic cage



SANS Region
Short range order of MOF cage filling

WANS Region
Evolution of unit cell size

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Experimental Setup

- **Sample Environment**
  High-pressure setup up to 100 MPa

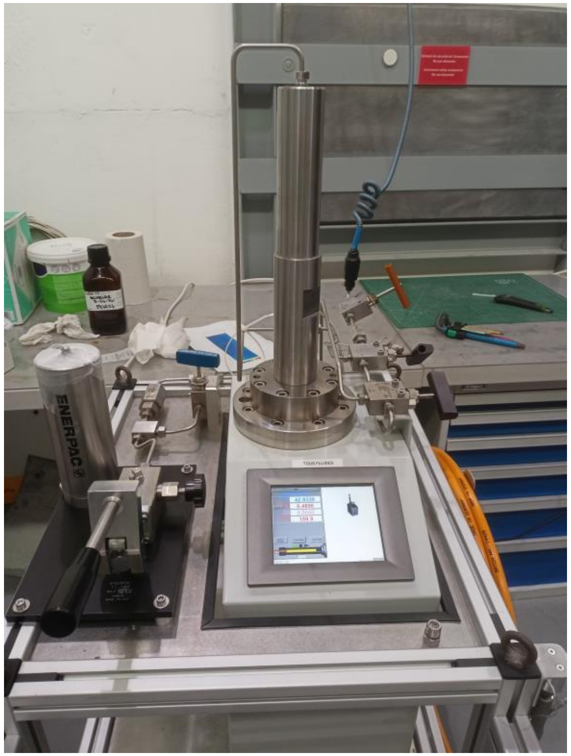


Fig. 6 Syringe pump setup

- **Neutron Scattering**
  D16 Line with "Orange ILL" cryostat

Fig. 7 Sample environment with "Orange cryo"

Results - Structural Changes

- **Lattice Parameter**: Changes in lattice parameter depending on pressure.
- **Negative Compressibility**: Demonstrated in nanoporous framework during intrusion for both materials.

ZIF-8

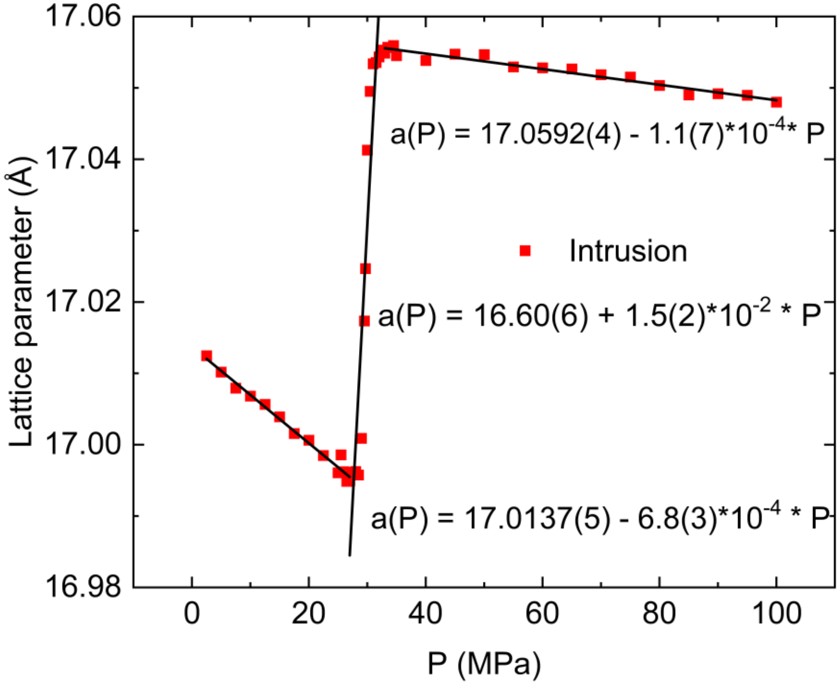


Fig. 8 Change of lattice parameter as a function of pressure during intrusion (compression) for ZIF-8 [E. Amayuelas, S. Kumar Sharma, J. Mor, L. Bartolomé, L. J. W. Johnson, D. Caporale, A. Le Donne, G. Sigolo, L. Scheller, V. Cristiglio, P. Zajdel, S. Meloni, Y. Grosu. *Submitted*.]

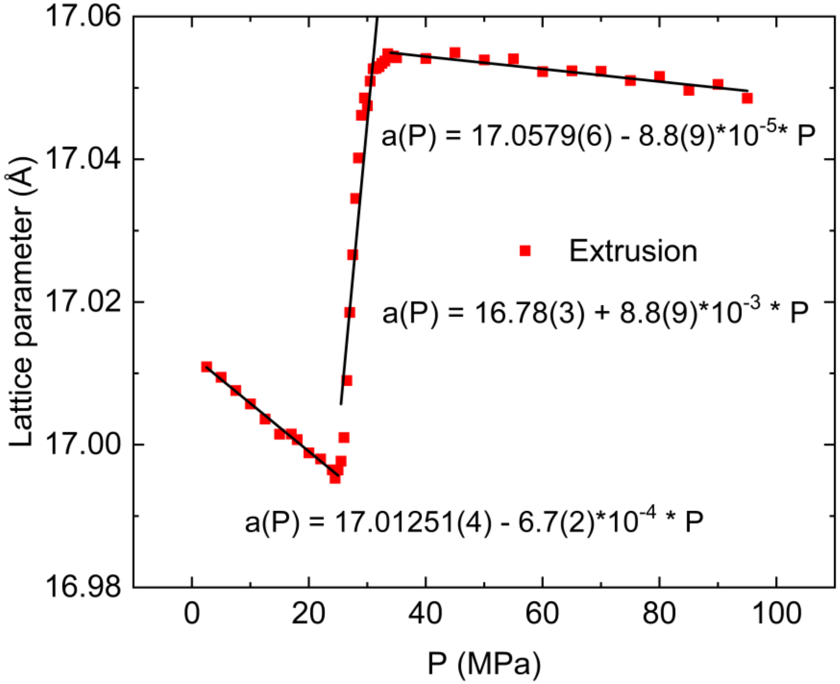


Fig. 9 Change of lattice parameter as a function of pressure during extrusion (decompression) for ZIF-8 [E. Amayuelas, S. Kumar Sharma, J. Mor, L. Bartolomé, L. J. W. Johnson, D. Caporale, A. Le Donne, G. Sigolo, L. Scheller, V. Cristiglio, P. Zajdel, S. Meloni, Y. Grosu. *Submitted*.]

ZIF-7-8

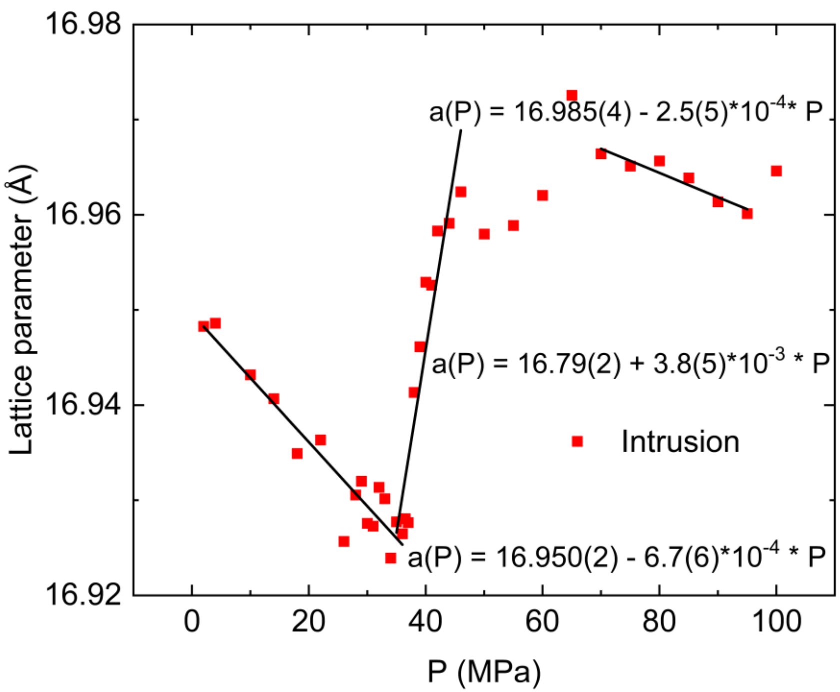


Fig. 10 Change of lattice parameter as a function of pressure during intrusion (compression) for ZIF-7-8

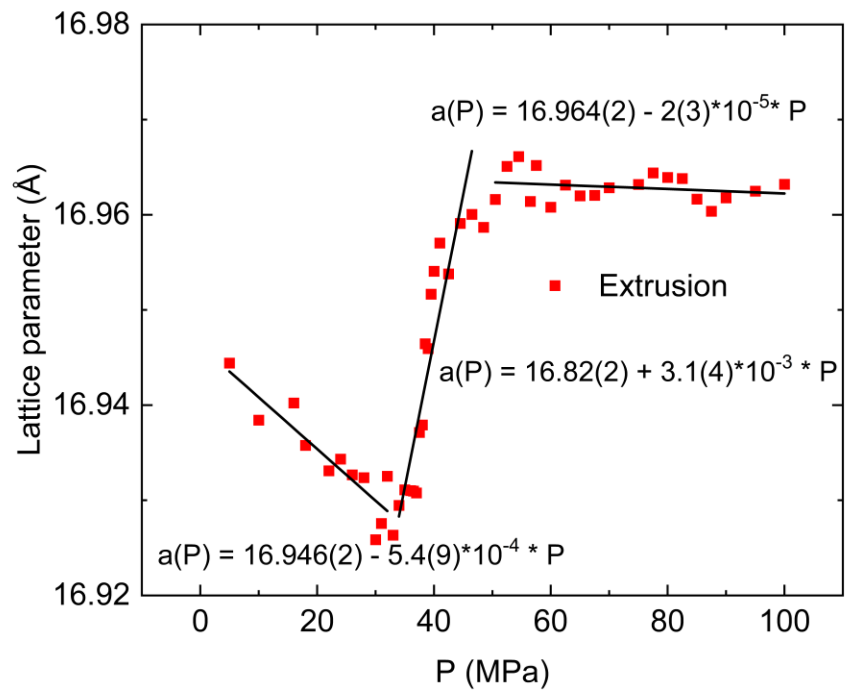


Fig. 11 Change of lattice parameter as a function of pressure during extrusion (decompression) for ZIF-7-8

ZIF-8

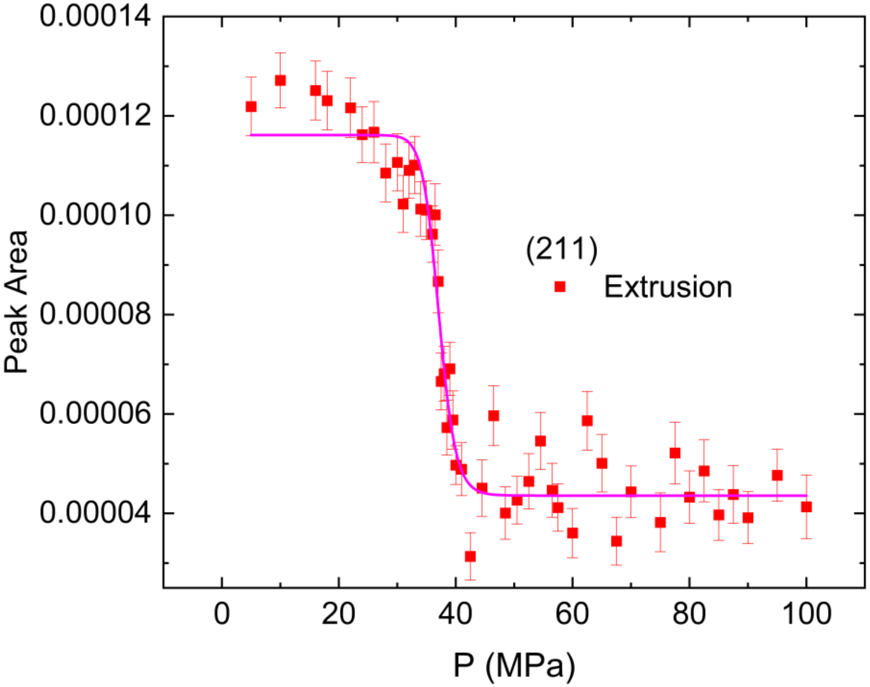


Fig. 12 Change of (211) peak area as a function of pressure during extrusion (decompression) for ZIF-8

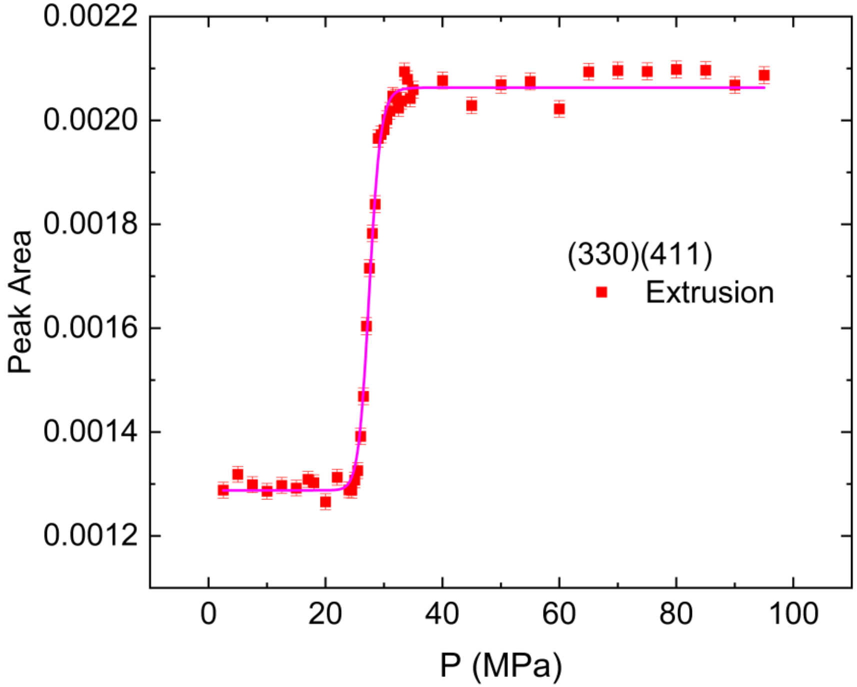


Fig. 13 Change of (330)(411) peak area as a function of pressure during extrusion (decompression) for ZIF-8

ZIF-7-8

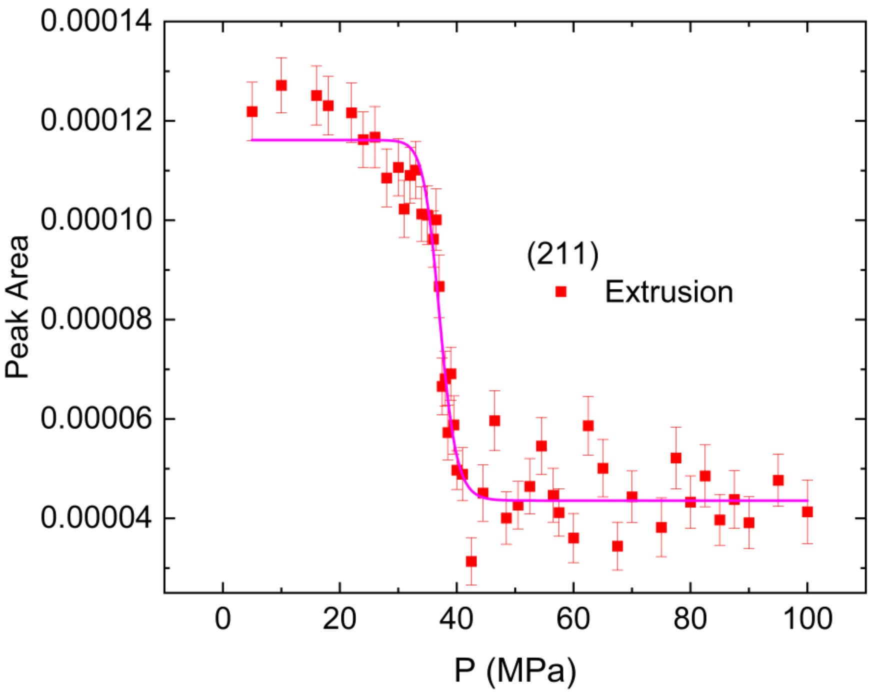


Fig. 14 Change of (211) peak area as a function of pressure during extrusion (decompression) for ZIF-7-8

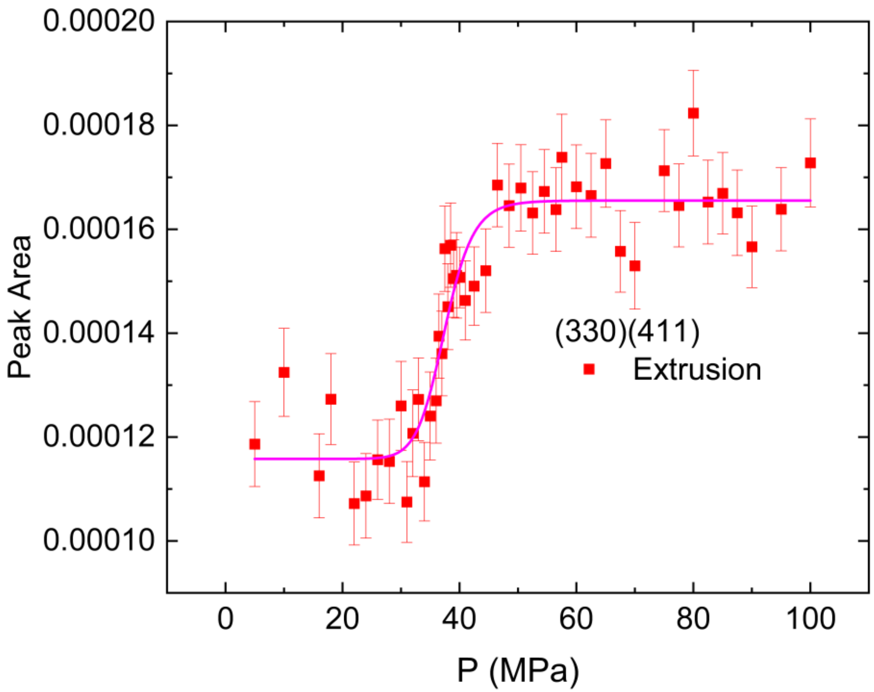
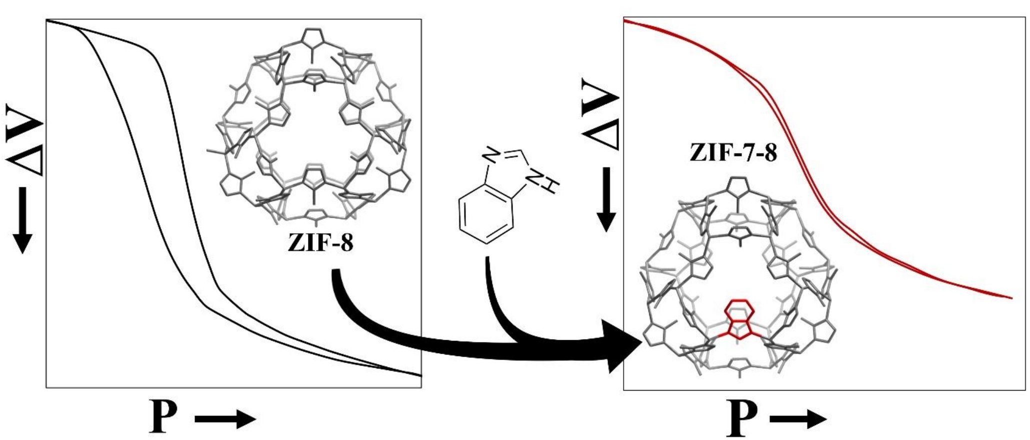


Fig. 12 Change of (330)(411) peak area as a function of pressure during extrusion (decompression) for ZIF-7-8

Hybrid ZIF-7-8 Findings

- **Non-Hysteretic Behavior**: Hybrid ZIF-7-8 MOF shows a non-hysteretic water intrusion-extrusion cycle, unlike ZIF-8 and ZIF-7.
- **Behavior Comparison**:
  - ZIF-8 and ZIF-7: Show pronounced hysteresis, acting as shock absorbers/bumper.
  - ZIF-7-8: Acts as a molecular spring.
- **Implications**: Potential for tuning wetting-dewetting hysteresis for various applications.



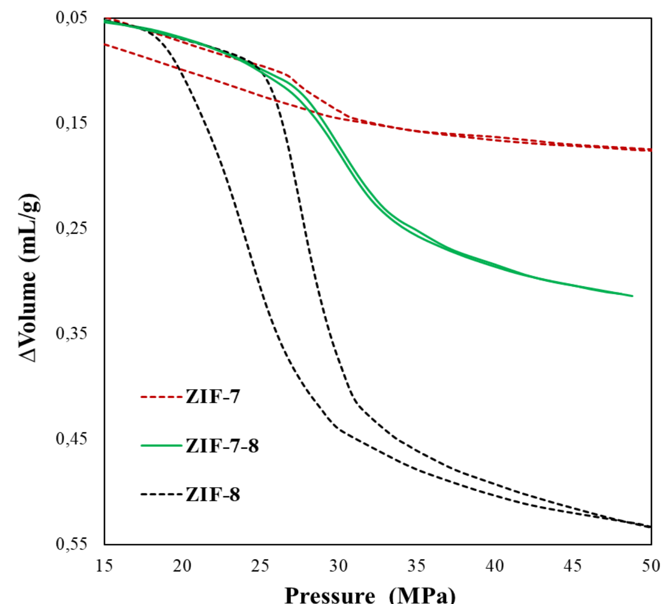


Fig. 15 *PV* isotherms [E. Amayuelas, S. Kumar Sharma, J. Mor, L. Bartolomé, L. J. W. Johnson, D. Caporale, A. Le Donne, G. Sigolo, L. Scheller, V. Cristiglio, P. Zajdel, S. Meloni, Y. Grosu. *Submitted*.]

Comparison

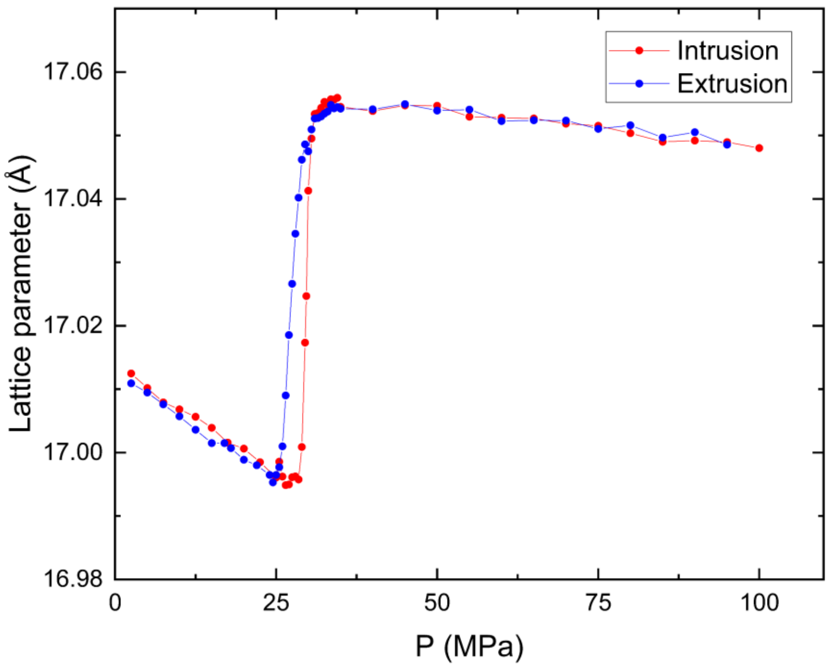


Fig. 16 Comparison of lat. par. change during intrusion/extrusion for ZIF-8

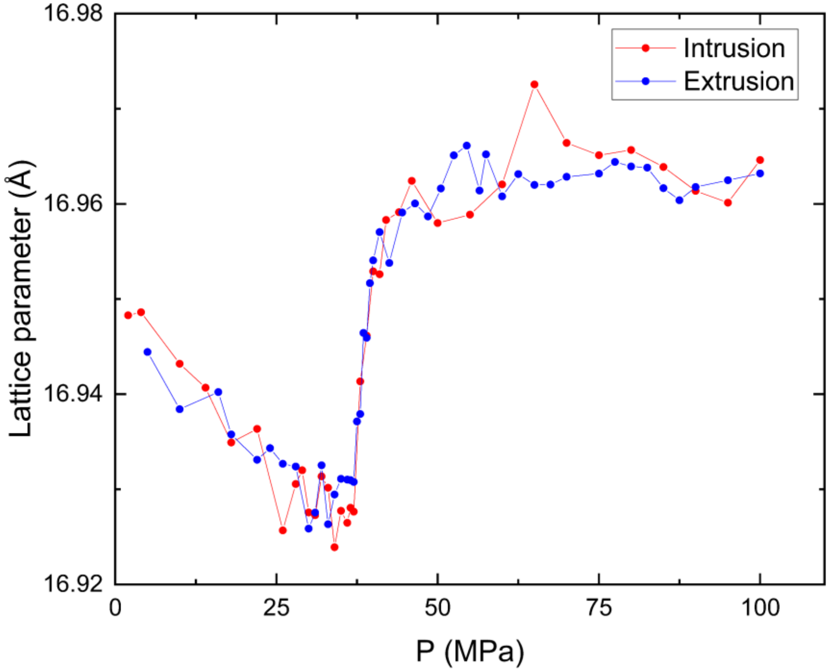


Fig. 17 Comparison of lat. par. change during intrusion/extrusion for ZIF-7-8

Comparison

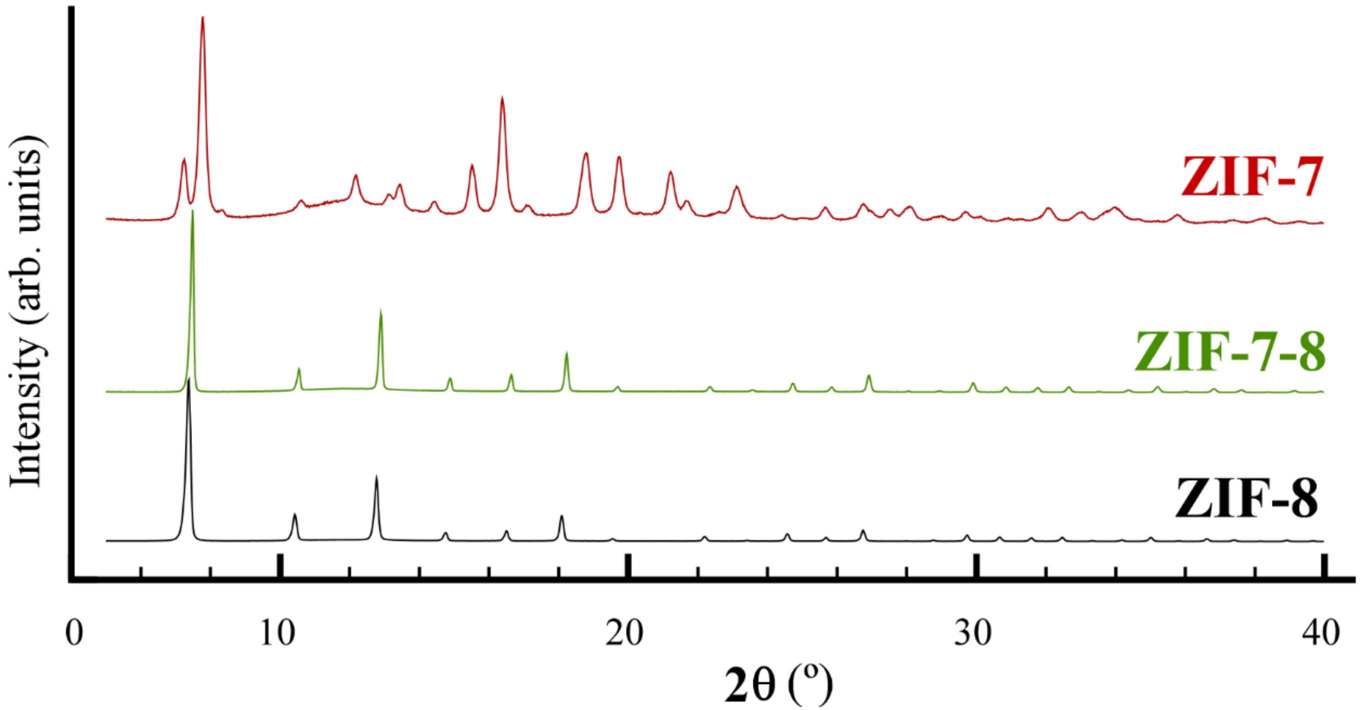


Fig. 18 XRD patterns for ZIF-7, ZIF-7-8 and ZIF-8. [E. Amayuelas, S. Kumar Sharma, J. Mor, L. Bartolomé, L. J. W. Johnson, D. Caporale, A. Le Donne, G. Sigolo, L. Scheller, V. Cristiglio, P. Zajdel, S. Meloni, Y. Grosu. *Submitted*.]

Conclusions

- **Macroscopic vs. Atomic Scale**: Linking intrusion parameters to atomic-scale phenomena.
- **Negative Compressibility**: Implications and significance in energy storage and dissipation.
- **New Insights**: Understanding transformation mechanisms from hysteretic to non-hysteretic behavior.

Conclusions

- **Summary**: Insights into the behavior of MOFs under varying pressures and the unique properties of hybrid ZIF-7-8.
- **Contribution**: Advancing understanding of energy storage mechanisms in porous materials.
- **Future Work**: Potential for more efficient and sustainable energy storage solutions and applications in tuning wetting-dewetting hysteresis.

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