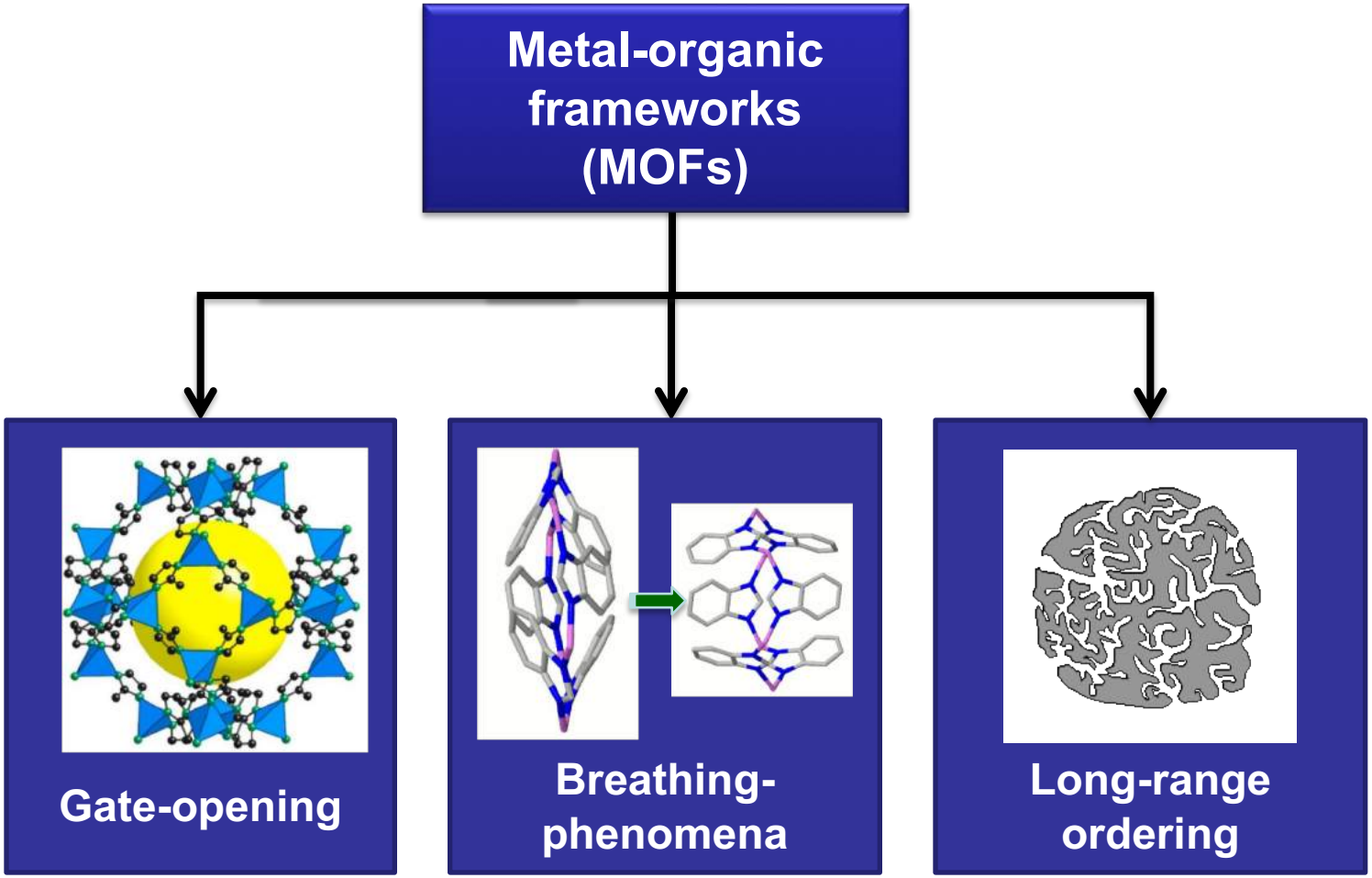




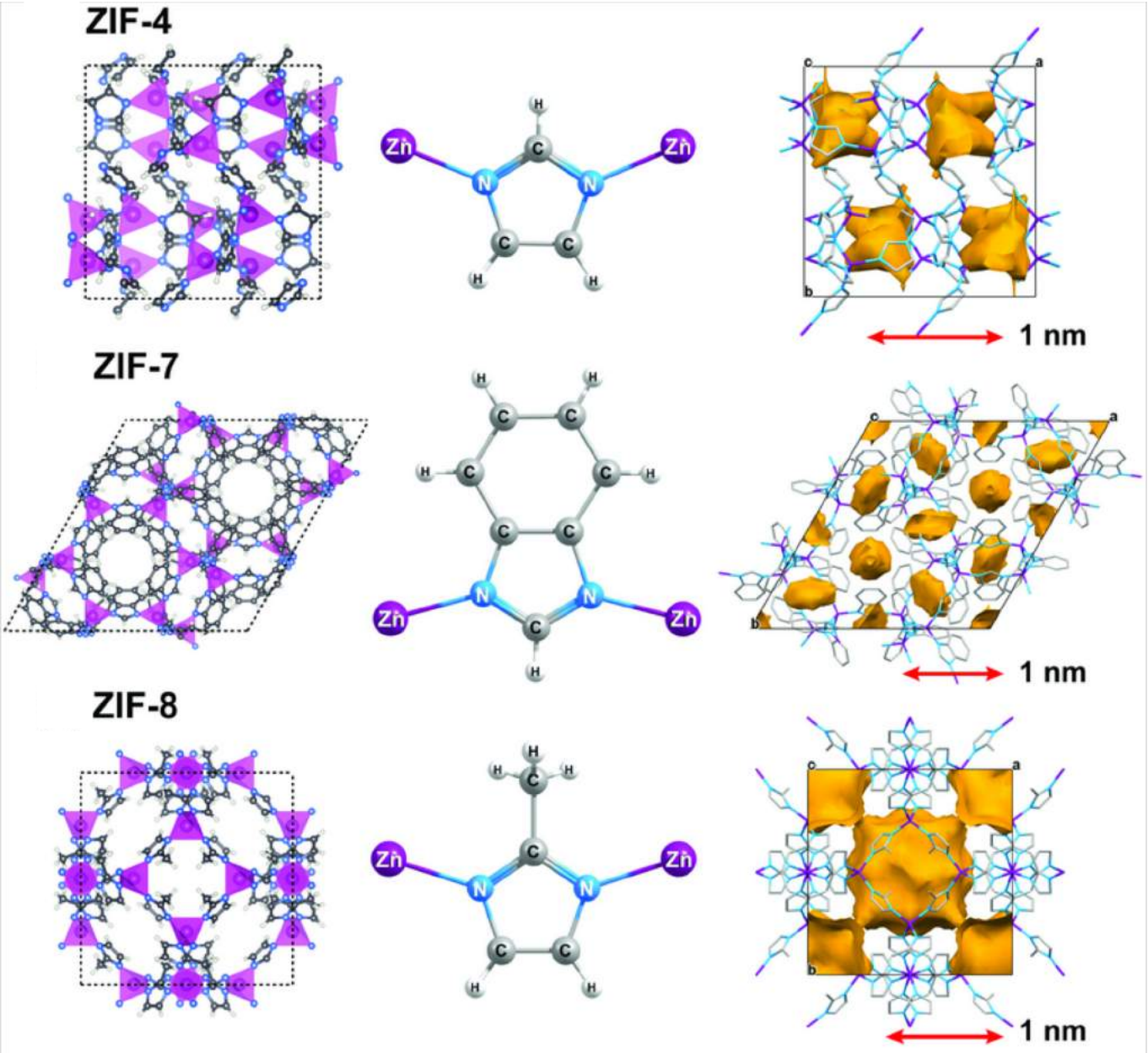
Structural flexibility in nanoporous solids upon gas adsorption

J. Silvestre-Albero
Laboratorio de Materiales Avanzados
Departamento de Química Inorgánica
Universidad de Alicante (Spain)

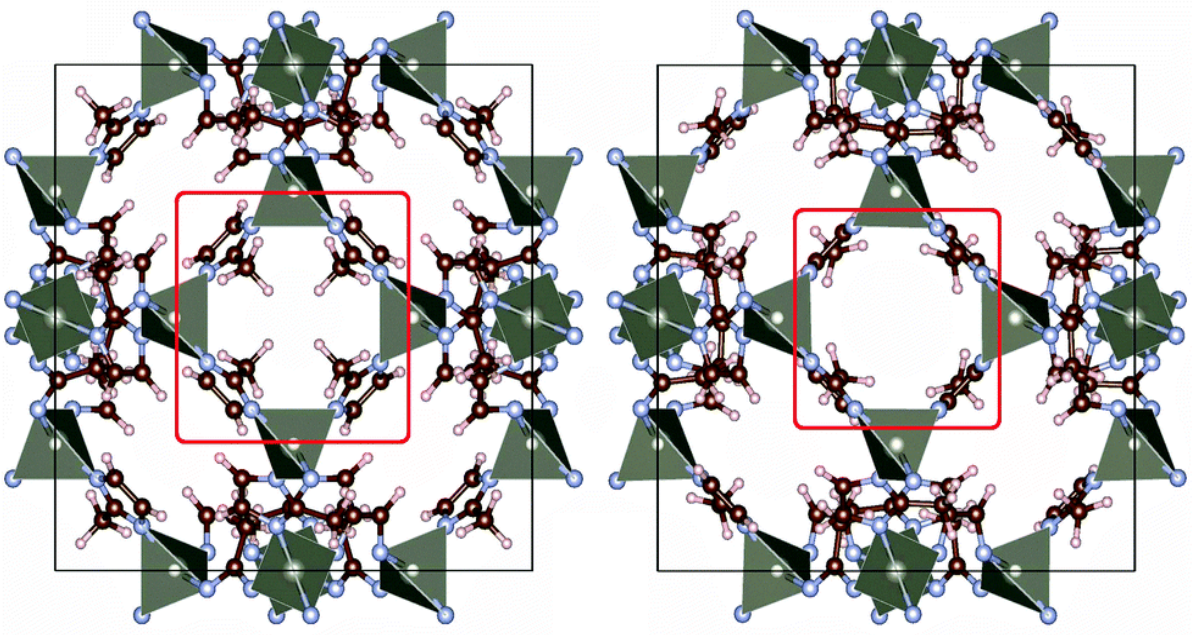
NanoMed


Metal-organic frameworks (MOFs)
Gate-opening
Breathing-phenomena
Long-range ordering

UA



GATE-OPENING ZIF-8

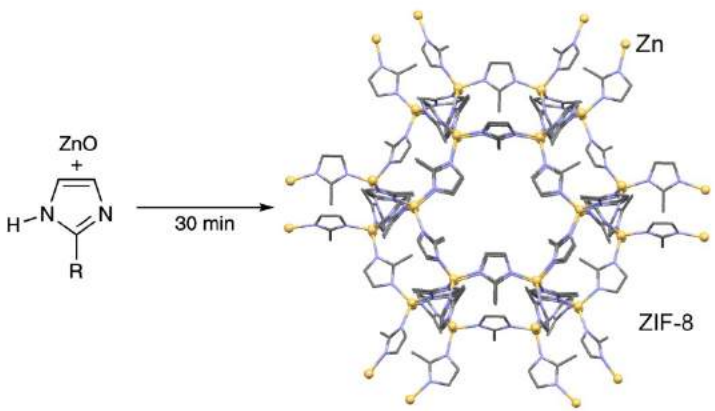


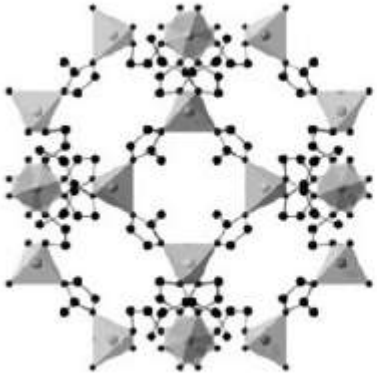
Casco et al., *Chem. Commun.* **2016**, 52, 3639

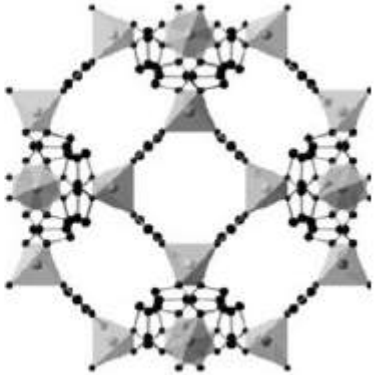
GATE-OPENING ZIF-8

UA

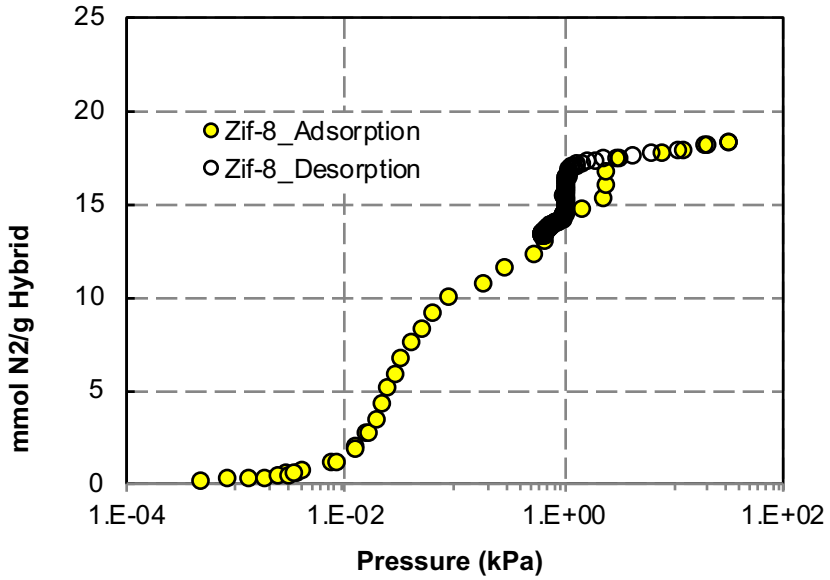
Synthesis of ZIF-8







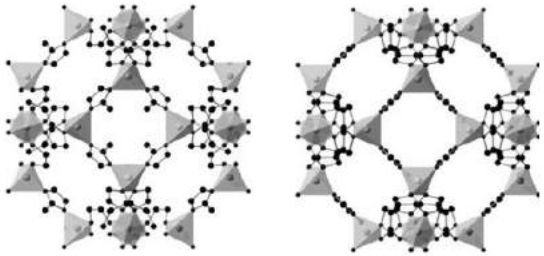
N2 adsorption isotherm ZIF-8

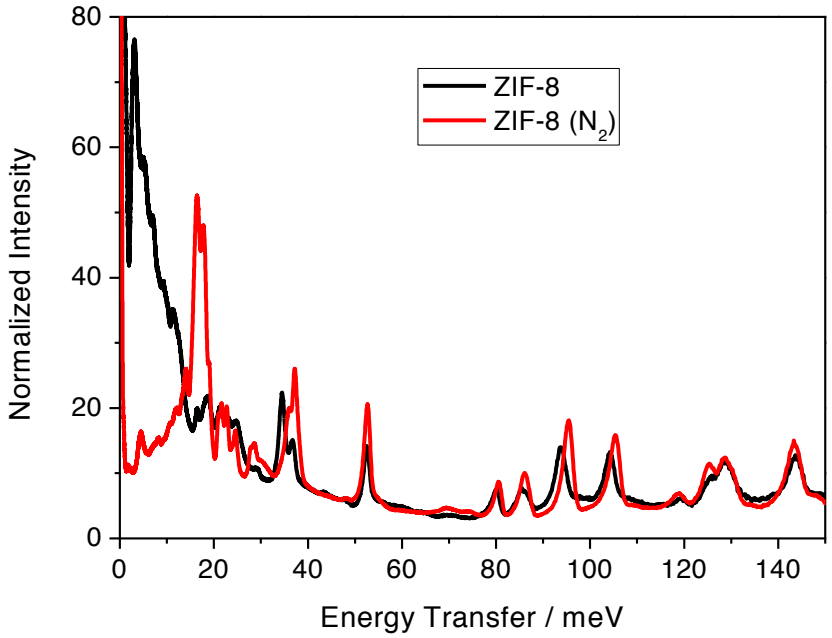


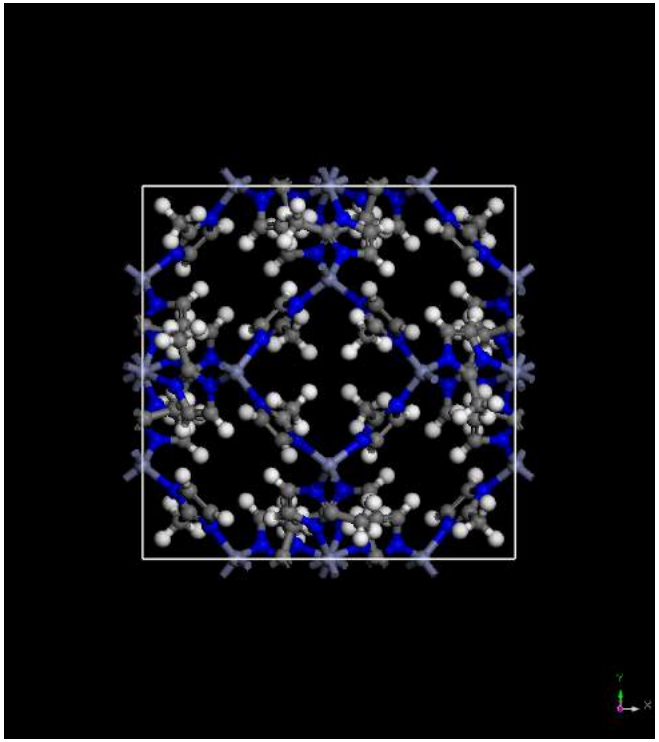
GATE-OPENING ZIF-8

UA

Inelastic neutron scattering in ZIF-8 before and after N_2





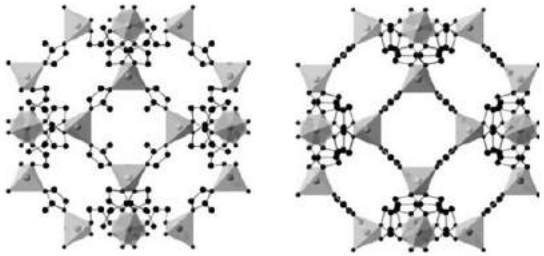


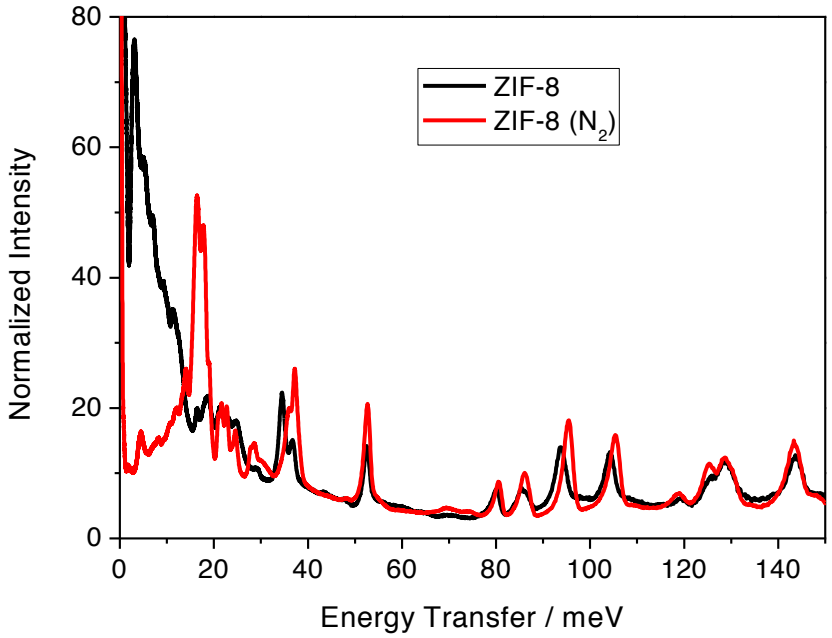
Casco et al., *Chem. Commun.* **2016**, 52, 3639

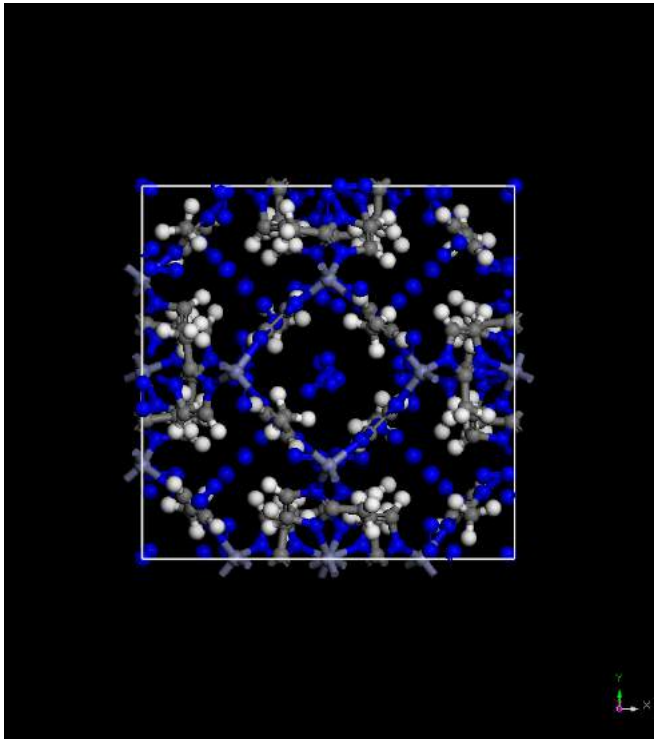
GATE-OPENING ZIF-8

UA

Inelastic neutron scattering in ZIF-8 before and after N_2





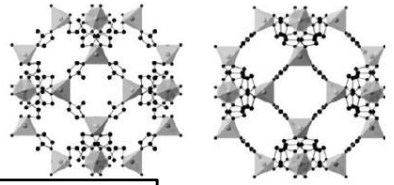


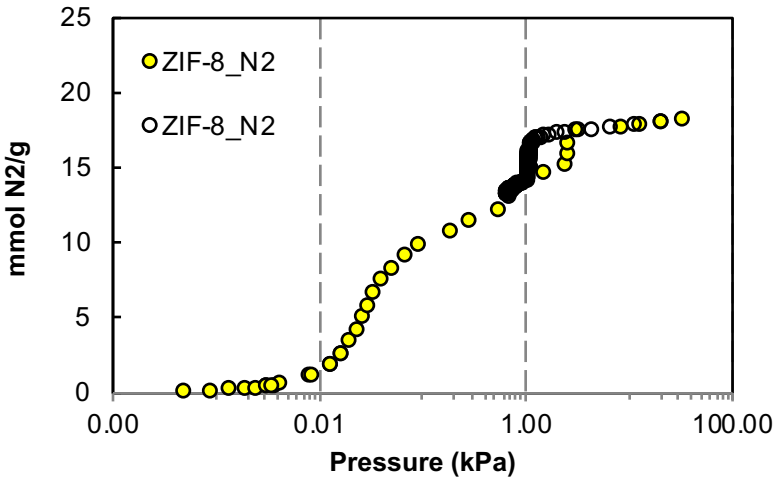
Casco et al., *Chem. Commun.* **2016**, 52, 3639

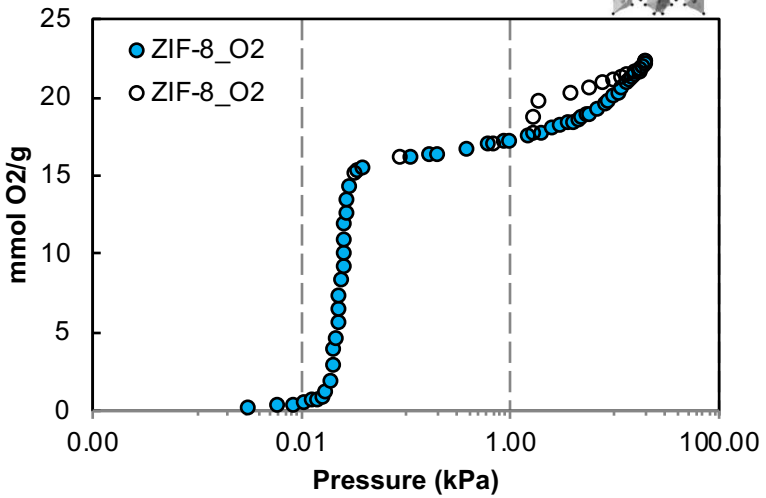
GATE-OPENING ZIF-8

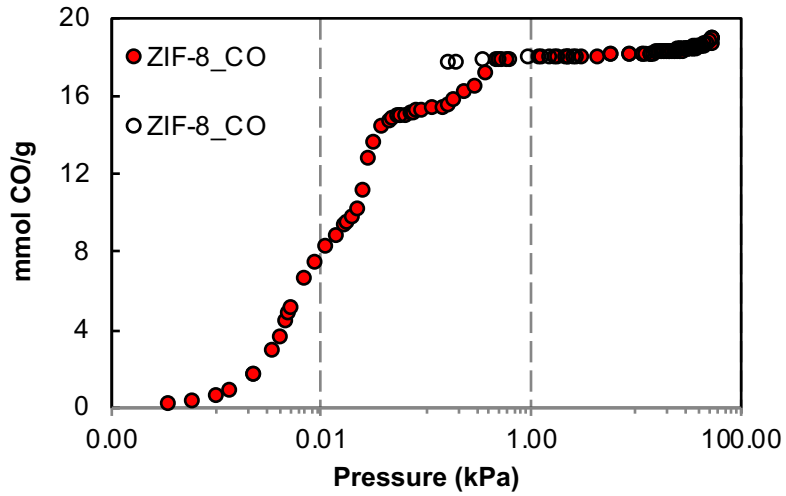
UA

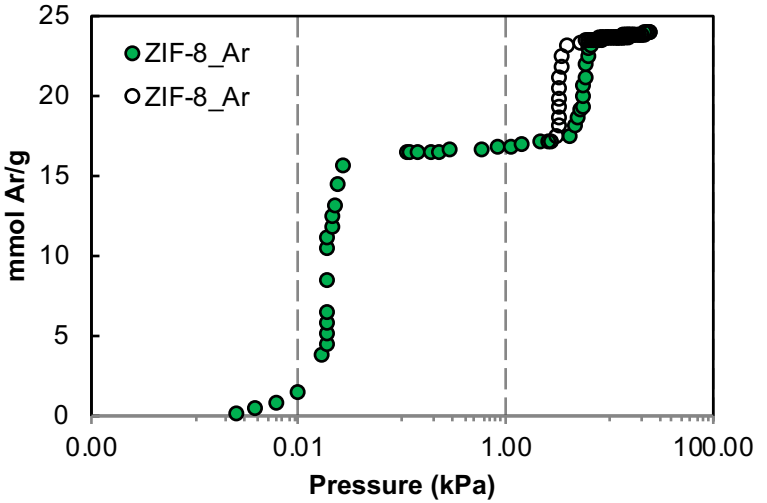
Inelastic neutron scattering in ZIF-8 before and after N_2, Ar, CO and O_2









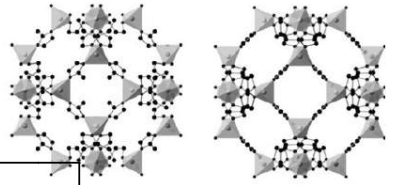


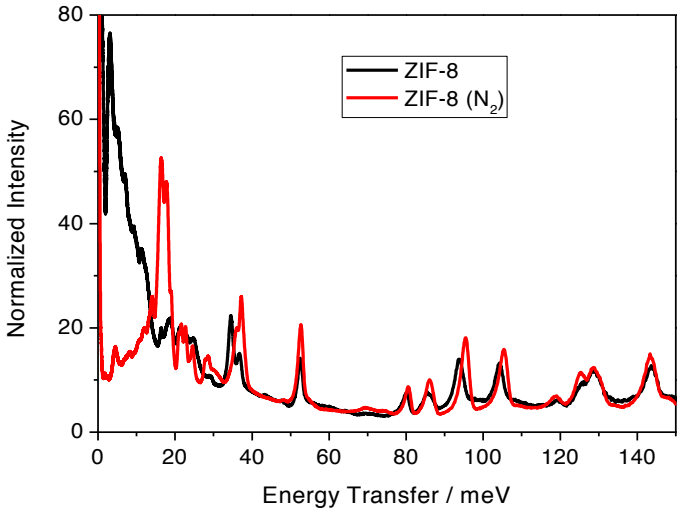
Casco et al., *Chem. Select* **2017**, 2, 2750-2753

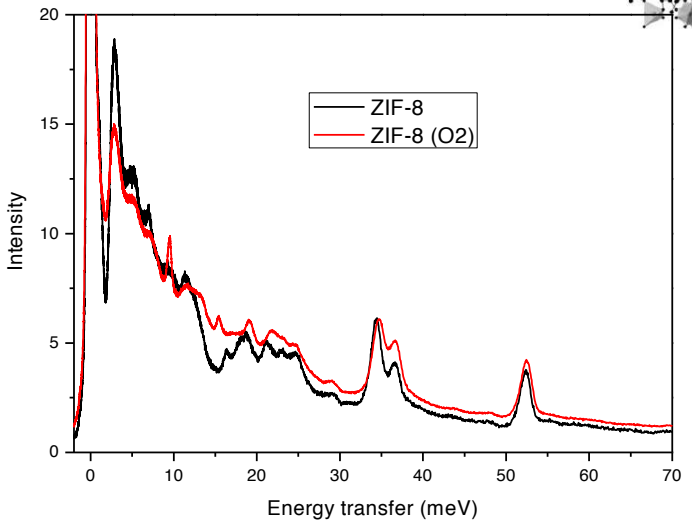
GATE-OPENING ZIF-8

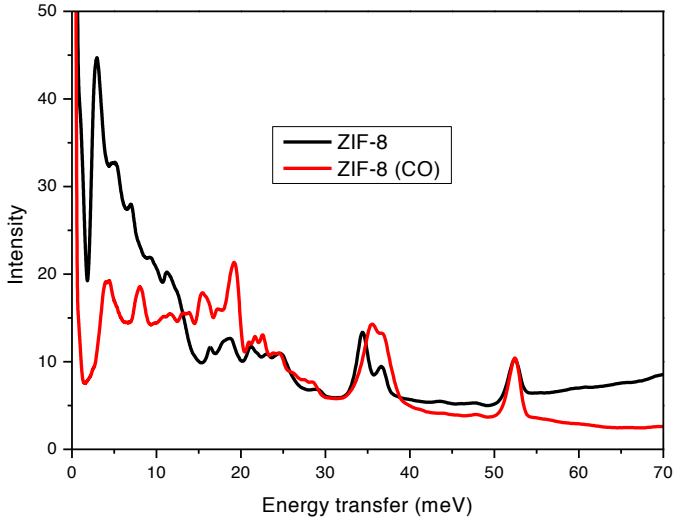
UA

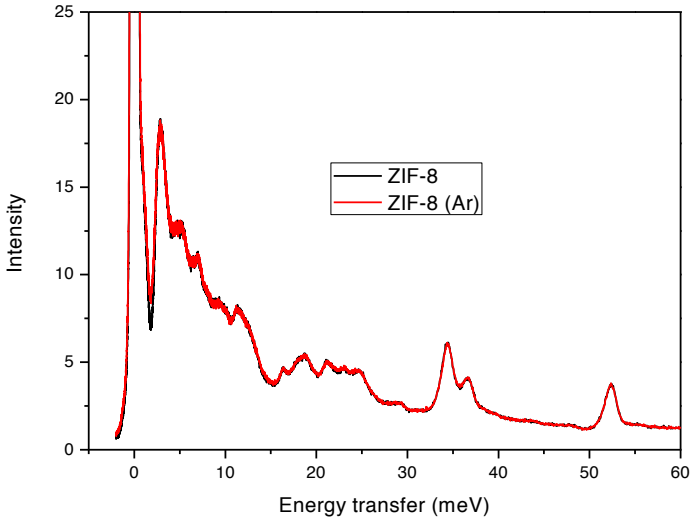
Inelastic neutron scattering in ZIF-8 before and after N_2, Ar, CO and O_2











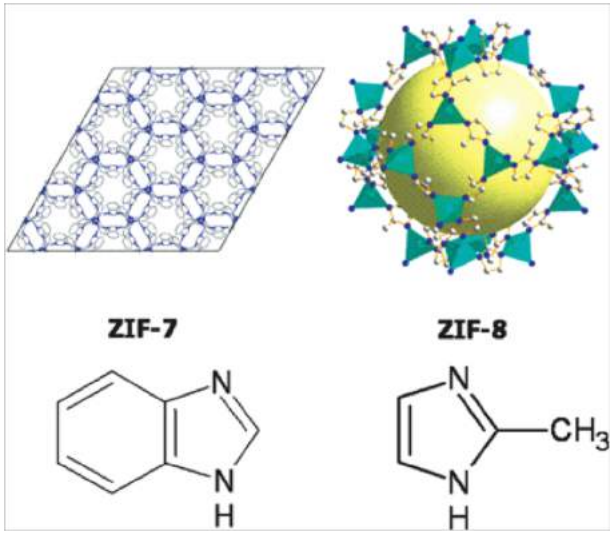
Casco et al., *Chem. Select* **2017**, 2, 2750-2753

Adsorption induced breathing phenomena in zeolitic-imidazolate frameworks (ZIF-7)

BREATHING ZIF-7

UA

Structure



SOD SOD

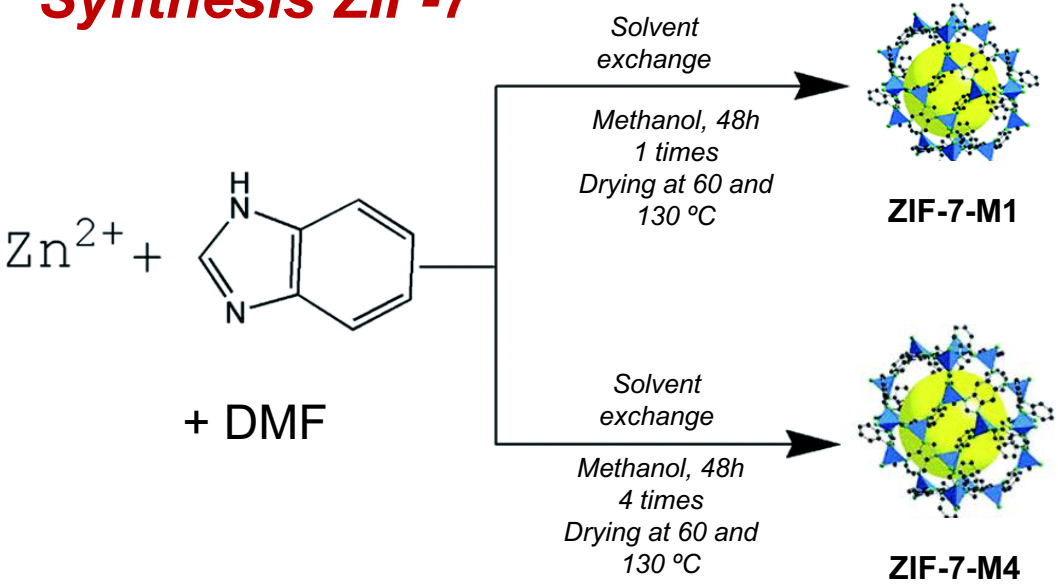
Crystal structure:

- ***Trigonal symmetry***

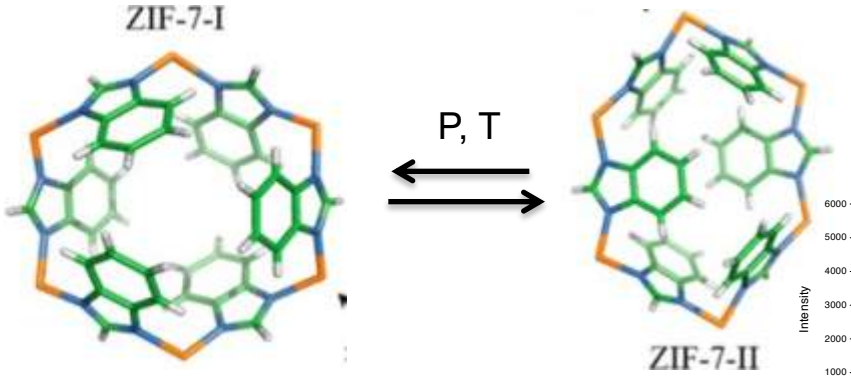
Crystal structure:

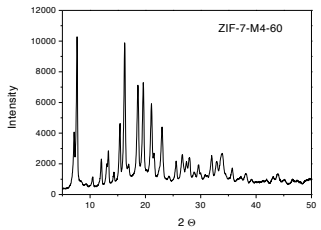
- ***Cubic structure***

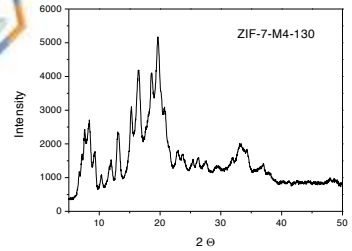
Synthesis ZIF-7



Structural transformation



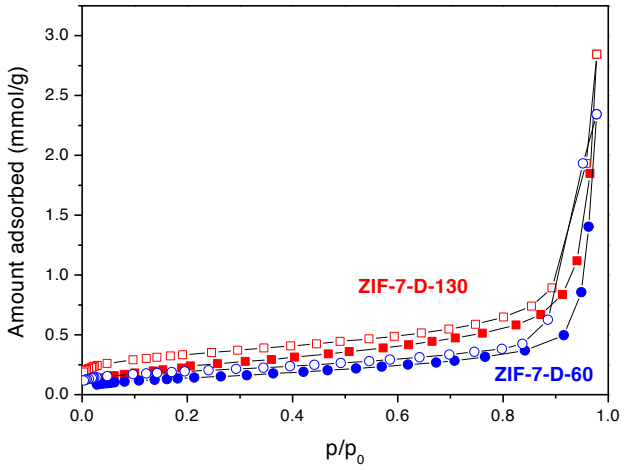


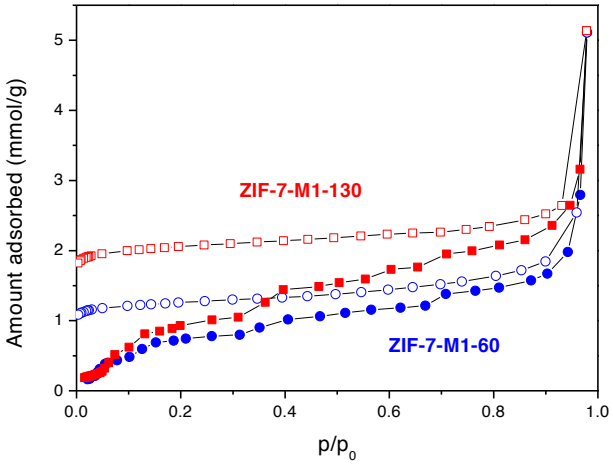


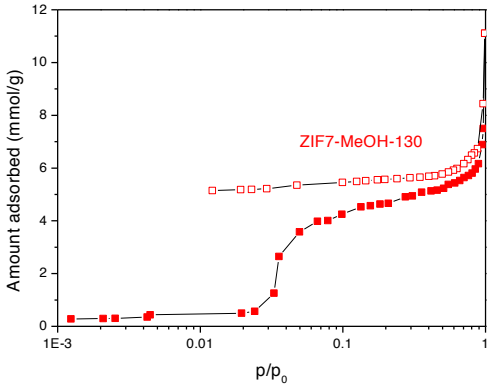
BREATHING ZIF-7

N2 adsorption isotherms at 77K

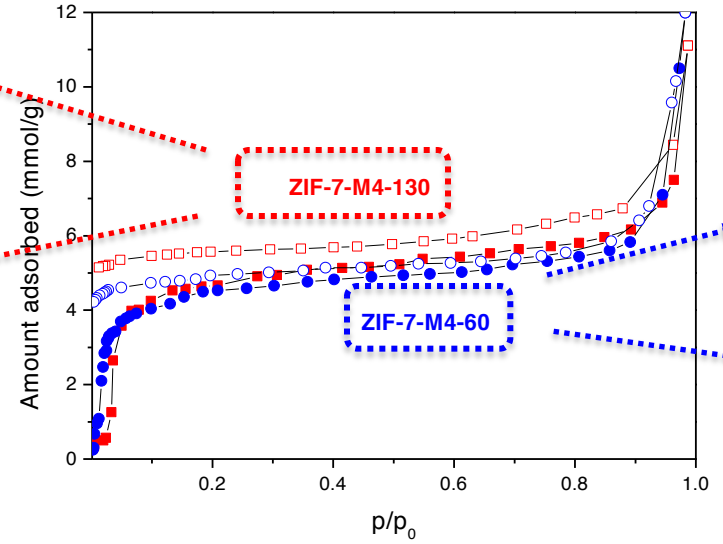
Theoretical S_{BET} = 400 m²/g

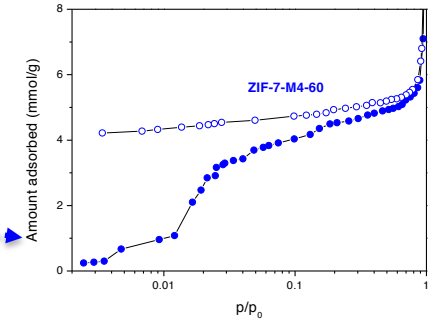






S_{BET} = 370 m²/g





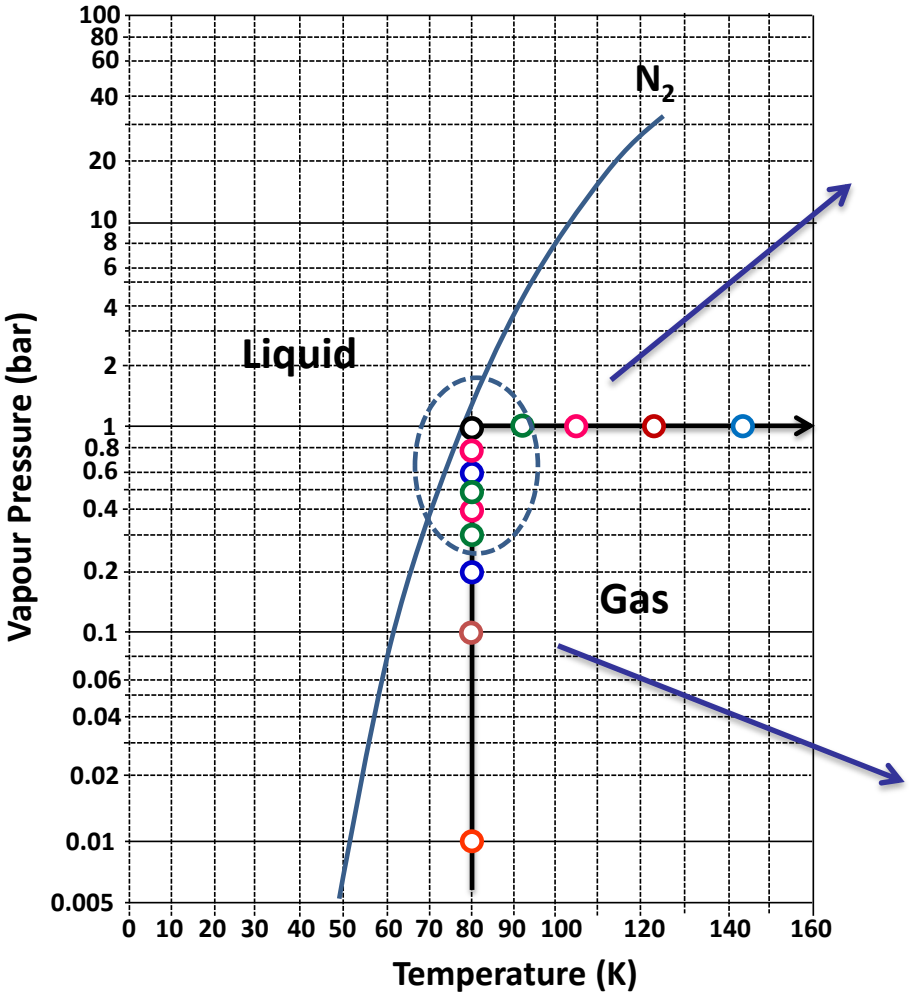
S_{BET} = 380 m²/g

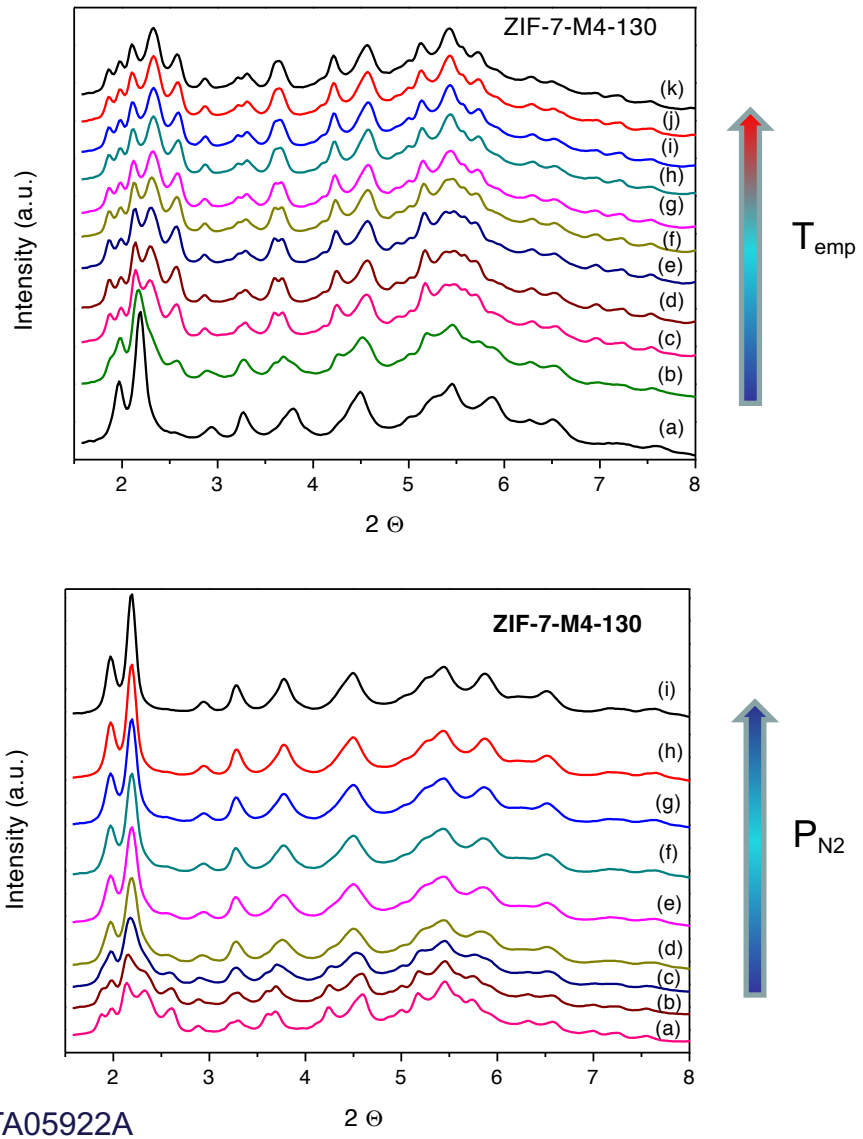
Cuadrado-Collados et al., *J. Mater. Chem. A* **2017**, DOI: 10.1039/C7TA05922A

BREATHING ZIF-7

UA

Synchrotron X-ray Diffraction (N_2)



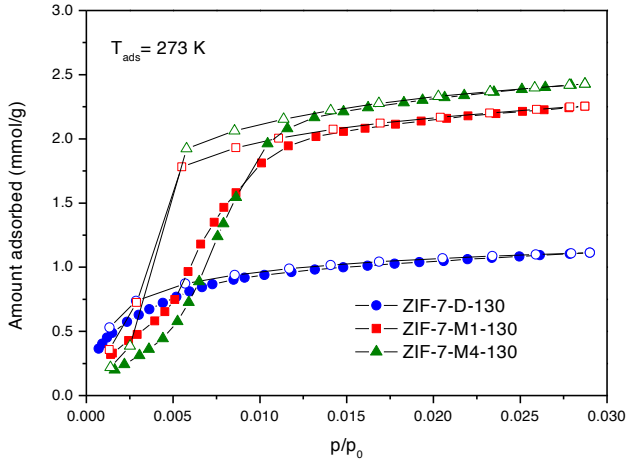


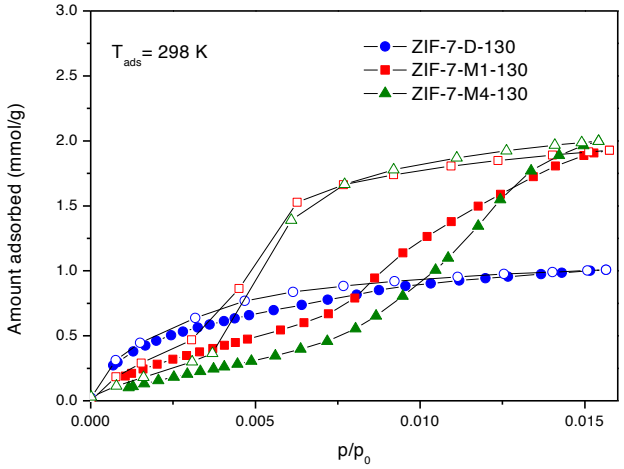
Cuadrado-Collados et al., *J. Mater. Chem. A* **2017**, DOI: 10.1039/C7TA05922A

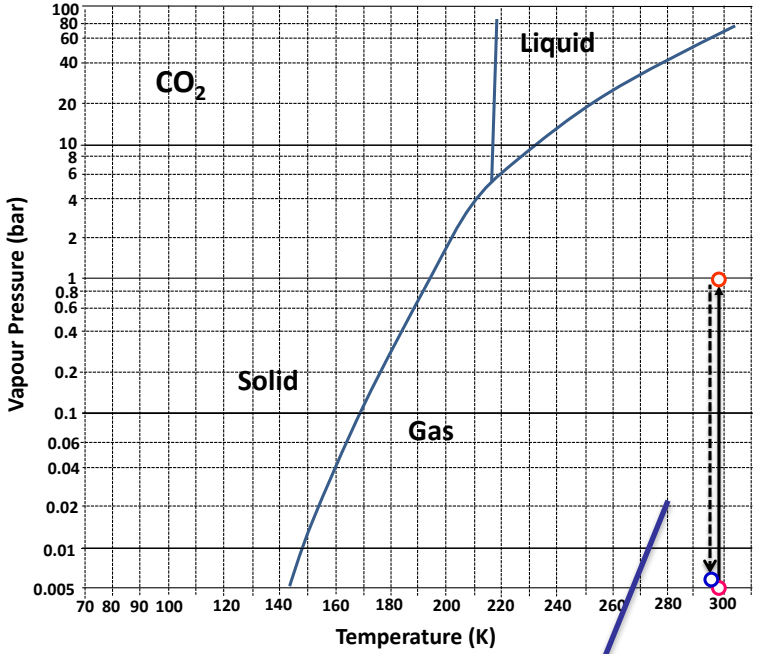
BREATHING ZIF-7

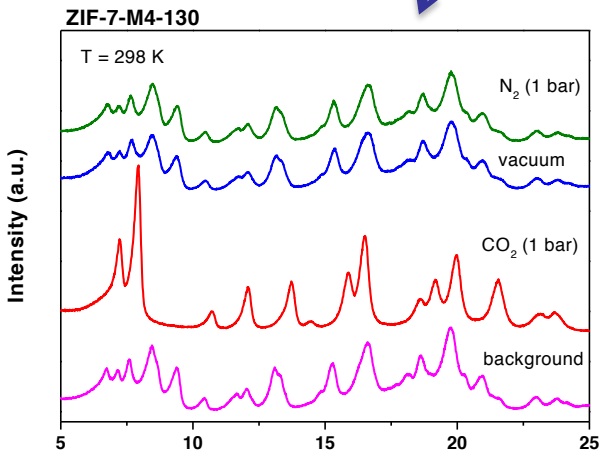
UA

CO_2 adsorption isotherms









Cuadrado-Collados et al., *J. Mater. Chem. A* **2017**, DOI: 10.1039/C7TA05922A

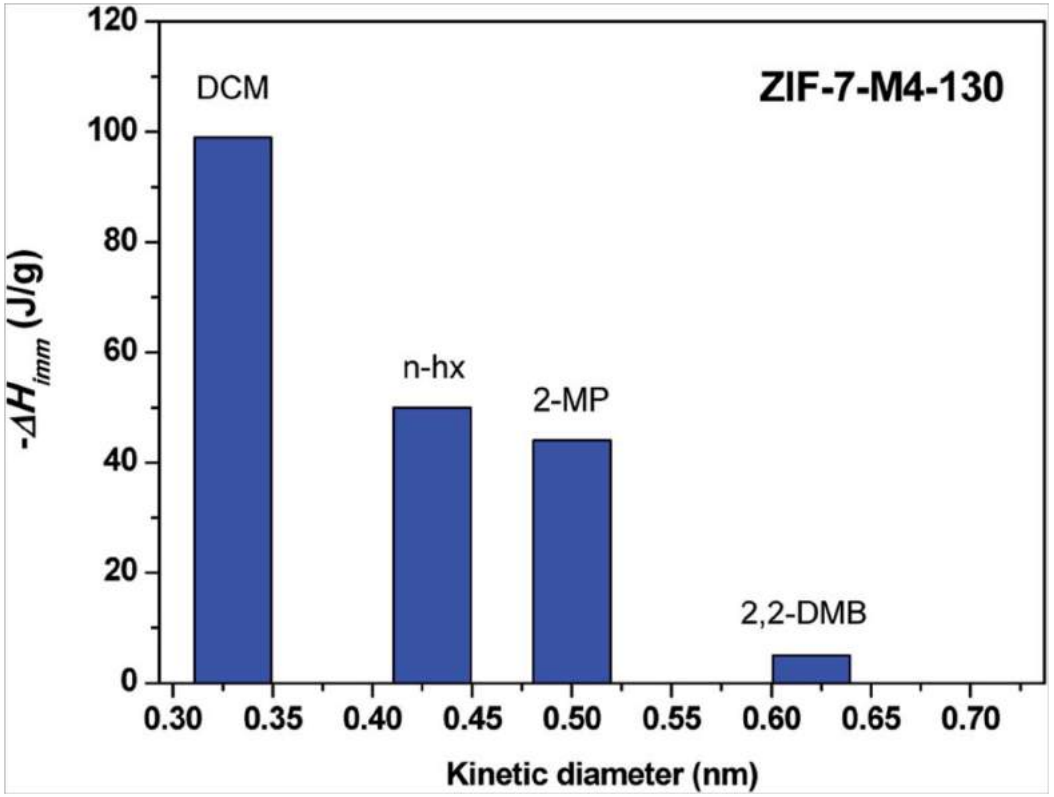
BREATHING ZIF-7

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Immersion calorimetry

Theoretical calculations predict a six-membered ring (6MR) pore entrance of ≈ 0.3 nm (cavity A).

Calorimetric measurements anticipate two different cavities in ZIF-7, one with a window diameter below 0.4 nm (cavity A) and one with a pore size of around 0.6 nm.



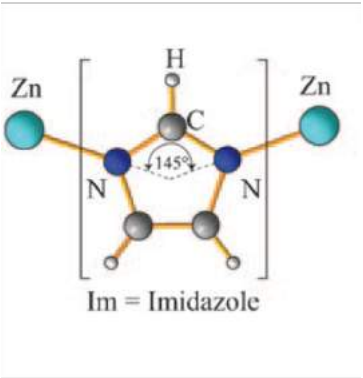
Cuadrado-Collados et al., *J. Mater. Chem. A* **2017**, DOI: 10.1039/C7TA05922A

Adsorption induced Structural Changes in zeolitic-imidazolate frameworks (ZIF-4)

BREATHING ZIF-4

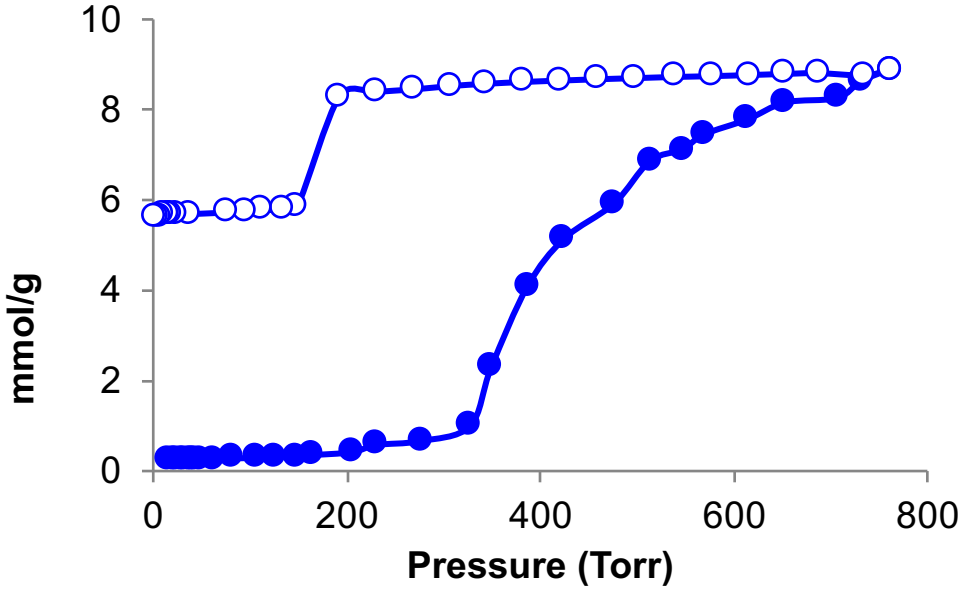
UA

Structure

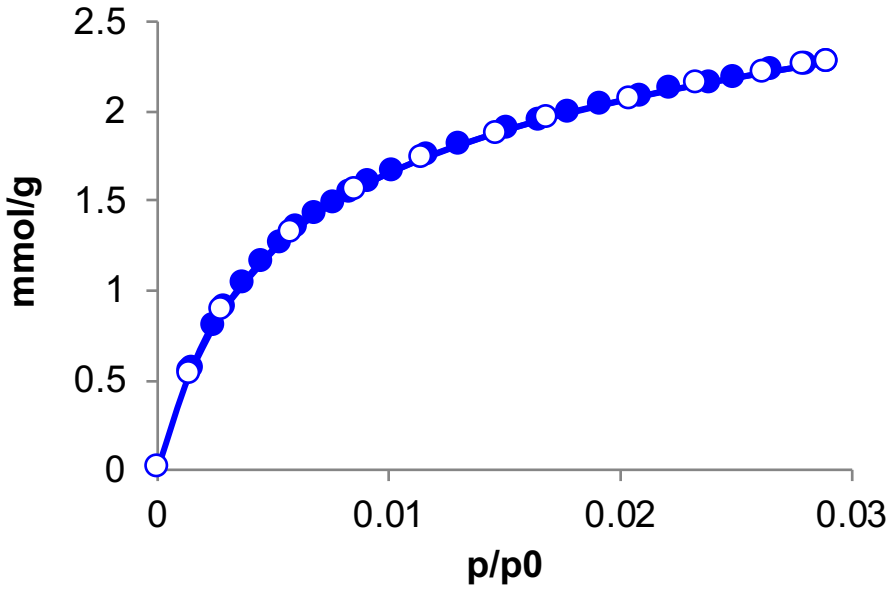




N_2 adsorption at 77K



CO_2 adsorption at 273K



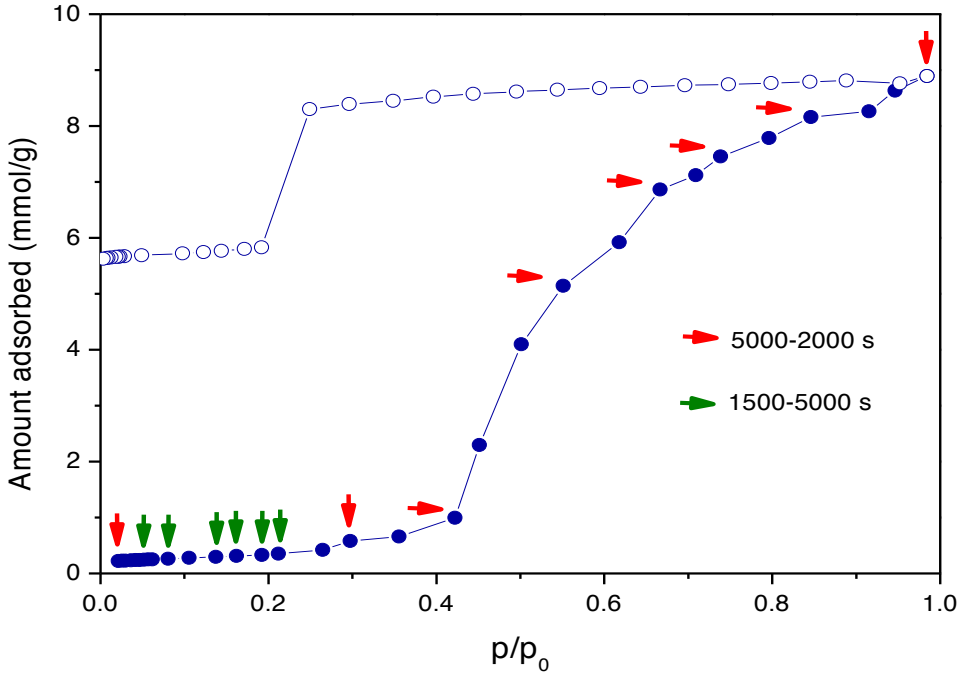
Gandara Loe et al., *in preparation*

BREATHING ZIF-4

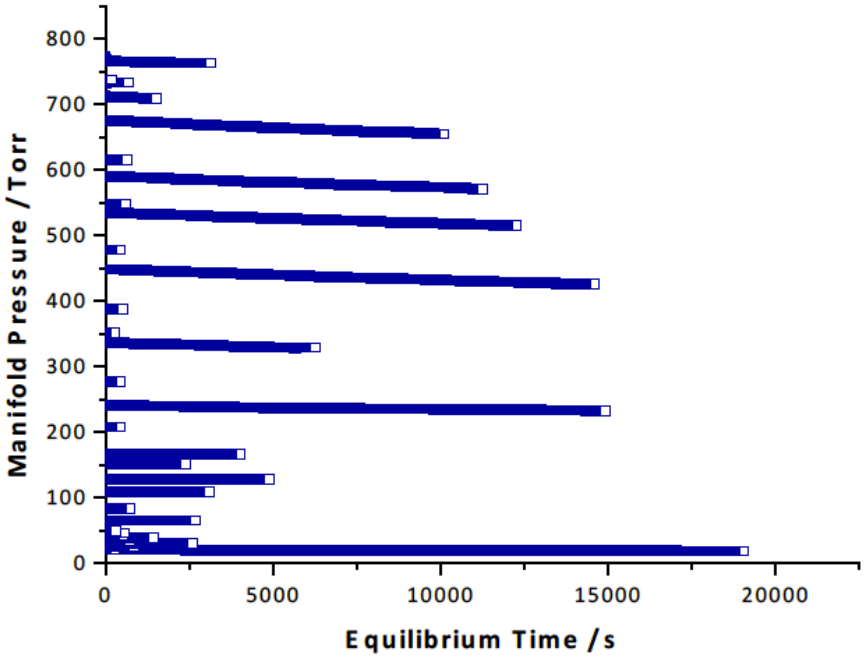
UA

N_2 adsorption at 77K

Adsorption isotherm



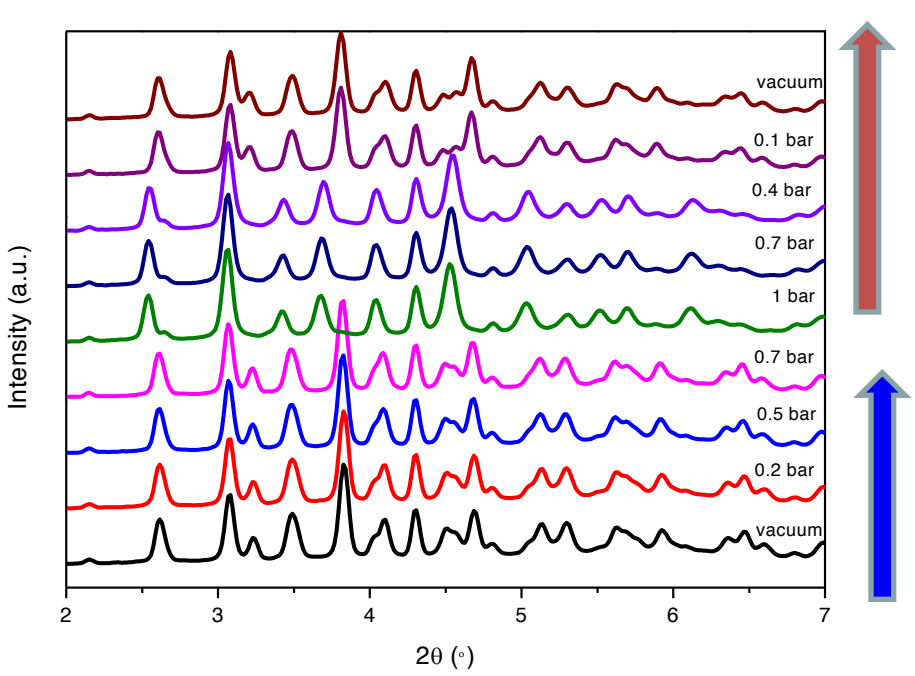
Adsorption kinetics

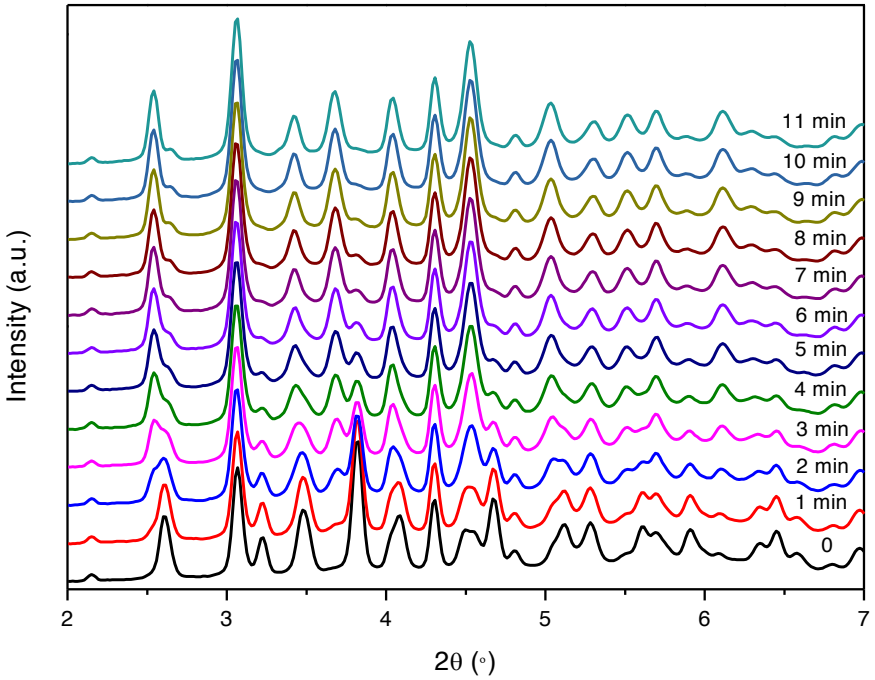


Gandara Loe et al., *in preparation*

BREATHING ZIF-4

Synchrotron XRD data under N_2 exposure



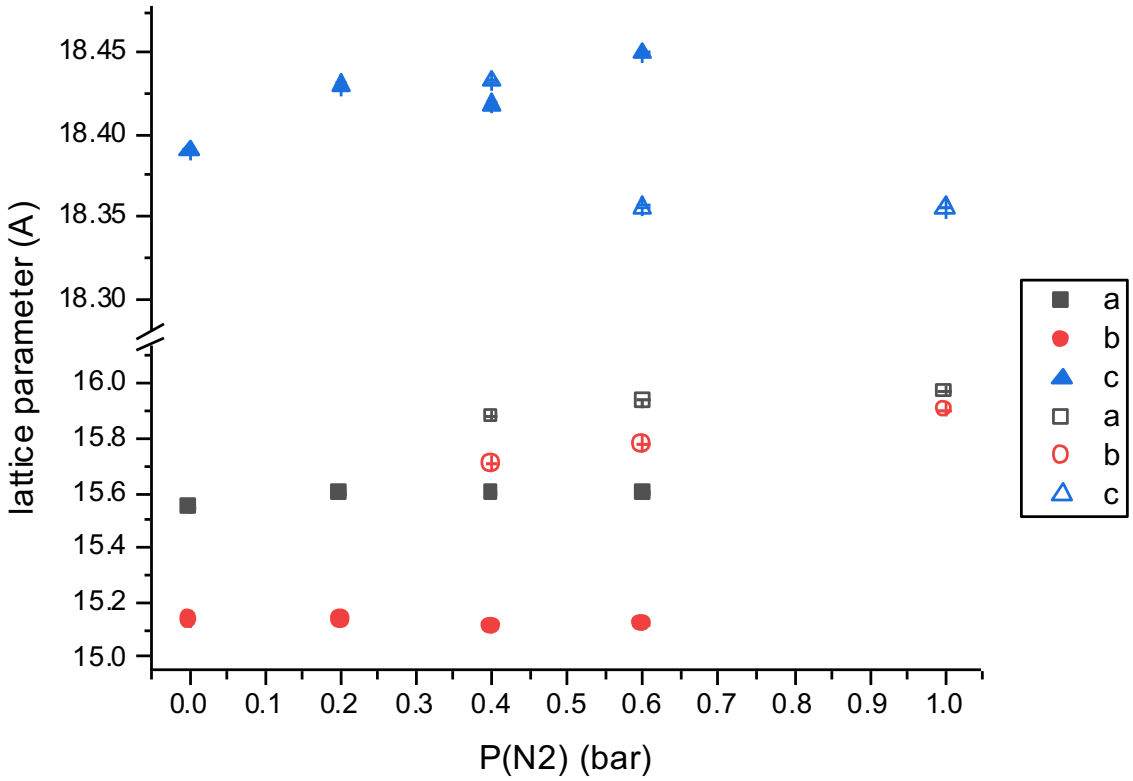


Gandara Loe et al., *in preparation*

BREATHING ZIF-4

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Synchrotron XRD data under N_2 exposure



Cell parameters:

Gate-closed
A= 15.54615
B= 15.13612
C=18.39033

Gate-opened

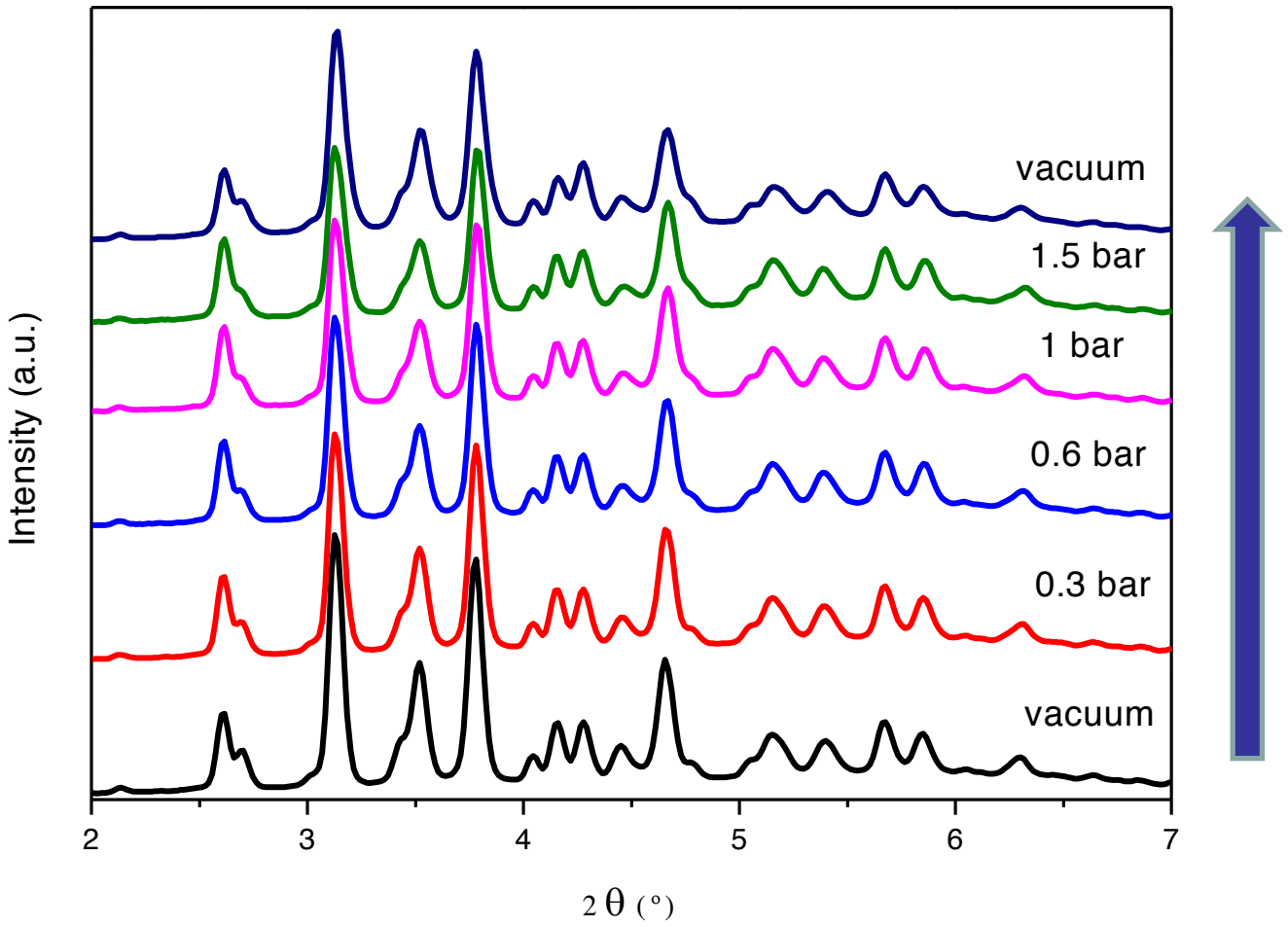
A = 15.9723
B = 15.90475
C= 18.35561

Gandara Loe et al., *in preparation*

BREATHING ZIF-4

UA

Synchrotron XRD data under CO_2 exposure



Gandara Loe et al., *in preparation*

CONCLUSION

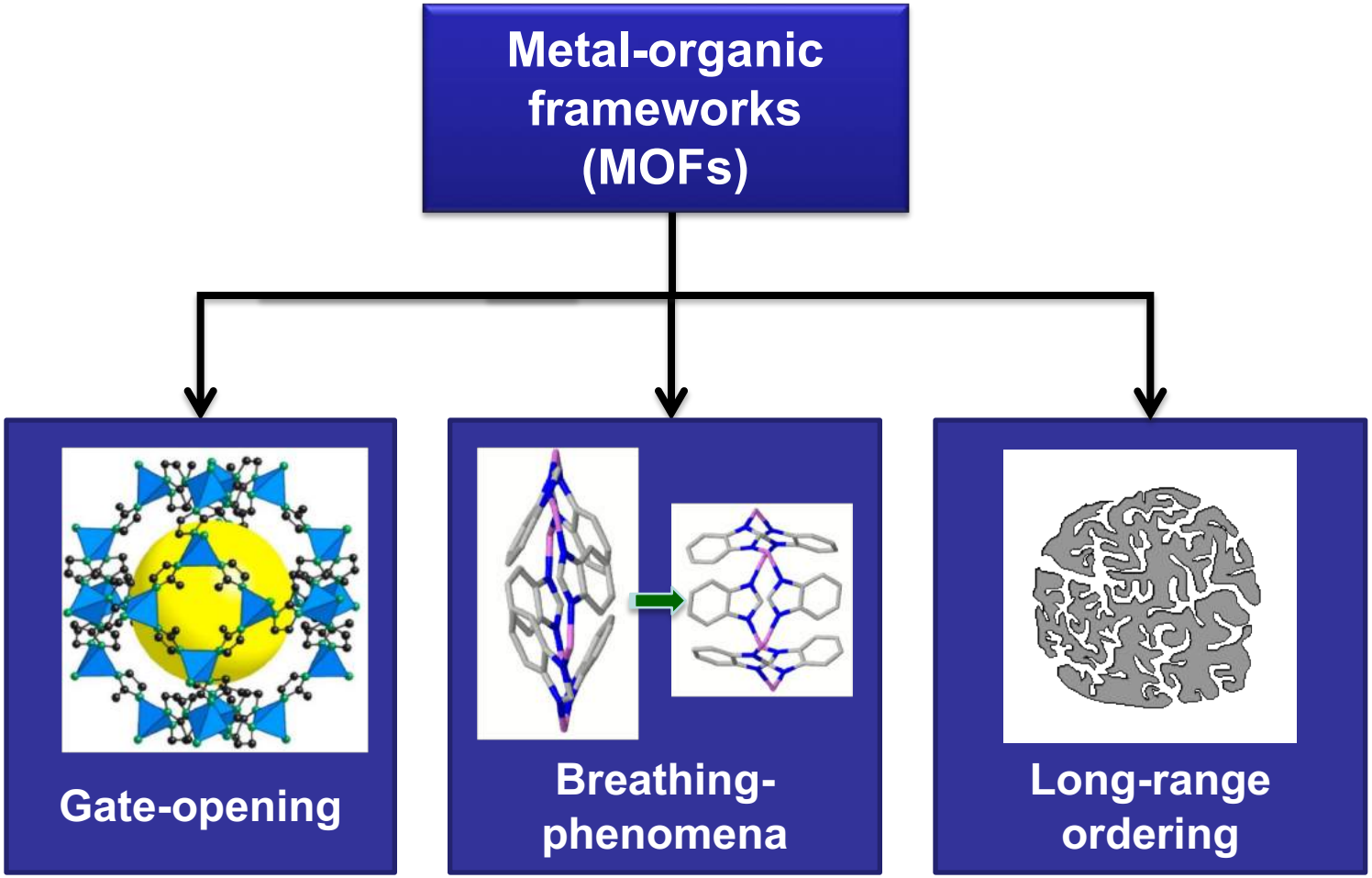
UA

✓*ZIFs materials constitutes an exciting class of flexible materials with an unusual response upon an external stimuli (e.g. upon gas adsorption).*

✓*Combination of gas adsorption and inelastic neutron scattering measurements under operando conditions constitute a extremely useful tool to evaluate gate-opening effects in ZIFs. The swinging of the –CH_3 in ZIF-8 is sensitive to temperature, pressure and to the nature of the adsorbed gas.*

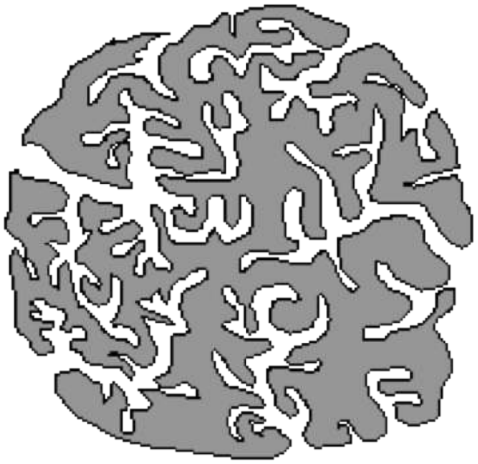
✓*Contrary to the expectations in the literature, ZIF-7 is able to adsorb N_2 provided that the material can be properly exchanged with methanol. N_2 and CO_2 adsorption is accompanied by a structural change from phase II (narrow pore) to phase I (open pore).*

✓*In the specific case of ZIF-4 the presence of closed porous structure gives rise to a unusual gate-opening only in the specific case of N2, whereas CO2 is able to access the porosity even at low pressures.*


Metal-organic frameworks (MOFs)
Gate-opening
Breathing-phenomena
Long-range ordering

ACTIVATED CARBONS

UA



Slit-shaped micropores

Porosity can be tailored

Rather “inert” surface

Adsorption of non-polar species favoured,

Surface chemistry can be easily modified,

Many physical forms (granular, pellets, fibres, cloth, felt, monoliths, etc.)

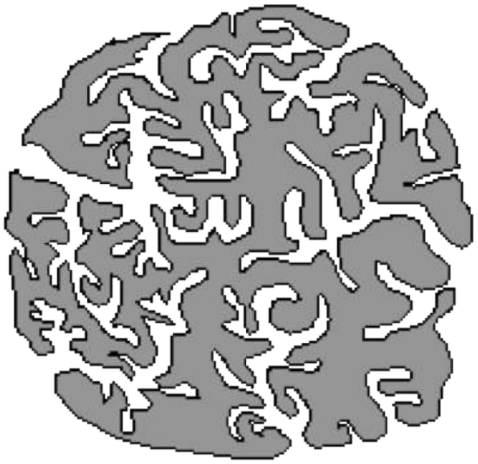
⇩

Unparallelled flexibility

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ACTIVATED CARBONS

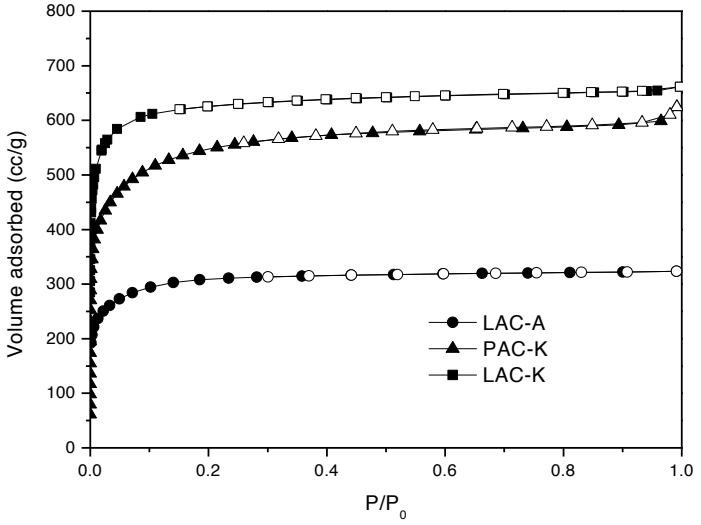
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- Lignocellolosic-based activated carbon prepared using H_3PO_4 – LAC-A
- Lignocellolosic-based activated carbon prepared using KOH – LAC-K
- Petroleum-based activated carbon prepared using KOH – PAC-K

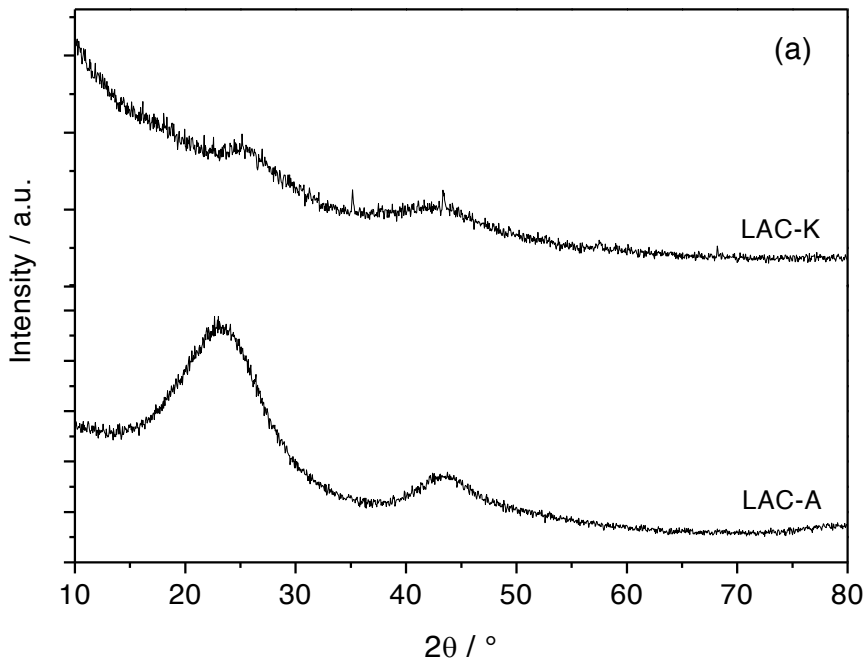
Sample	BET (m^2/g)	$V_T(cm^3/g)$	$V_0(cm^3/g)$
LAC-A	1180	0.50	0.43
LAC-K	2490	1.01	0.94
PAC-K	2000	0.87	0.76

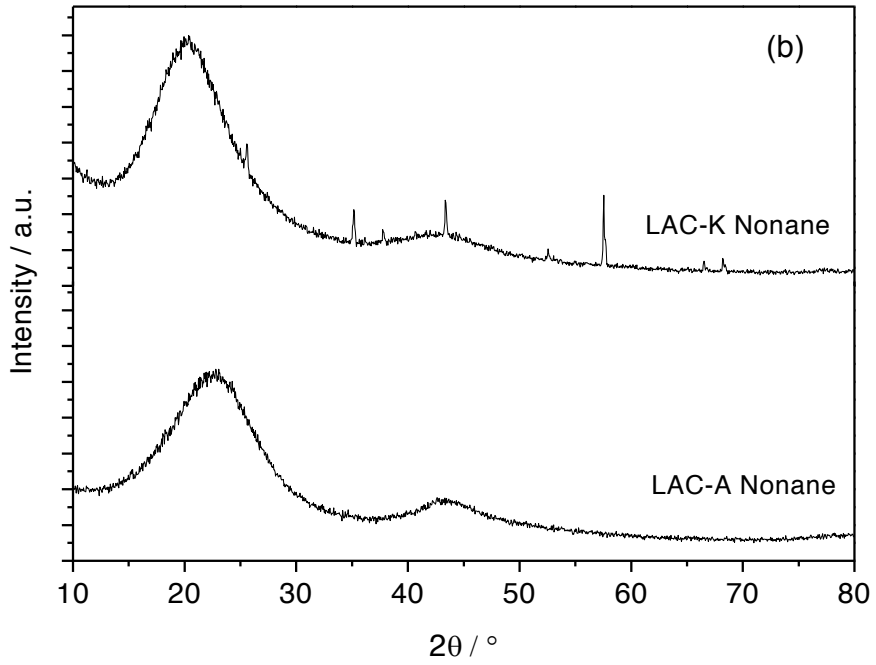
N_2 adsorption isotherms at 77K



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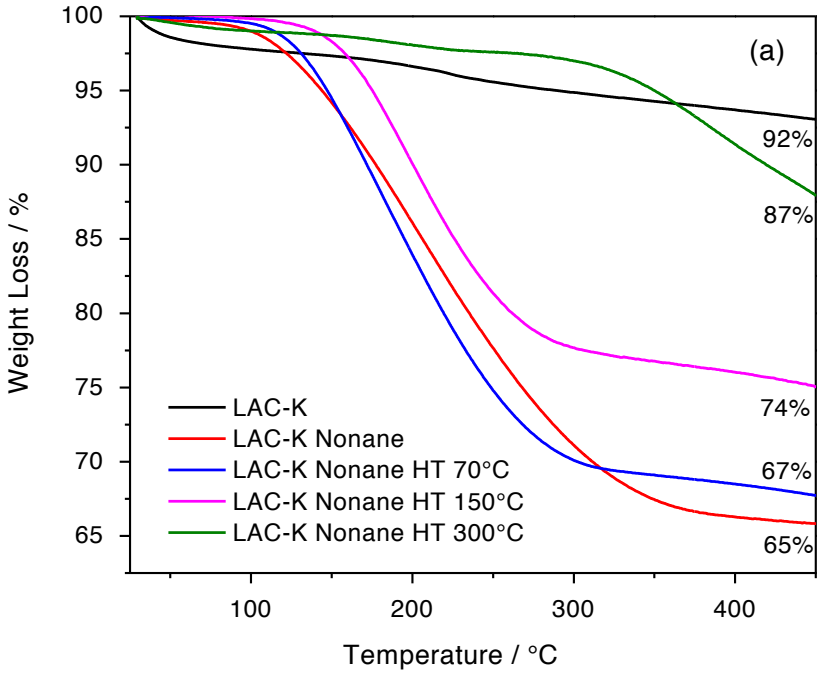
XRD pattern for lignocellulosic-based carbons before and after n-nonane adsorption

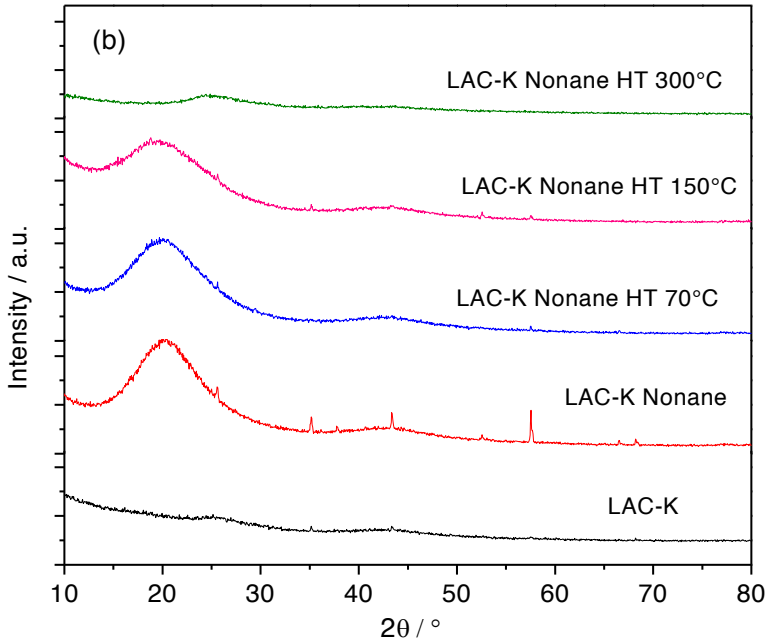




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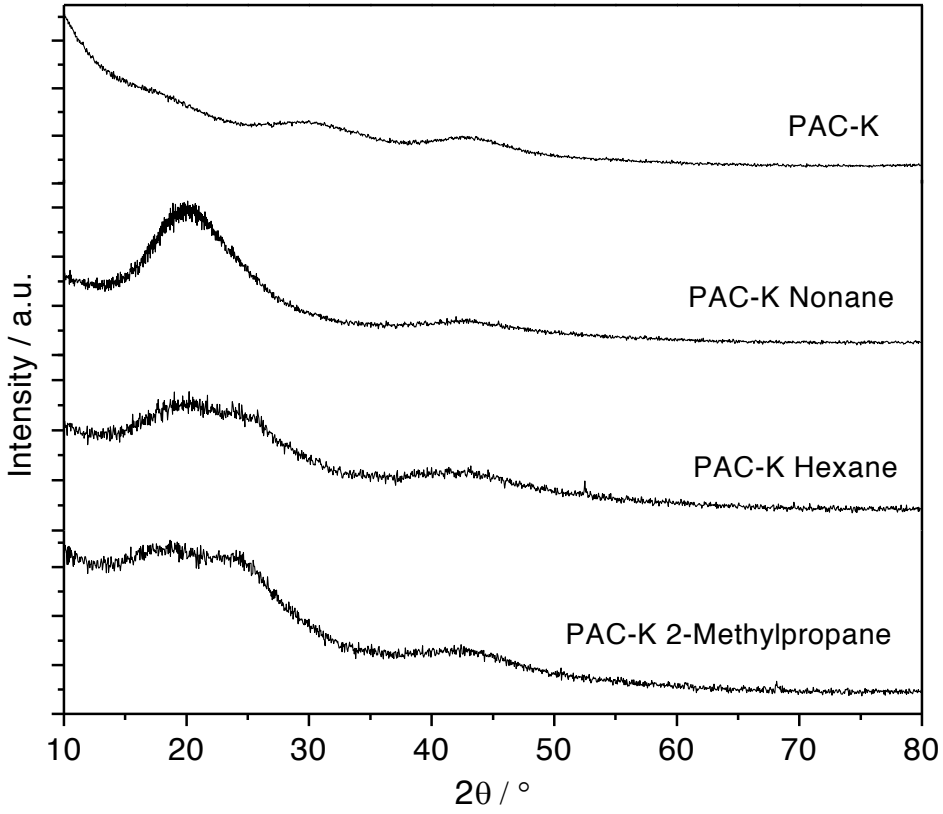
Effect of the amount of n-nonane in the long-range ordering





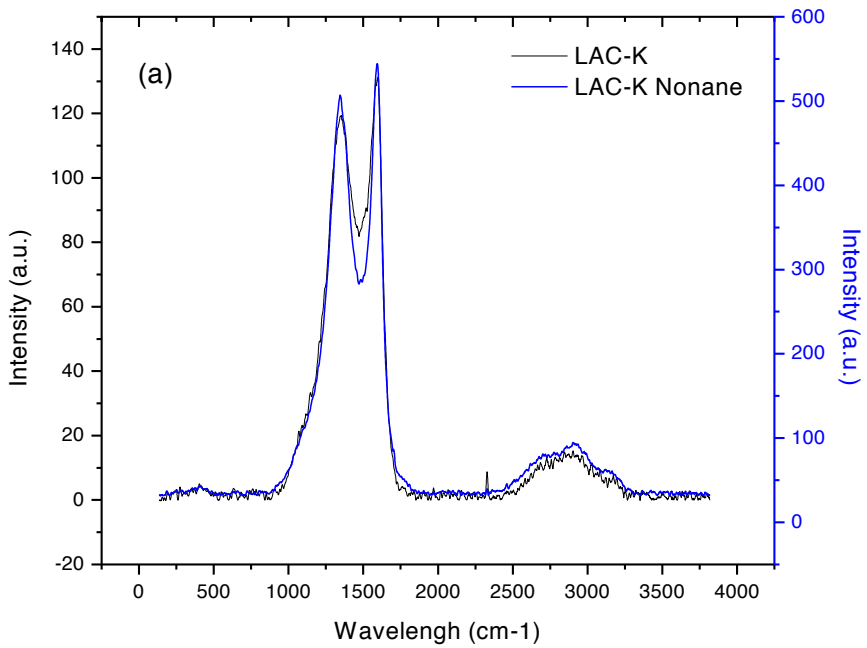
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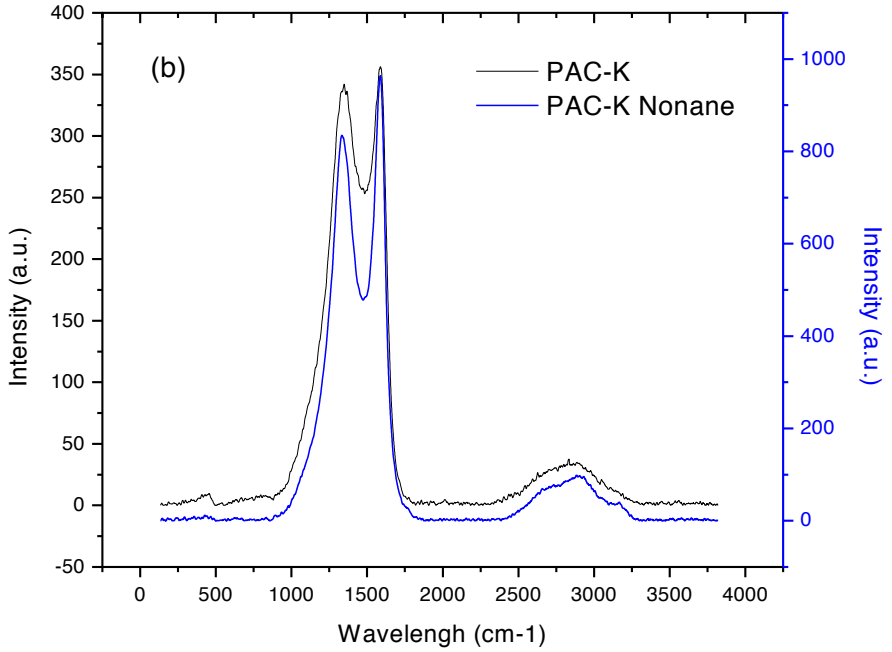
Effect of the nature of the organic solvent in the long-range ordering



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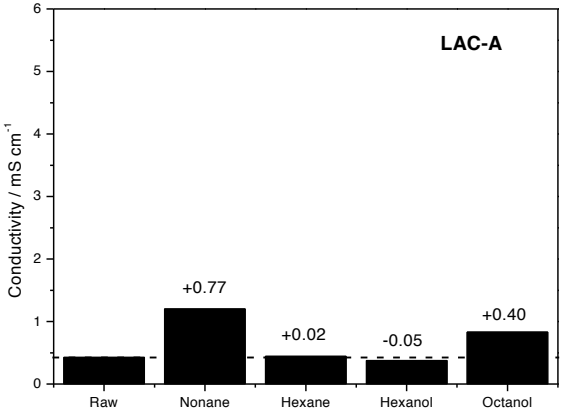
Raman spectra of two different carbon materials before and adter adsorption of n-nonane

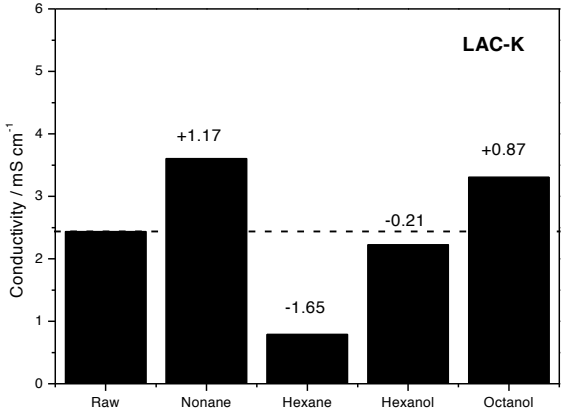


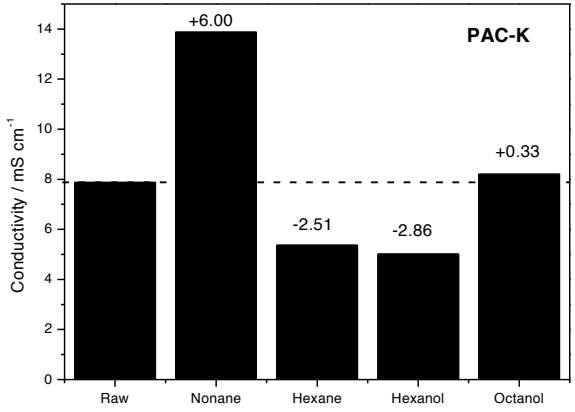


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Electrical conductivity upon adsorption of different organic molecules







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Conclusions

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✓***Even though activated carbon is considered a rigid material, XRD results shows that this is not the case for KOH – derived systems.***

✓***Upon adsorption of hydrocarbons and/or alcohols, graphite microdomains exhibit an important flexibility.***

✓***Flexibility depends on the nature of the organic molecule adsorbed.***

✓***The structural re-orientation is reflected in an important change in the electrical conductivity of the synthesized ACs.***

✓***The large selectivity of the electrical conductivity to the nature of the organic molecule opens the gate towards the application of these carbon materials as sensing devices.***

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Collaborations

Prof. Kaneko, Research Centers for Exotic Nanocarbon, Shinshu University, Japan
Prof. Rey, ITQ-UPV, Valencia, Spain
Prof. Ramirez-Cuesta, Oak Ridge National Laboratory, USA
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Thank you very much!!!

email: joaquin.silvestre@ua.es

Antelope Canyon-Reserva de los indios navajos (USA)