# Pore Architecture of Zeolitic Imidazolate Frameworks: An Investigation using Positron Annihilation Spectroscopy

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PPC 12.5

## Introduction

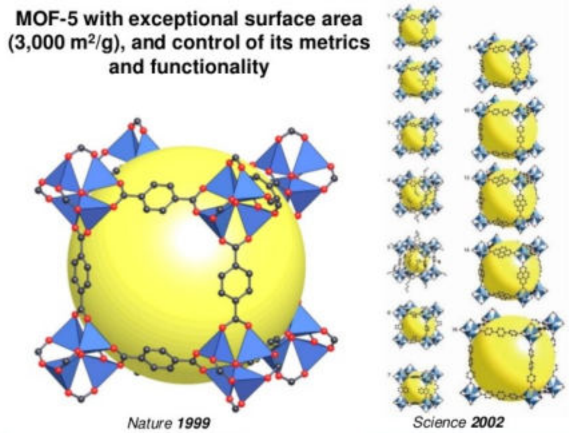
- MOFs, ZIFs and their pore architecture
- Issues with pore analysis of ZIFs

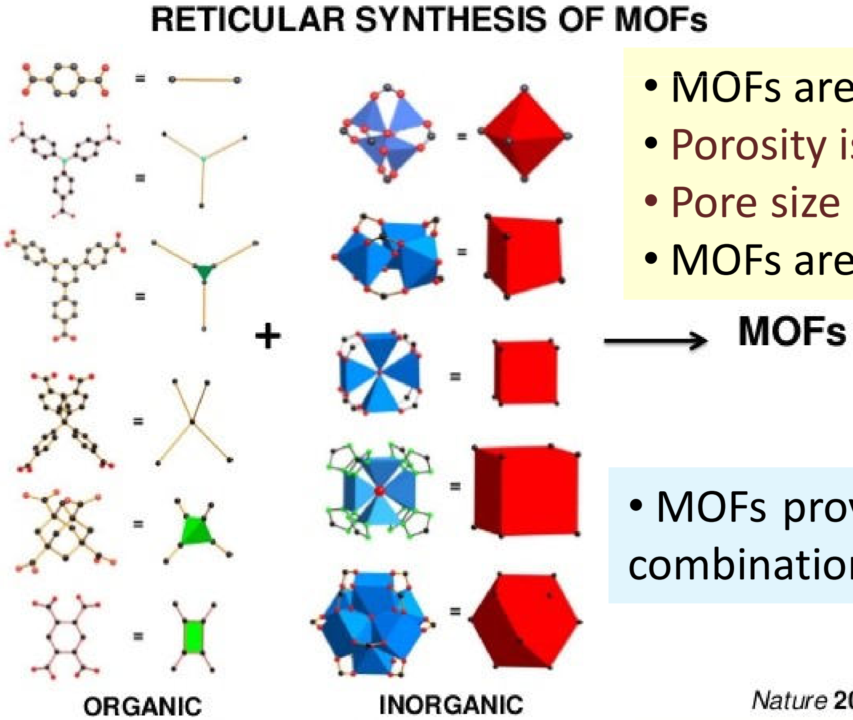
## Application of positron annihilation spectroscopy in ZIFs

- Effect of external pressure
- Crystal size induced modifications
- Mixed ligand induced tuning of pore architecture
- Positronium diffusion in ZIF-8 films

## Conclusions and outlook

# Metal Organic Frameworks



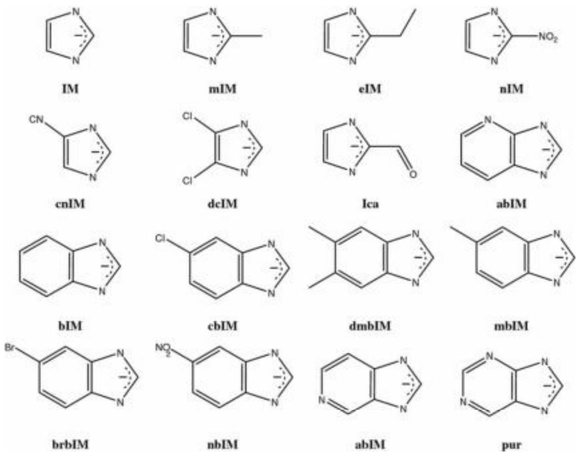

- MOFs are highly porous with very high surface area.
- Porosity is due to crystal structure.
- Pore size can be tuned using different metals and ligands.
- MOFs are thermally stable.

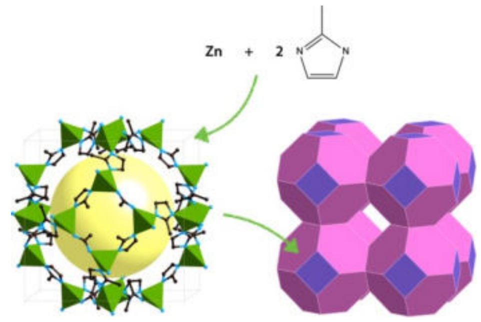
- MOFs provide immense possibilities as a result of infinite combination of metals and ligands.

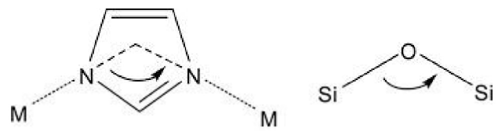
*Nature* 2003

# Zeolitic Imidazolate Framework

- Topology of Zeolites; M-Im-M bond similar to Si-O-Si bond

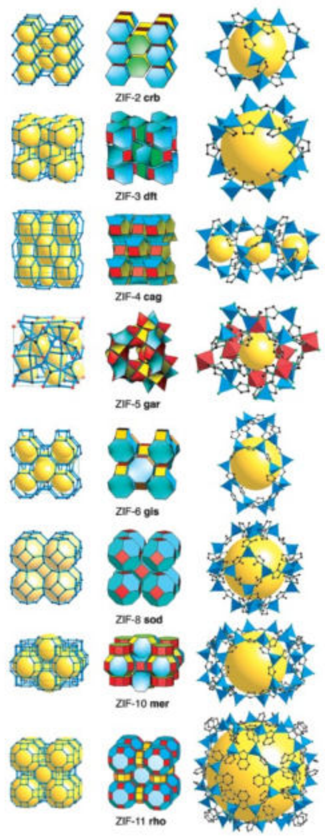



M - IM - M
1

Si - O - Si
2

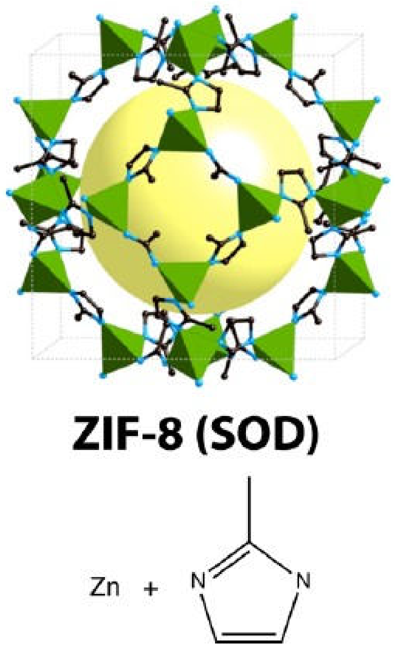



| ZIF-*n* | Composition | Net* | Zeolite† | *T*/*V*,‡ $nm^{-3}$ | *d*,§ Å | *N*¶ |
|---|---|---|---|---|---|---|
| ZIF-1 | $Zn(IM)_2$ | **crb** | BCT | 3.64 | 6.94 | 12 |
| ZIF-2 | $Zn(IM)_2$ | **crb** | BCT | 2.80 | 6.00 | 12 |
| ZIF-3 | $Zn(IM)_2$ | **dft** | DFT | 2.66 | 8.02 | 16 |
| ZIF-4 | $Zn(IM)_2$ | **cag** | — | 3.68 | 2.04 | 20 |
| ZIF-5 | $In_2Zn_3(IM)_{12}$ | **gar** | — | 3.80 | 3.03 | 20 |
| ZIF-6 | $Zn(IM)_2$ | **gis** | GIS | 2.31 | 8.80 | 20 |
| ZIF-7 | $Zn(PhIM)_2$ | **sod** | SOD | 2.50 | 4.31 | 24 |
| ZIF-8 | $Zn(MeIM)_2$ | **sod** | SOD | 2.47 | 11.60 | 24 |
| ZIF-9 | $Co(PhIM)_2$ | **sod** | SOD | 2.51 | 4.31 | 24 |
| ZIF-10 | $Zn(IM)_2$ | **mer** | MER | 2.25 | 12.12 | 24 |
| ZIF-11 | $Zn(PhIM)_2$ | **rho** | RHO | 2.01 | 14.64 | 48 |
| ZIF-12 | $Co(PhIM)_2$ | **rho** | RHO | 2.01 | 14.64 | 48 |

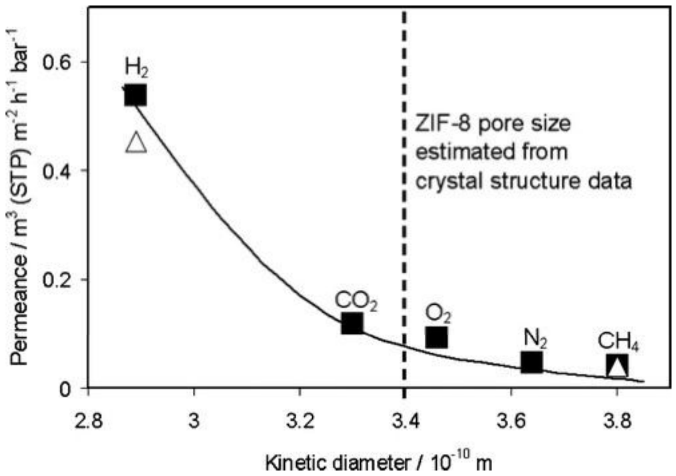
PNAS 2006 (103) 10186-10191

# ZIF-8

Single crystallography: Central cavity of 1.16 nm connected through 0.34 nm



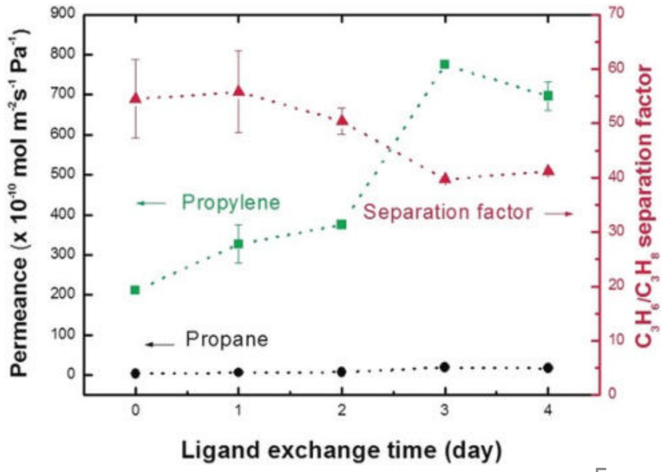

$CO_2$ (0.33) < Pore aperture <$CH_4$ (0.38)




J. Am. Chem. Soc. 2009, 131, 16000-16001

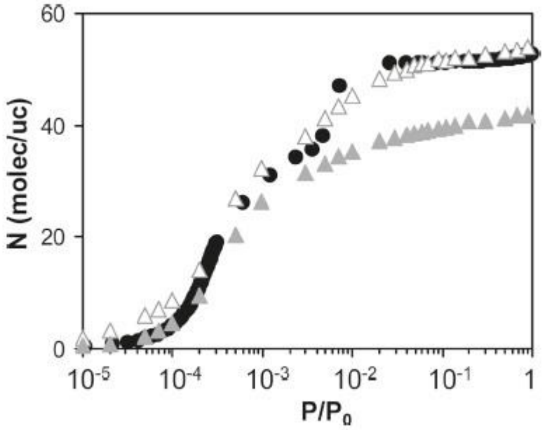
Poor selectivity

Large size molecules are passing through.

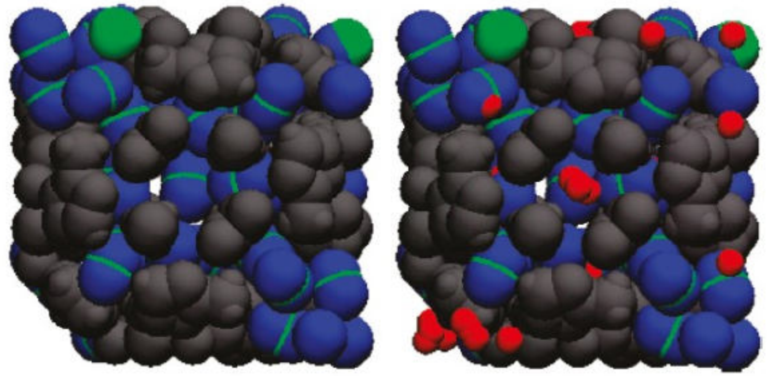



Angew. Chem., 2018, 57, 156-161

# Gate Opening: Flexible framework

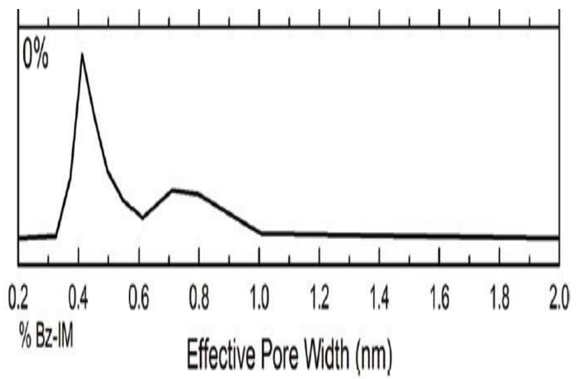


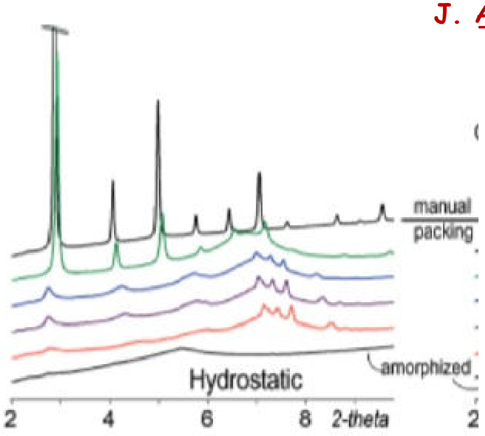

$N_2$ Adsorption at 77 K

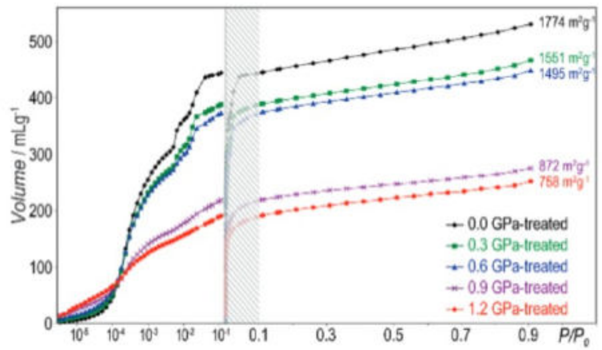


Structural Changes at high pressure

J. Am. Chem. Soc. 2011, 133, 8900-8902



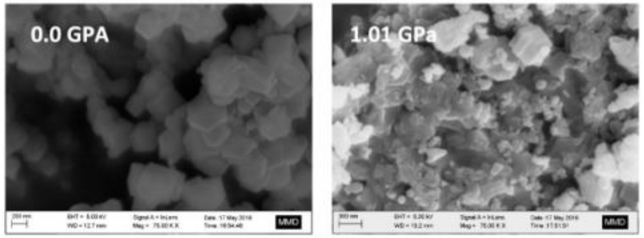

Pore size determined using $N_2$ adsorption does not match the crystallographic data.

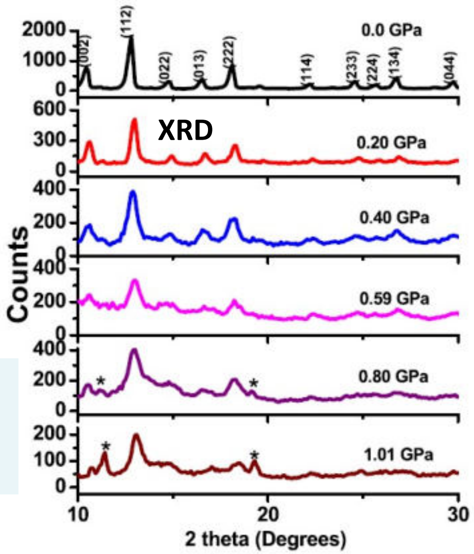
Pressure induced Irreversible amorphization
Amorphous phase remains porous.

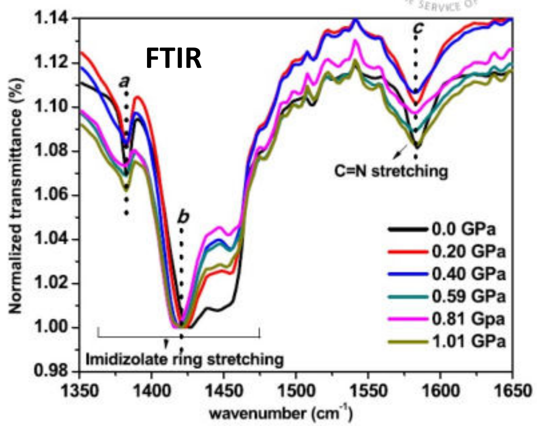
Chem. Mater. 2012, 24, 1930-136

J. Am. Chem. Soc. 2009, 131, 17546-17547

# Compression induced change in porosity

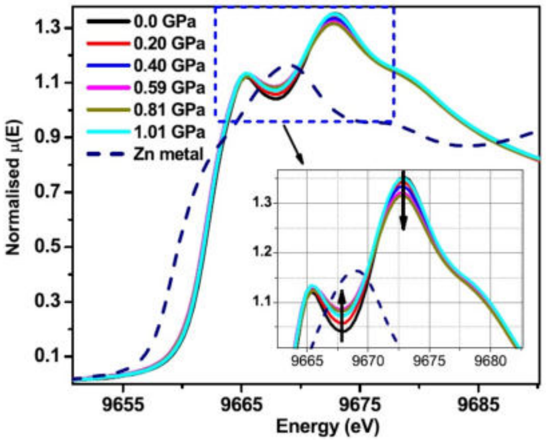


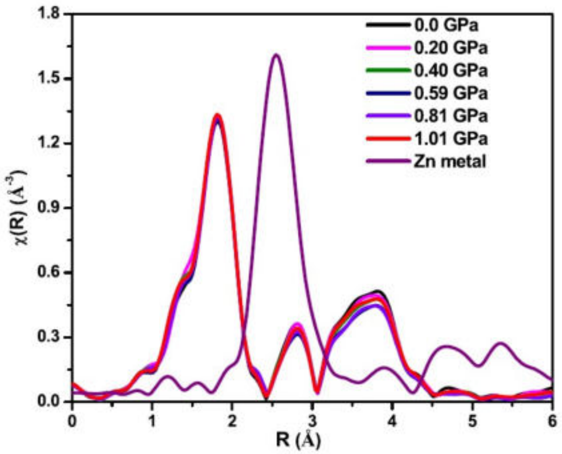



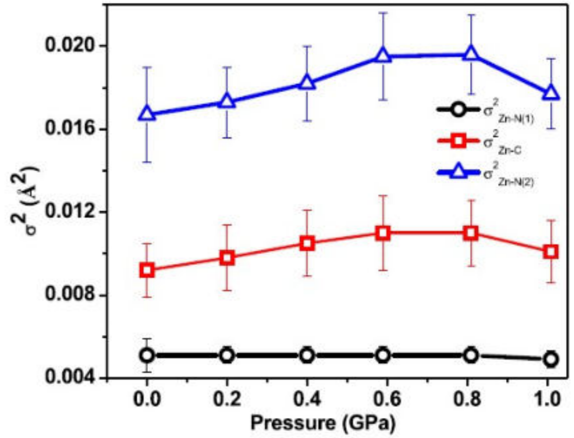




- Irreversible amorphization
- Deformation in Imidazolate ring bonding

**X-ray Absorption spectroscopy:**

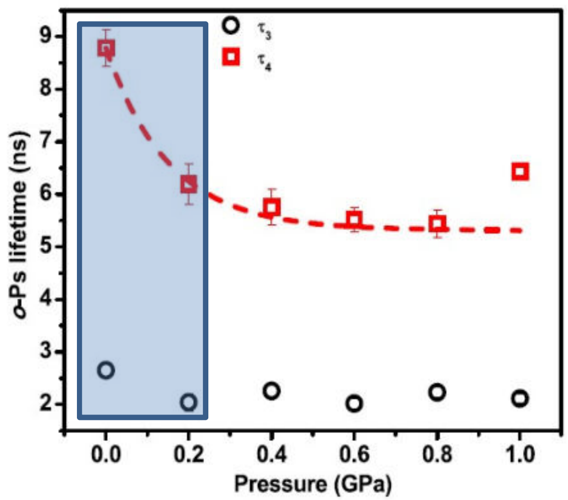


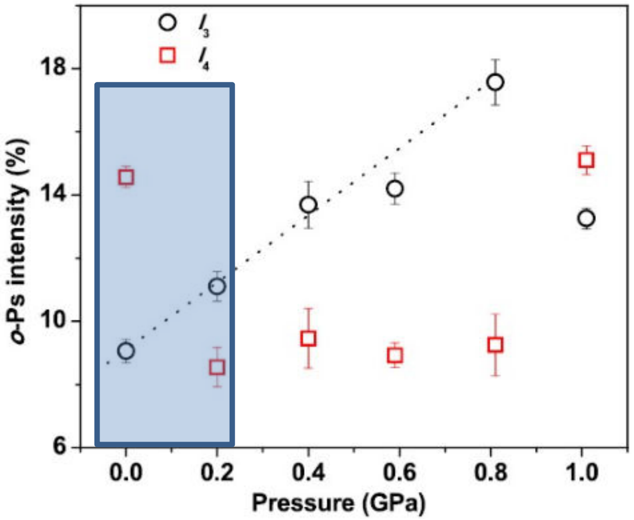




- Retention of Zn-N tetrahedral arrangement in amorphous state.

# Positron annihilation lifetime measurements:



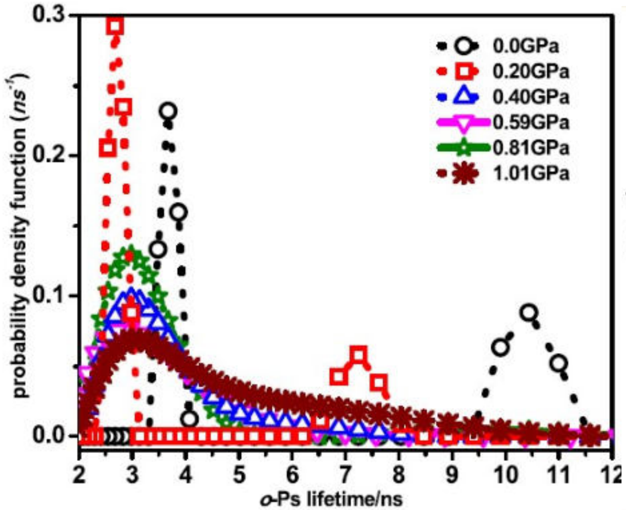



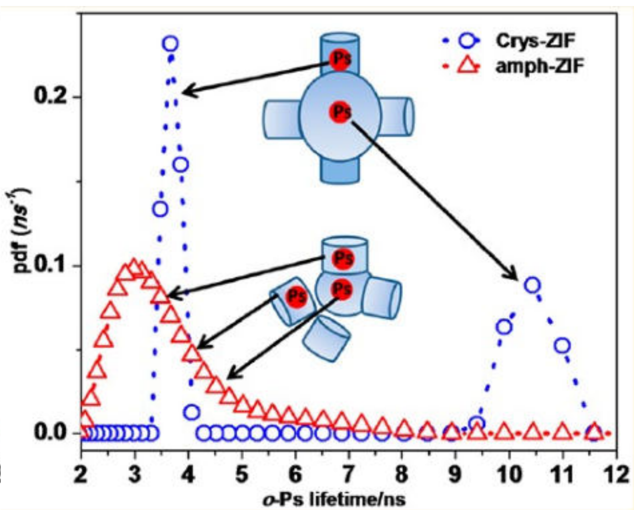

**Lower pressure:**

Partial collapse of open volume

**Higher pressure:**

Cataclysmic modifications



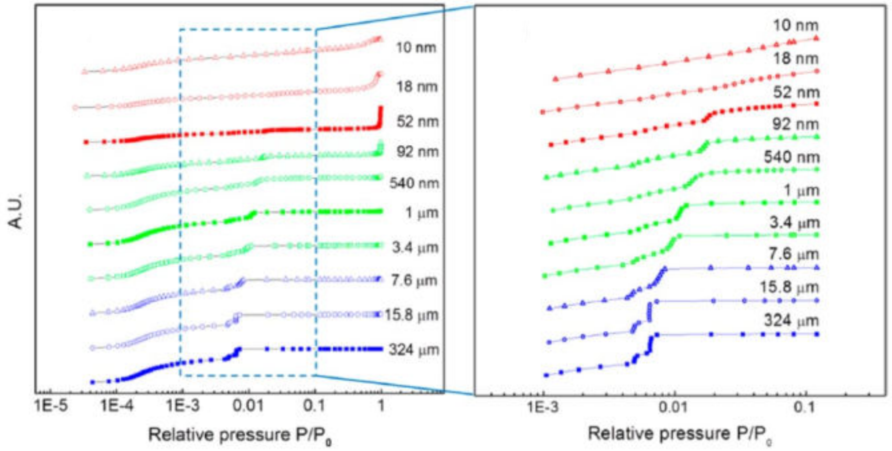



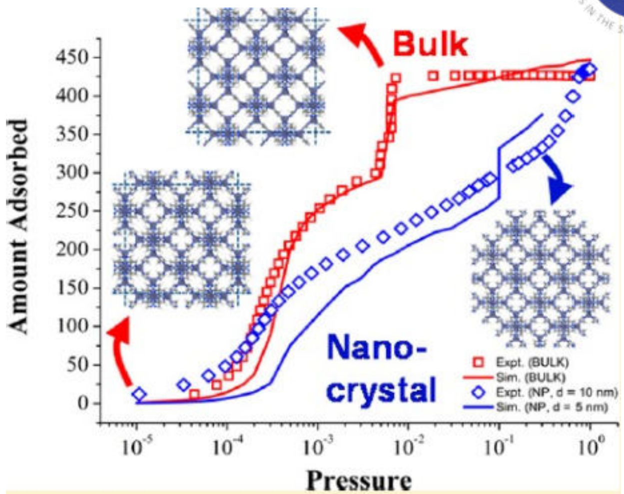

**Amorphous phase:**

Continuous random network of open volume of broader size distribution

Sharma et al. J. Phys. Chem. C 123 (2019) 22273-22280

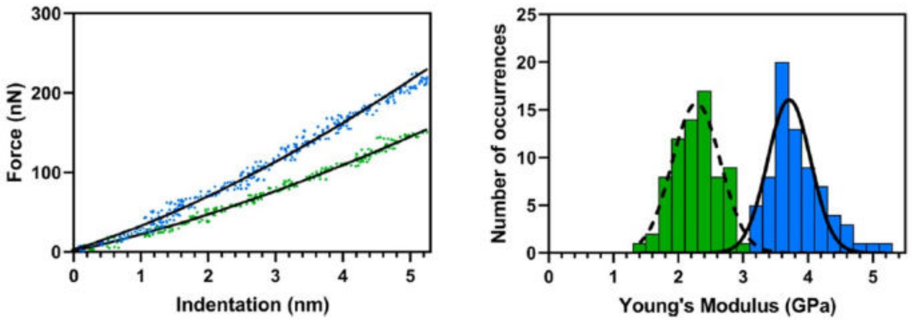
# Crystal size dependent porosity

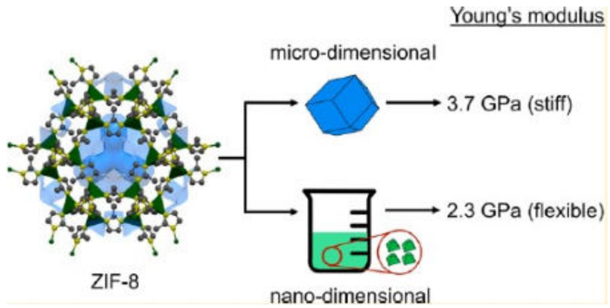



J. Phys. Chem. C 118 (2014) 20727-20733

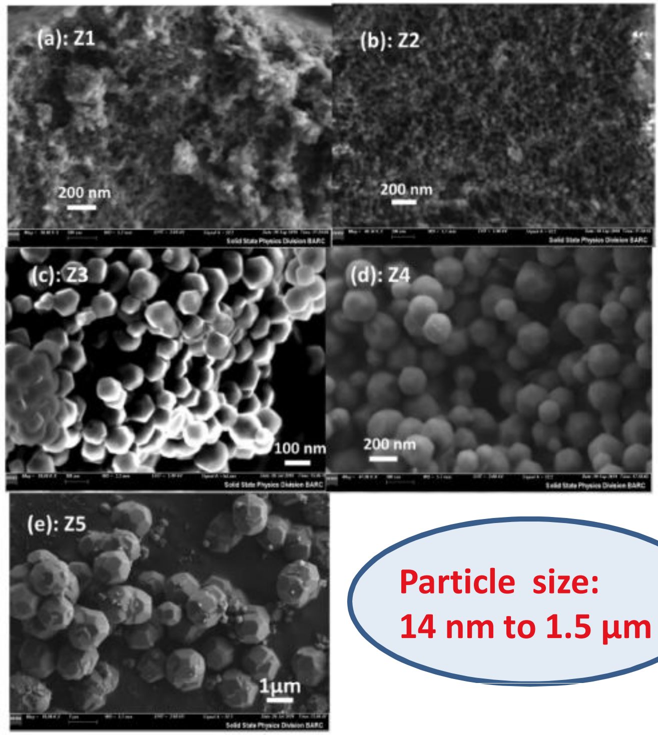
- Flexibility is reduced with reduction in crystal size
- Pore size distribution of solvated crystals ??



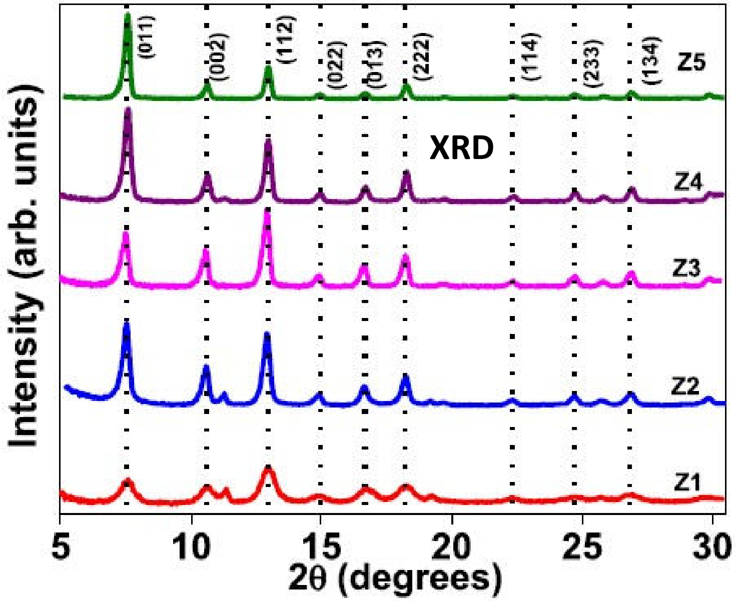



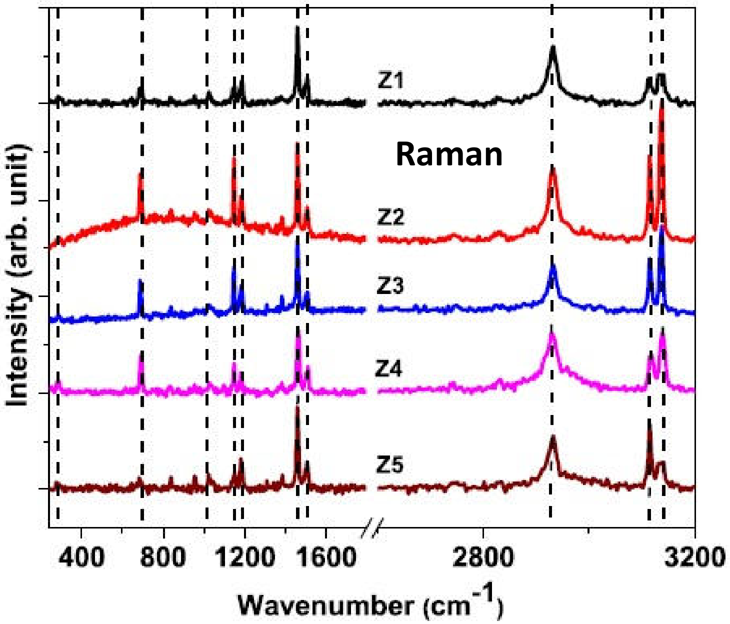

- Nanocrystals are more flexible.

ACS Nano Letters 19 (2019) 6140-6143



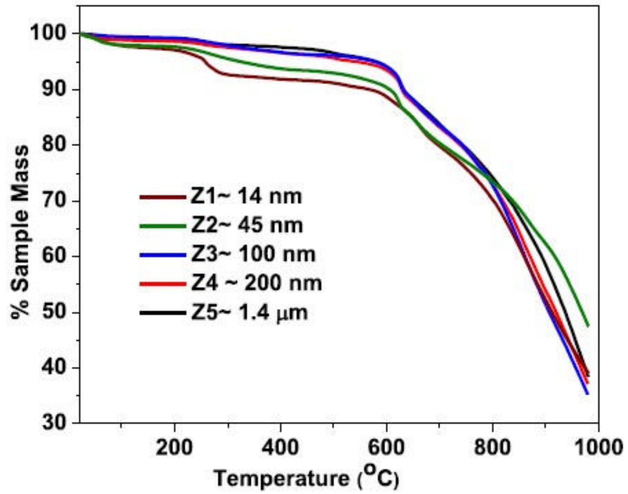

Particle size:
14 nm to 1.5 μm



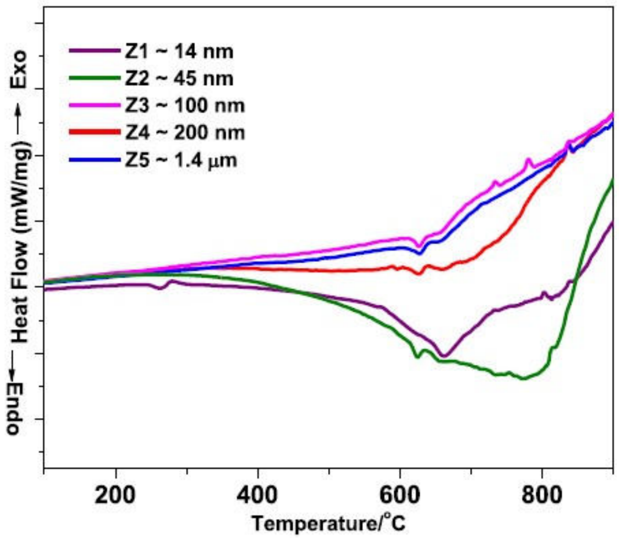

- **Phase pure ZIF-8 of 14 nm to 1.5 μm were synthesized.**
- **Chemical bonding and structure are intact.**

# Thermal analysis




- Decomposition temperature remains nearly invariant.
- Thermal stability of nanocrystals is similar to larger crystals.

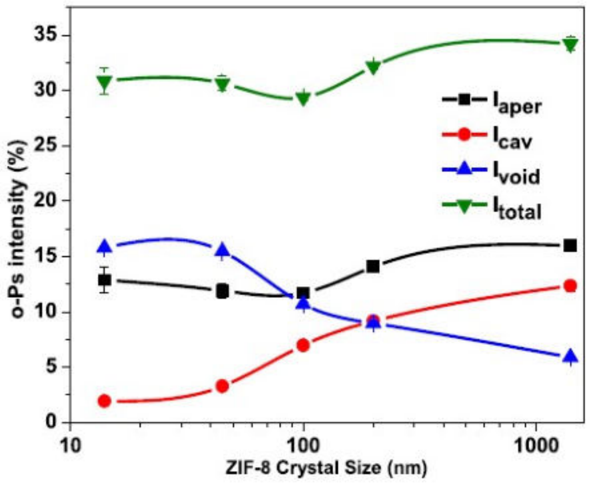
- No impurity phase.
- No additional phase transition.
- Decomposition of ZIF-8 ~ 750°c.



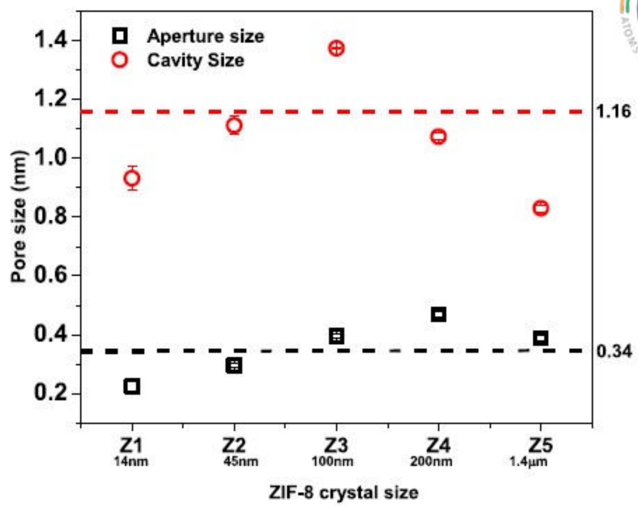

- Nanocrystals shows broader endothermic peak corresponding to decomposition.

- Surface characteristics and pore architecture of nanocrystals are different.

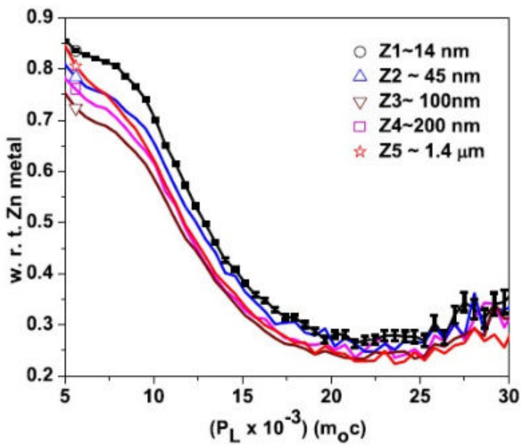
# Positron annihilation lifetime measurements:



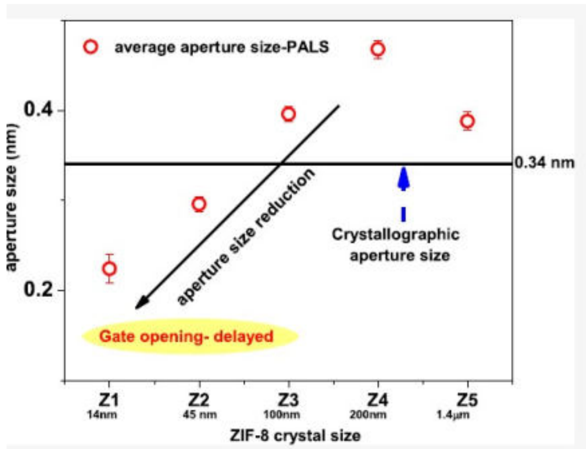

Pore interconnectivity is altered with crystal size.




- Average size is different from crystallographic size.
- Defective crystals during synthesis.



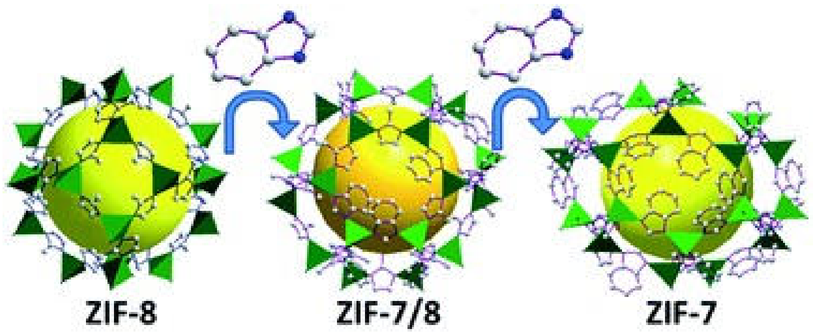

Nanocrystals have Zn enriched surface.



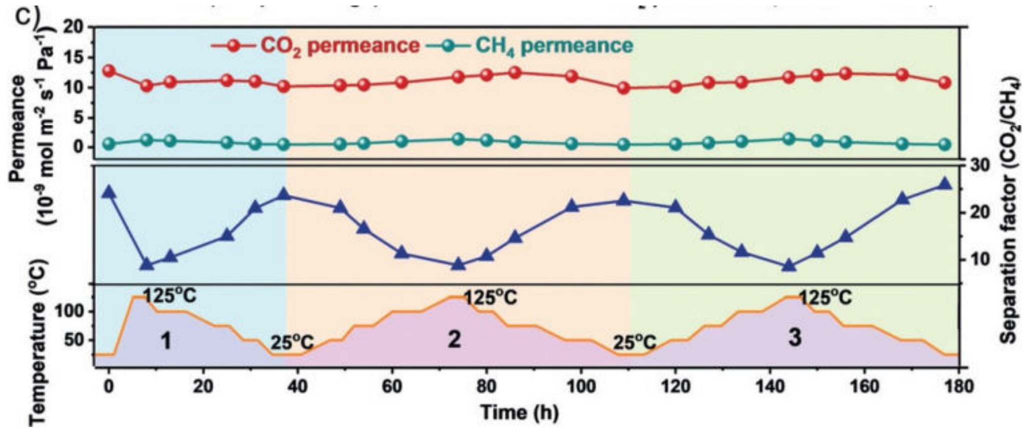

Delayed gate opening due to restricted pore aperture.

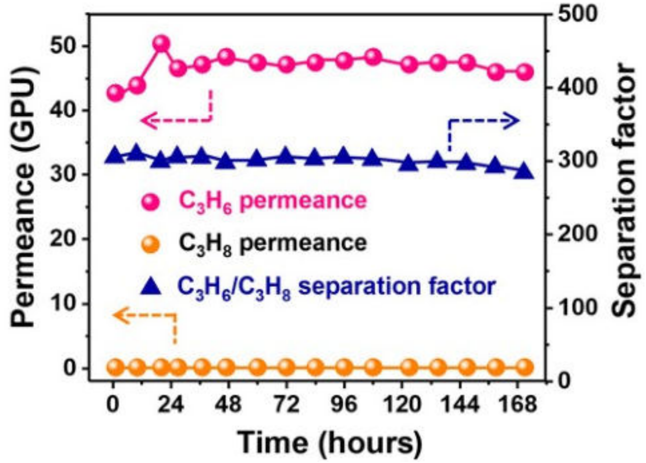
Sharma et al. J. Phys. Chem. C 124 (2020) 25291-25298

# Pore tuning with mixed ligand strategy




J. Mater. Chem. A 5 (2017) 25601

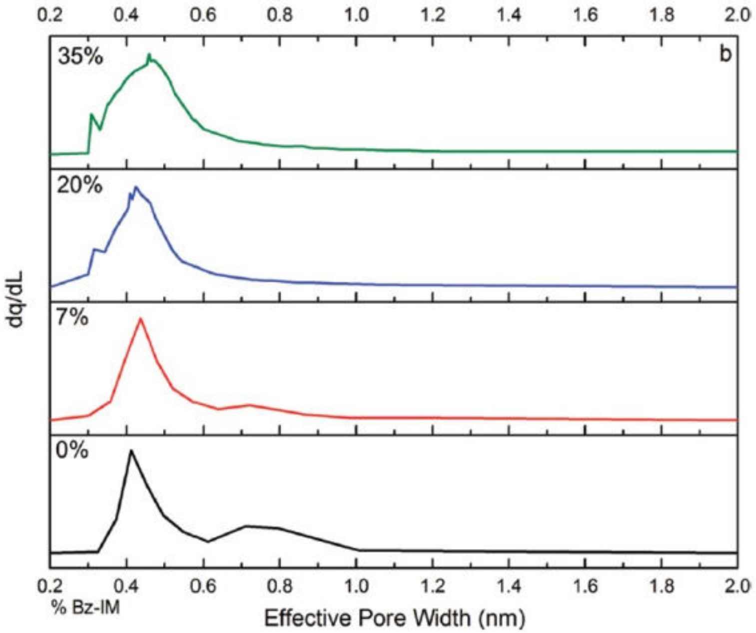


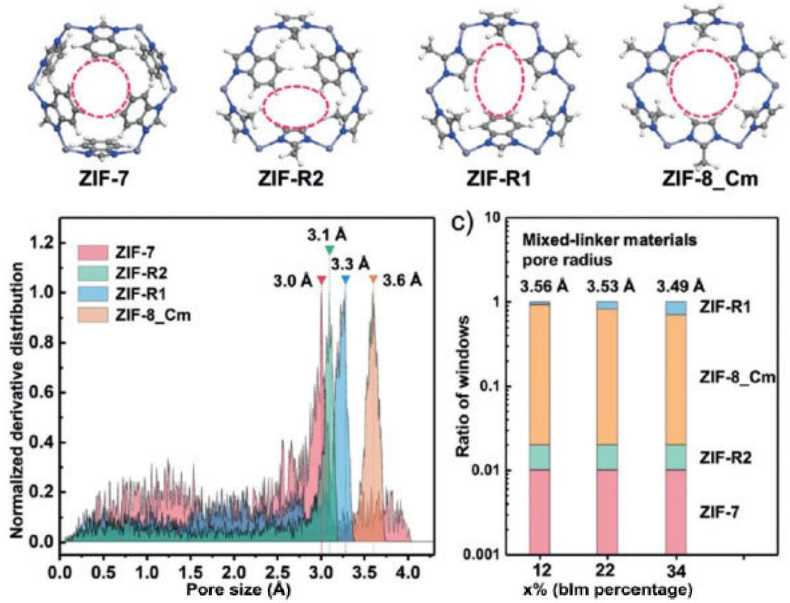

Angew. Chem. 58 (2019) 327-331

Science Advances 4 (2018) eaau 1393

**Pore tuning of a stiffened phase using mixed ligand strategy is possible.**




Chem. Mater. 2012, 24, 1930-136

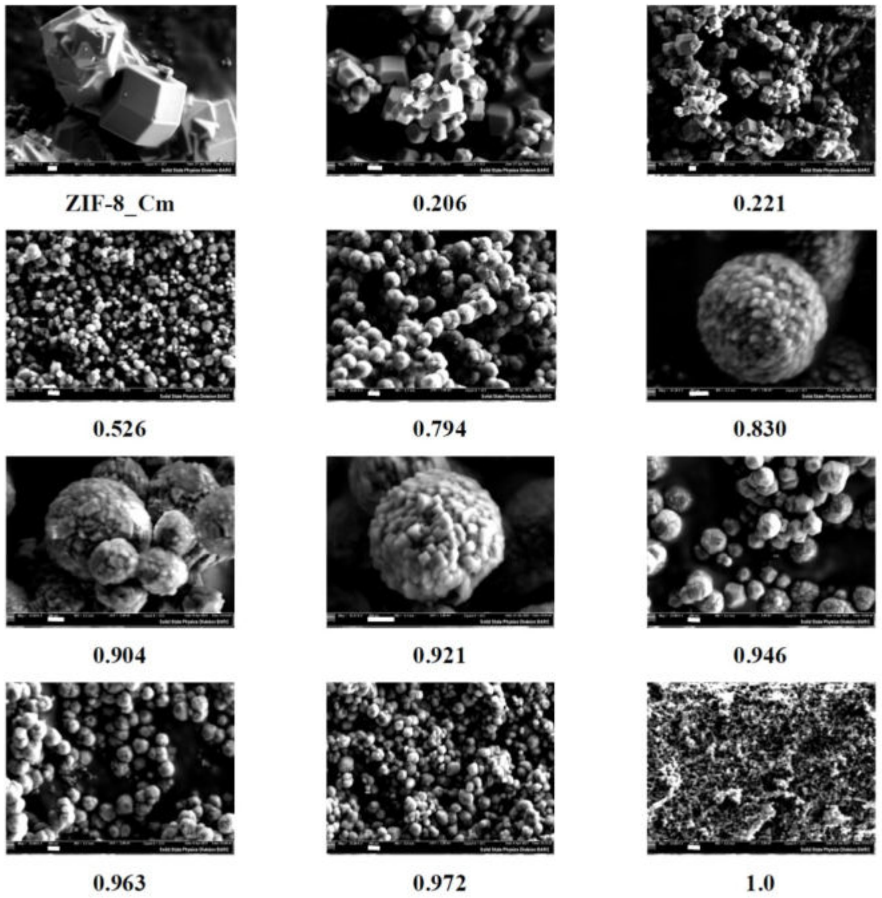


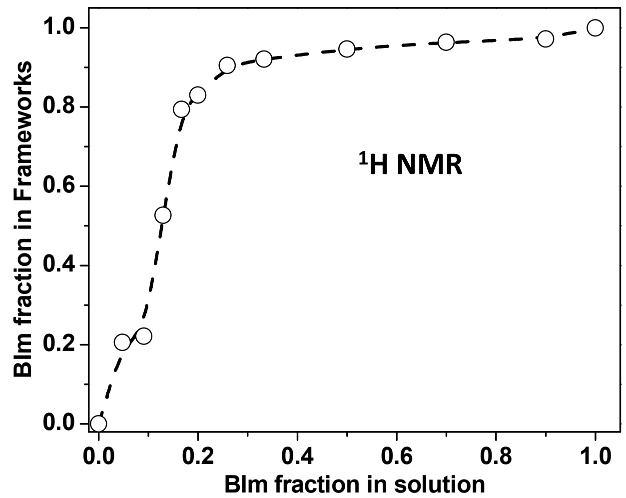

Angew. Chem. 58 (2019) 327-331

• Pore size determined using gas adsorption is not absolute due to framework-gas interaction induced pore openings.

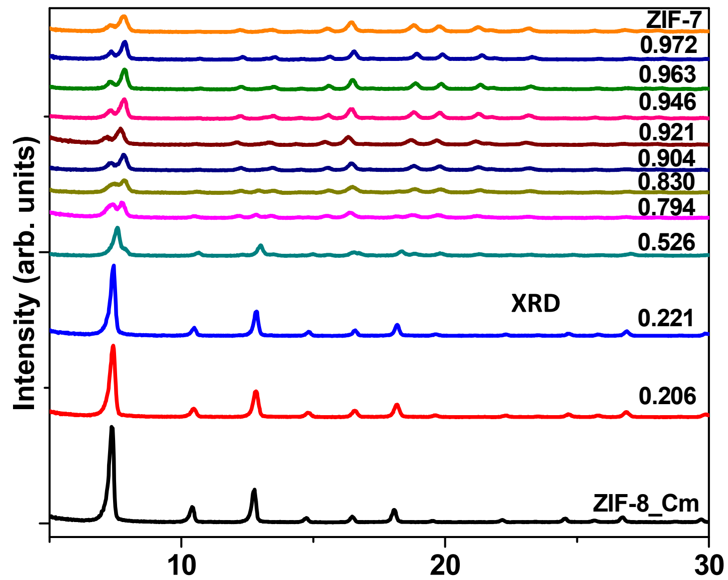
• Pore size from theoretical modeling does not represent the average pore sizes.

Morphology of ZIF-$7_x$-8 frameworks:



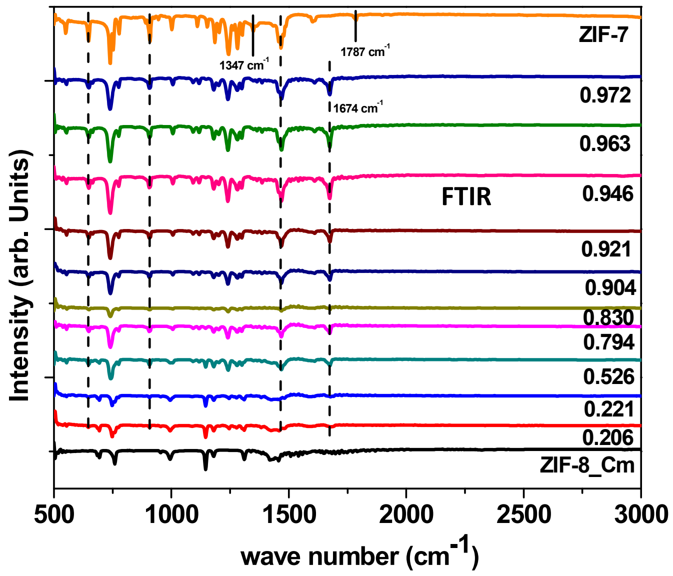



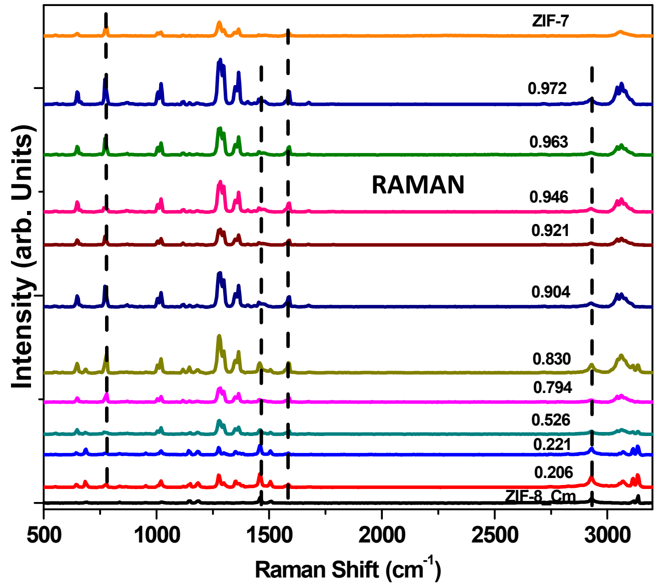

**bIm is incorporated in ZIFs preferentially.**




With increase in bIm fraction in frameworks

- Morphology changes drastically.
- Phase changes from ZIF-8_Cm to ZIF-7 (R3).

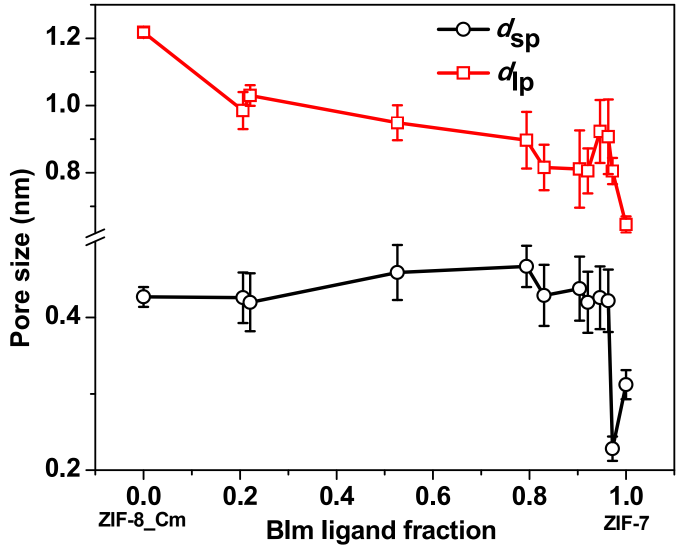


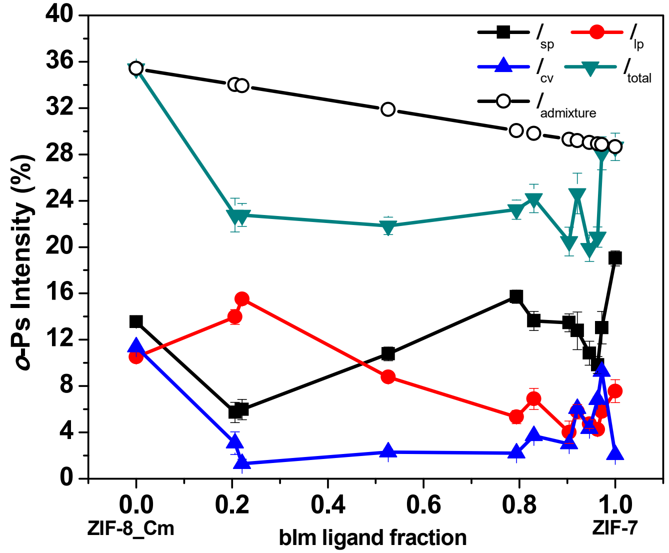




- Peaks from bIm and 2-mIm are present in all the samples.
- NMR also confirms presence of both the ligands.
- Single morphology of each sample.

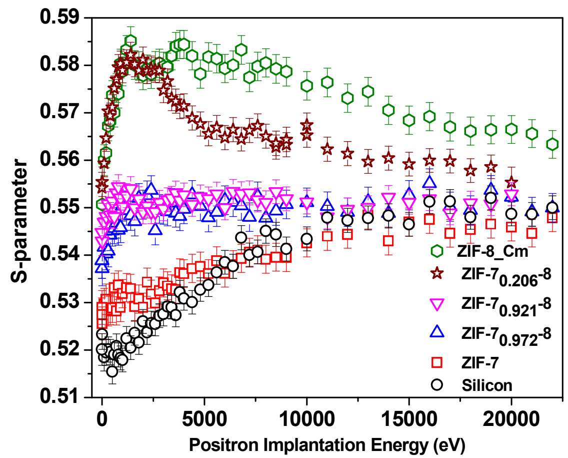
**The synthesized ZIF-7$_x$-8 frameworks are single phase materials having randomly distributed ligand and not the mixture.**

# Positron annihilation measurements:



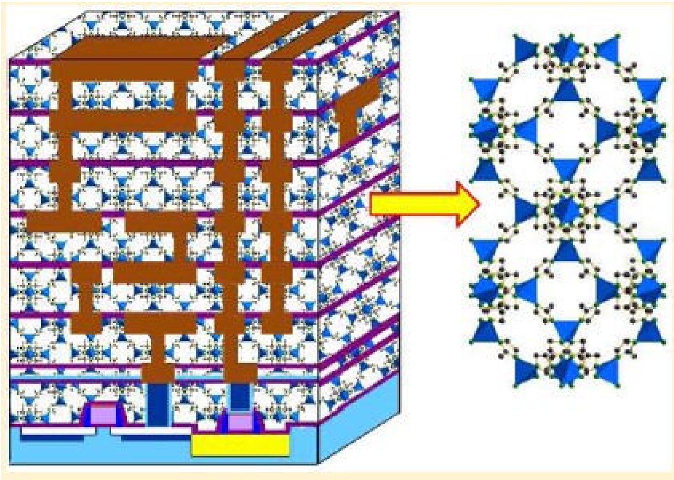



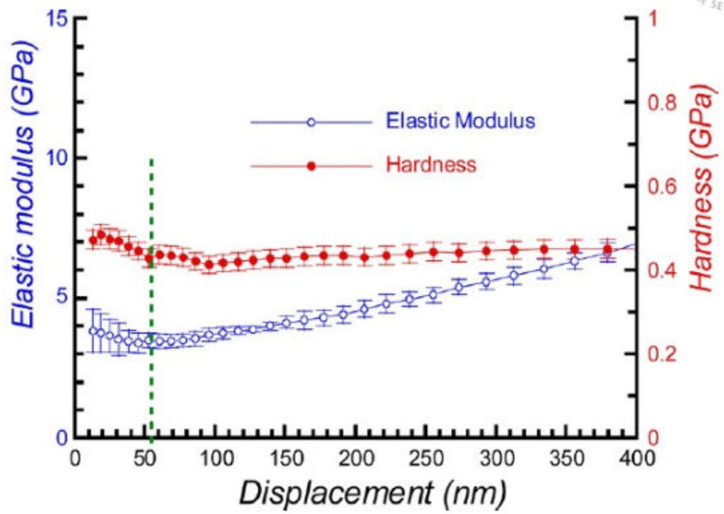

- The pore size for pure ZIF-7 and ZIF-8_Cm match very well.
- The pore size varies with bIm ligand incorporation.
- Intensity does not follow the admixture rule of two components confirming that material is single phase.
- Pore interconnectivity is also hampered in mixed ligand network.

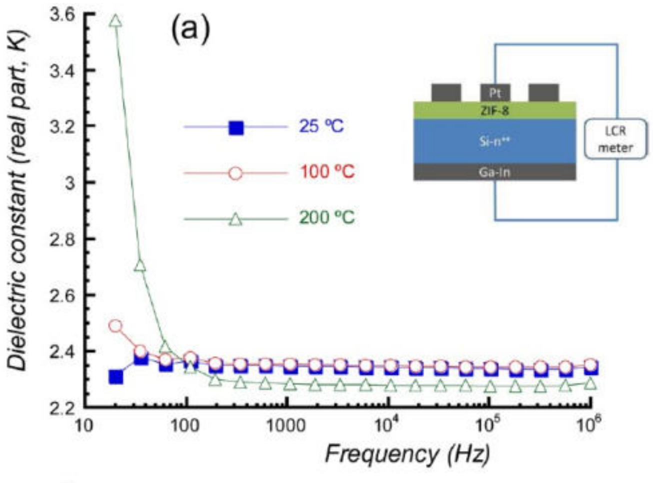



Sharma et al. Mic. Meso. Mater. (Revision submitted)

# ZIF films as low k dielectric





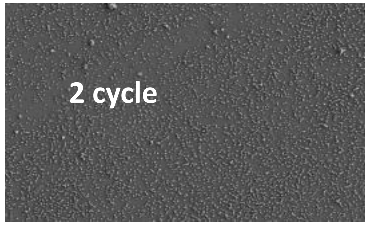

**Dielectric constant = 2.33 at 100 kHz**

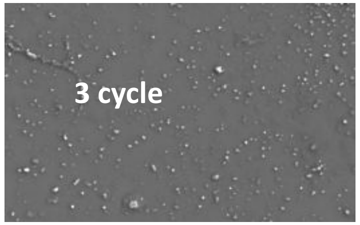
**Elastic modulus > 3 GPa**

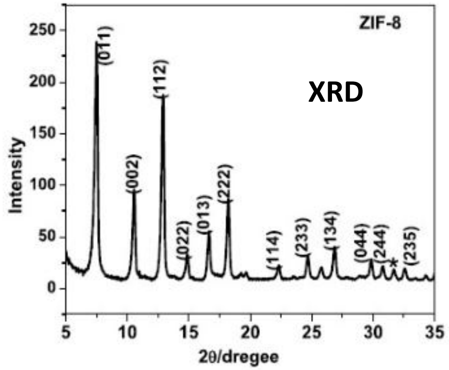
**Dielectric constant and applicability of the films will depend on the pore architecture.**

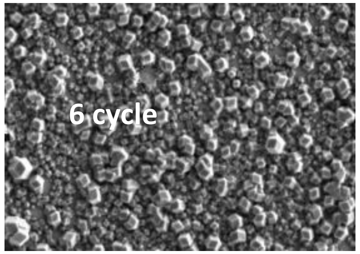


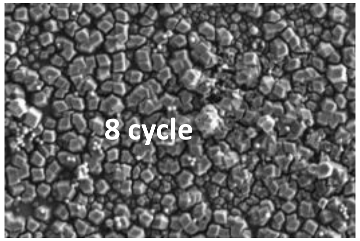
Chem. Mater. 25 (2013) 27-33.

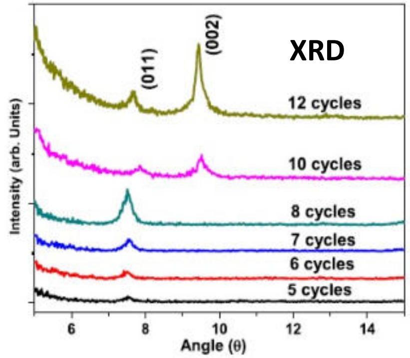


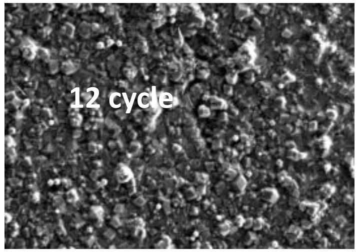



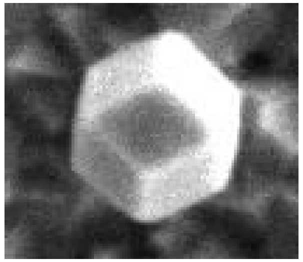



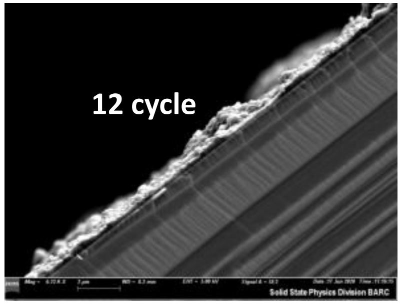



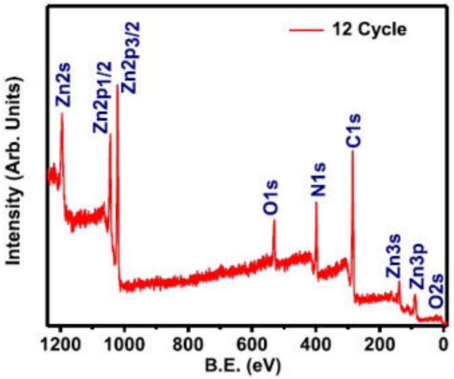



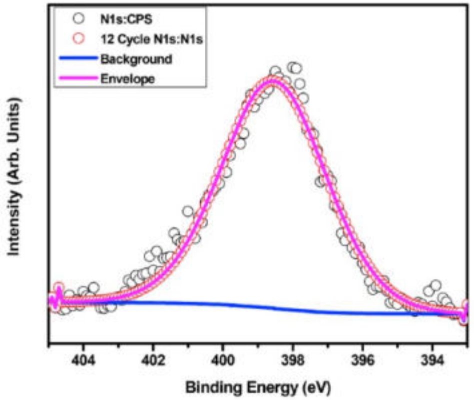



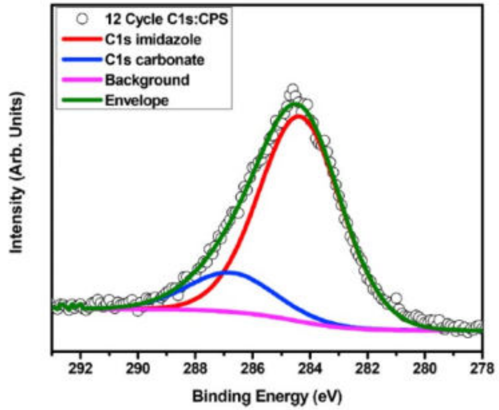


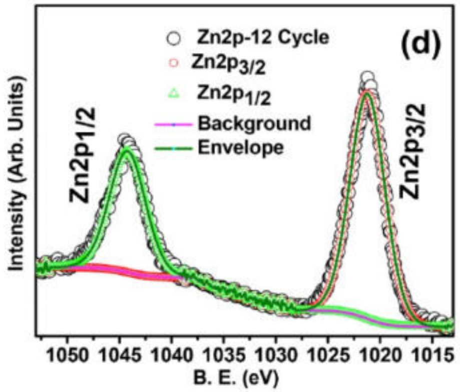

- ZIF-8 can be deposited at room temperature.
- ZIF-8 nuclei density increases in initial cycles and thickness growth occurs in later cycles.
- Preferential growth occurs in (002) direction.

# XPS analysis:



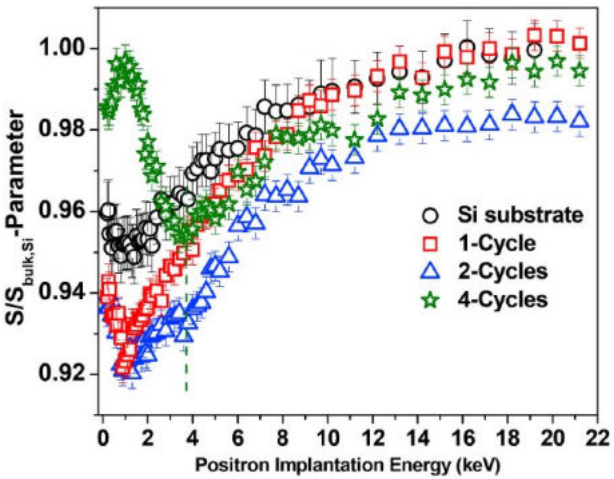



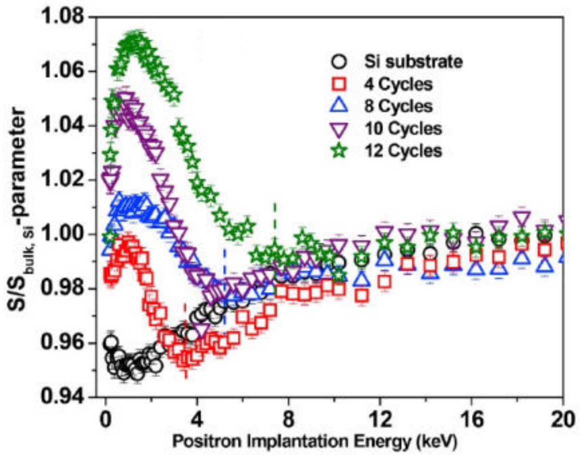



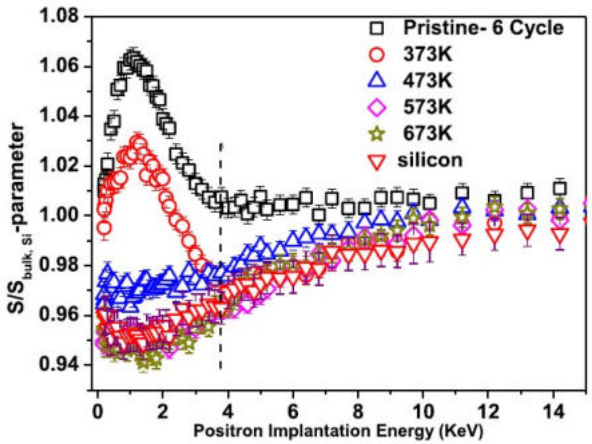

| Element | At. % | Atomic Ratio | |
|---|---|---|---|
| | | Experimental | Theoretical |
| Zn2p | 5.69 | 1 | 1 |
| N1s | 17.62 | 3.1 | 4 |
| O1s | 7.06 | 1.2 | 0 |
| C1s | 69.62 | 10.2 | 8 |

- ZIF-8 nanocrystals surface (~ 3-4 nm) are enriched by Zn as compared to Imidazolate.
- Nanocrystals have different gas adsorption characteristics as compared to large size.




- Initial cycles: Annihilation from the particles surface or particle-substrate interface.
- Later cycles: Peak in S-parameter profiles shows positronium diffusion to interface
- Positronium diffusion length: ~ 1.4 micrometer which is consistent with literature.




On annealing: Collapsing of pore interconnectivity starts before the lattice decomposition

Sharma et al. Mic. Meso. Mater. 307 (2020) 110519

## Conclusions and outlook:

- Positron annihilation spectroscopy is highly useful for experimental investigation of pore architecture

- ZIF-8 porosity depends on the external stimuli such as temperature, pressure and crystal size

- Pore size and porosity can be fine controlled using different strategies making ZIF-8 suitable for gas storage and gas separations.

- A systematic comparison of PAS data with other technique is required to establish the findings (gas adsorption does not work).

- ZIFs are proposed to be used in the form of membranes; pore aperture size using positron beam close to surface will be highly relevant for the gas separation efficiency.

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