Water Harvesting with Metal-Organic Frameworks (MOFs)

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Ibn Khaldun Fellowship for Saudi Arabian Women
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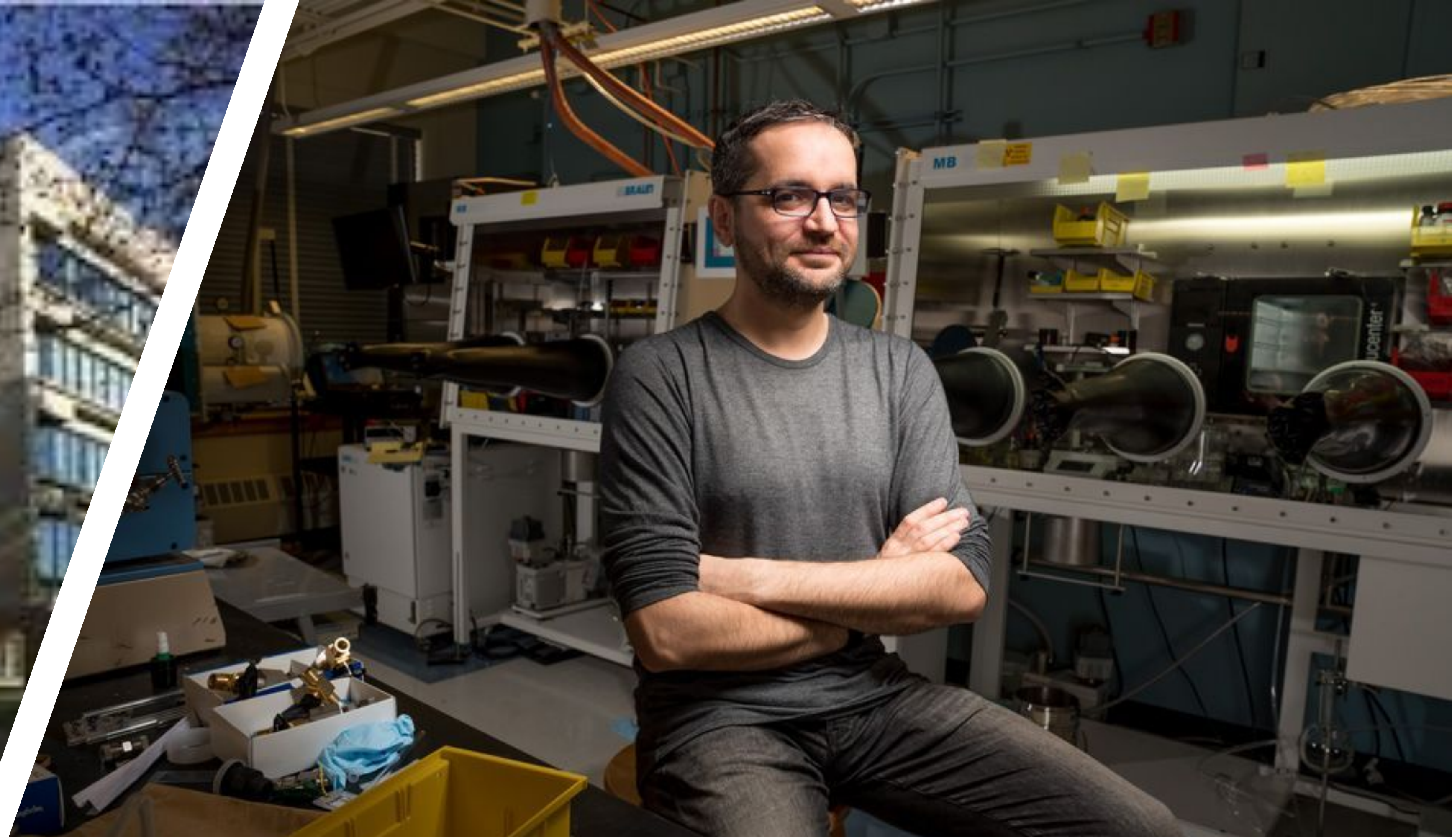
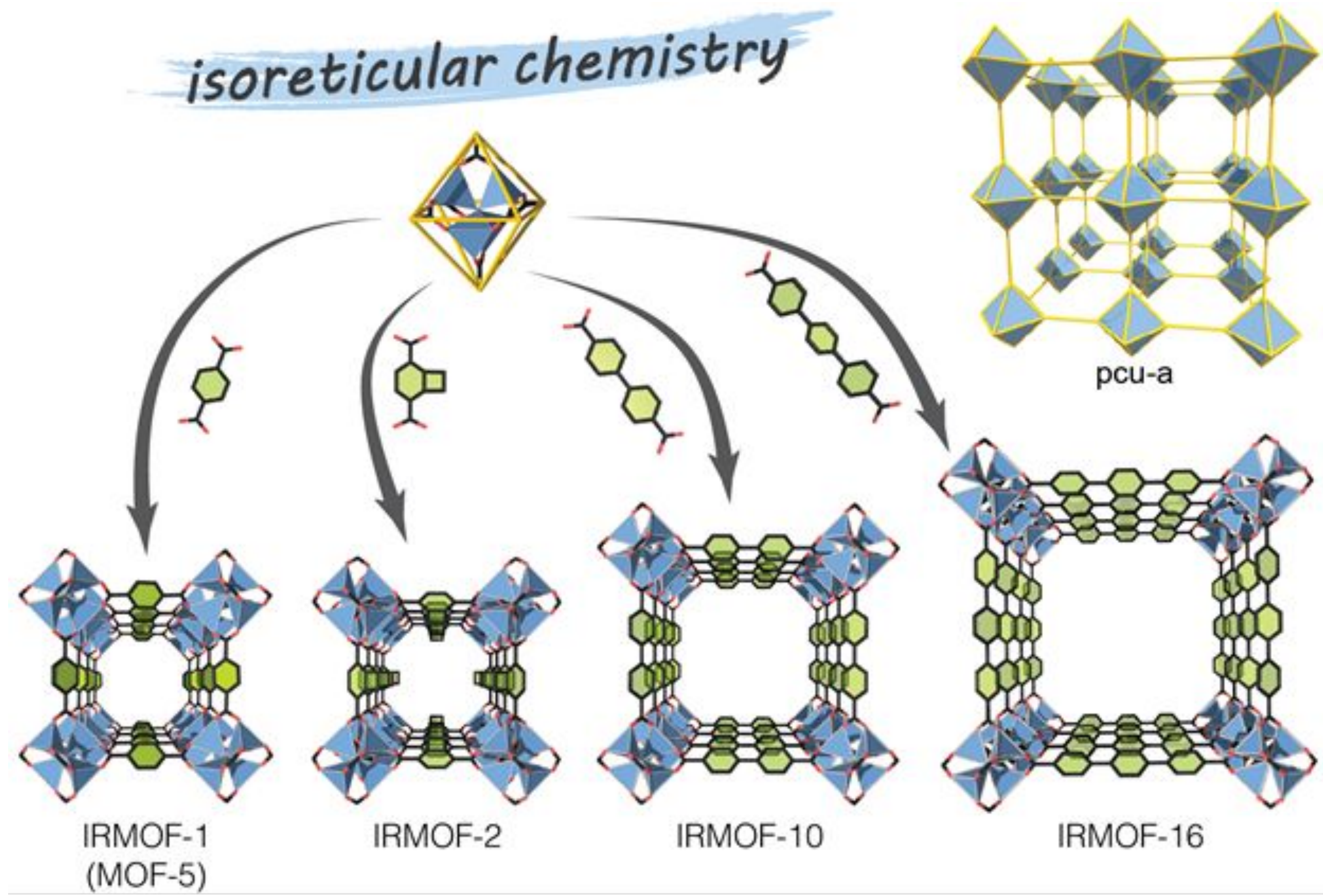


the dincă group

Metal-Organic Frameworks (MOFs)

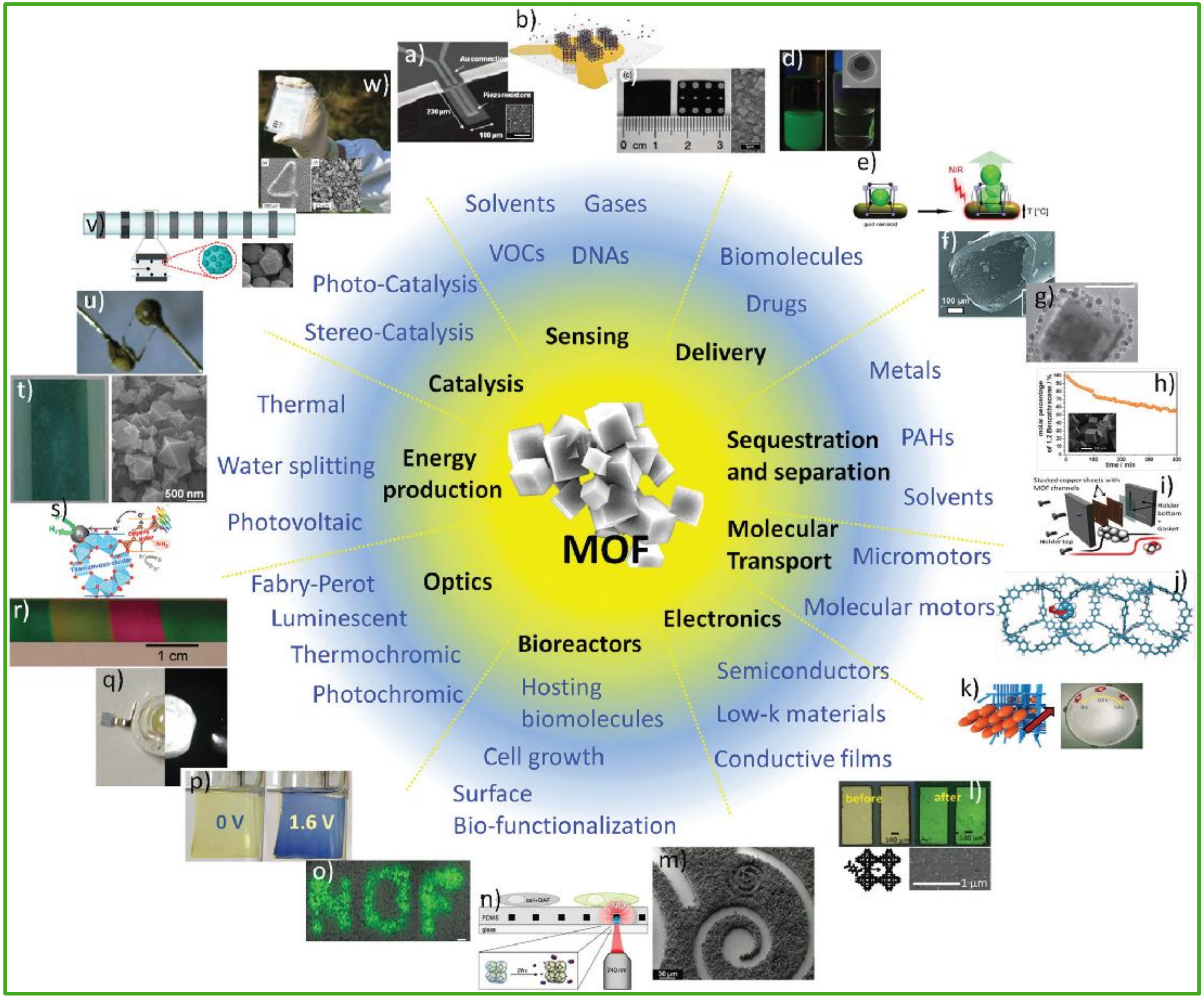
MOFs can be rationally designed by choosing a proper ligand and targeting a suitable cluster.

- **Crystalline extended hybrid solids**
- **Rational Assembly (building block approach)**
- **Modular, can be functionalized prior or after the assembly**
- **Unprecedented apparent surface areas (up to 7000 m^2/g)**
- **Controlled pore size (from ultra-micropores to mesopores up to 5nm)**

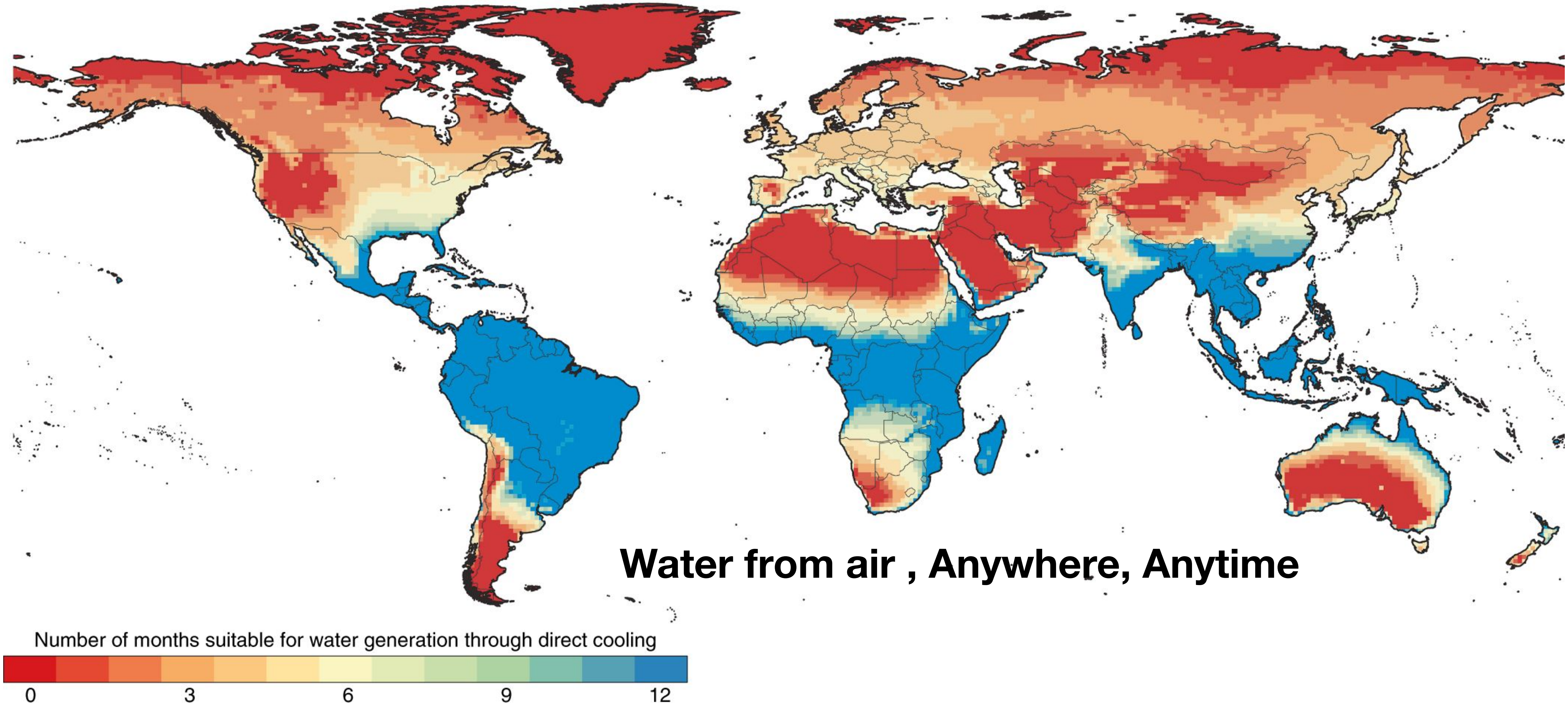


- Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. Science, **2002.**, Jiang, H.; Alezi, D.; Eddaoudi, M. *Nat. Rev. Mater.*, **2021**

MOFs Applications



Water insecurity necessitates new sources of clean water



Water from air , Anywhere, Anytime

The areas marked in yellow to red are often water-stressed

Hanikel, N., Prévot, M.S. & Yaghi, O.M. MOF water harvesters. Nat. Nanotechnol. 15, 348–355 (2020).

Potential solution:

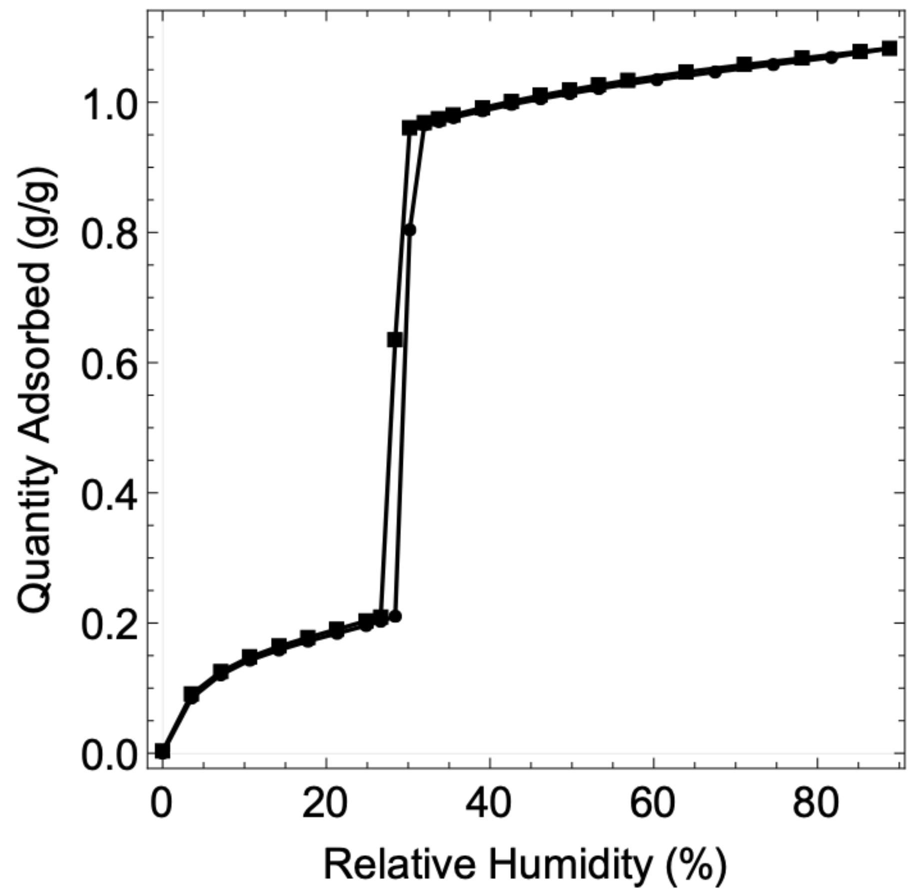
Harvesting water from air

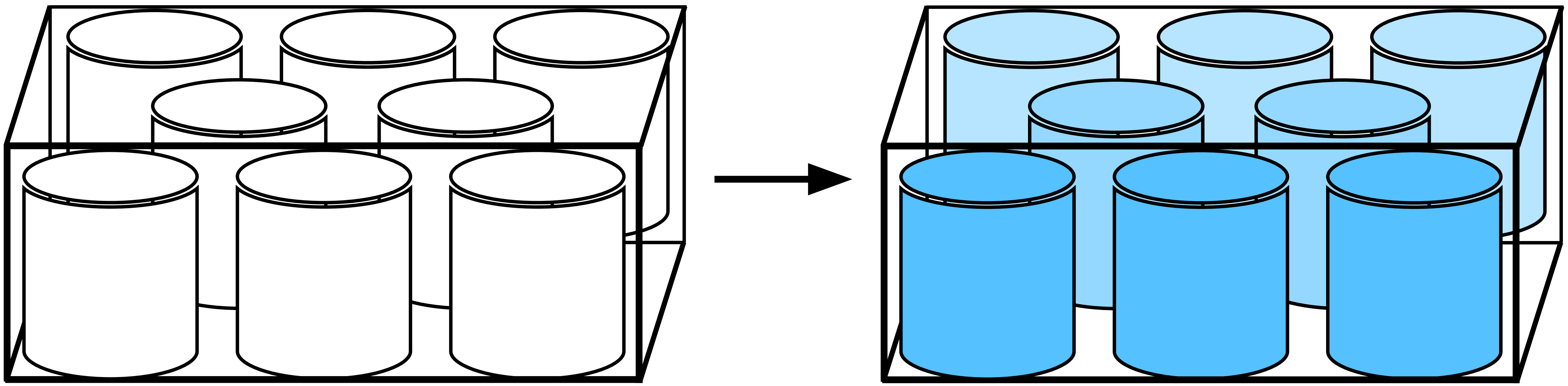
12.900 cubic kilometers (km^3)

of water in the air at any time

Sorbents with uniform micropores often have steep water uptake

Sudden pore filling is called *capillary condensation*

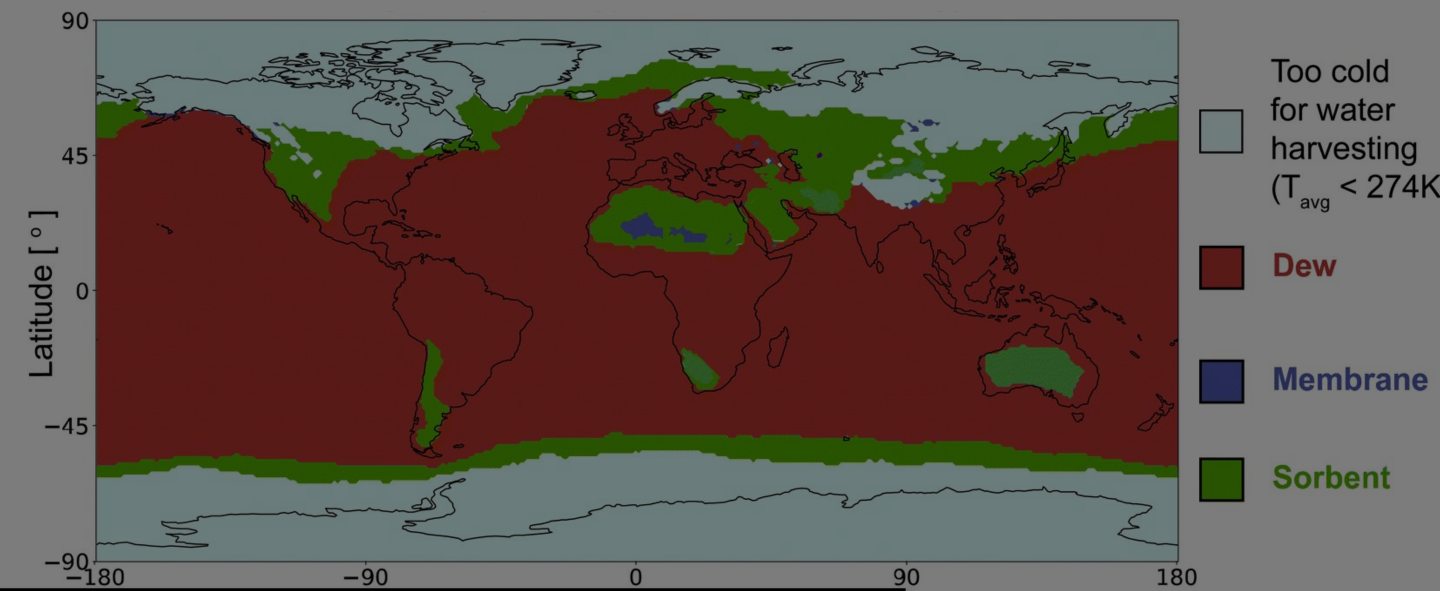




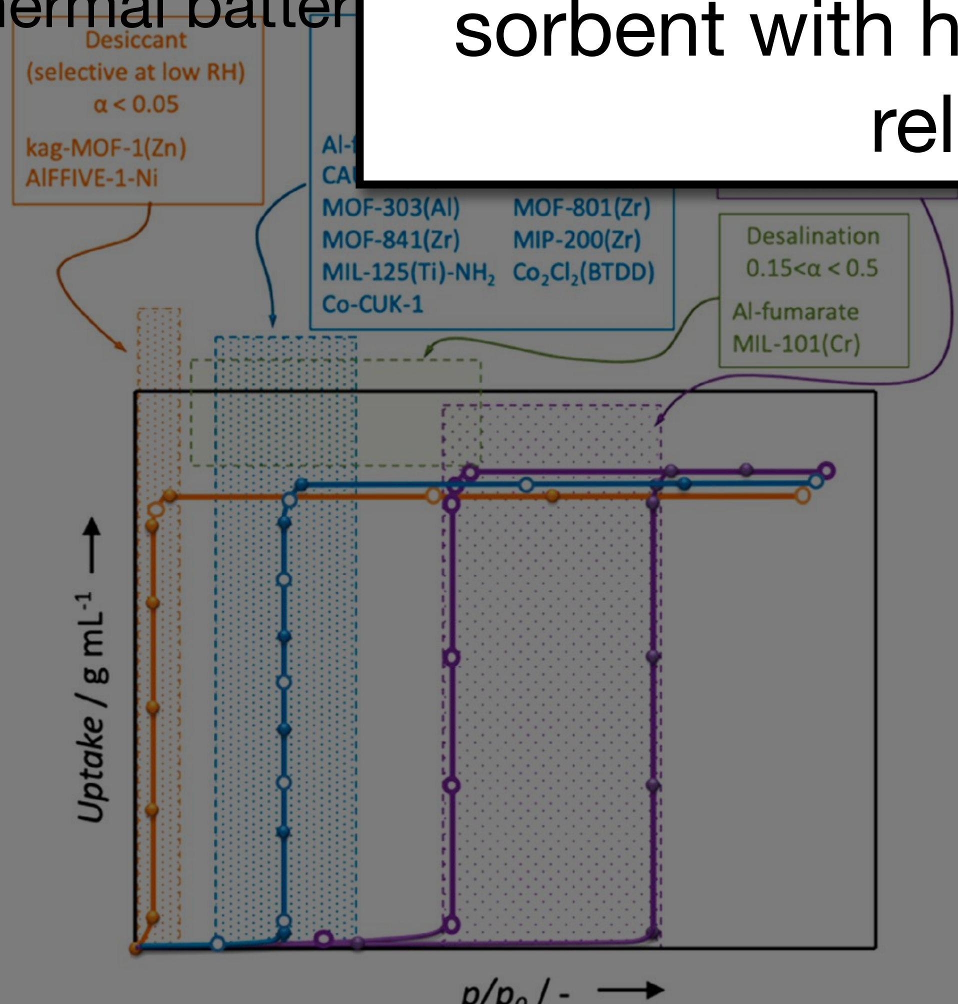
Water sorbents can be used for a wide range of desirable applications

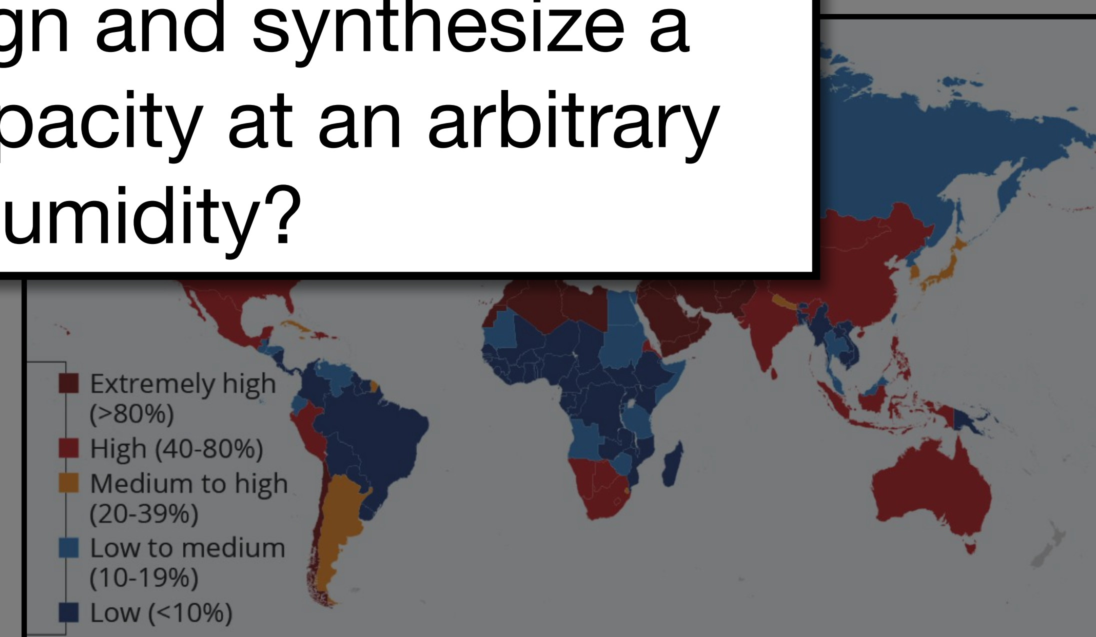
Applications enabled by sharp uptake operate at a variety of relative humidity

- Heat pumps (air conditioning)
- Desiccants
- Desalination
- Humidity contr
- Thermal batter



How does one design and synthesize a sorbent with high capacity at an arbitrary relative humidity?

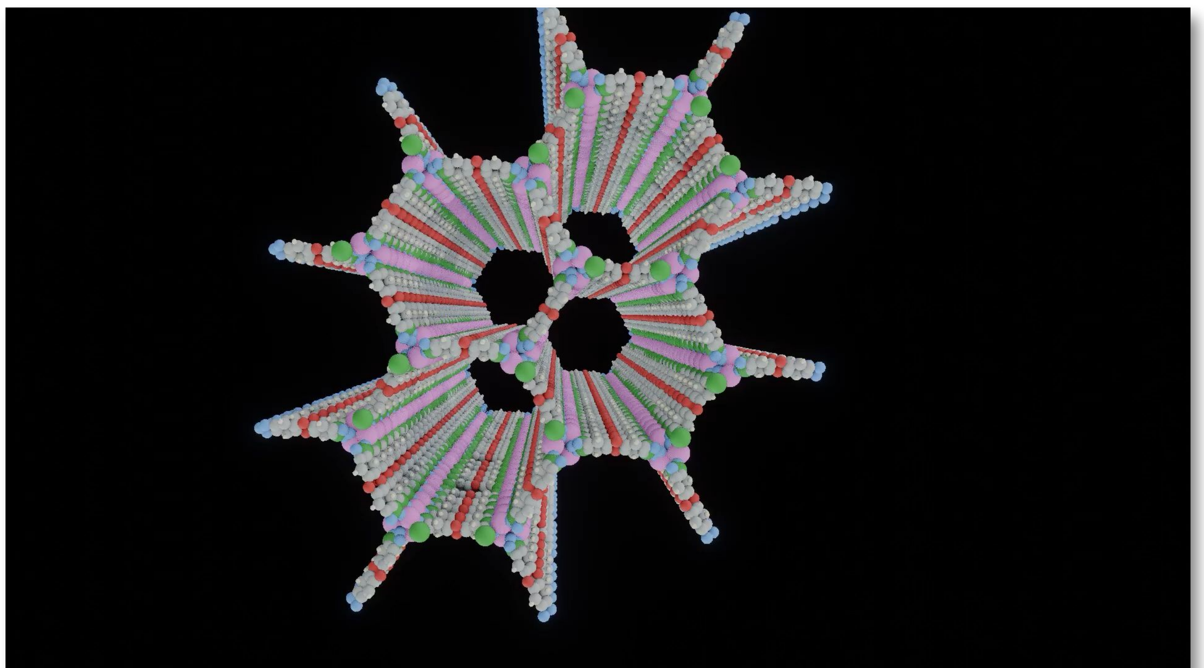


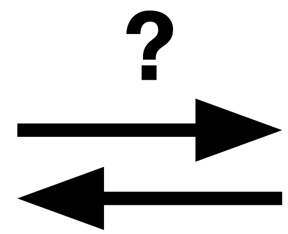


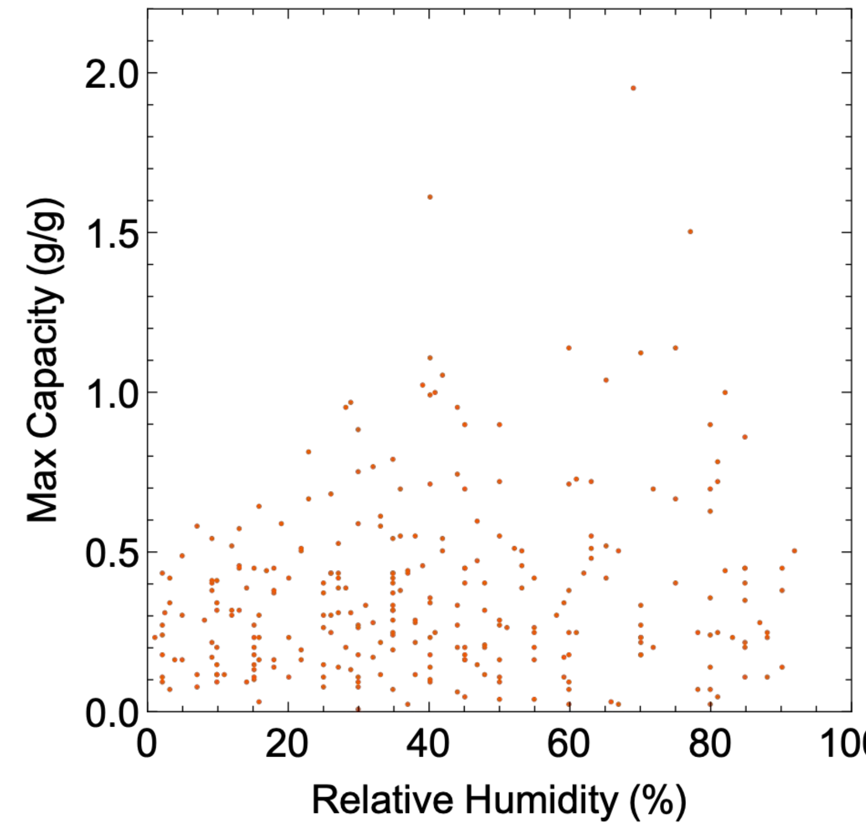
- Regions of water insecurity are primed for sorbent water harvesting
- However, the is a distinct lack of sorbents that operate at 10 – 30% RH

Energy Environ. Sci., 2022,15, 4025-4037
Chem. Rev. 2020, 120, 16, 8303–8377

What is the structure-function relationship?



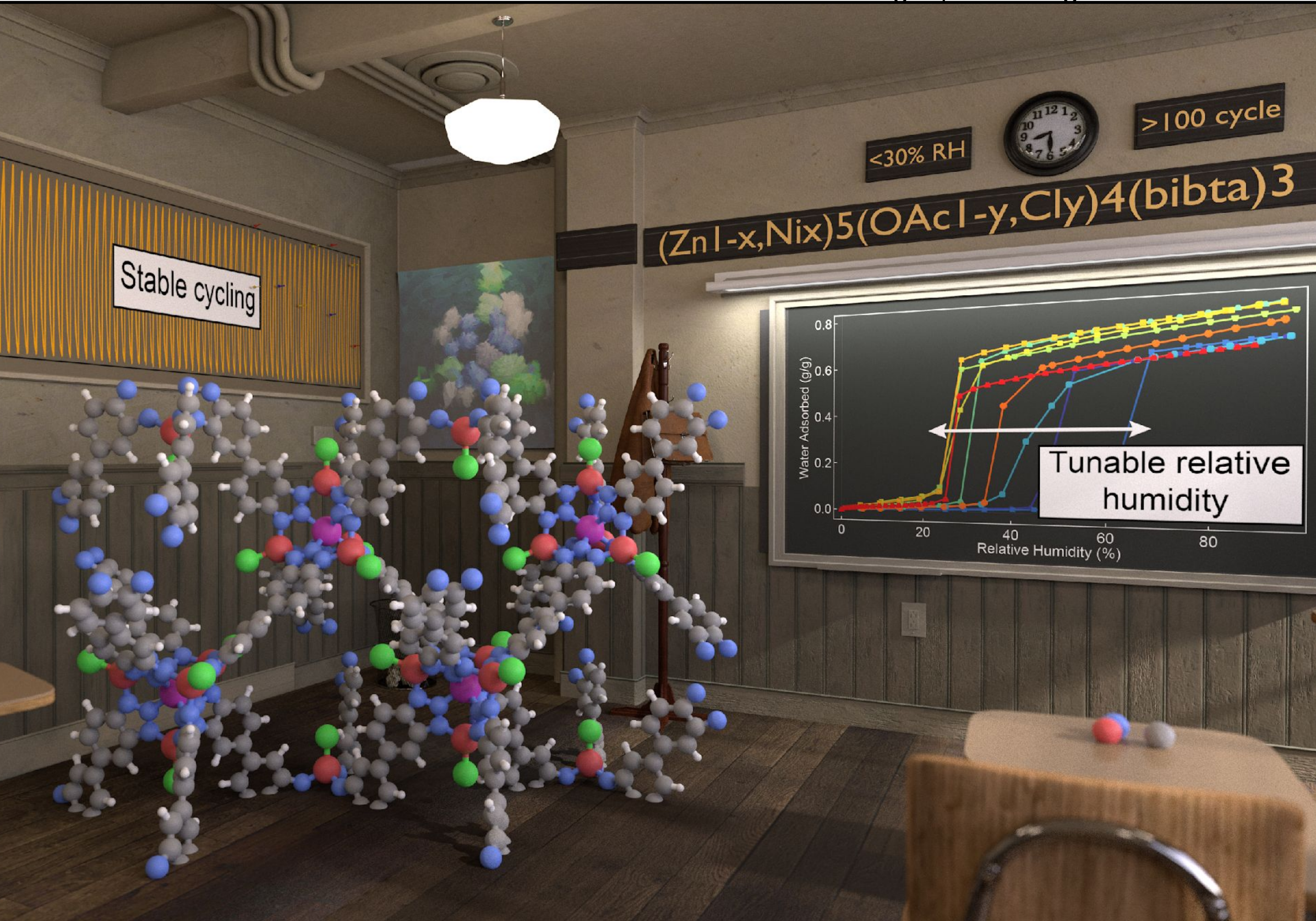




The fundamental parameters include

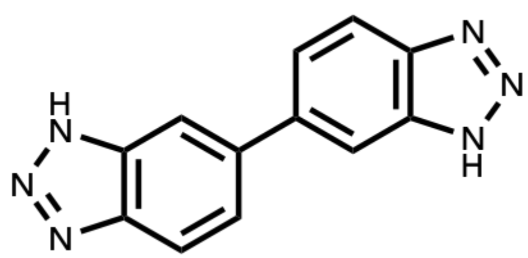
1. Relative humidity of capillary condensation
2. Working capacity
3. Relative humidity – capacity relationship
4. Hysteresis
5. Cycling stability
6. Environmental impact of the material and its synthesis
7. Costs associated with MOF synthesis and use

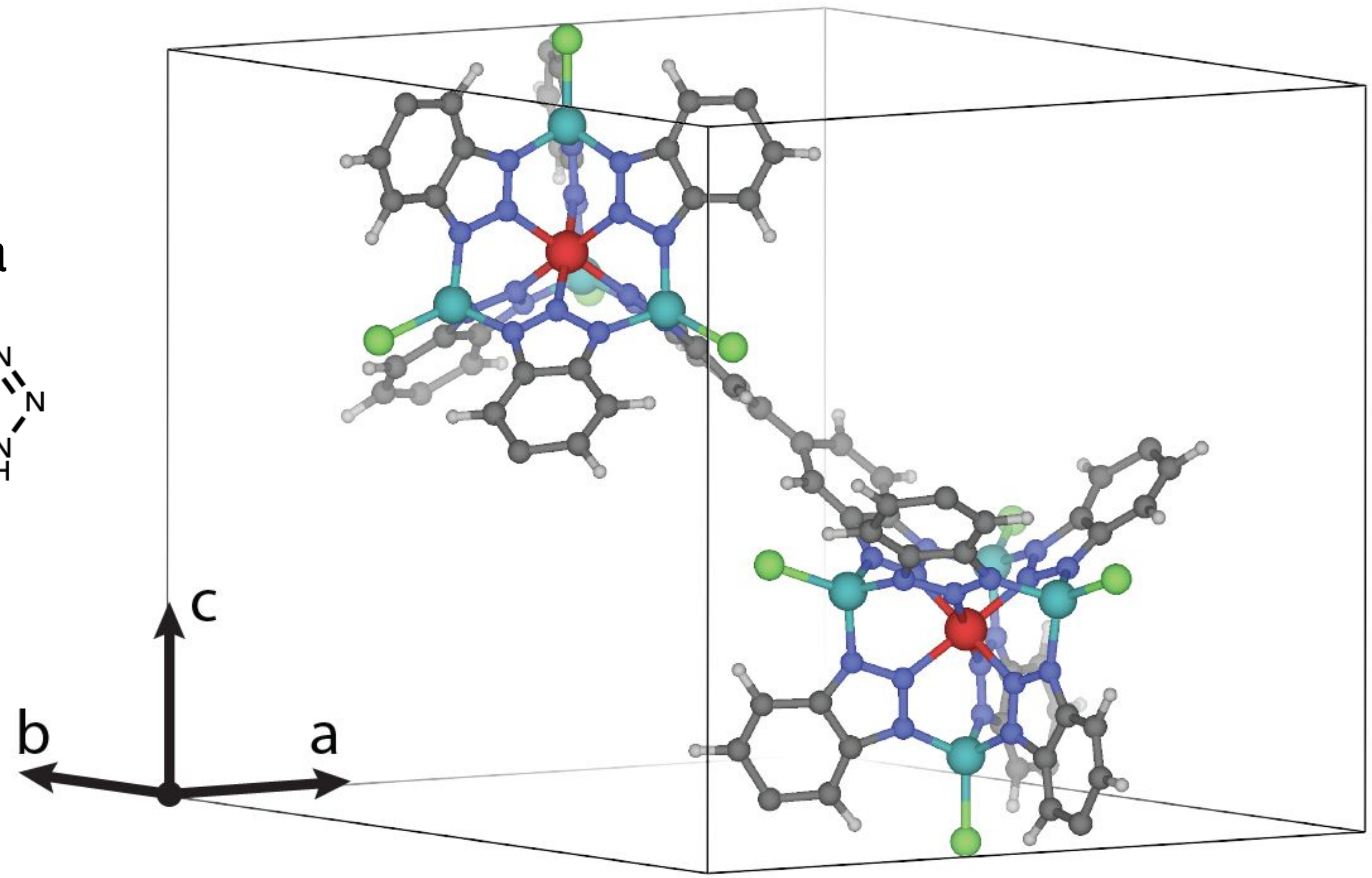
Water adsorption in a bibenzotriazole MOFs, $M_5X_4(bibta)_3$

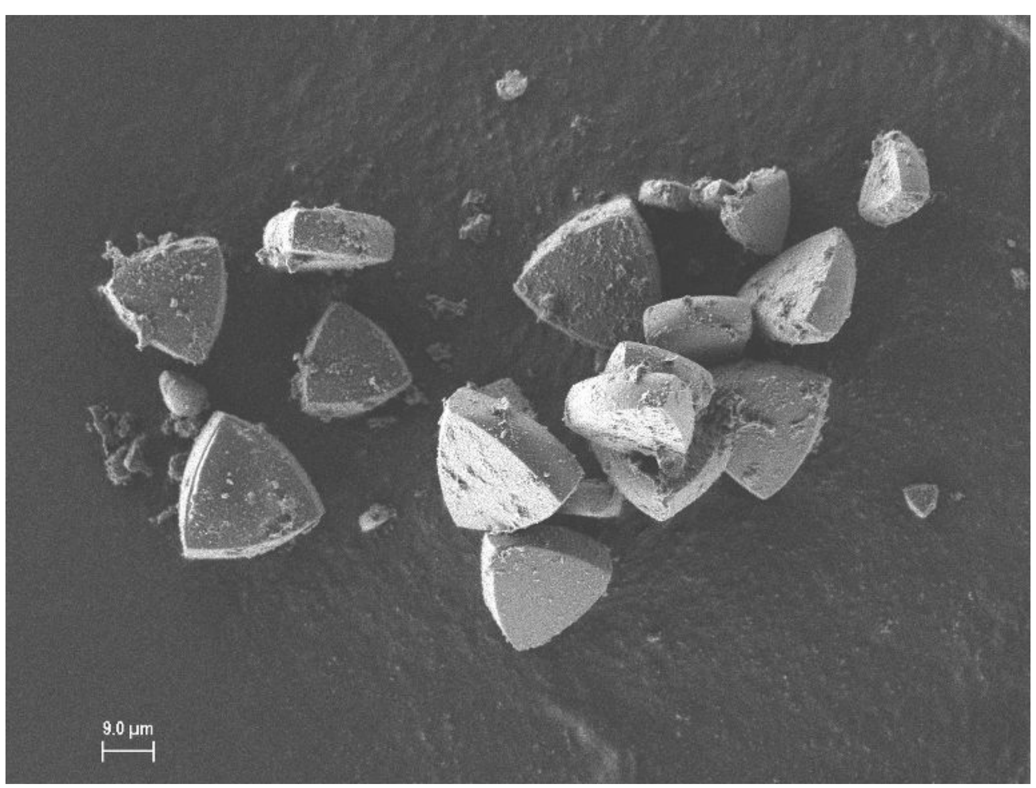


CFA-1. A cheap modular framework

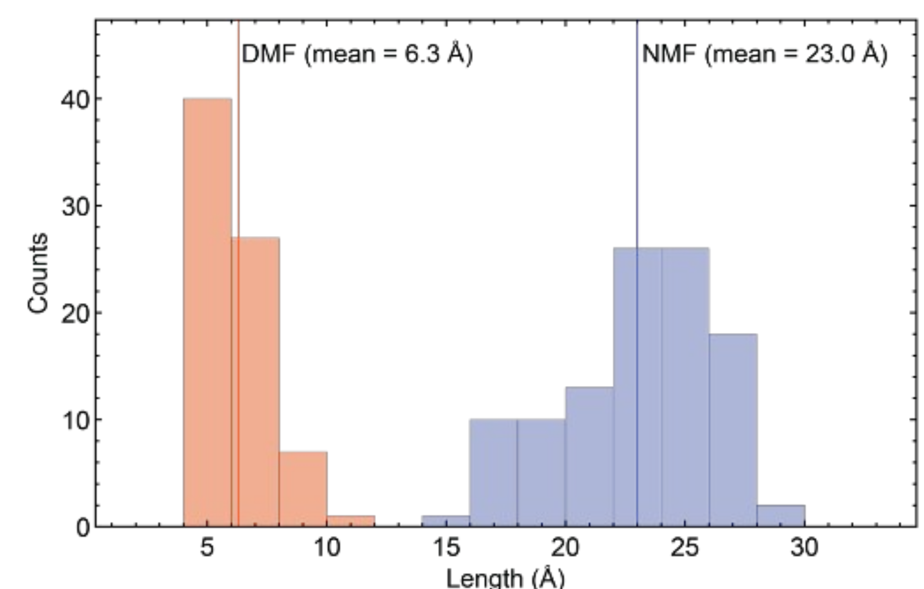
Linker: H_2bibta





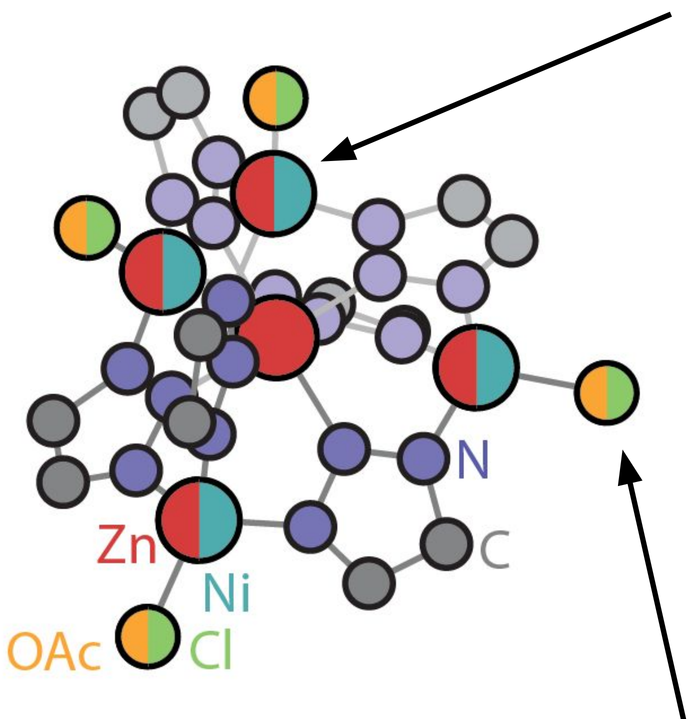


Particle size controlled by synthetic conditions

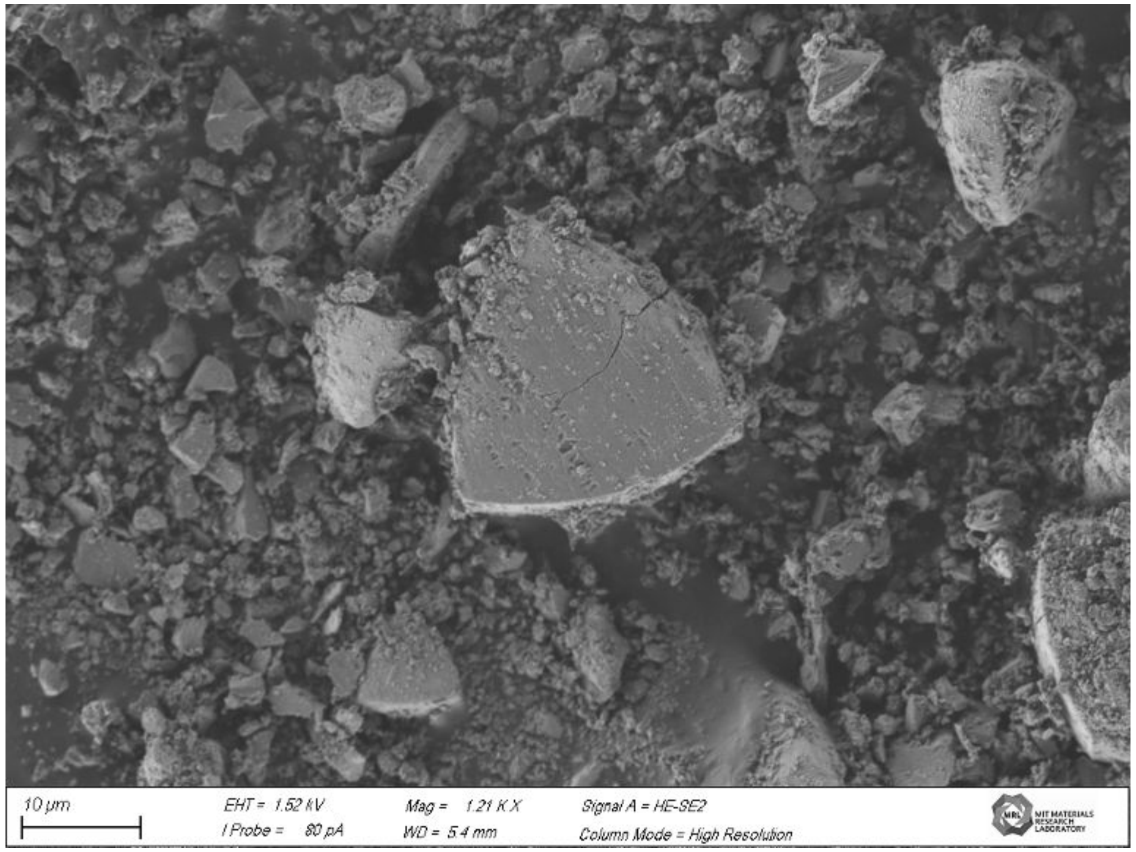


$Zn_5OAc_4(bibta)_3 \rightarrow (Zn_{1-x},Ni_x)_5(OAc_{1-y},Cl_y)_4(bibta)_3$

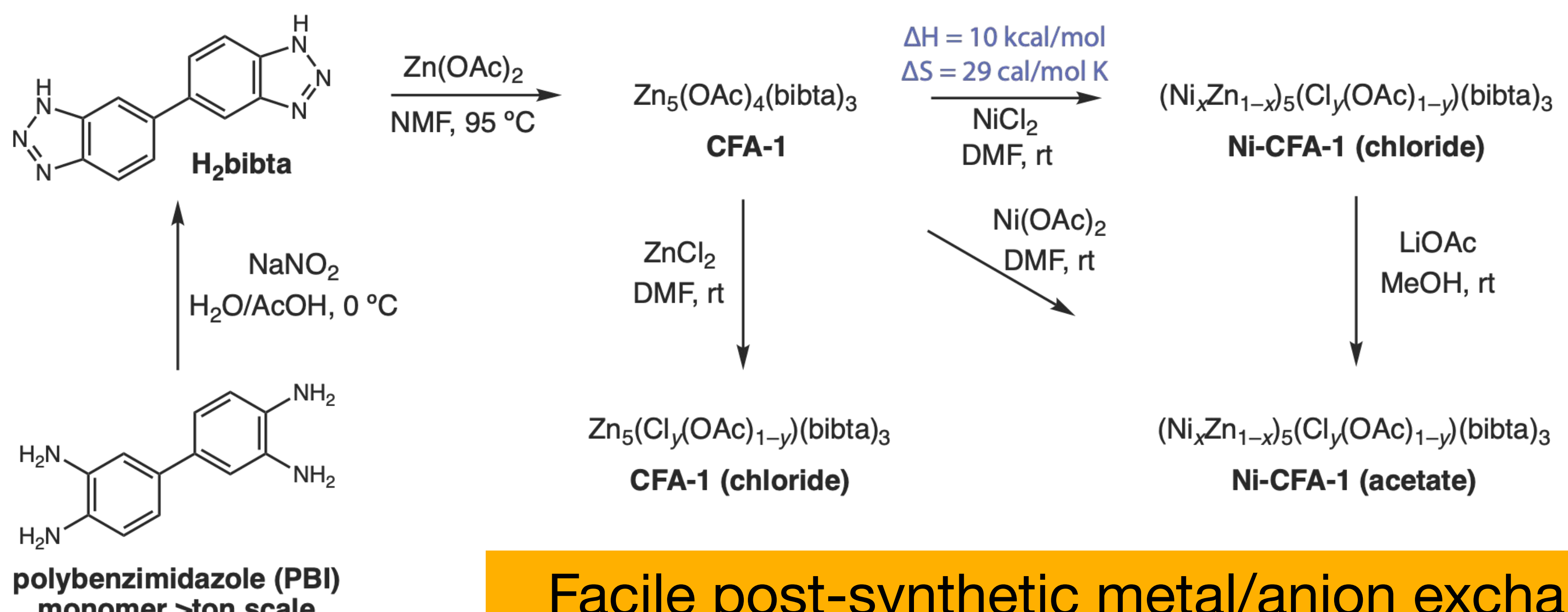
Multivariate metal



Multivariate anion



Particle remain intact after exchange

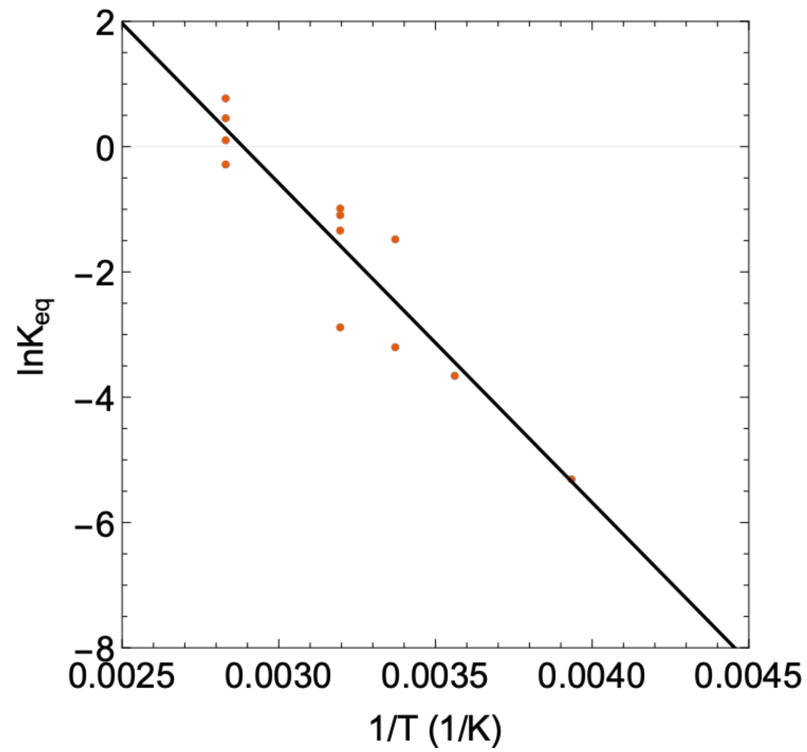


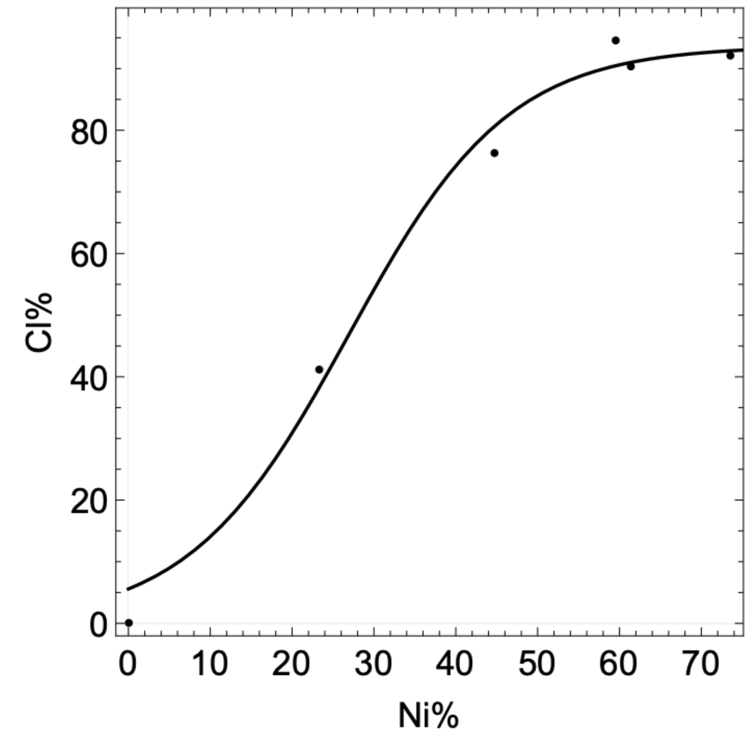
Facile post-synthetic metal/anion exchange

$Zn_5OAc_4(bibta)_3 \rightarrow (Zn_{1-x},Ni_x)_5(OAc_{1-y},Cl_y)_4(bibta)_3$

Quantification of post-synthetic metal exchange thermodynamics enables synthesis of arbitrary composition

ΔH = 10.1 ± 1.8 kcal/mol
ΔS = 29.2 ± 3.8 cal/molK



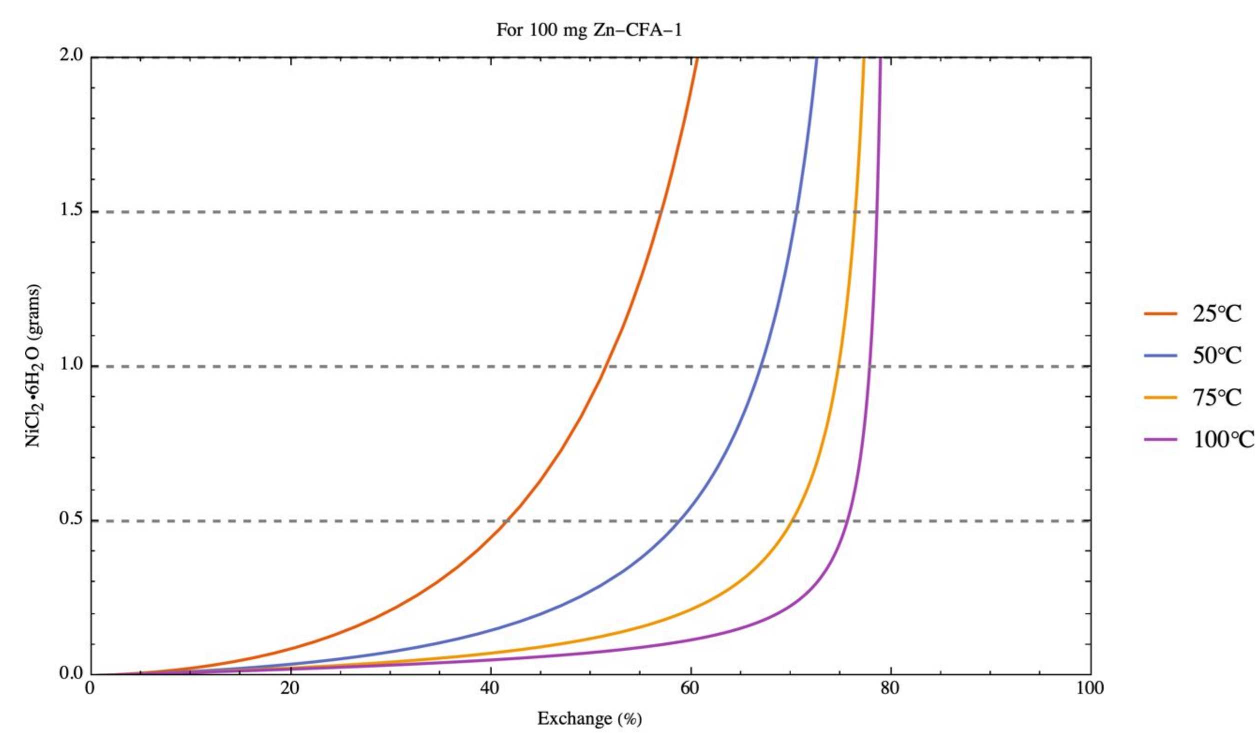


Chloride content increases monotonically with nickel content

$$\ln K_{eq} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

$$K_{eq} = \frac{Z_{Ni}S_{Zn}}{Z_{Zn}S_{Ni}} = \frac{c_{Ni}^2 m_{Zn}}{c_{Ni}m_{Ni}c_{Zn} + m_{Ni}c_{Zn}^2 - c_{Ni}c_{\ldots}}$$

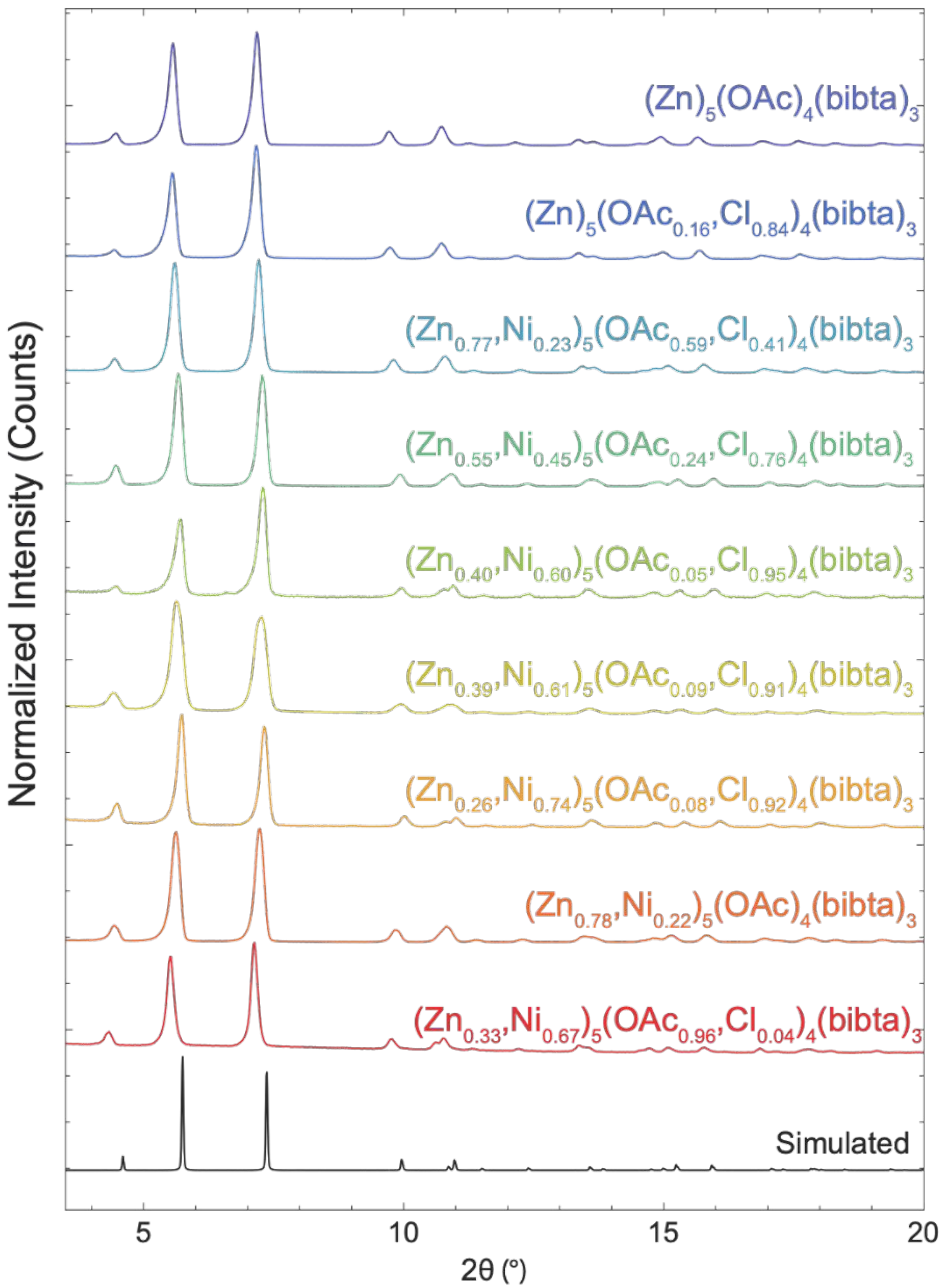
c_M = moles of metal in the MOF
m_M = moles of metal in the original solution

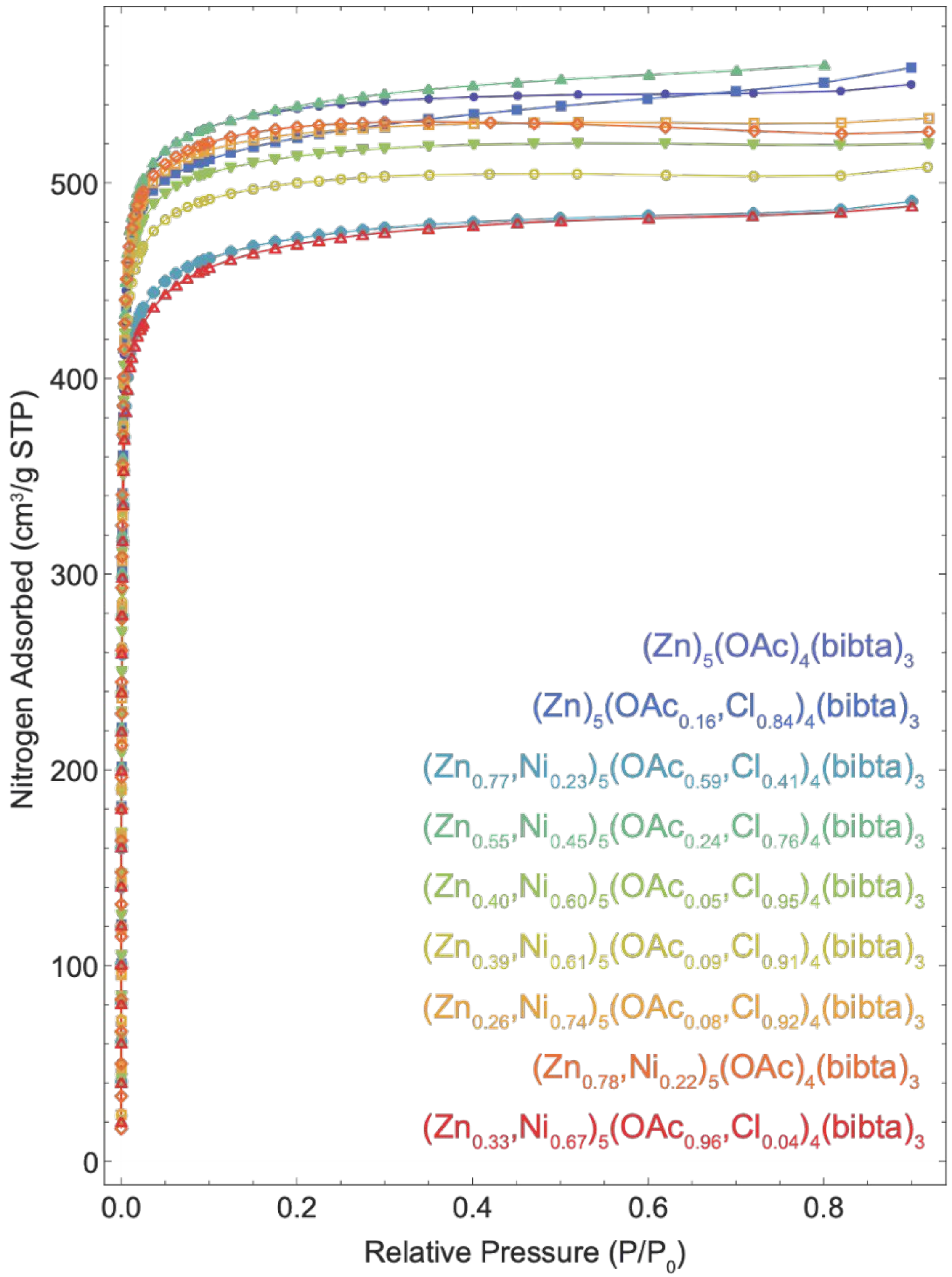


ΔH and ΔS provide guidelines for synthetic design

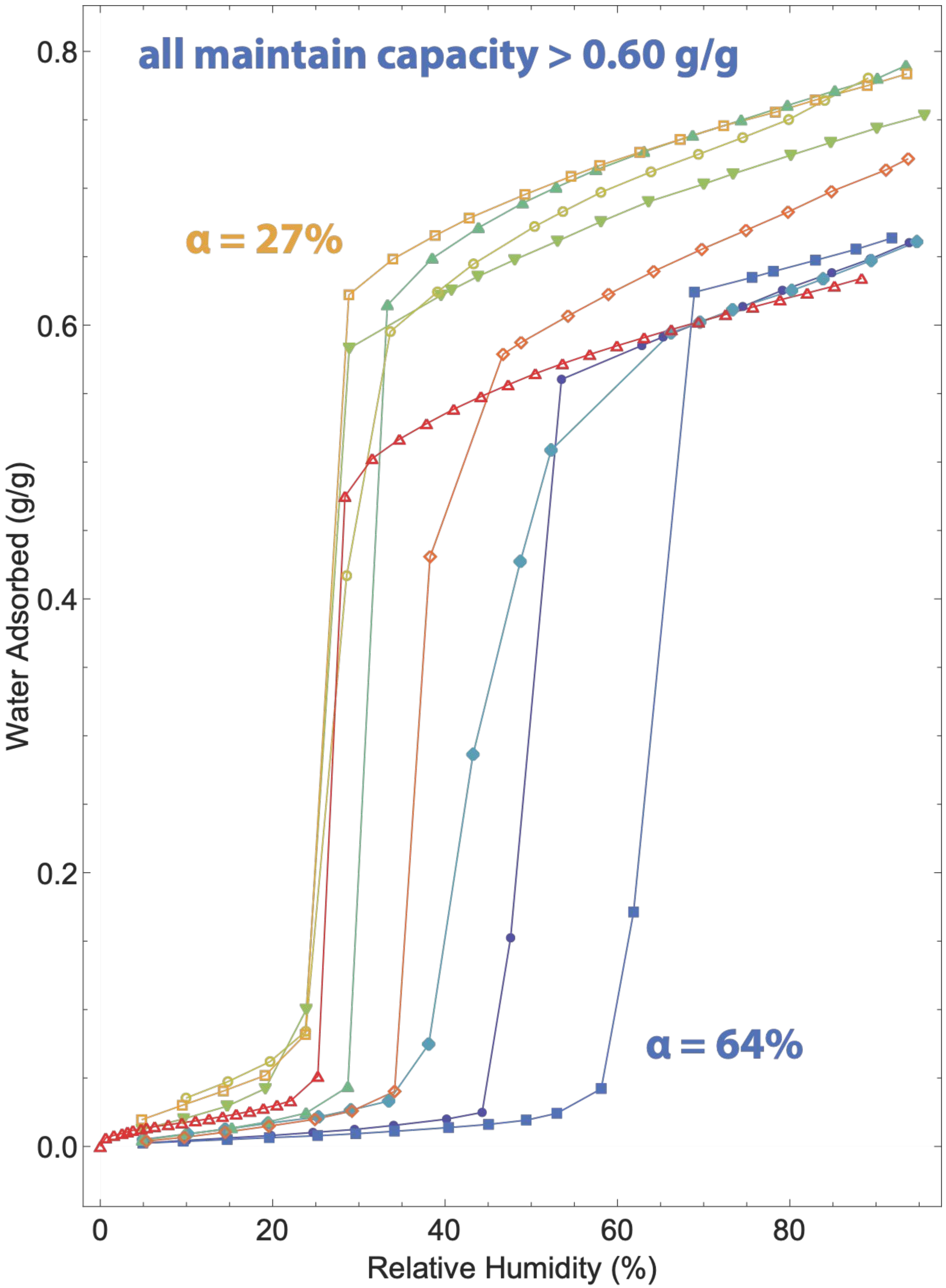
Post-synthetic exchanged material retains porosity and structure of parent

Experimentally, we manage to access to 0–74% Ni (all Td metal sites), 0–95% Cl

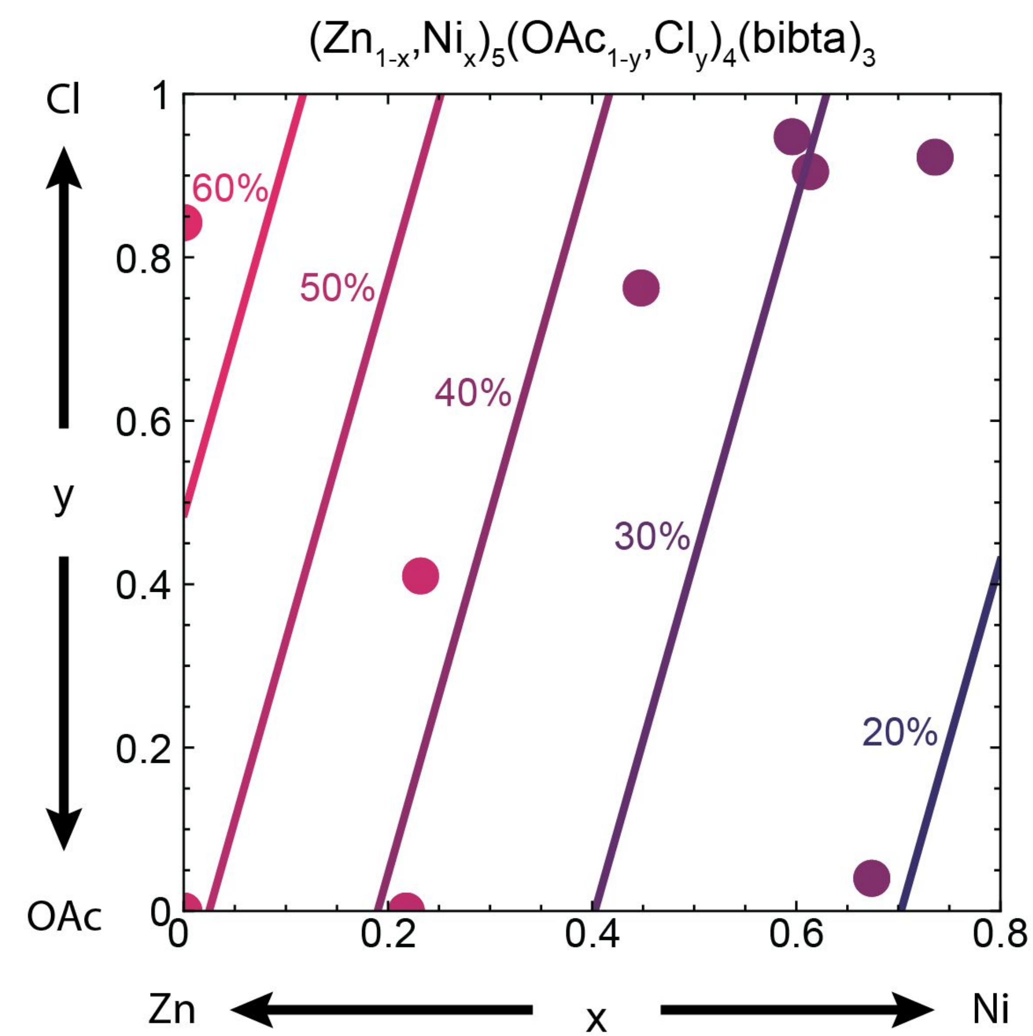




Tunable water sorption



Critical pressure – composition obey the derived thermodynamic relationship



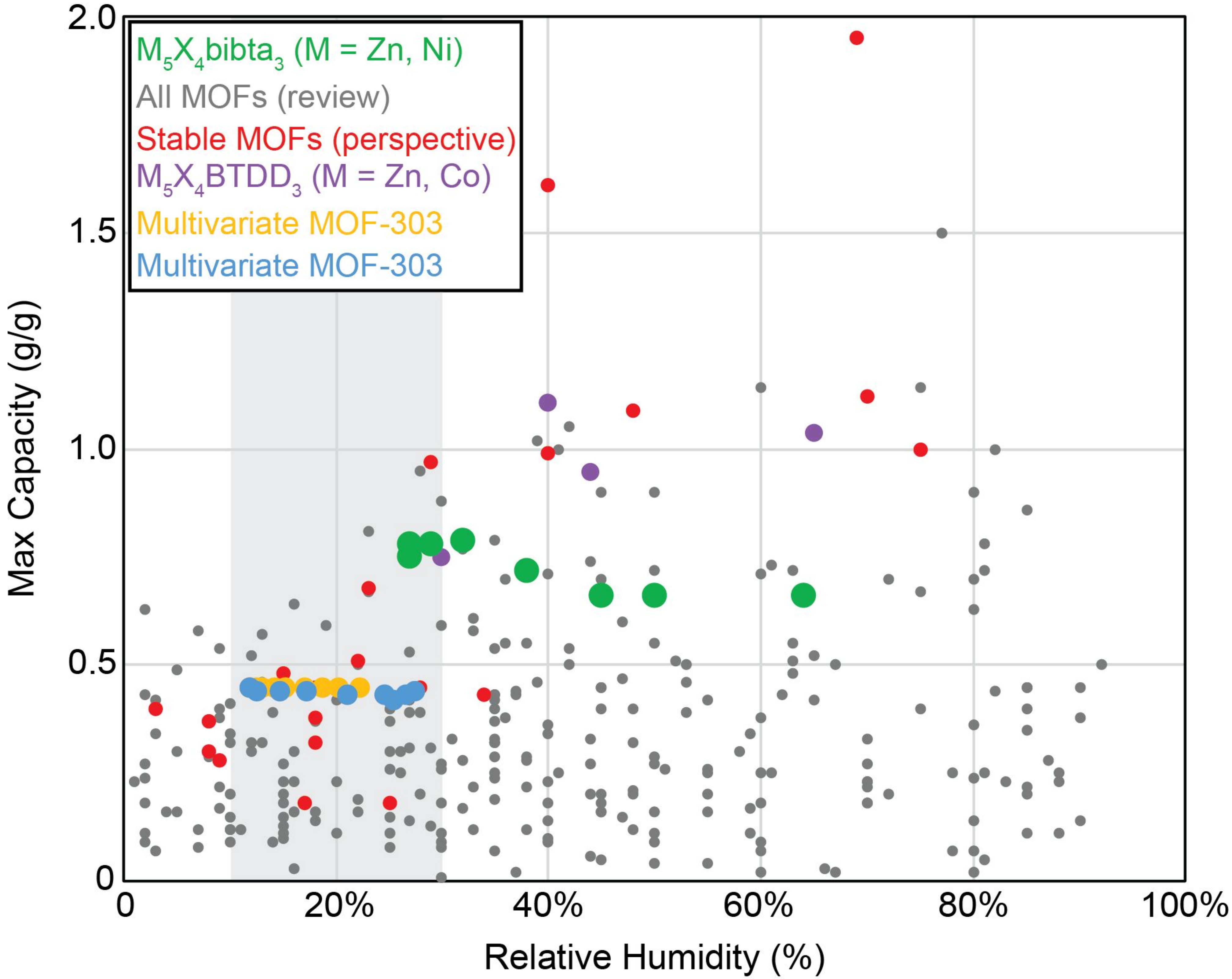
$$\ln \frac{P}{P_{sat}} = \frac{V}{ArkT} \Delta G_{in}$$

$$\Delta G_{Ni} < \Delta G_{Zn}$$

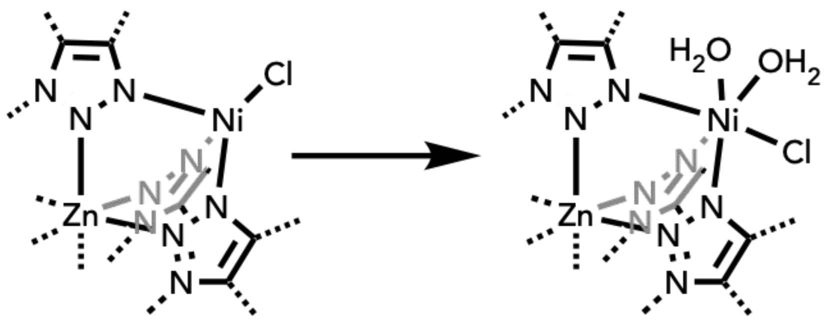
$$\Delta G_{OAc} < \Delta G_{Cl}$$

$$\Delta G_{int} = x\Delta G_{Ni} + (1-x)\Delta G_{Zn} + y\Delta G_{Cl} + (1-y)\Delta G_{OAc} + \Delta G_{back}$$

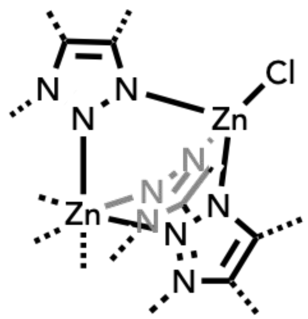
The capacity of $(Zn_{1-x},Ni_x)_5(OAc_{1-y},Cl_y)_4(bibta)_3$ is remarkably high

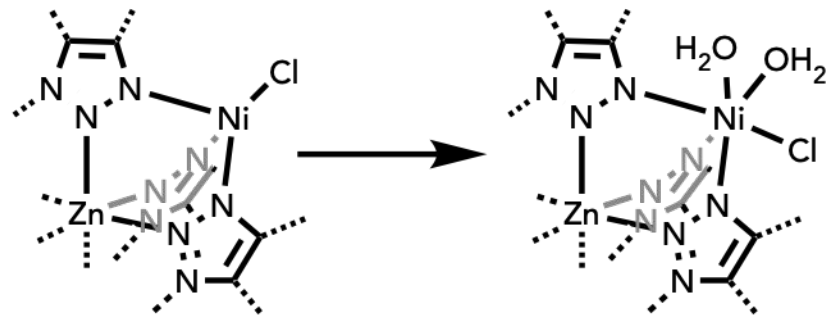


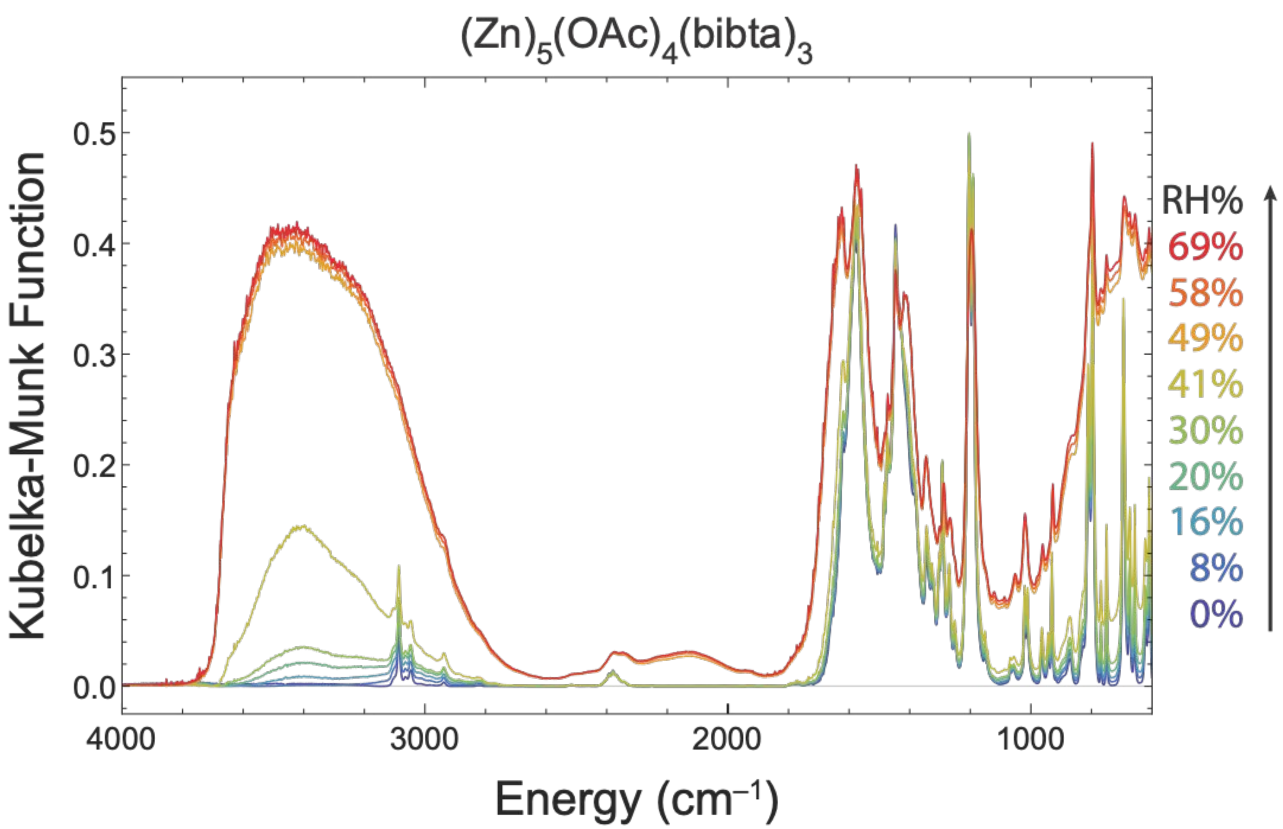
Colorimetric change upon water sorption

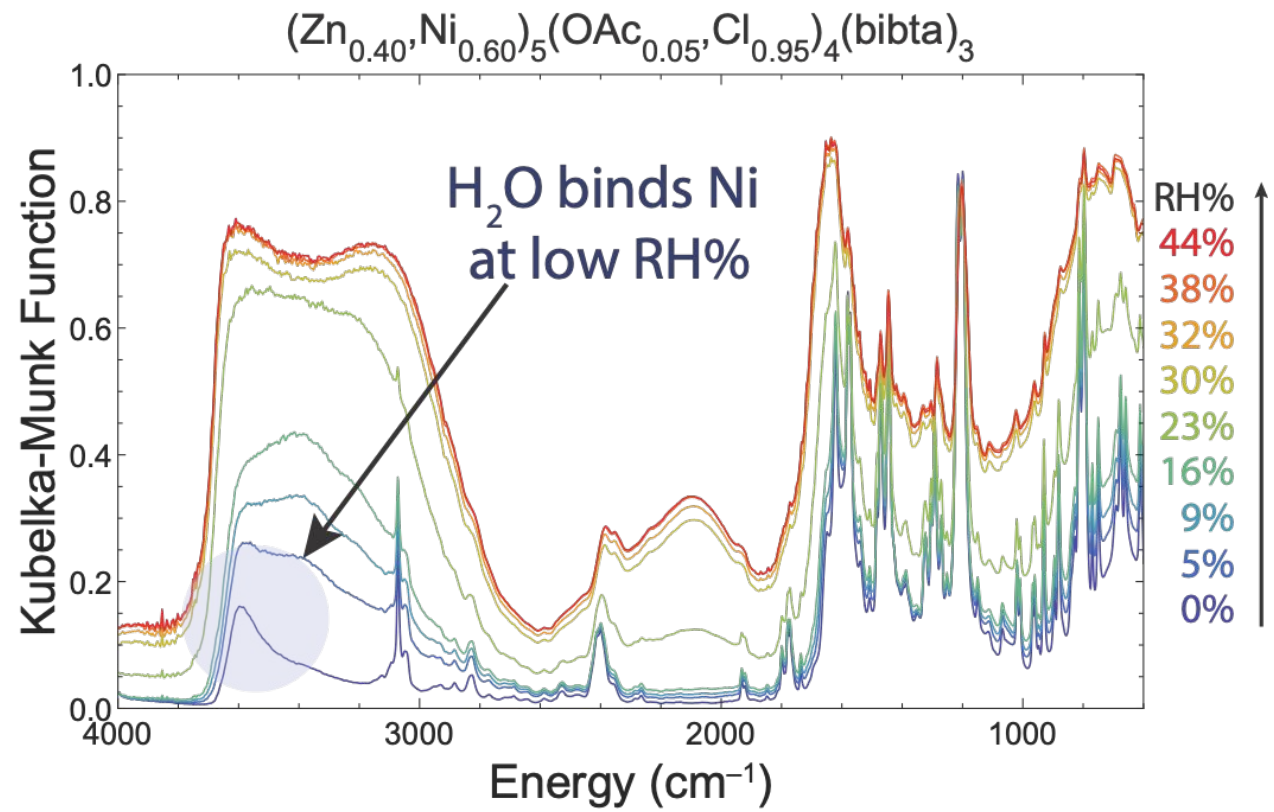


Coordination to water at low relative humidity seeds condensation









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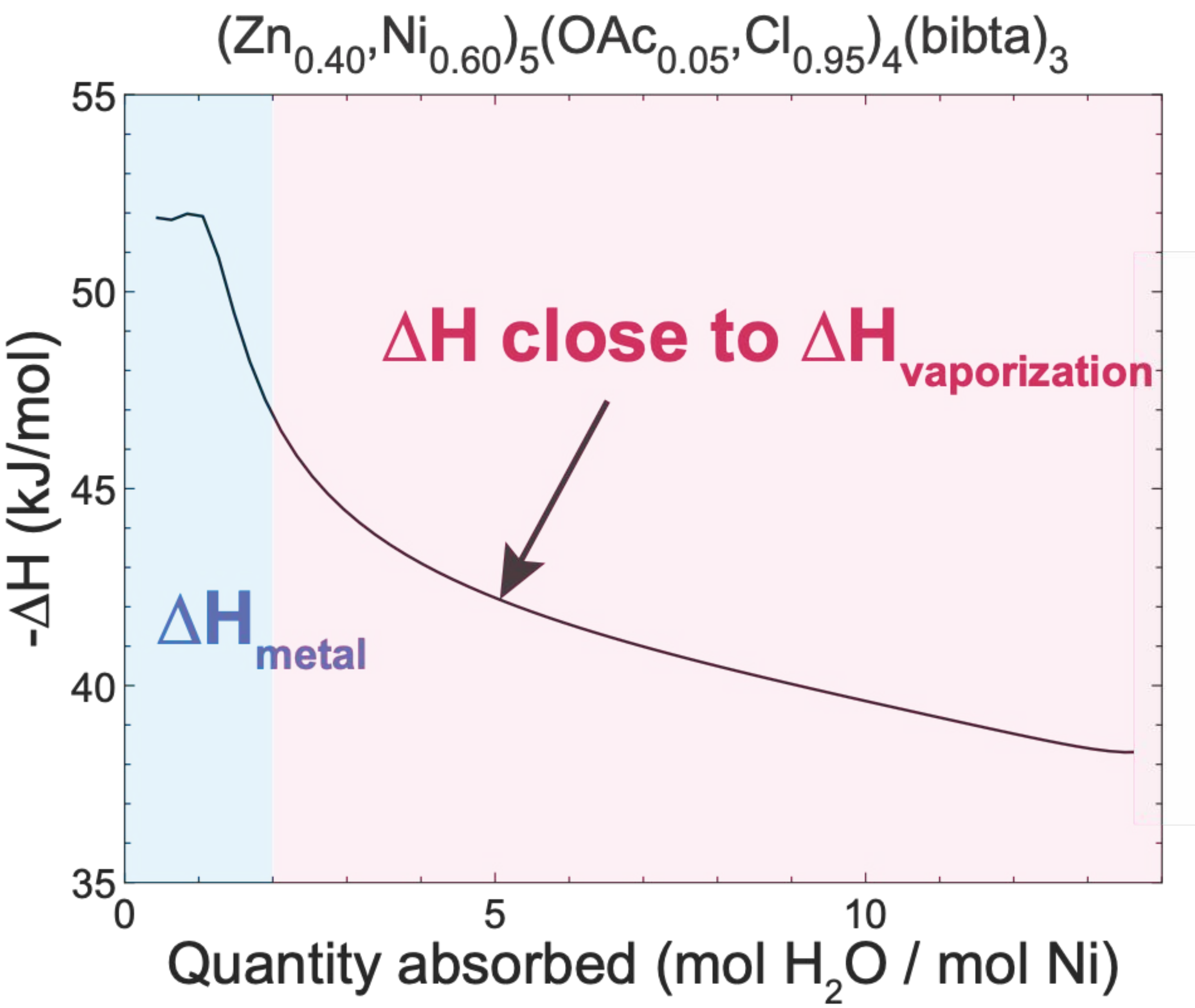
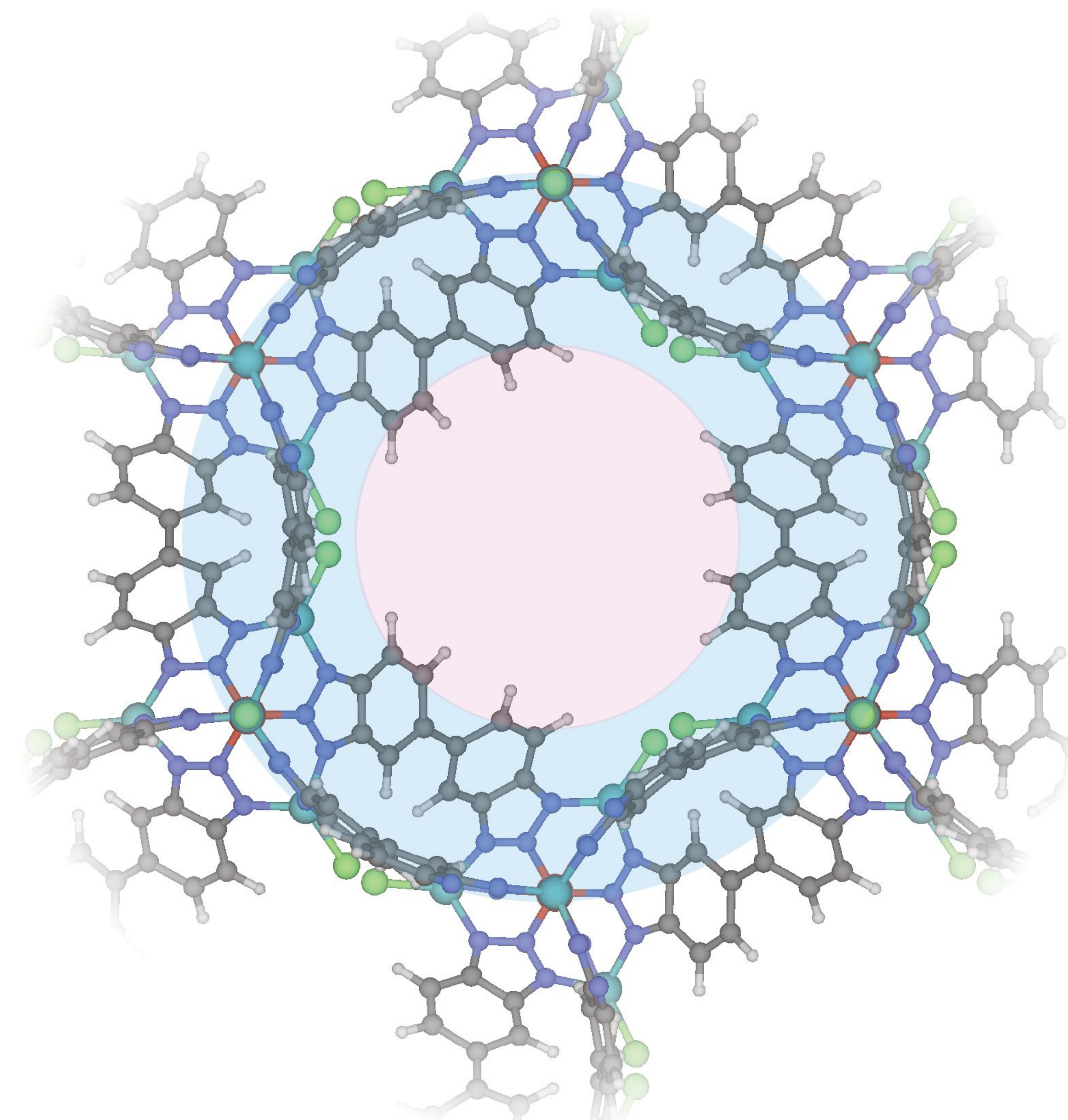
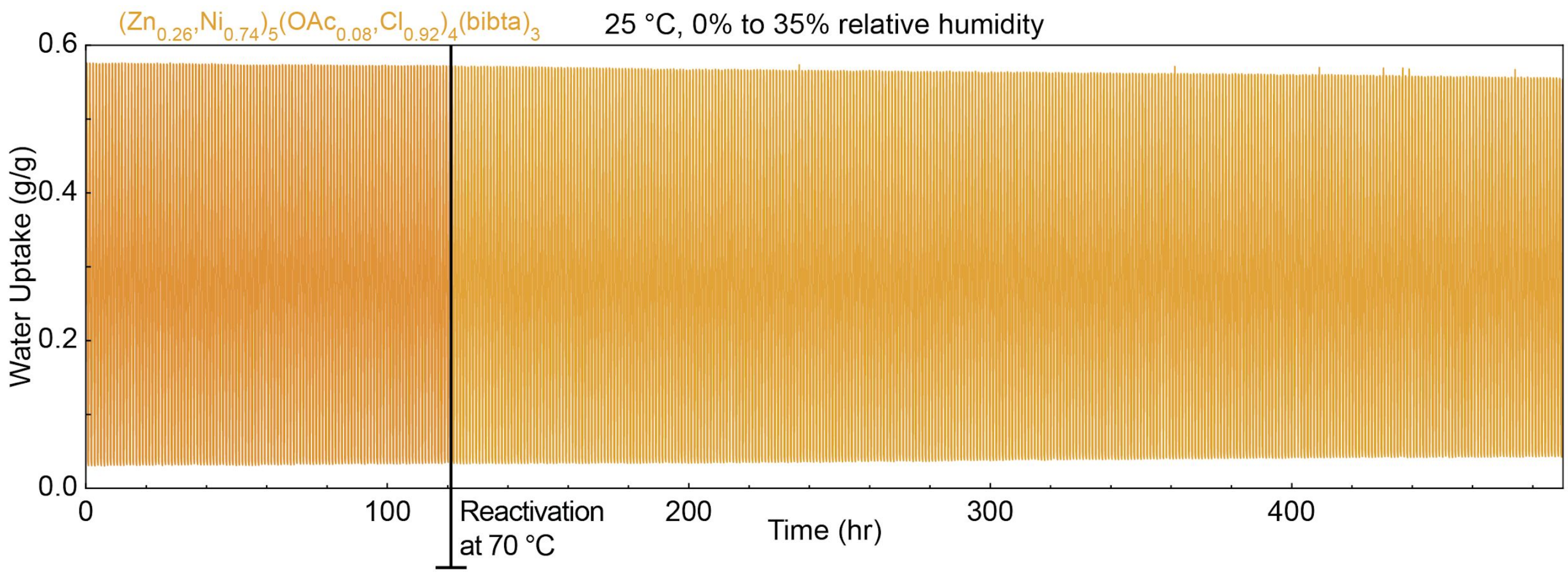


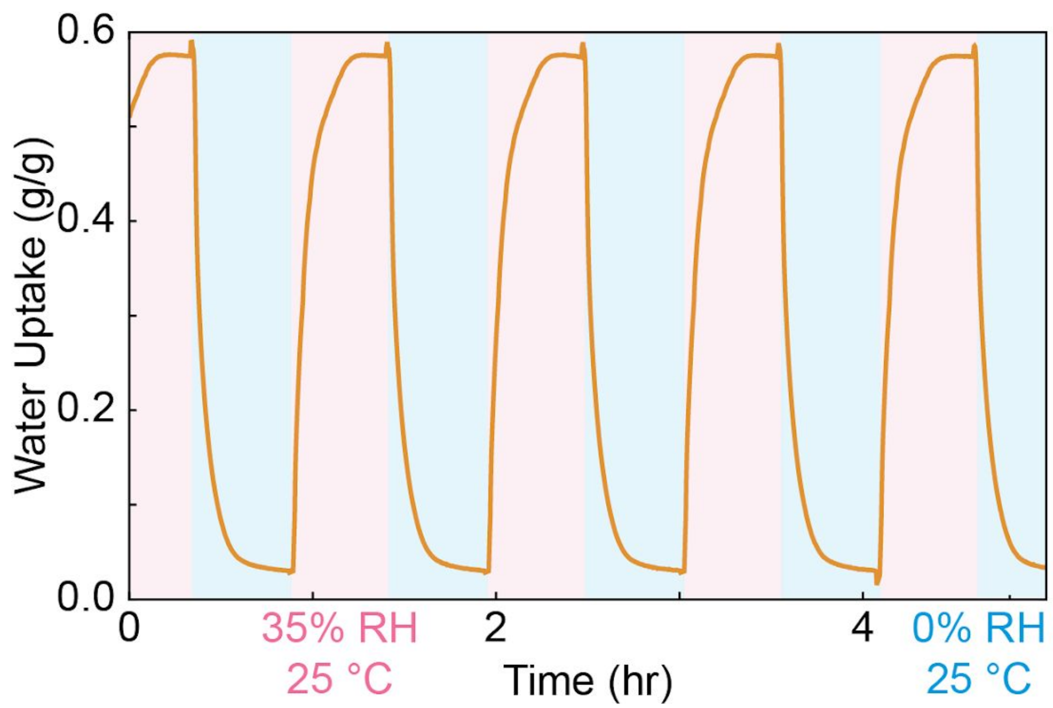


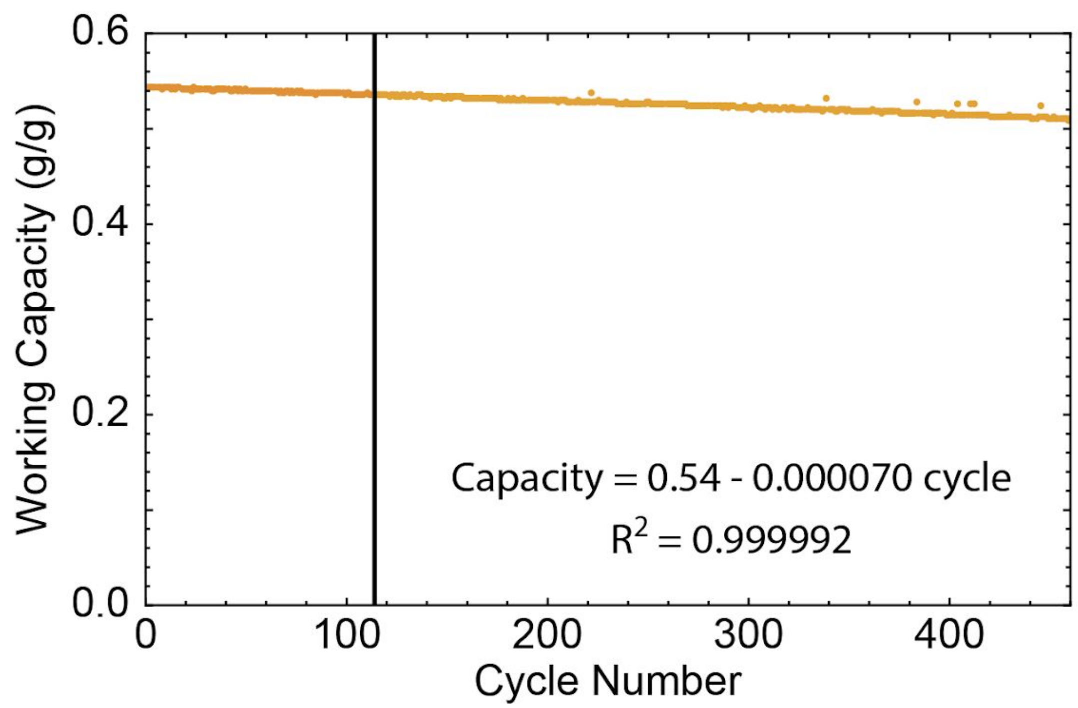
Monolayer adsorption, 2 mol/mol 52 kJ/mol	Bulk adsorption, > 2 mol/mol ~40 kJ/mol

Highly stable to cycling

minimal loss, 5.7% in working capacity after more than 450 cycles

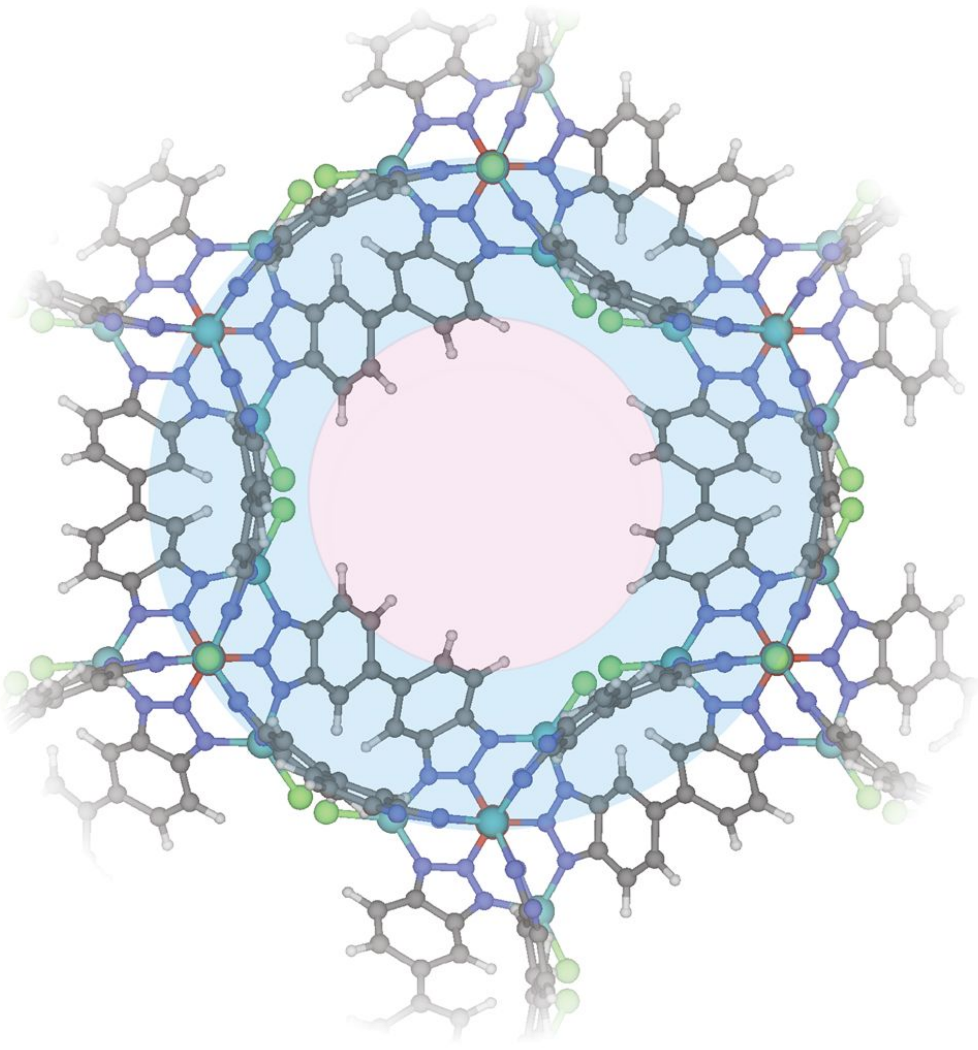






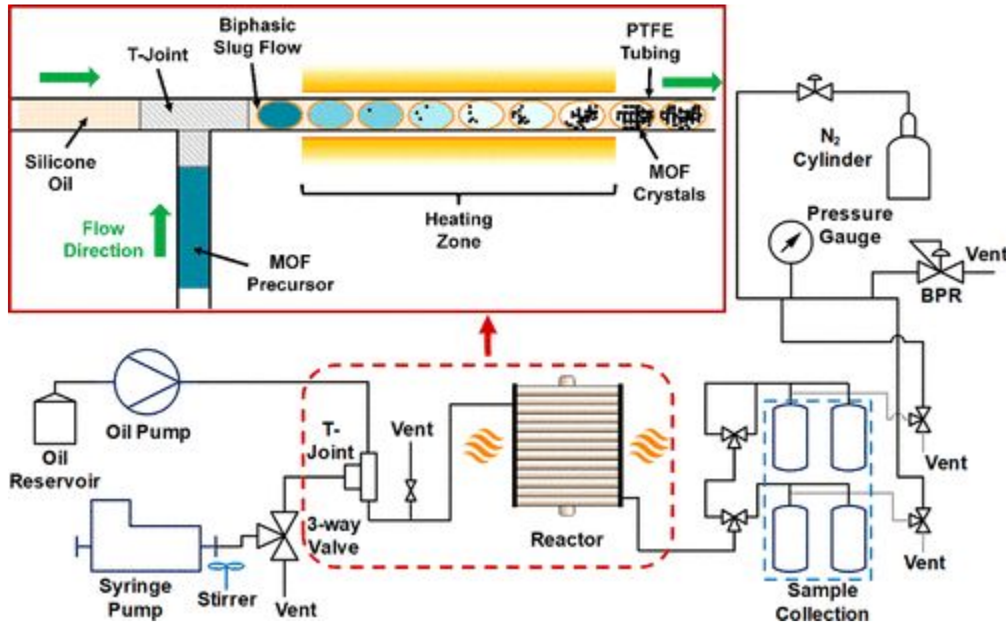
Summary

- We introduced a promising class of new adsorbent compositions characterized by their high-water capacity, particularly at low relative humidity levels (<30%)
- The hydrophilicity of $M_5X_4(bibta)_3$ can be controlled by post-synthetic metal/anion exchange
- Cycling stability increases by exchange from Zn to N
- The nickel exchanged frameworks are stable over 500 cycles with minimal loss in capacity



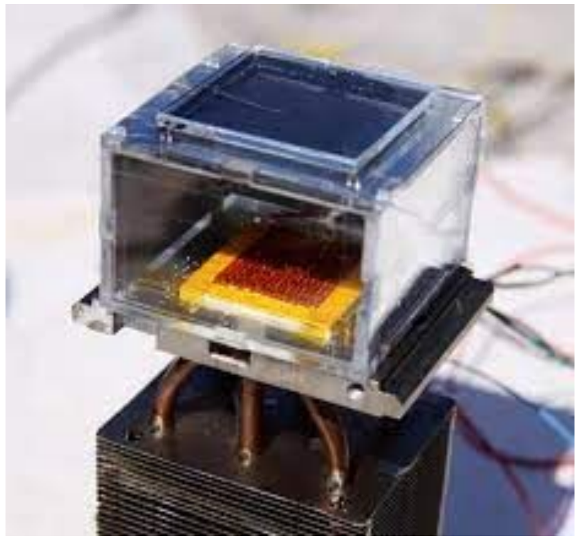
What's next!!!

- Optimization of flow synthesis in progress: with Roman lab



- Altering relative humidity with other anions

- Device level study of materials: in collaboration Wang lab at MIT



Tunable low–relative humidity and high–capacity water adsorption in a bibenzotriazole metal-organic framework

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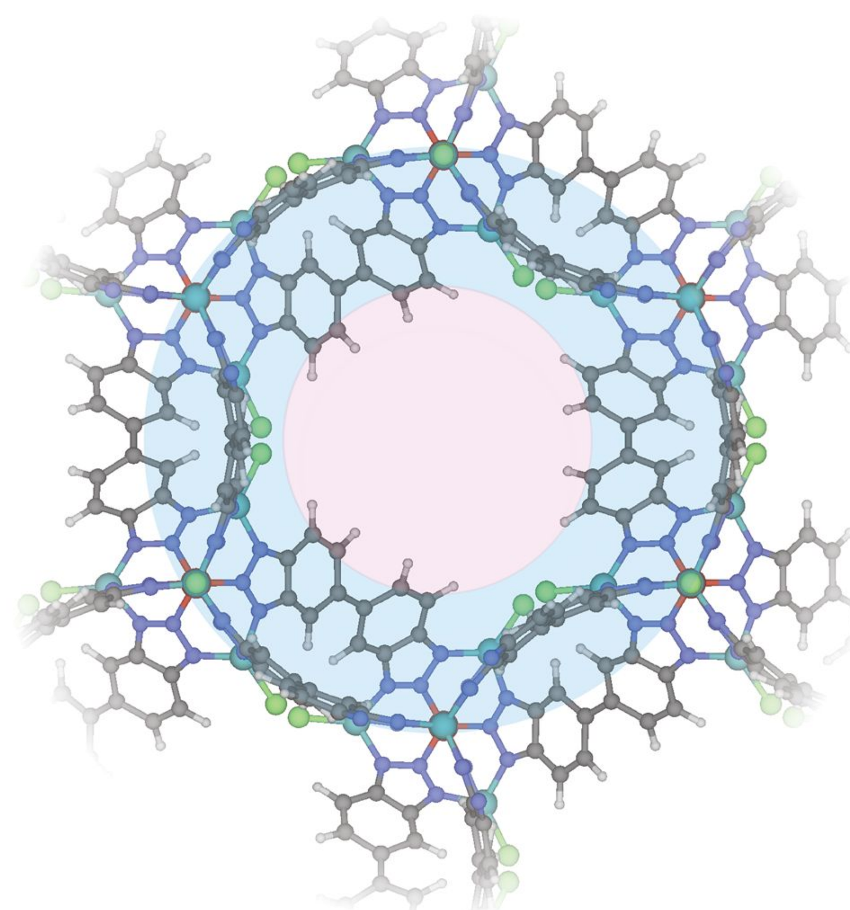
‡These authors have contributed equally

KEYWORDS: Metal-organic framework, water sorption, post-synthetic exchange, atmospheric water harvesting

Submitted

Patent filed " Sorbents for the Tunable Capture and Release of Water" Dalal Alezi, JuliusJ.Oppenheim, PatrickJ.Sarver, Andrei Iliescu, Mircea Dincă. MIT-25178-PR



Research outputs

Cooperative Interactions with Water Drive Hysteresis in a Hydrophilic Metal-Organic Framework

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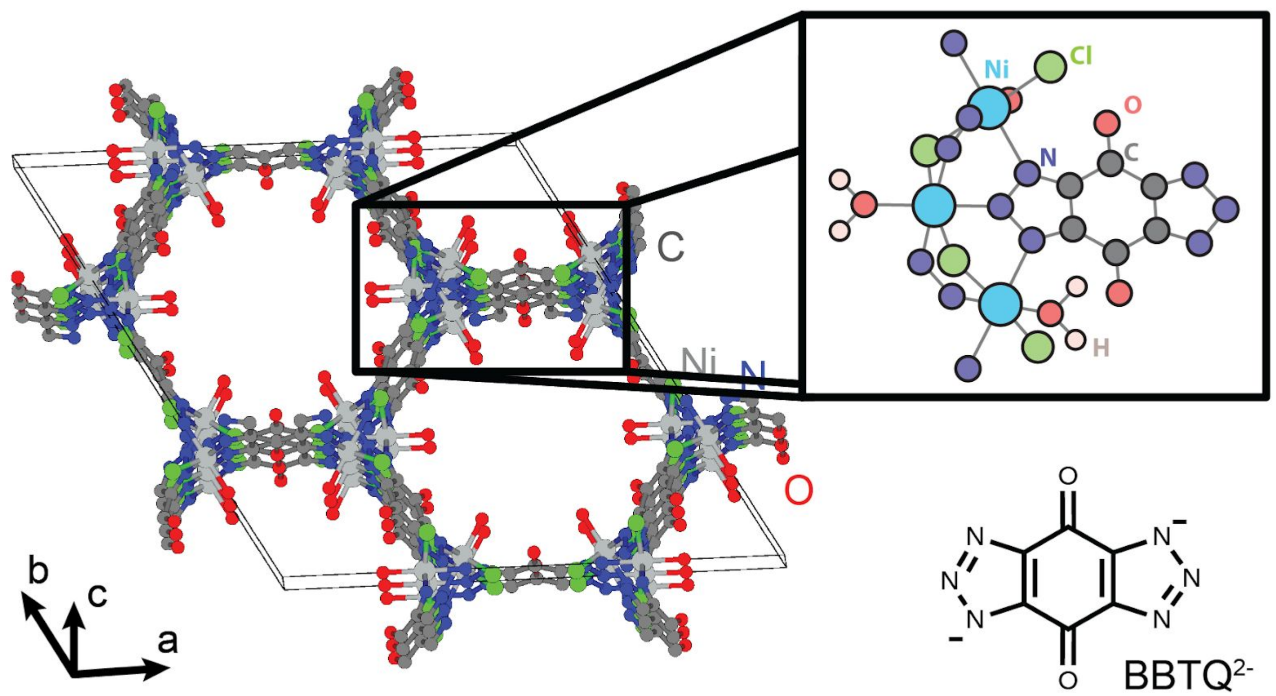
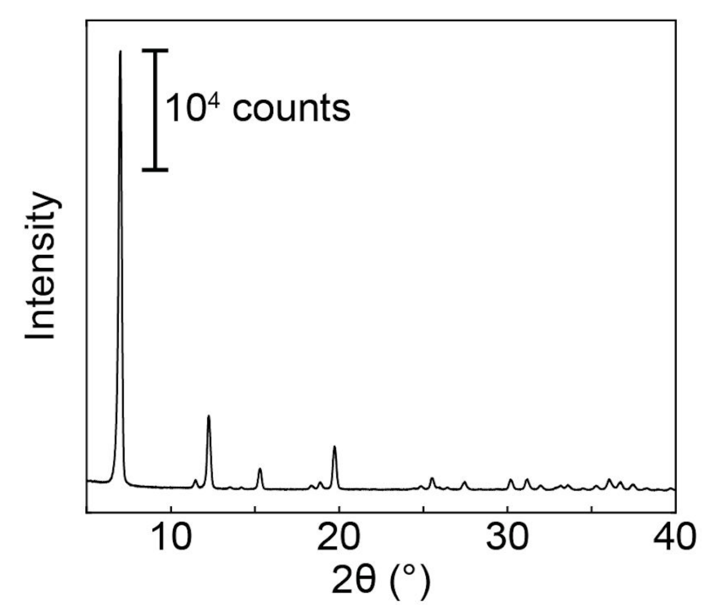
KEYWORDS. Metal-organic frameworks, sorption, water, hysteresis

Submitting soon





Professional developments

▪ Teaching

MIT's Kaufman Teaching Certificate Program, MIT

▪ Professional development

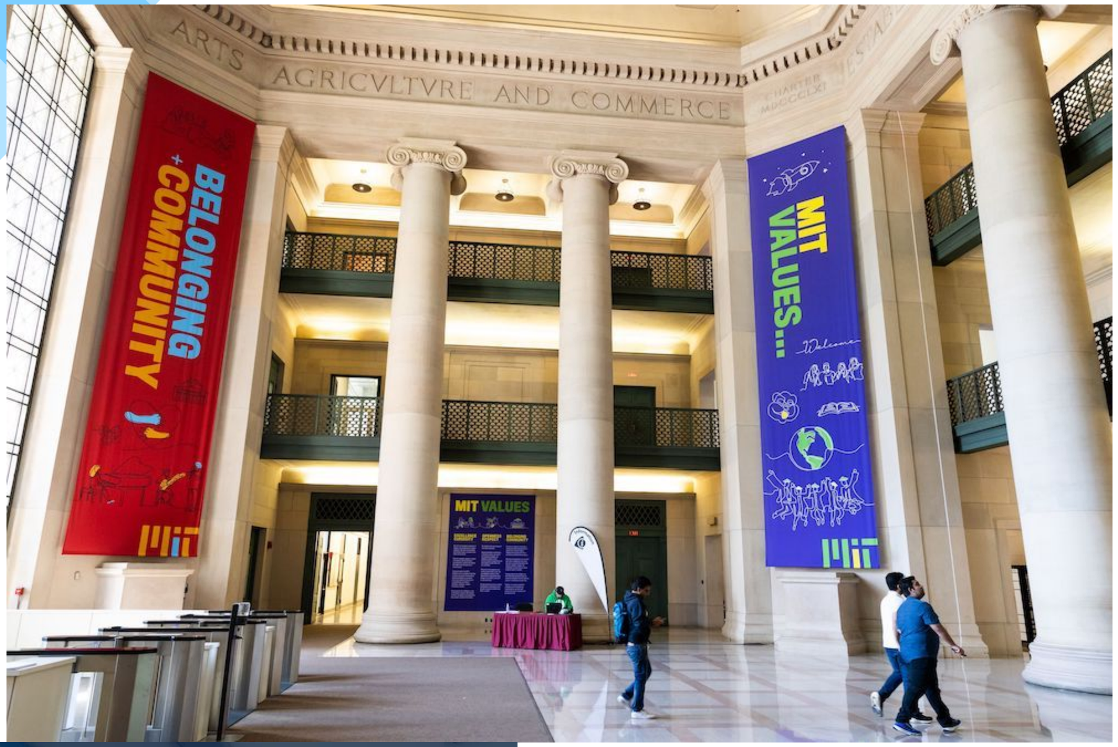
- **Certified ChatGPT Expert, Blockchain Council**
- **McKinsey Forward program, McKinsey & company**
- **Artificial Intelligence: Implications for Business Strategy Program, MIT Sloan**
- **Cybersecurity Leadership for Non-Technical Executives, MIT Sloan**
- **Mindfulness and wellbeing: Search Inside Yourself, MIT**

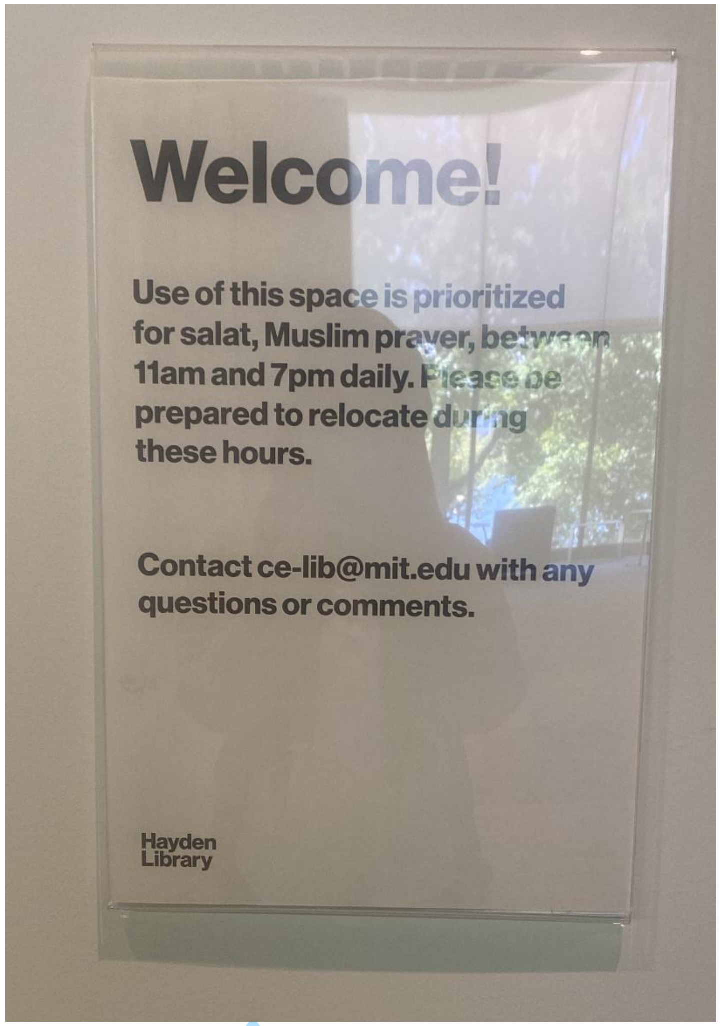
MIT Values

Excellence and Curiosity

Openness and Respect

Belonging and Community





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JuliusJ.Oppenheim


Thanks for
Listening!
Question?