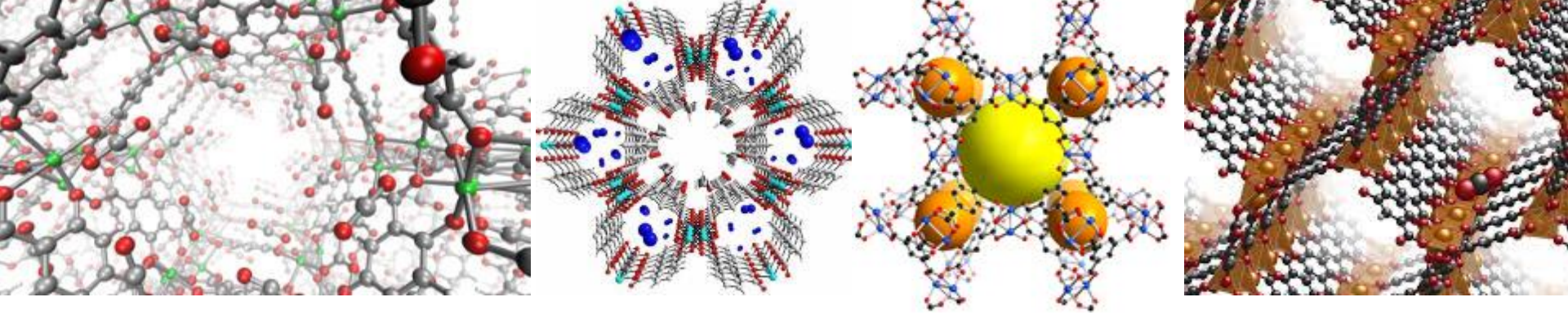

Current perspectives on advanced solid sorbents for CCS: the case of hybrid metal organic framework

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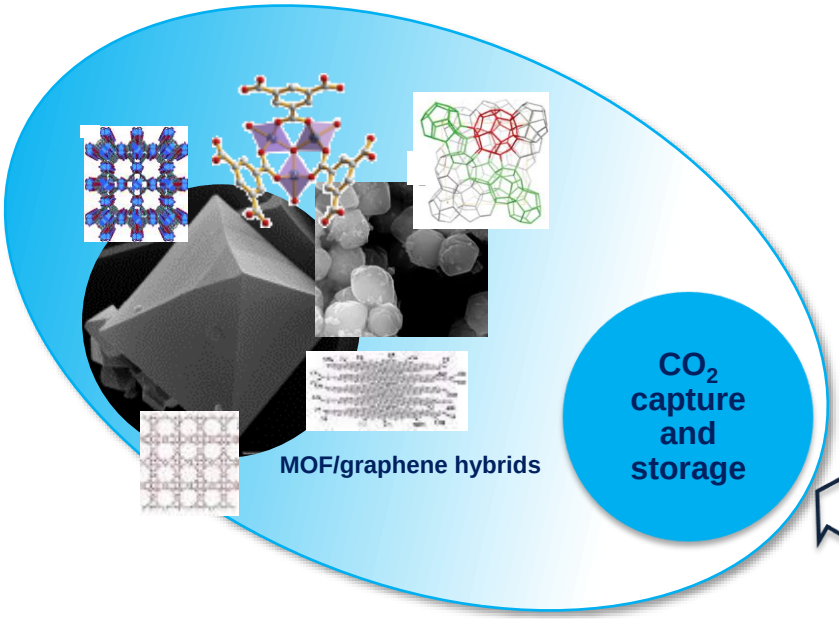
Institute of Science and Technologies for Sustainable Energy and Mobility
CNR – STEMS, Naples, Italy

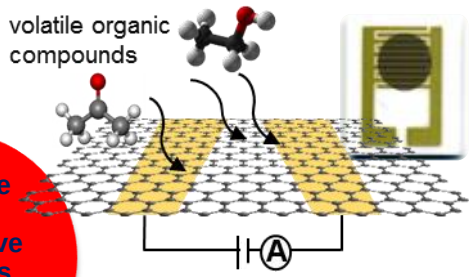
Design and development of new concept materials

from carbon-rich end-of-life materials to engineered materials



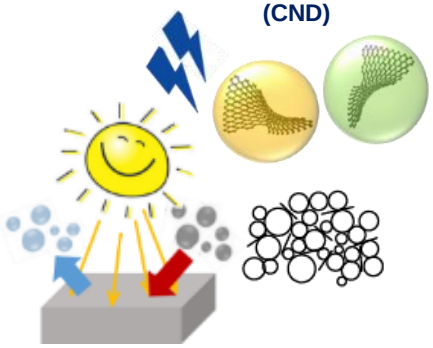
MOF/graphene hybrids

CO_2 capture and storage



Sensitive and conductive thin films (VOC detection)

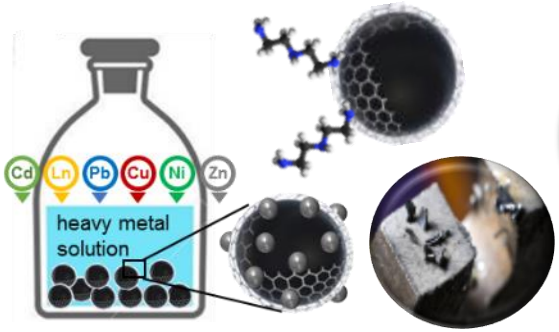
Photoactive materials (PLE enhancers, selective photo catalysts)



Carbon nanodots (CND)

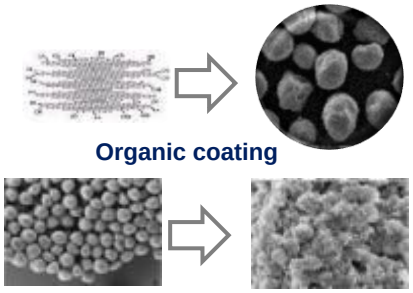
carbon-rich materials for...

Water remediation (heavy metal capture)



Surface - tailored (also magnetic) carbon- based nanoparticles

Coating of planar and non-planar surfaces (cells, particles)



Organic coating

Biocompatible and bioinspired materials

Eumelanin-based conductive layers

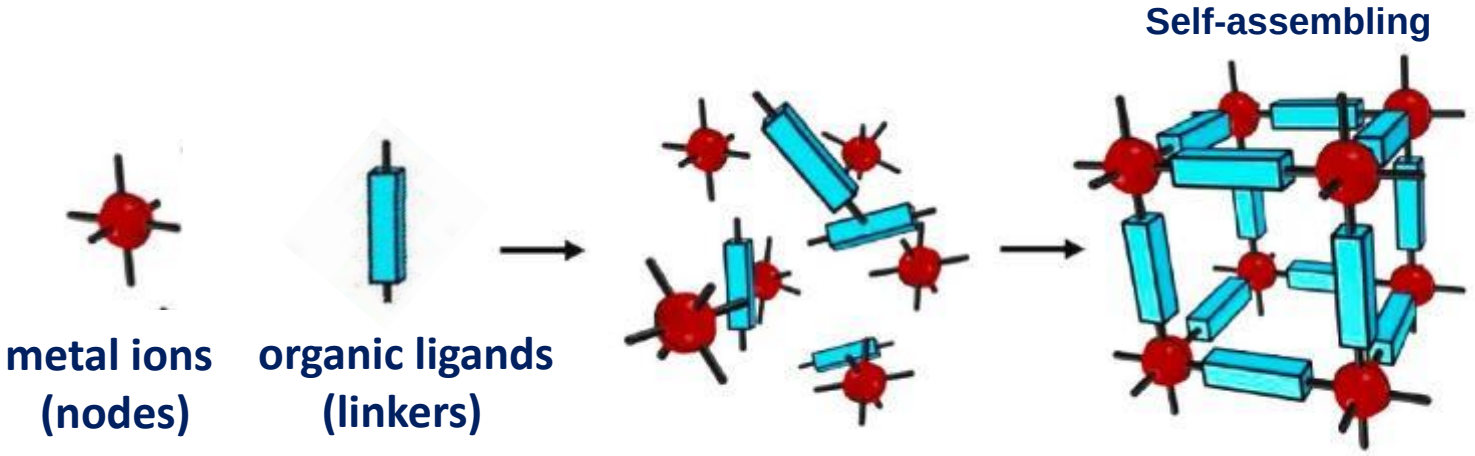
Consiglio Nazionale delle Ricerche

STEMS

Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili

Introducing Metal Organic Frameworks (MOF)

- **MOF** are porous coordination polymers (PCP) in the form of crystalline materials obtained by the self-assembly reactions between metal ions (nodes) and organic ligands (linkers) leading to strong coordination bonds;

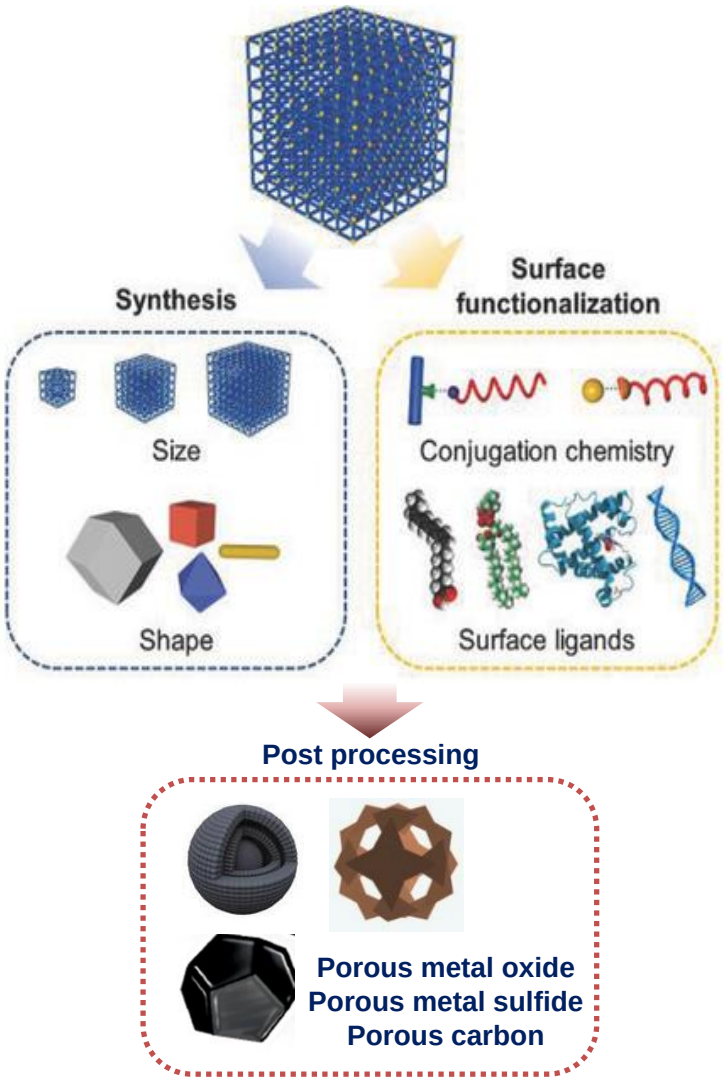


- the majority are built up from divalent or trivalent cations (Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Fe^{3+}, Al^{3+}) and are typically based on **carboxylates, phosphonates or N donating linkers**, or a combination of them.

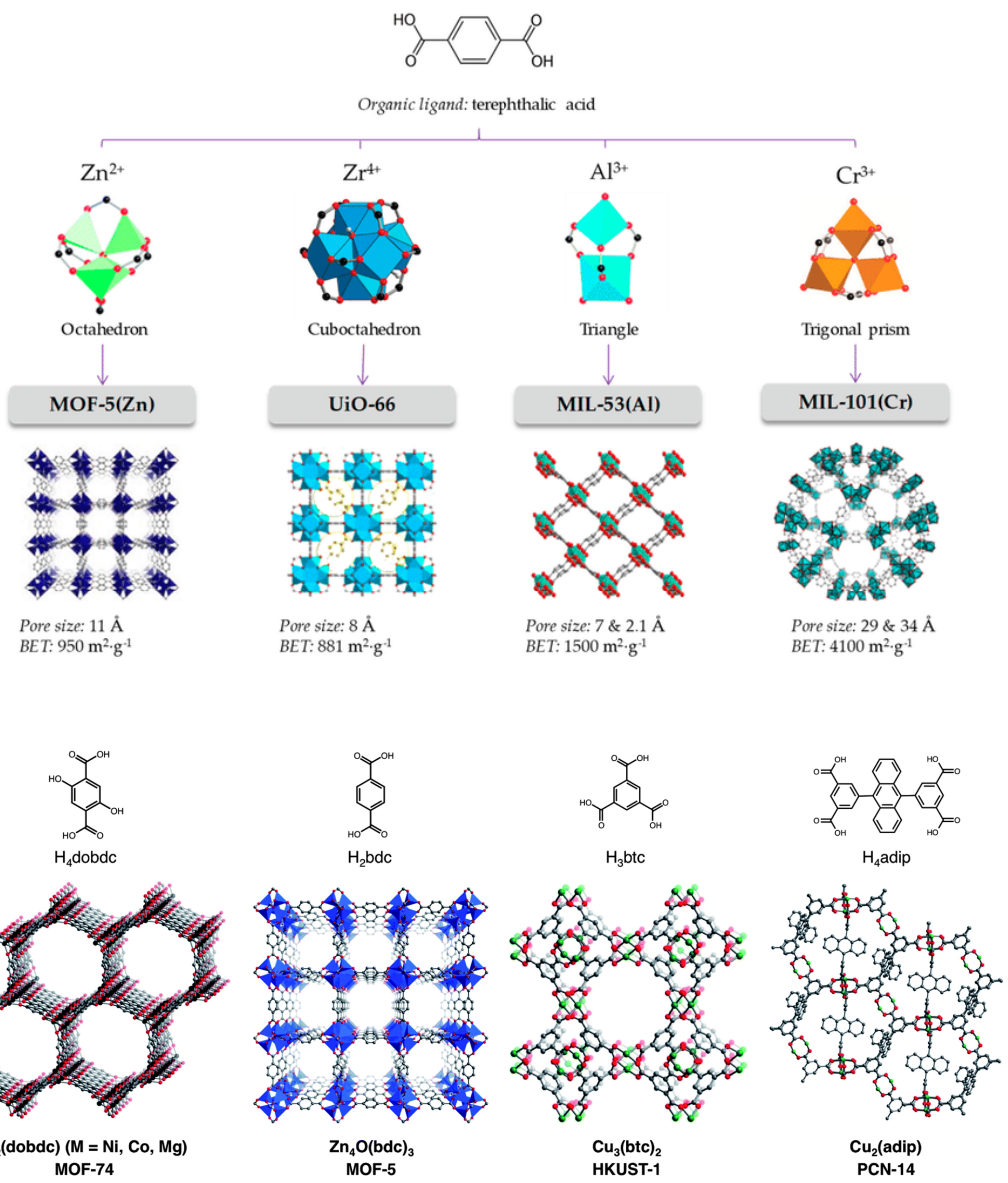
This leads to MOFs with a ***wide range of structure types and pore sizes*** (up to now the number of MOF is around 20,000; the higher porosity ever recorded is 10,000 m^2/g), from the micro- to the meso-domain and with or without functional groups on the organic spacers.

Introducing Metal Organic Frameworks (MOF)

3D-polymer network



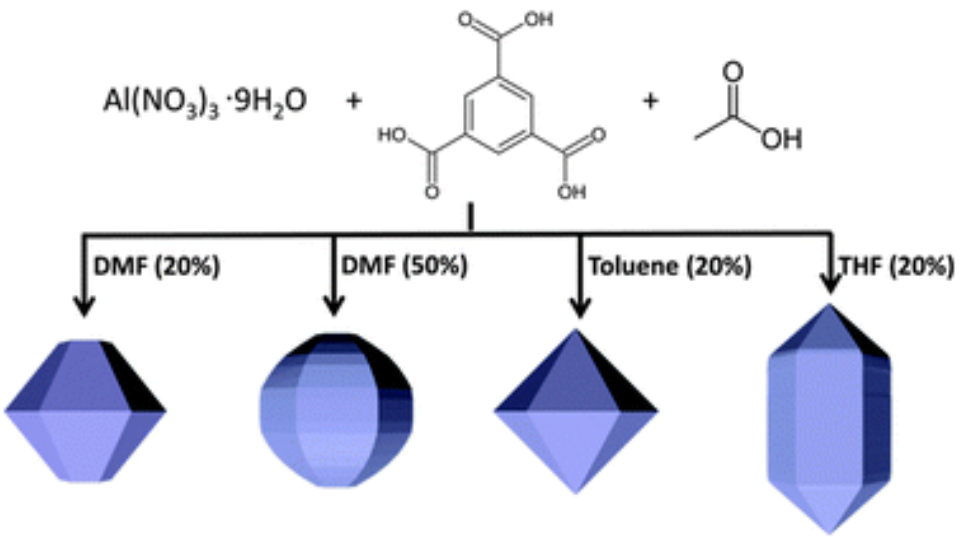
with the same ligand…

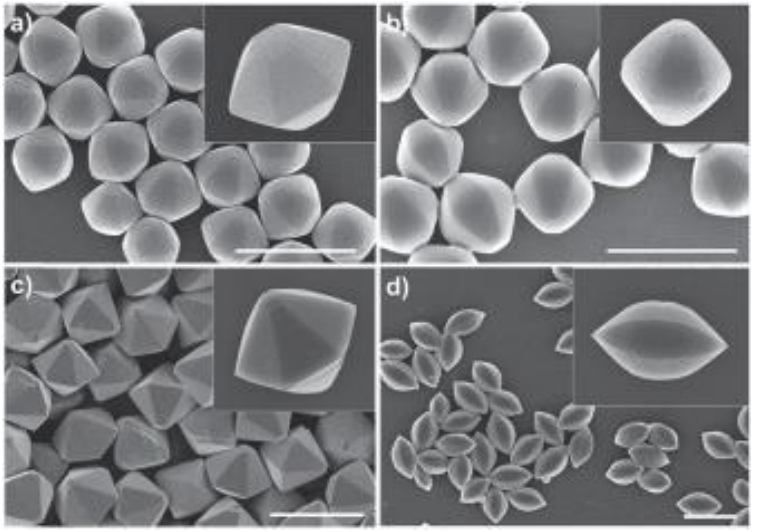


Introducing Metal Organic Frameworks (MOF)

Structure tunability within the same MOF

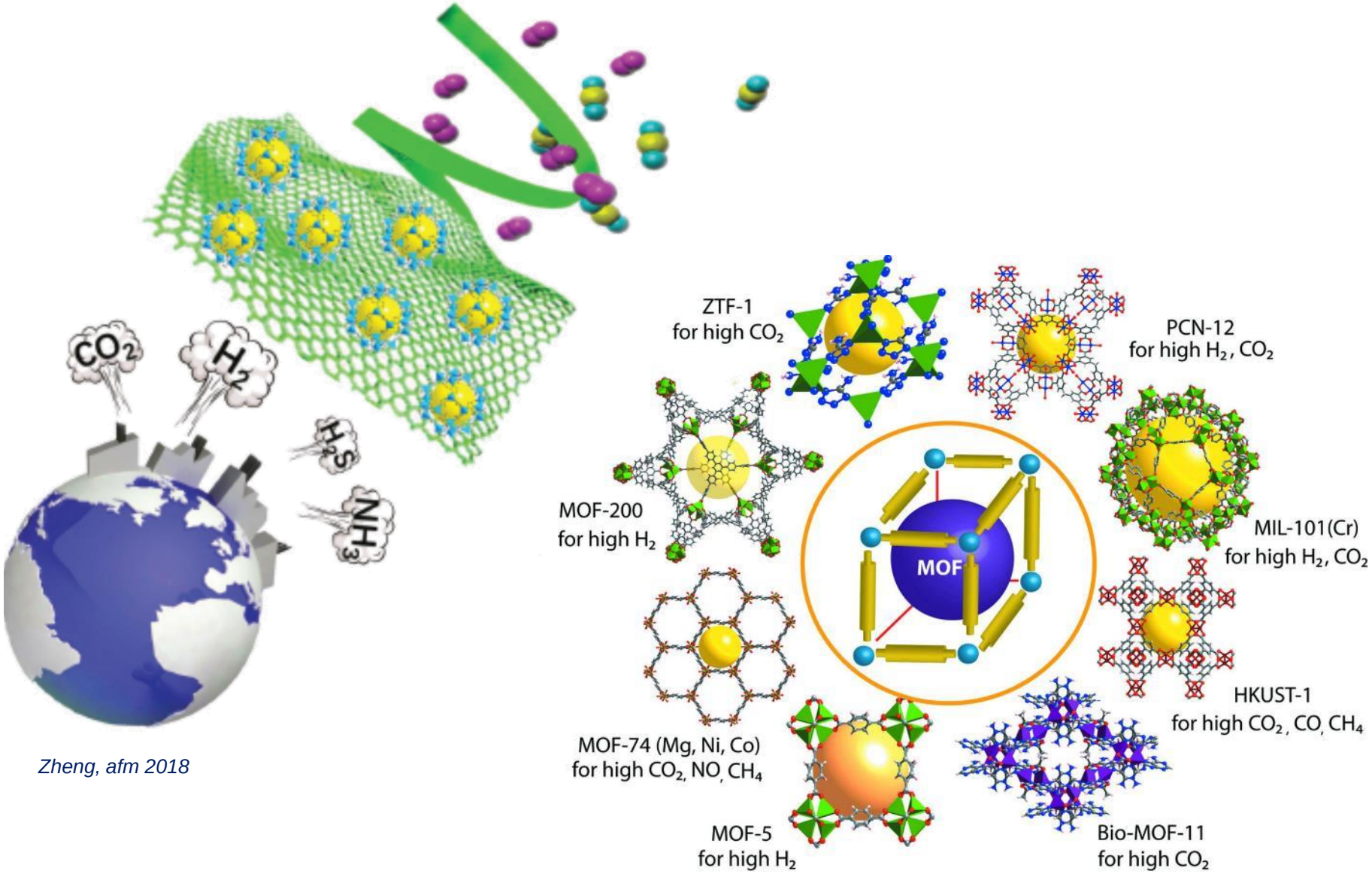
The structures and properties of MOFs are easily tuned by changing the typology, geometry, size, and functionality of the building bricks or the synthetic medium (pH, concentration, solvent, pressure, presence of modificants) in pre-design or in post-synthetic modification





Sindoro, M., Chem. Comm., 2013

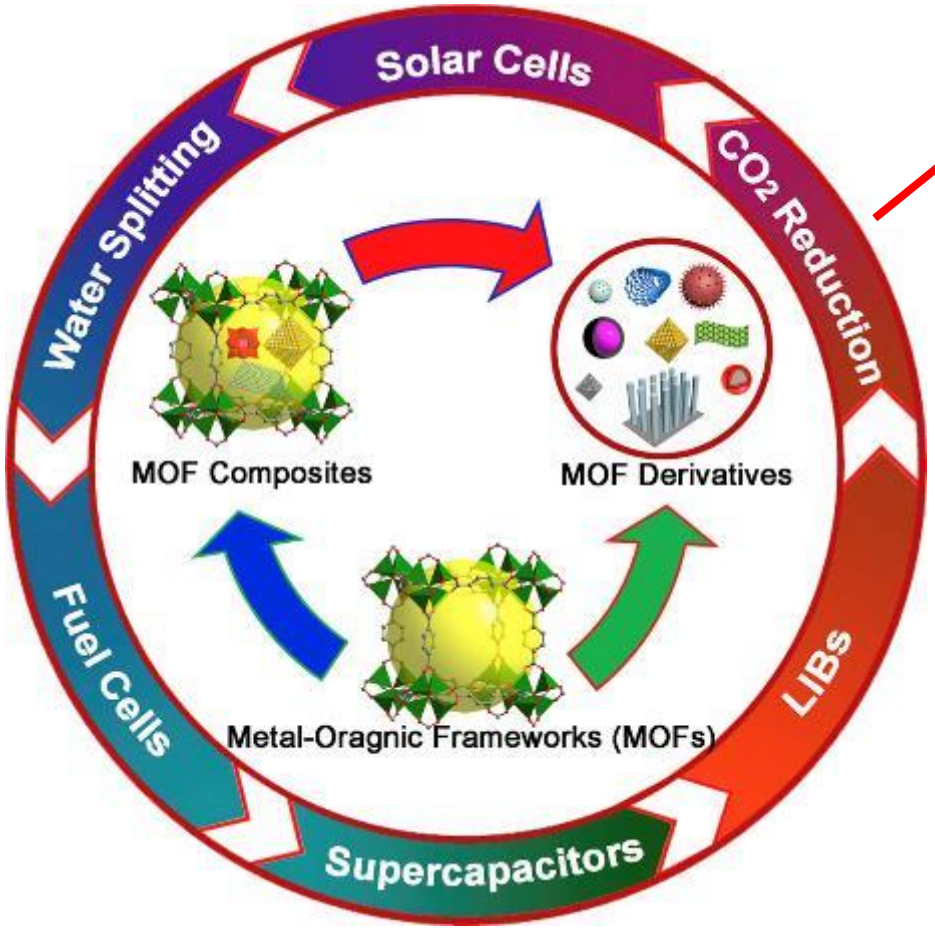
Metal Organic Framework (MOF) shapes for gas sorption



Zheng, afm 2018

Metal Organic Frameworks (MOF) and hybrids

MOFs allow obtaining, in a quite easy way, hybrid or composite materials with tunable chemico-physical properties (porosity, ionic and electrical conductivity, catalytical behaviour…)



Wang, H. et al. Chem, 2017

MOFs main characteristics are suitable for gas adsorption:

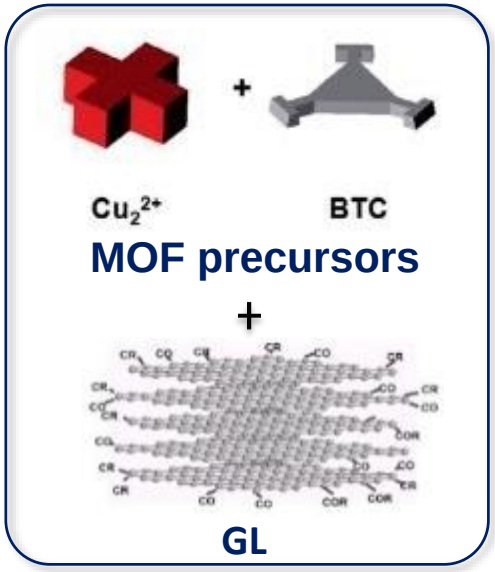
- large surface area
- permanent porosity
- tunable pore size/functionality
- easy formulation of **hybrids**

Continuous need of new approaches for the fabrication of tailored MOF structures to meet the market and technological requests

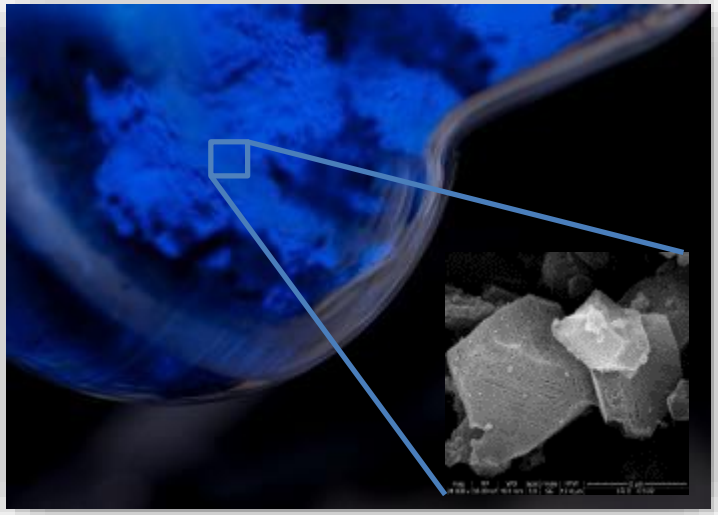
Embedding GRM (graphene related materials as graphene oxide, graphite…) in the MOF network.

Metal Organic Framework (MOF) GRM hybrids

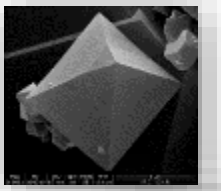
HKUST-1/GL as case study



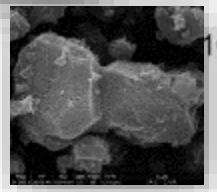
Solvothermal method

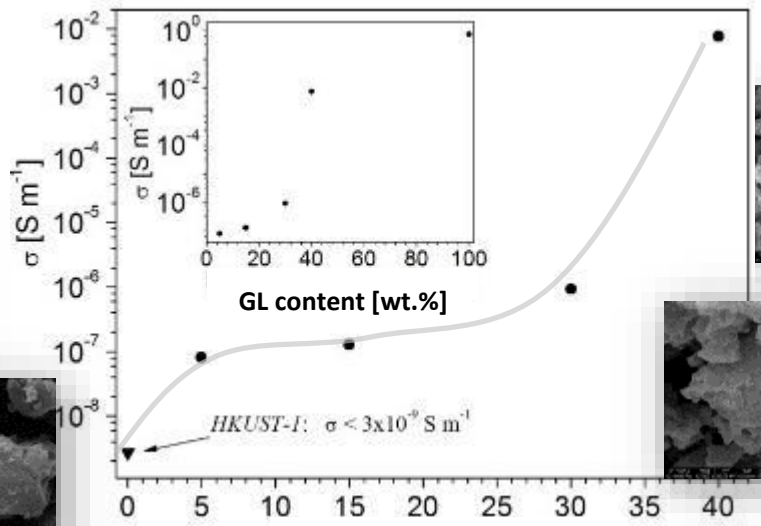


neat HKUST-1

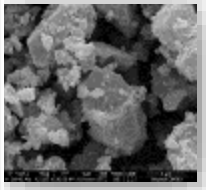


15 wt.% GL layers

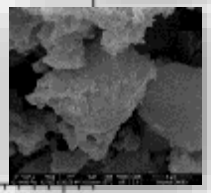




40 wt.% GL layers



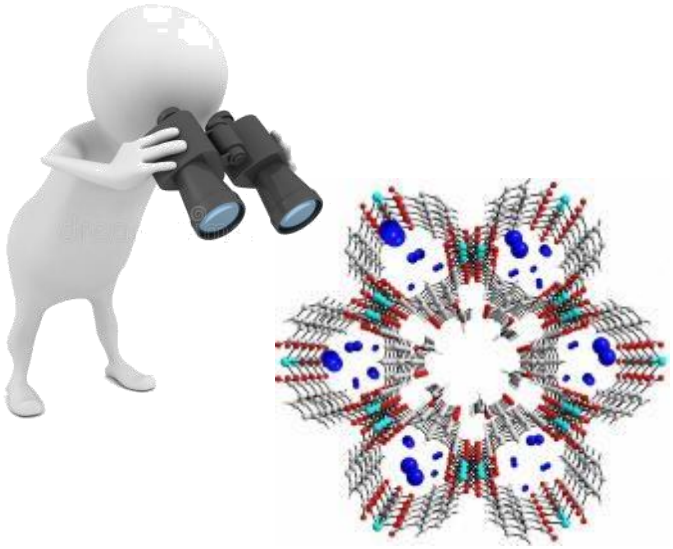
30 wt.% GL layers



Alfè et al. Mat. Chem.Phys. 2014

Questions:

- What happens when a GRM (not amenable to adsorb CO_2) is introduced in a MOF structure?
- What about the role of the metallic center?



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Solid sorbents for CO_2 and CH_4 adsorption: The effect of metal organic framework hybridization with graphene-like layers on the gas sorption capacities at high pressure

M. Alfe [a,*], A. Policicchio [b,c,d], L. Lisi [a], V. Gargiulo [a]

Table 1 (continued)

MOF type	GRM type	GRM (wt%)	Synthetic method	SSA (m^2/g)	Test methodology	Adsorption results	Selectivity	Reference
		10		1260		4.11 mmol/g		
HKUST-1	MWCNTs	0	microwave synthesis and activation with supercritical CO_2	1587	Apparatus: gravimetric analyzer; Conditions: CO_2, 298 K and 18 bar.	0.15 mmol/g		[89]
		0.2 mg MWCNT and 5 g copper nitrate		1458		0.31 mmol/g		
MIL-100(Fe)	MWCNTs	0	hydrothermal	1093	Apparatus: fixed bed; Conditions: CO_2, 298 K and 100 kPa.	−0.9 mmol/g	–	[90]
		0.1		1248		−1.2 mmol/g		
		0.25		1464		−1.2 mmol/g		
		0.5		1060		−0.9 mmol/g		
UiO-66(Zr)	GO	0	hydrothermal	936	Apparatus: static volumetric analyzer; Conditions: CO_2, 298 K and 1 bar.	2.27 mmol/g		[91]
		1		923		−2.5 mmol/g		
		5		1184		3.37 mmol/g		
		10		1012		−3 mmol/g		
UiO-66(Zr)	GO	0	hydrothermal	1110	Apparatus: gravimetric analyzer; Conditions: CO_2, 298 K and 0–4 bar.	1.50 mmol/g (1 bar) 3.82 mmol/g (4 bar)		[42]
		10		1016		1.05 mmol/g (1 bar) 3.00 mmol/g (4 bar)		
MOF-5	GO	0	solvothermal	420	Apparatus: gravimetric analyzer; Conditions: CO_2, 298 K and 4 bar.	0.64 mmol/g	–	[87]
		10		408		1.06 mmol/g		
MOF-200(Zn)	GO	0	solvothermal	3624	Apparatus: static volumetric analyzer; Conditions: CO_2, CH_4	CO_2: 1.17 mmol/g CH_4: 0.15 mmol/g	CO_2/CH_4 13.93	[66]
		n.a.		3259	298 K and 1 bar.	CO_2: 1.34 mmol/g CH_4: 0.20 mmol/g	CO_2/CH_4 10.37	

Table 1
MOF/GRM hybrid characteristics and related adsorption performances.

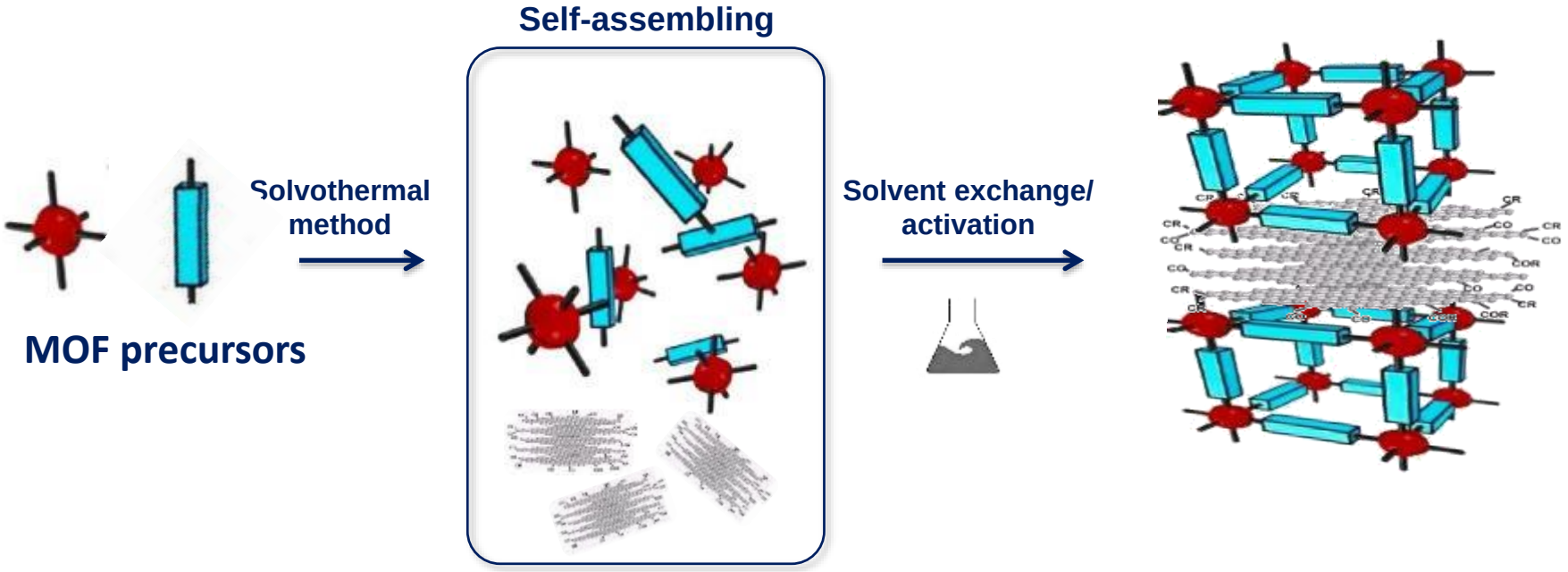
MOF type	GRM type	GRM (wt%)	Synthetic method	SSA (m^2/g)	Test methodology	Adsorption results	Selectivity	Reference
MIL-101(Cr)	GNPs	0	solvothermal	2486	Apparatus: homemade volumetric system; Conditions: CO_2, 298 K and 40 bar.	14.38 mmol/g		[92]
		10		3032		20.62 mmol/g		
MIL-101(Cr)	GO	0	hydrothermal	2486	Apparatus: volumetric analyzer; Conditions: CH_4, CO_2, 298 K and 40 bar.	−19.5 mmol/g (CO_2); −5 mmol/g (CH_4)		[94]
		−2.5		2543		−19.8 mmol/g (CO_2); −5.2 mmol/g (CH_4)		
		−5		2672		−19.3 mmol/g (CO_2); −5.5 mmol/g (CH_4)		
		−10		2351		−20.1 mmol/g (CO_2); −4.7 mmol/g (CH_4)		
MIL-101(Cr)	rGO	0	hydrothermal	2670	Apparatus: magnetic suspension balance; Conditions: CO_2, CH_4, 298 K and 25 bar.	14.6 mmol/g (CO_2); −6.3 mmol/g (CH_4)	CO_2/CH_4 (10:90) −6	[61]
		1 rGO: 10 Cr $(NO_3)_3{\cdot}9H_2O$		2950		22.4 mmol/g (CO_2); −7.5 mmol/g (CH_4)	CO_2/CH_4 (10:90) −7.5	
MIL-101(Cr)	MWCNTs	0	hydrothermal	1270	Apparatus: volumetric analyzer; Conditions: CO_2, 298 K and 25 bar.	0.84 mmol/g		[88]
		10		1240		1.35 mmol/g		
MIL-53(Al)	GNPs	0	hydrothermal	1132	Apparatus: homemade volumetric system; Conditions: CO_2, 298 K and 40 bar.	9.61 mmol/g		[91]
		2.5		1196		11.75 mmol/g		
		5		1201		12.95 mmol/g		
		10		974		9.13 mmol/g		
MIL-53(Cr)	rGO	0	solvothermal	1197	Apparatus: magnetic suspension balance; Conditions: CO_2, CH_4, 298 K and 25 bar.	−10.6 mmol/g (CO_2); −5.3 mmol/g (CH_4)	CO_2/CH_4 (10:90) −1	[62]
		1		1270		−13.5 mmol/g (CO_2); −5.3 mmol/g (CH_4)	CO_2/CH_4 (10:90) −1	
		10		1182		−10.6 mmol/g (CO_2); −5.3 mmol/g (CH_4)	CO_2/CH_4 (10:90) −9	
ZIF-8	GO	0	solvothermal	1120	Apparatus: static volumetric analyzer; Conditions: CO_2, 195 K and ambient pressure.	wt.%: 27.2		[64]
		1		919		wt.%: 32.4		
		2		675		wt.%: 35.1		
		4		450		wt.%: 46.4		
		10		360		wt.%: 55.3		
		20		269		wt.%: 72.4		
MOF-505	GO	0	solvothermal	1104	Apparatus: static volumetric analyzer; Conditions: CO_2, CH_4, 298 K and 100 kPa.	2.87 mmol/g (CO_2); −0.75 mmol/g (CH_4)	CO_2/CH_4 27.8	[70]
		2		1249		3.46 mol/g		
		5		1276		3.94 mmol/g (CO_2); −0.9 mmol/g (CH_4)	CO_2/CH_4 37.2	
		8		1236		−3.3 mmol/g		
		10		1208		−3.25 mmol/g		
HKUST-1	GO	0	hydrothermal	1048	Apparatus: static volumetric analyzer; Conditions: CO_2, 305 K and 5 atm.	1.8 mmol/g		[86]
		10		1015		2.5 mmol/g		
HKUST-1		0	hydrothermal	1137	Apparatus: volumetric analyzer; Conditions: CH_4, 298 K and 65 bar.	217 cm^3 (STP)/cm^3		[93]
	GO	10		1259		247 cm^3 (STP)/cm^3		
	rGO	10		1271		270 cm^3 (STP)/cm^3		
HKUST-1	GO	0	hydrothermal	404	Apparatus: gravimetric analyzer; Conditions: CO_2, 298 K and (0–4 bar).	1.59 mmol/g (1 bar) 3.45 mmol/g (4 bar)		[42]
		50		369		0.98 mmol/g (1 bar), 1.86 mmol/g (4 bar)		
HKUST-1	GO	0	room-temperature ultrafast synthesis under ultrasound	1760	Apparatus: static volumetric analyzer; Conditions: CO_2, 298 K and 1 bar.	5.33 mmol/g		[96]
		2		1620		5.12 mmol/g		
		5		1520		4.79 mmol/g		

Due to the wide MOF characteristics, a systematization of the effects when GRMs **(GO, rGO, nanotubes…)** are included into MOF structure is far to be achieved

Metal Organic Framework (MOF) hybrids

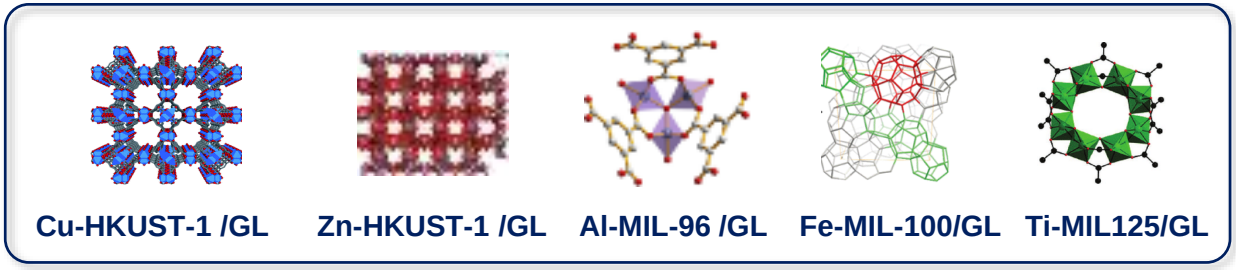
Our approach

One - pot synthesis



GL layers are embedded into the MOF crystal

The combination of MOF and carbonaceous GL layers allows obtaining conductive hybrid materials with tunable porosity

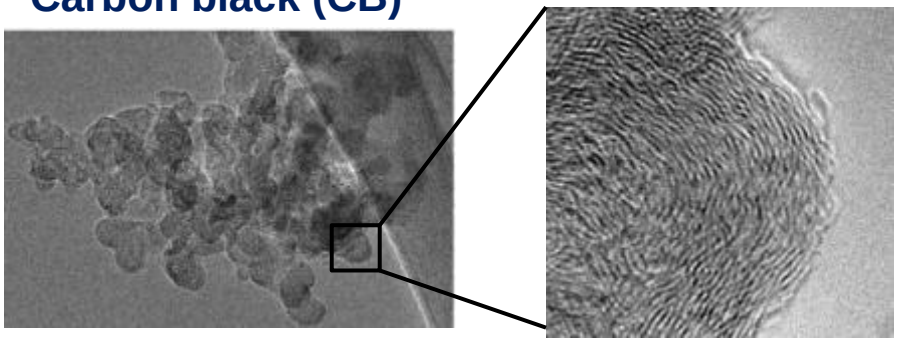


Alfè et al. Mat. Chem.Phys. 2014
Raganati et al. Chem.Eng.J, 2014
Gargiulo et. al. Fuel 2018
Alfè et. al. RSER 2021

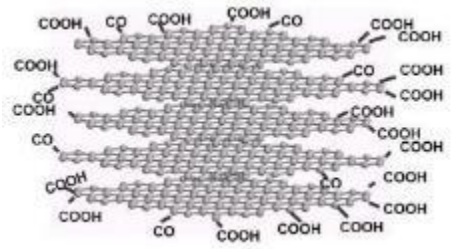
Graphene-like (GL) layers from carbon black

A new-concept graphene related material (GRM) was recently produced from carbon black

Carbon black (CB)

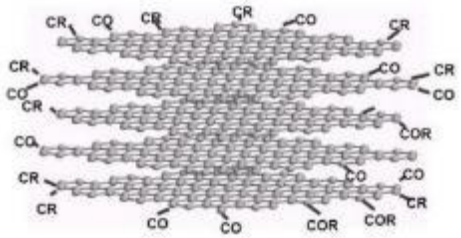


100°C, 90 h
HNO_3



oxygen-rich GL

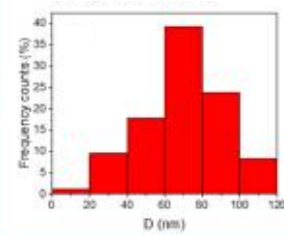
100°C, 24 h
$NH_2NH_2 \cdot H_20$

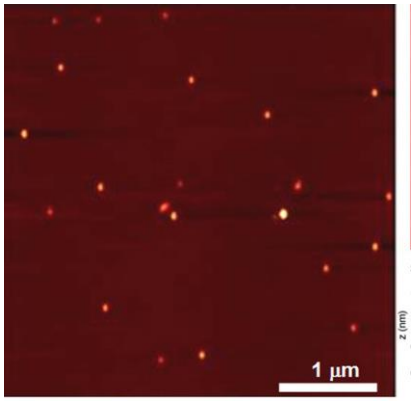


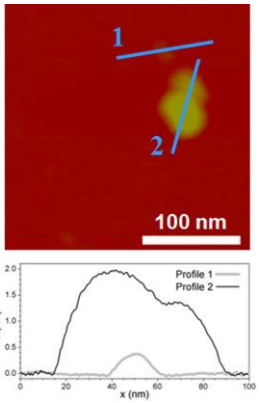
GL

R: =N-NH_2 (hydrazone)

Top-down demolition of the CB backbone





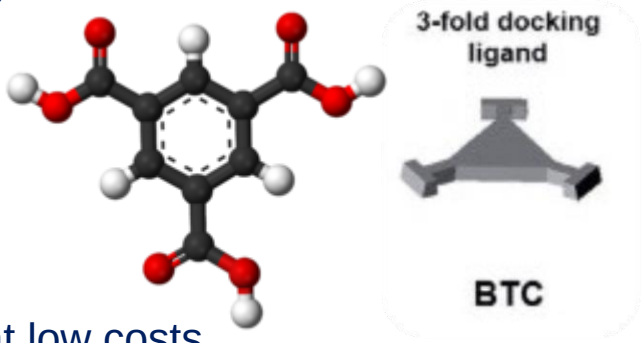


- Functionalization at the edge of the basal planes
- Mild condition
- Stability in water over a wide pH range (suitable for the fabrication of hybrid materials in aqueous media)

Alfè et al. App. Mat. Interfaces 2012
Alfè et al. App. Surf. Sci. 2015
Alfè et al. App. Cat. A, 2014
Gargiulo et al. J App Phys, 2018
Giordani et al. Nanomaterials, 2020

In this work

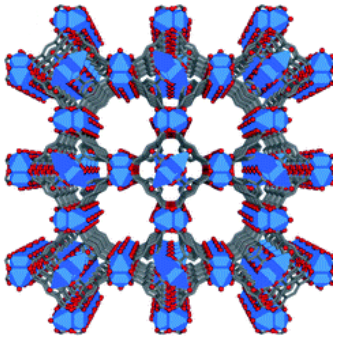
We selected three **1,3,5-benzenetricarboxylic acid (BTC)** based MOFs differing for the metallic center (**Cu, Al, Fe**)



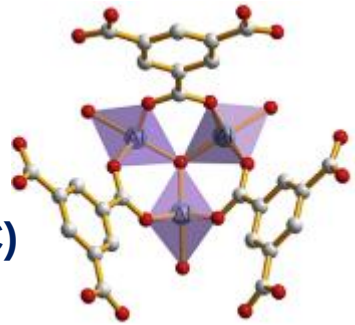
- Very simple synthesis at low costs
- Solvothermal approach
- HF-free synthesis

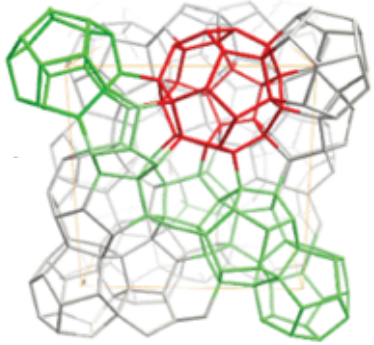
The three MOFs (**Cu-HKUST-1, Al-MIL-96 and Fe-MIL-100**) present different morphology and textural properties

Cu(BTC)



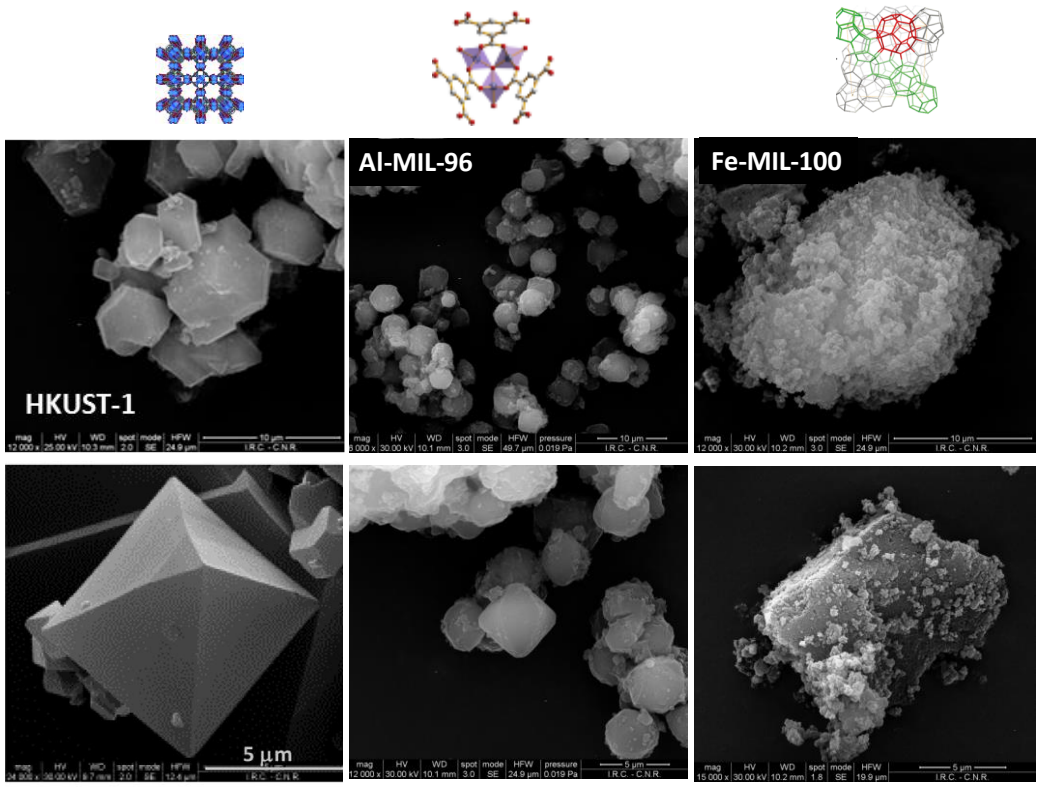
Al(BTC)





Fe(BTC)

Morphology of the pristine MOFs

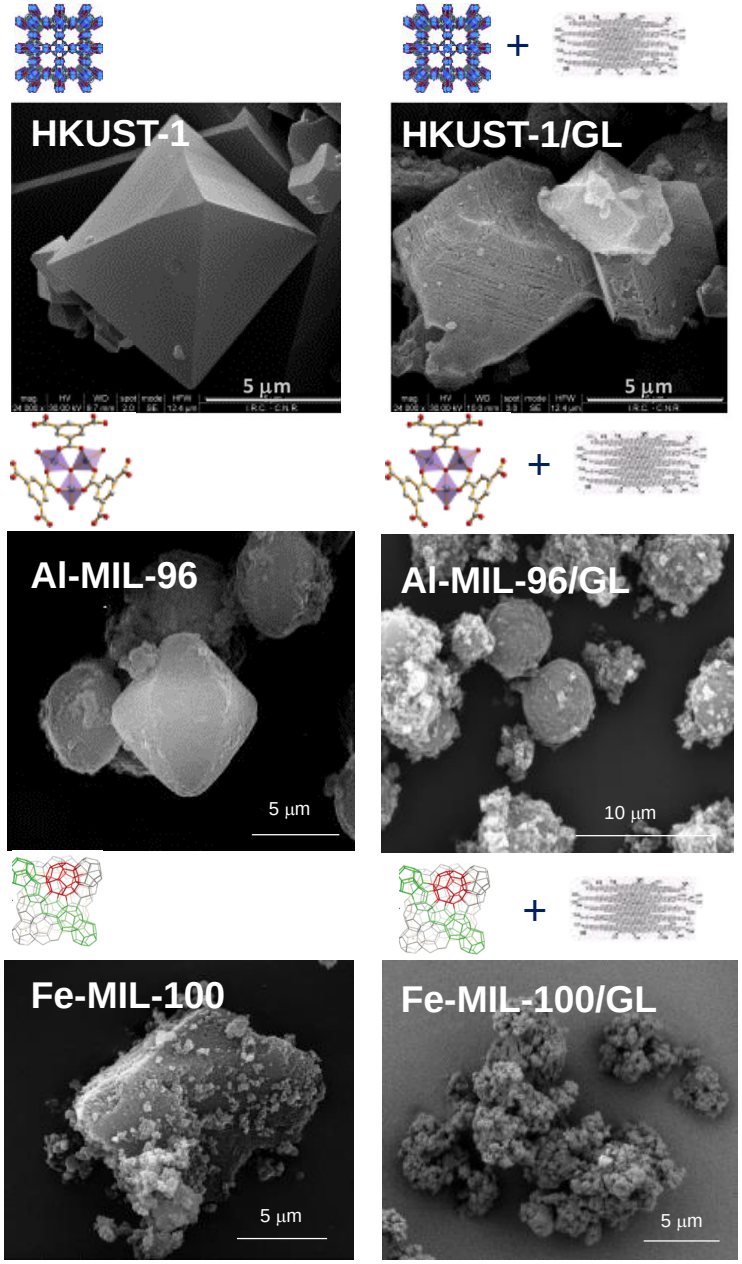


HKUST-1 is characterized by octahedral crystals of different sizes with relatively smooth surface.

Al-MIL-96 crystals are characterized by a truncated octahedral shape.

Fe-MIL-100 showed agglomerates of particles with a no defined shape, as found for other Fe-MIL-100 samples produced in HF-free conditions. The HF-free conditions probably did not favor the formation of octahedral crystal as reported for Fe-MIL-100 prepared in presence of HF.

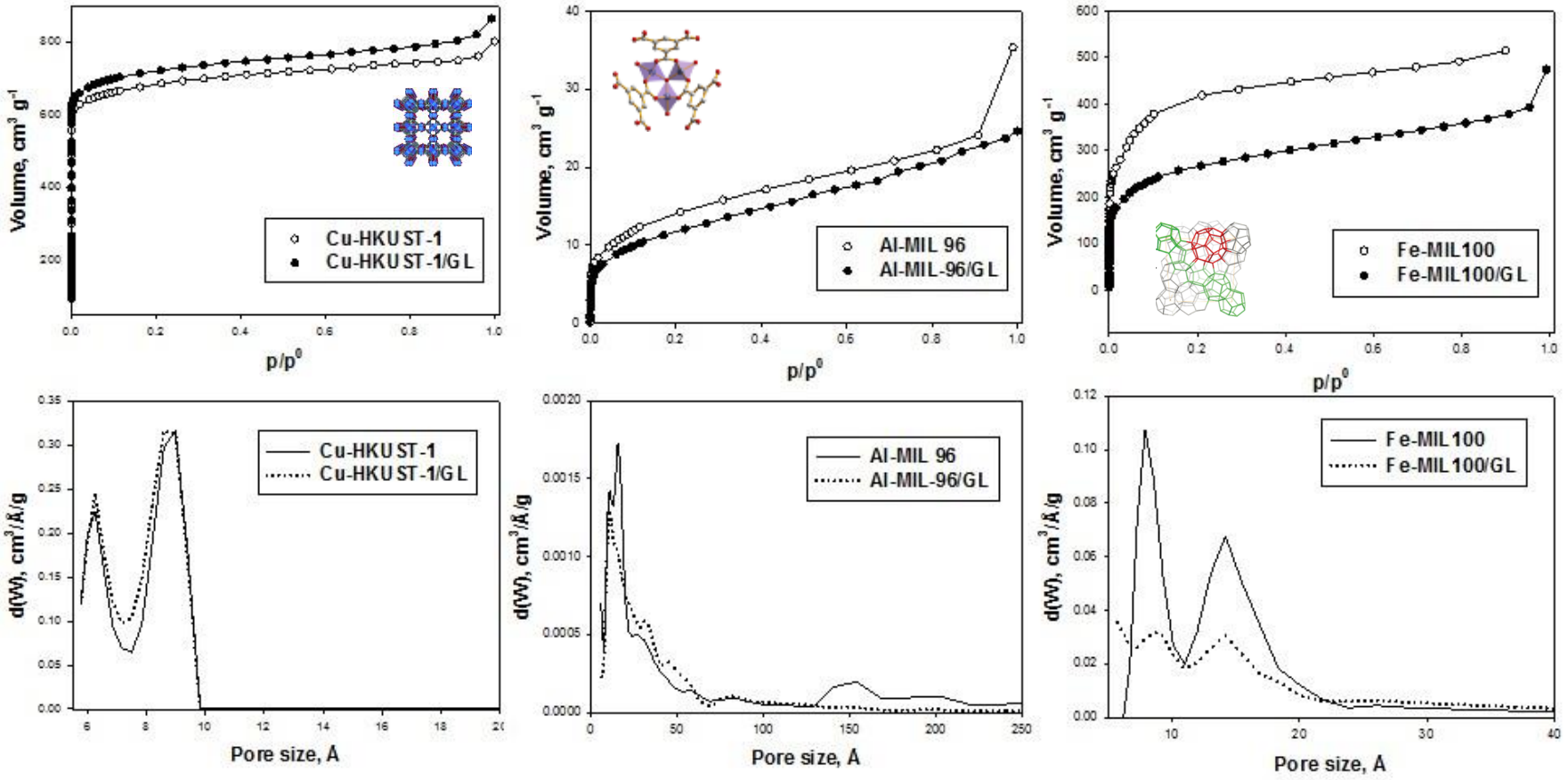
Morphology of the MOFs/GL hybrids



Elemental analysis demonstrated a complete incorporation of the carbonaceous layers into the hybrid structures.

Overall the incorporation of GL in MOFs structure does not affect the formation of the characteristic crystals even if the crystal shape appears slightly distorted. The crystalline phase is confirmed by XRD analysis.

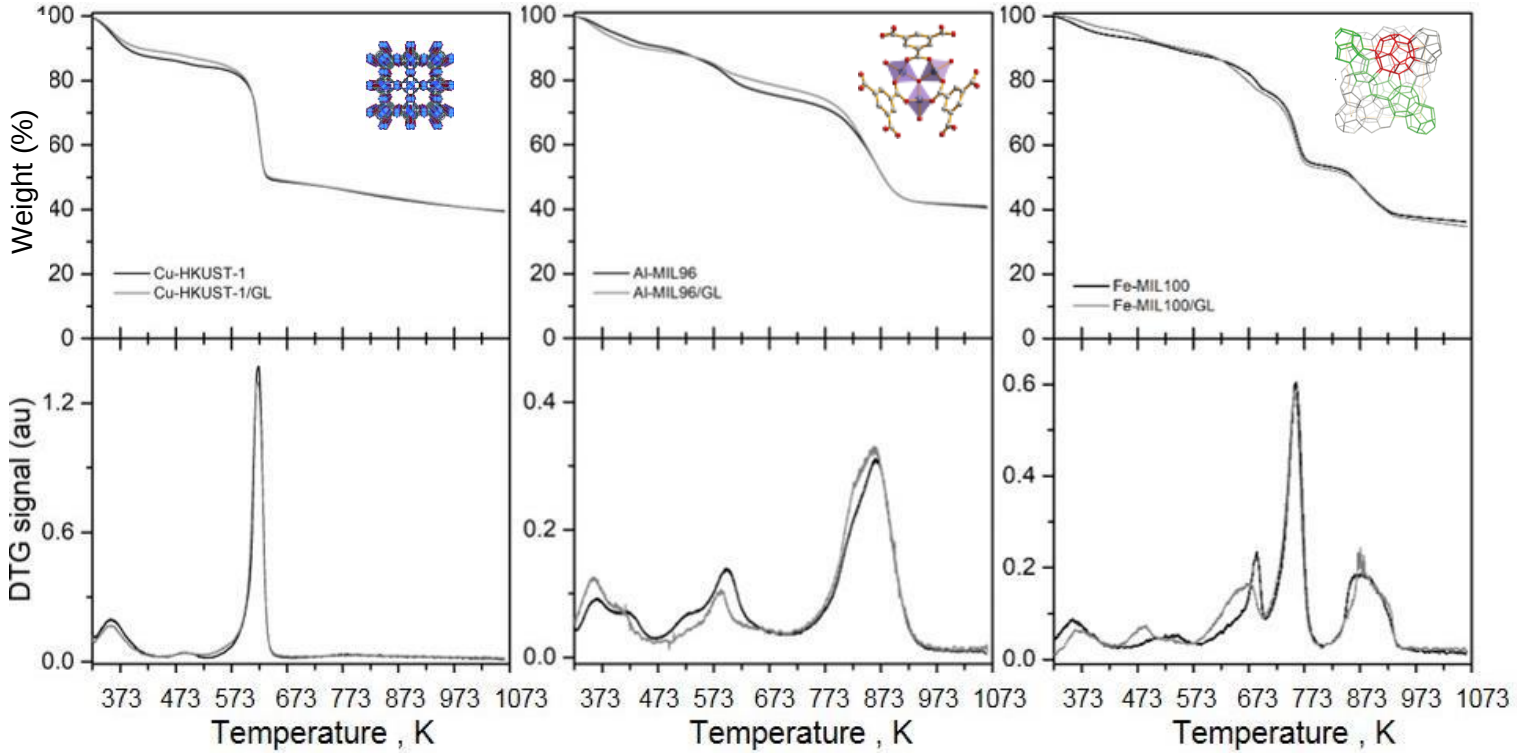
SA and pore size distribution



Sample	Skeletal Density g/mL	Specific surface area (SSA) m^2/g	Total pore volume cm^3/g	Micropores volume cm^3/g
Cu-HKUST-1	2.32	2632	1.11	0.99
Cu-HKUST-1/GL	1.45	2768	1.20	1.03
Al-MIL96	1.57	51	0.047	0.018
Al-MIL96/GL	1.62	47	0.035	0.013
Fe-MIL100	2.05	1105	0.74	0.60
Fe-MIL100/GL	1.86	959	0.59	0.36

The **surface area** slightly increase after the incorporation of GL in the case of Cu-HKUST-1 and Al-MIL-96 while it drops down in the case of Fe-MIL100

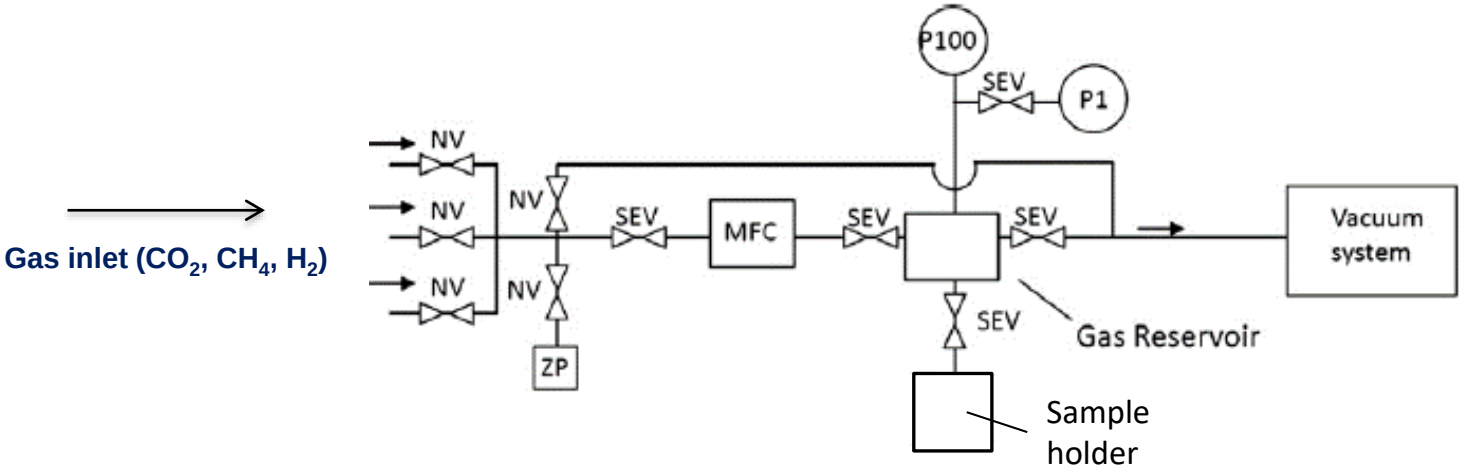
Thermal stability



- **Cu- HKUST-1:** weight loss (2 wt.%) @ **200-280 °C** → water or co-solvent (DMF) desorption
  main weight loss @ **450°C** → collapse of MOF network
- **Al-MIL-96:** weight loss @ **270 - 320 °C** → release of solvent molecules (DMF)
  weight loss @ **500 - 650 °C** → collapse of the MOF network
- **Fe-MIL-100:** weight loss @ **300 - 400 °C** → release of solvent molecules
  main weight loss @ **460 °C** → collapse of the MOF network
  weight loss @ **620 °C** → progressive decomposition of BTC ligands

Gas adsorption performances

All measurements have been acquired using an optimized Sievert-type (volumetric) apparatus f-PcT, equipped with two pressure transducers Bourdon Haenni with end scale of 0.1 MPa and 10 MPa (accuracy is 0.001 and 0.00001 respectively). The apparatus allows collecting measurements in a temperature range 77–800 K.



The adsorption/desorption tests have been carried out at room temperature (**297 K**) and in the pressure range:

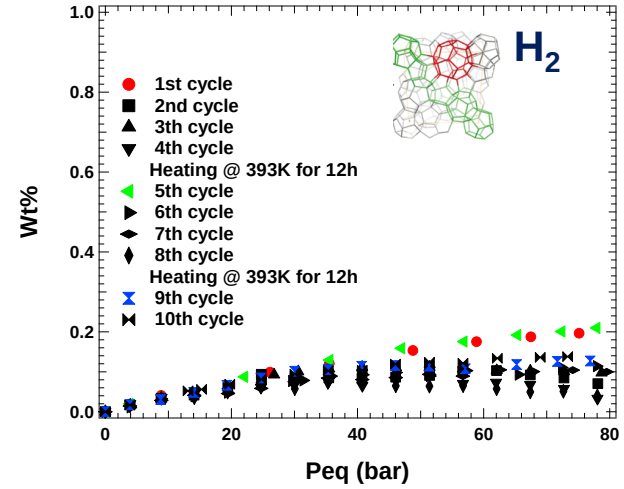
- 0 ÷ 80 bar for H_2,
- 0 ÷ 50 bar for CH_4
- 0 ÷ 15 bar for CO_2

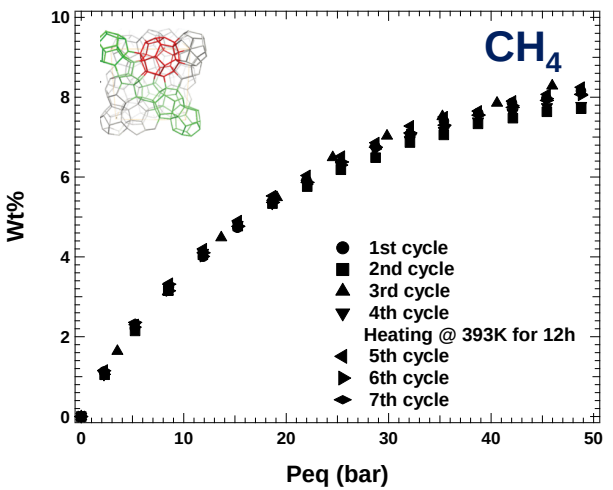
Each sample, before each measurement, was previously vacuum-cleaned under mild heating (12 hours, 393 K, < 10^{-6} mbar) to eliminate water traces.

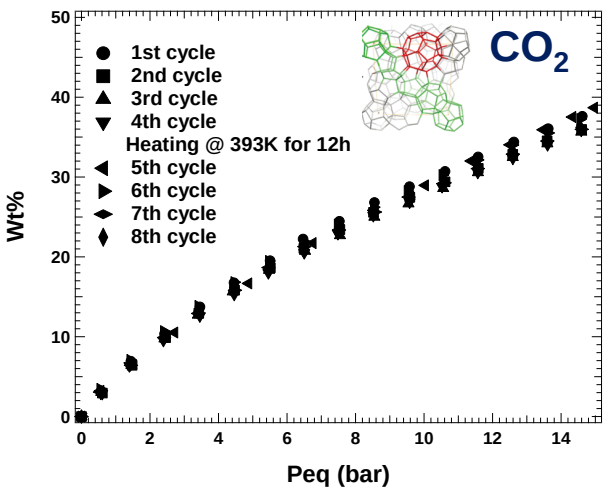
Policicchio et al., Fuel 2013
Policicchio et al., Review of scientific Instruments 2013

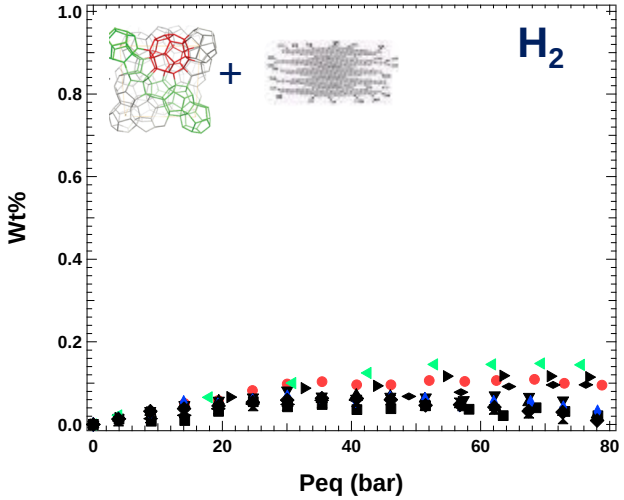
Gas adsorption performances

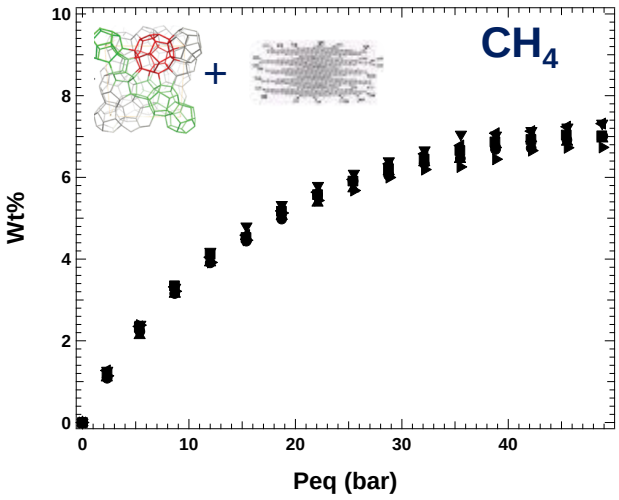
Fe-MIL100 and hybrid

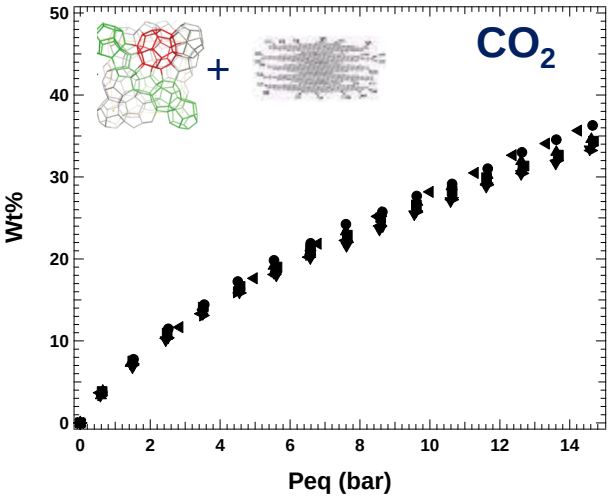










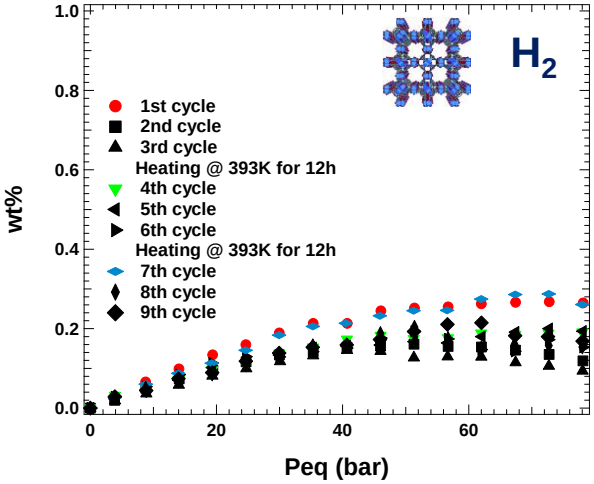


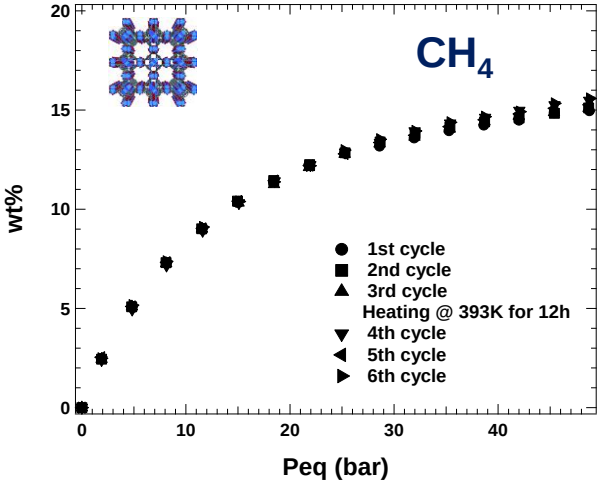
Negligible H_2 adsorption

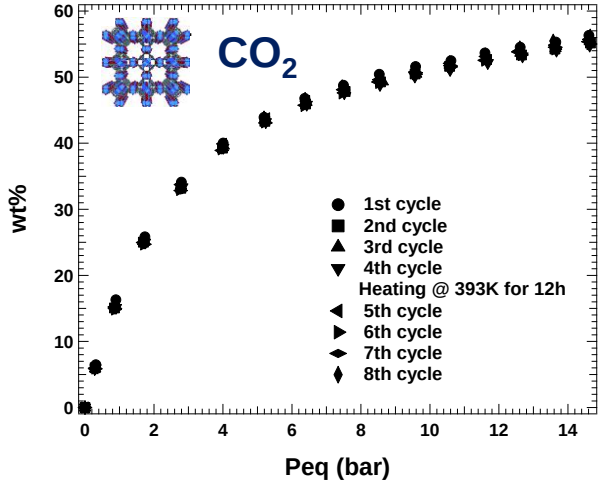
CH_4 and CO_2: cycles following the first, apparently, do not show changes and/or lowering of the maximum adsorption capacity. A simple vacuum pumping allows a complete sample recovery indicating **physisorption** phenomena.

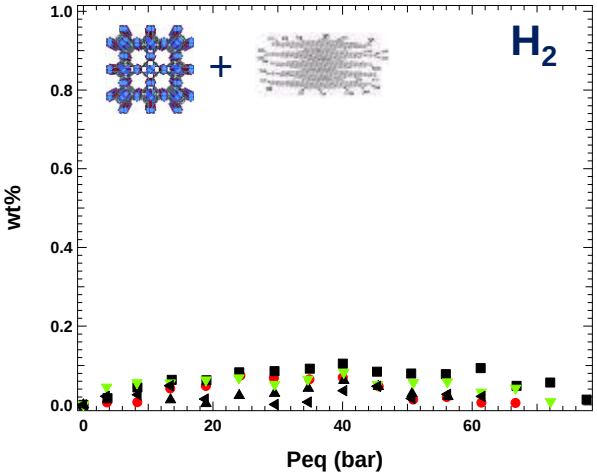
Gas adsorption performances

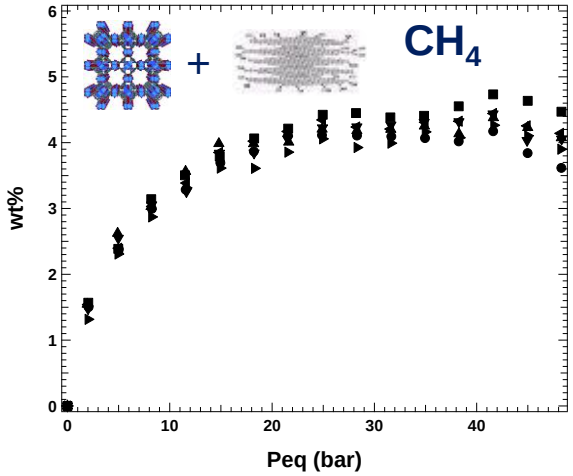
Cu-HKUST-1 and hybrid

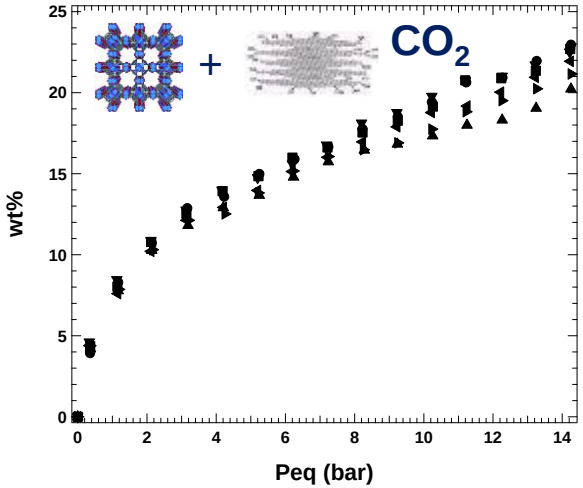










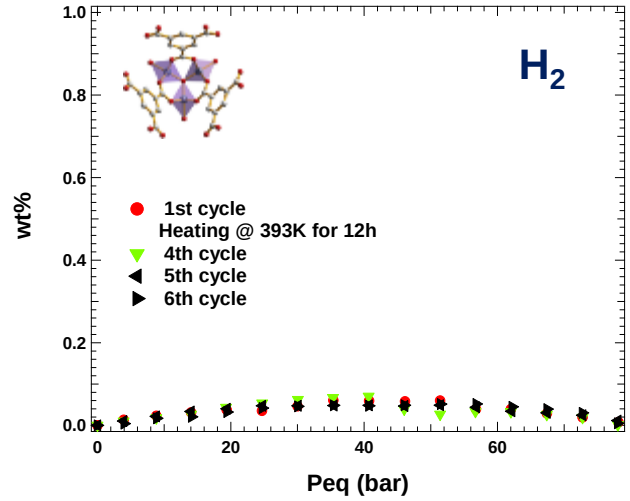


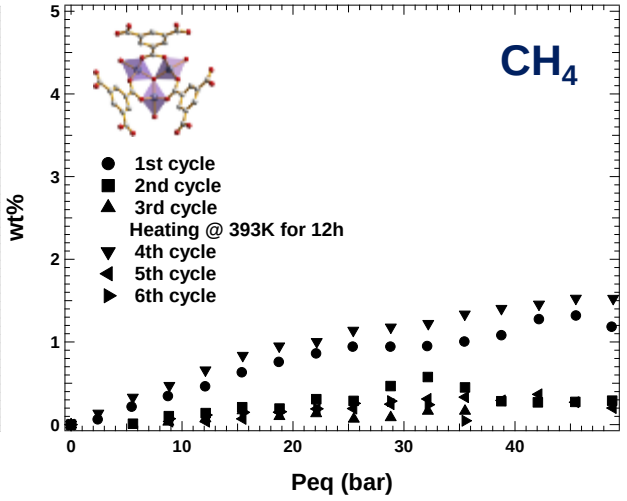
CH_4 and CO_2: completely recovered after multiple cycling. **Weak chemisorption** phenomena in the case of hybrid (recovered combining vacuum and heating at 120 *C);

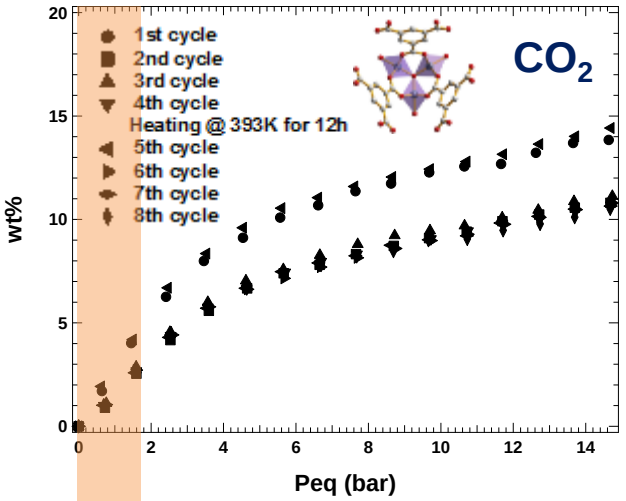
CH_4 adsorption comparable to High Surface Activated Carbon (HSAC, 1400-1600 m^2/g) and commercial AC samples (5-16 wt%).

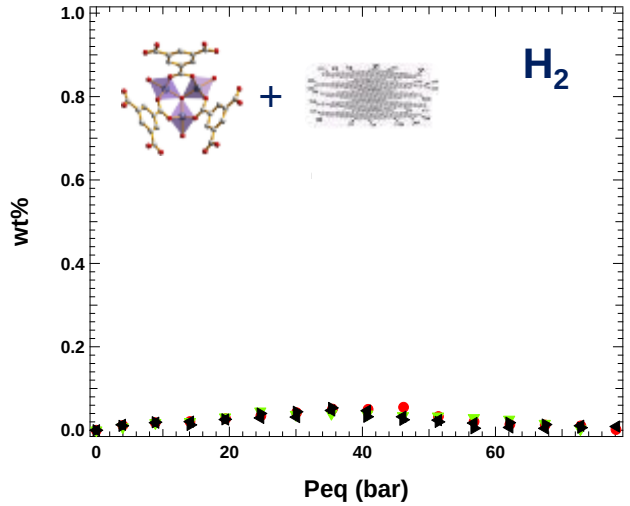
Gas adsorption performances

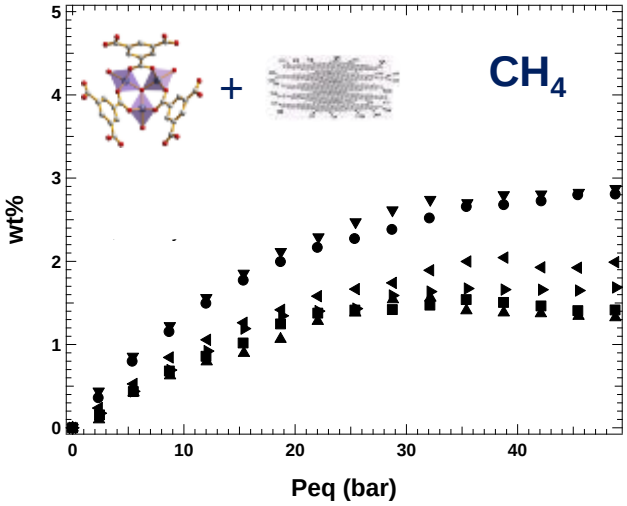
Al-MIL96 and hybrid

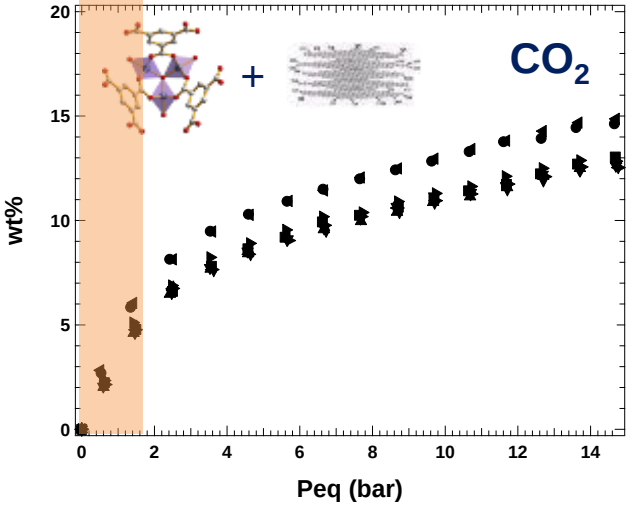










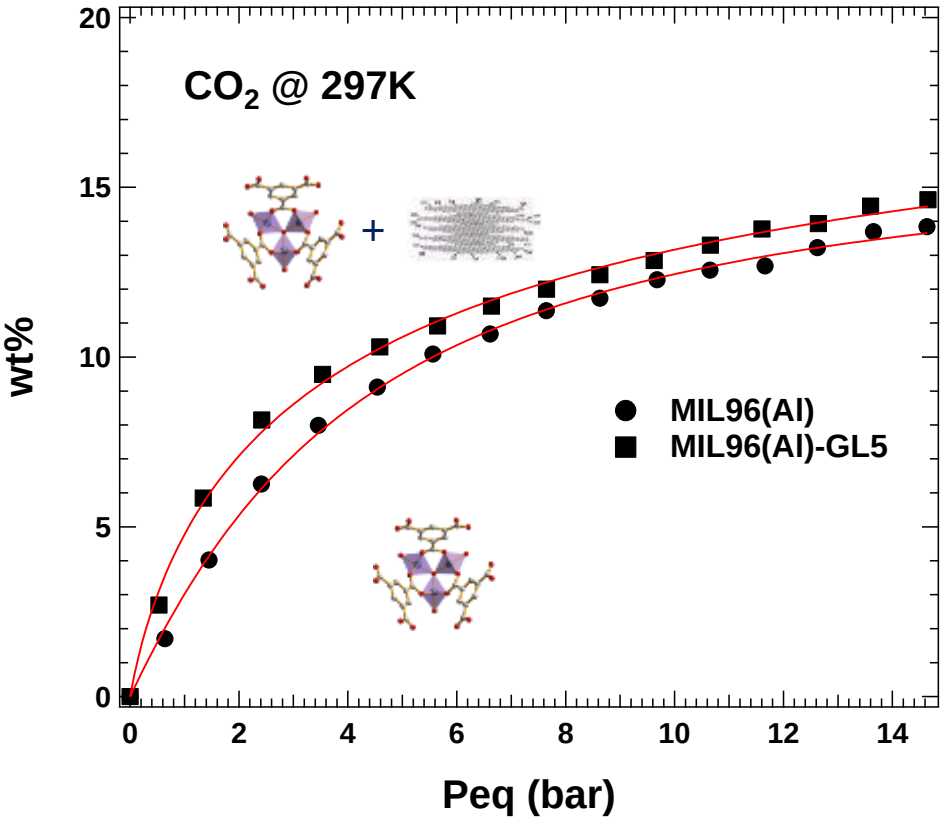


Negligible H_2 adsorption

CH_4 and CO_2: adsorption/desorption cycles following the first lead to a lowering in the maximum adsorption capacity that can be completely recovered combining vacuum and moderate heating (120 °C) indicating **chemisorption** phenomena

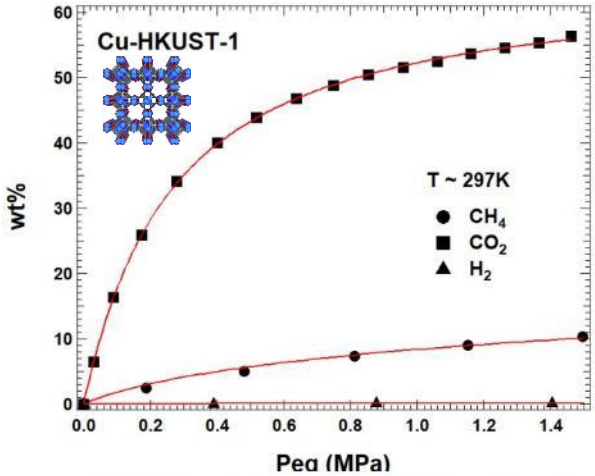
Gas adsorption performances

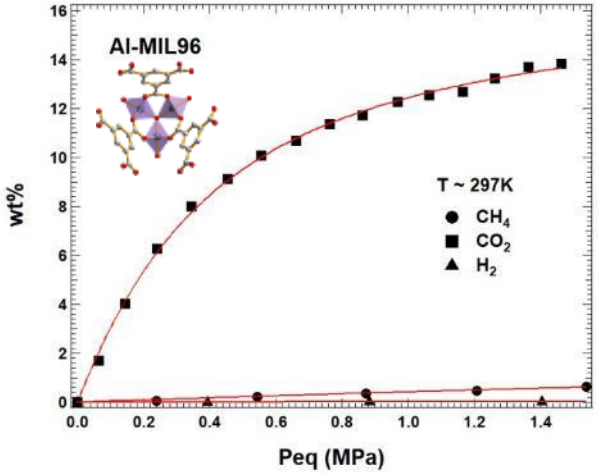
Al-MIL96 and hybrid, CO_2

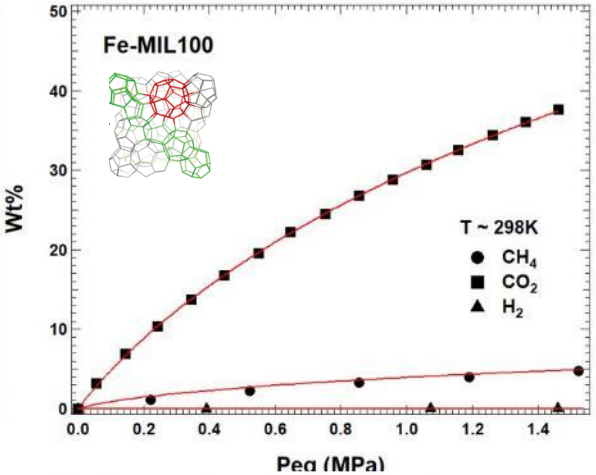


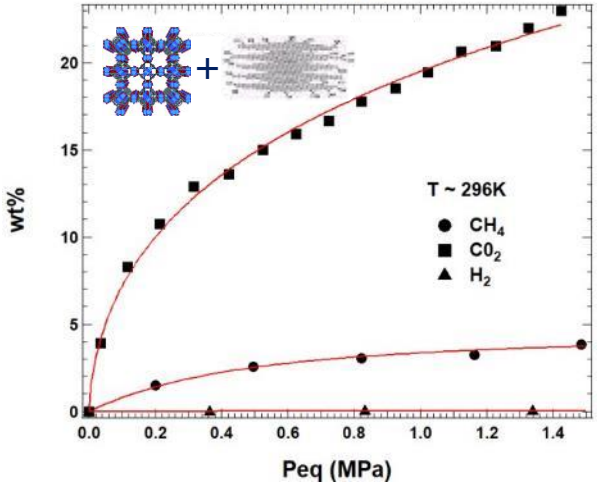
- Al-MIL96/GL shows an improvement of CO_2 absorption compared to Al-MIL96 over the entire pressure range;
- **at atmospheric pressure** Al-MIL96/GL exhibits a larger CO_2 uptake (25% higher compared to Al-MIL96 CO_2 uptake) indicating a higher interaction with the incoming gas molecules (this is even true for CH_4).

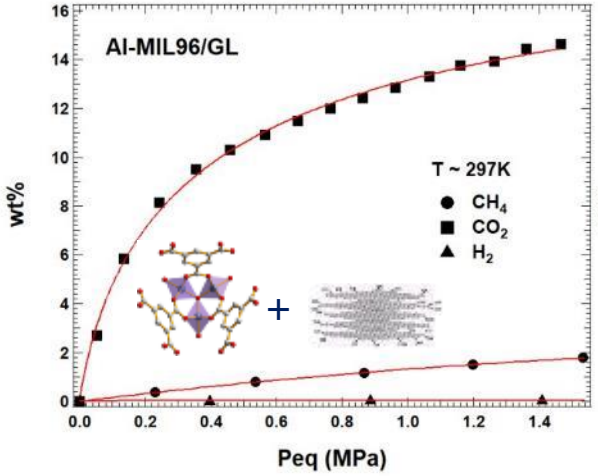
Gas adsorption performances: overview

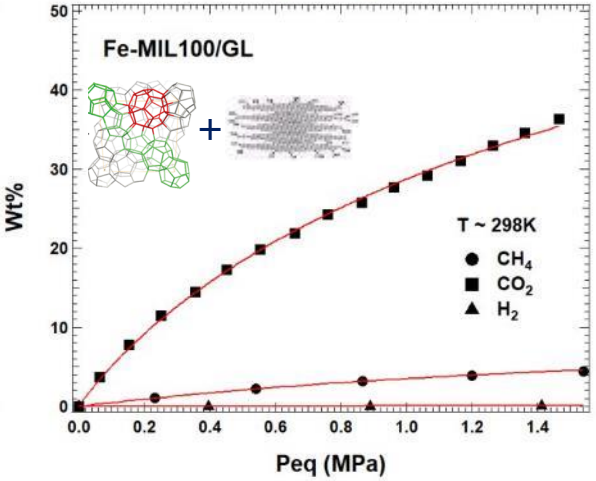




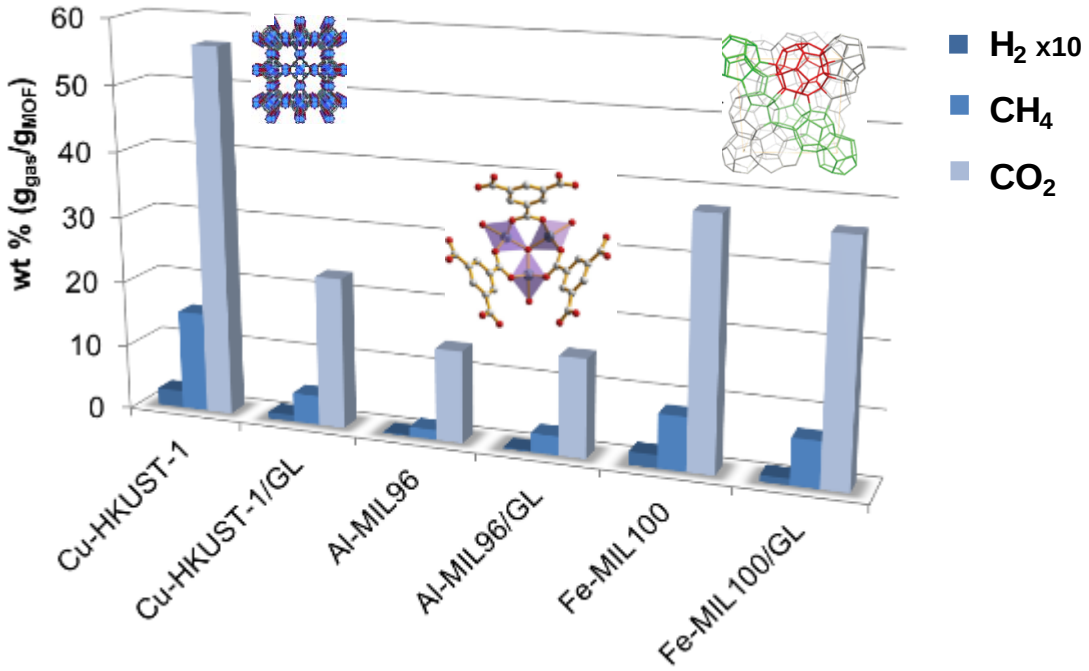






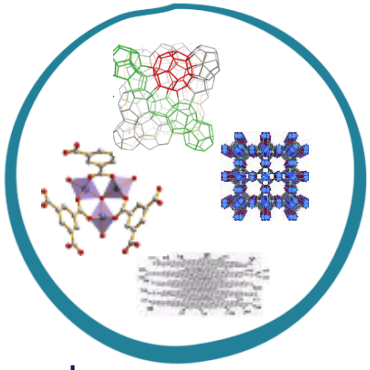


Gas adsorption performances overview



- Overall favorable interaction between the CO_2 and the frameworks.
- As a general trend the hybrid MOFs exhibit a quicker saturation for all the analyzed gases (negligible in the case of hydrogen).
- It was found that in all cases the neat samples did not reach saturation indicating the possibility of uptake improvement increasing pressure and/or changing working temperature conditions.
- **Chemisorption** (Cu-HKUST-1, Al-MIL96 and hybrids) and **physisorption** (Fe-MIL100 and hybrid) phenomena are evidenced.

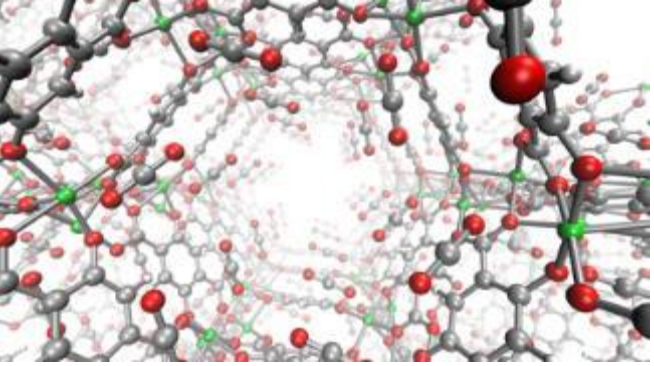
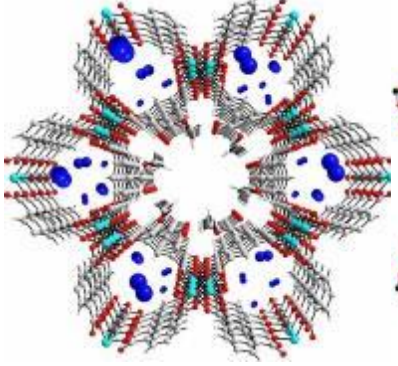
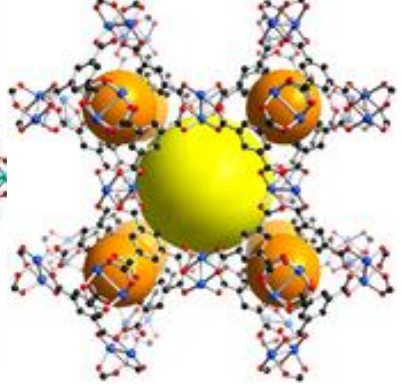
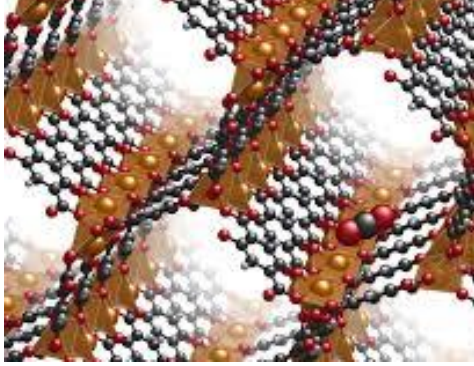
Final remarks and conclusions



- The incorporation of GL at 5 wt.% does not drastically affect the morphology and the characteristic crystallinity of the pristine MOFs.
- Overall **favorable and reversible** strong interaction between the CO_2 and the frameworks.
- The samples with the higher surface areas and enhanced microporous character (**Fe-MIL100** and **Cu-HKUST-1**) exhibit the highest CO_2 and CH_4 uptakes

Can the MOF hybridization with graphene-like layers improve the CO_2 adsorption at high pressure?

- The selectivity of CO_2 over H_2 and CH_4 on MOFs/GL does not show obvious advantage over that of the parent MOF in the **high-pressure range**.
- for **low-pressure applications** (< 2 bar) the introduction of GRM into the Al-MIL96 moiety, where chemisorption phenomena are established, is able to enhance the CO_2 and CH_4 adsorption.

Thank you!

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