Continuous one-step synthesis of porous M-XF_6-based metal-organic and hydrogen-bonded frameworks

Vincent Guillerm,[1] Luis Garzón-Tovar,[1] Amirali Yazdi,[1] Inhar Imaz,[1] Jordi Juanhuix[2] and Daniel Maspoch[1,3]

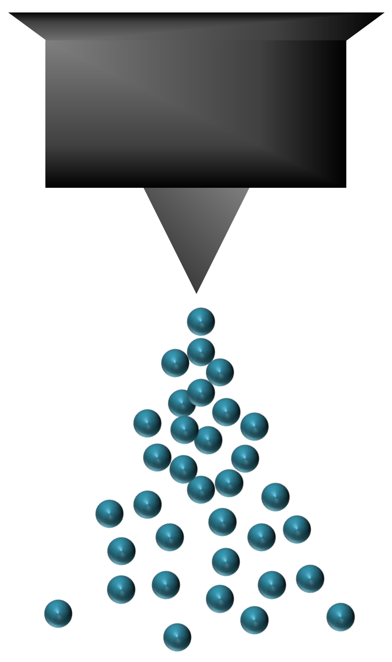
[1]Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Bellaterra;
[2]ALBA Synchrotron, Cerdanyola del Vallès; [3]ICREA, Barcelona

Supramolecular Nanochemistry and Materials - NANOUP

The Need For Efficient Synthetic Methods Of Useful Sorbents

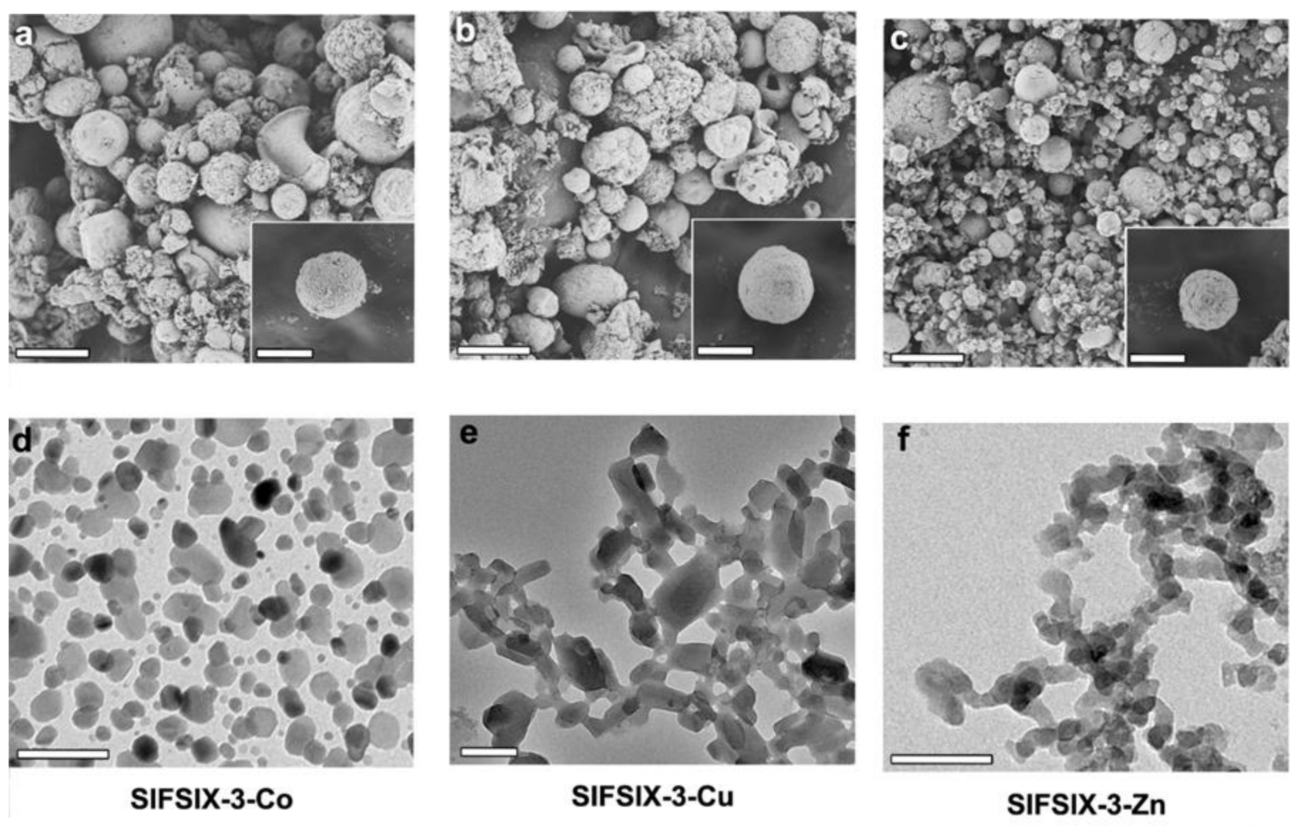
Addressing the current and future energy needs while mitigating the environmental impact has nowadays become a crucial challenge. The development of efficient CO_2 sorbents such as zeolites, activated carbons, metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs) for achieving cleaner combustible supplies is a promising solution. However, despite great developments, scientific community and industrials still need to join their efforts for transferring these materials from the laboratory to industry. A major step here is the optimization of their fabrication, which must envision fast and scalable one-step processes that produce ready-to-use products. Here we report a synthetic method that allows producing several isoreticular **M-XF_6**-based CO_2 sorbents fulfilling all these requirements.[1]

The spray-drying method for synthesizing M-XF_6 based MOFs

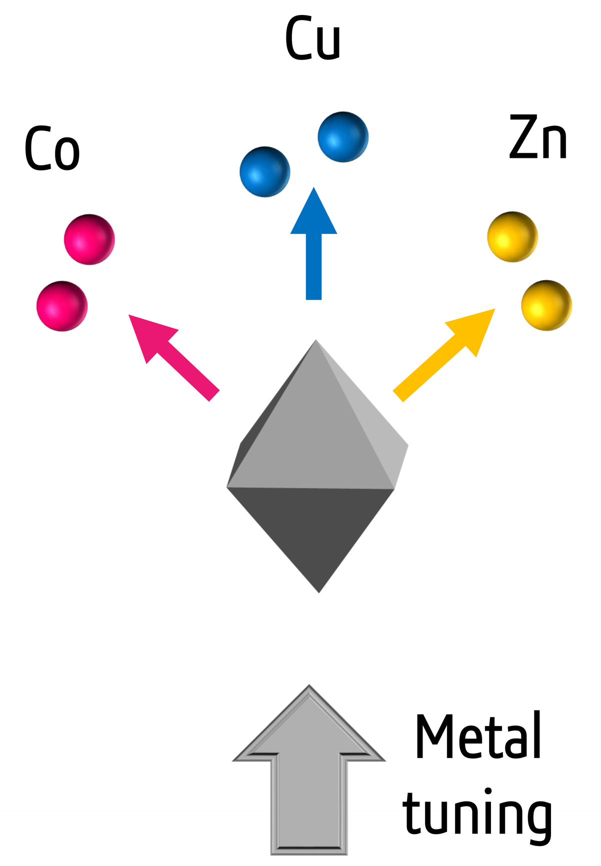


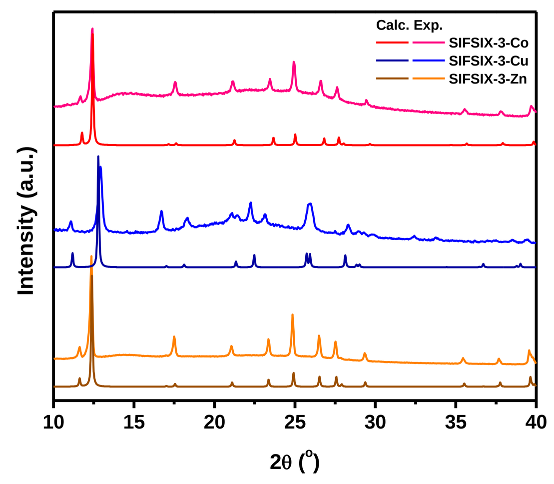
Our group is pioneer and experienced in the use of the industrially well-established spray-drying (SD) technique as a new synthetic way to prepare various MOFs spherical superstructures and nanocrystals.[2] The capital importance of the formation of the inorganic secondary building unit (SBU) for the nucleation and growth of MOFs,[3] convinced us that the premade pillars of the **M-XF_6** MOF platform would be ideal candidates for expanding the catalogue of MOFs synthesized by SD. Moreover, this old-fashioned class of fluorinated materials recently been brought back to the spotlights thanks to their exceptional uptake and selectivity towards CO_2 and hydrocarbons.[4]

Characterization of SIFSIX-3-M (M = Co, Cu, Zn)

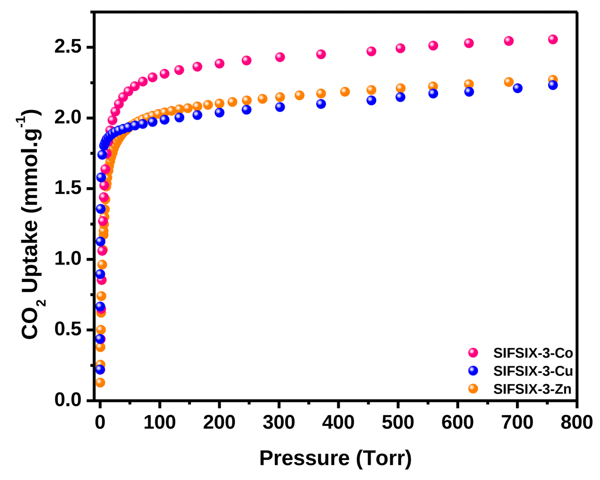


*Representative FE-SEM images of (**a**) **SIFSIX-3-Co**, (**b**) **SIFSIX-3-Cu**, and (**c**) **SIFSIX-3-Zn**. TEM images of (**d**) **SIFSIX-3-Co**, (**e**) **SIFSIX-3-Cu**, and (**f**) **SIFSIX-3-Zn**. Scale bars for FE-SEM: 15 μm and 5 μm (insets).Scale bars for TEM: 100 nm (**d, f**) and 200 nm (**e**)*





PXRD patterns (exp. vs calc.)

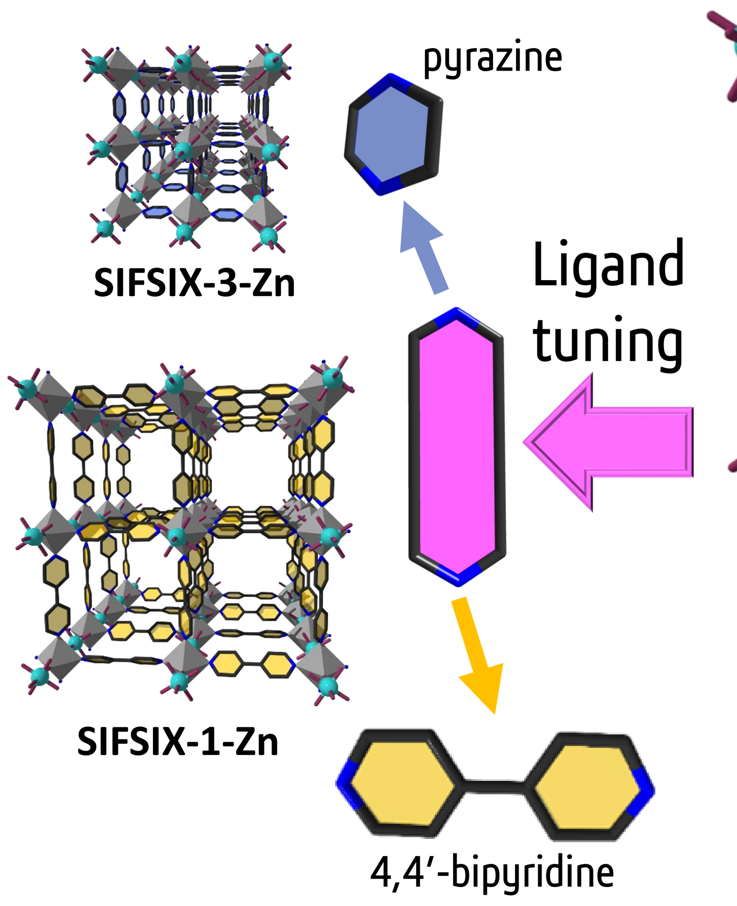


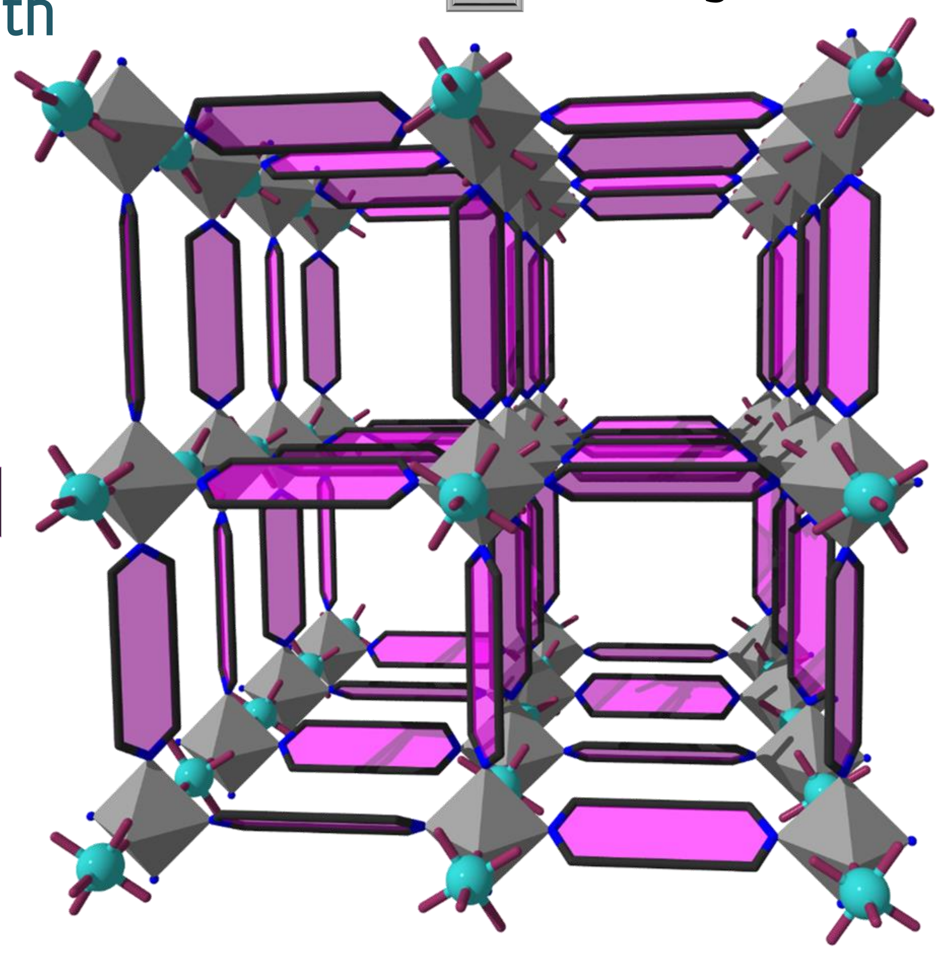
CO_2 adsorption isotherms (298 K)

CO_2 uptake at 760 torr and 298 K ($mmol.g^{-1}$)		
MOF	Bulk	Sprayed (% of bulk)
SIFSIX-3-Co	≈ 2.79	2.56 (92 %)
SIFSIX-3-Cu	≈ 2.40	2.23 (93 %)
SIFSIX-3-Zn	≈ 2.46	2.27 (91 %)

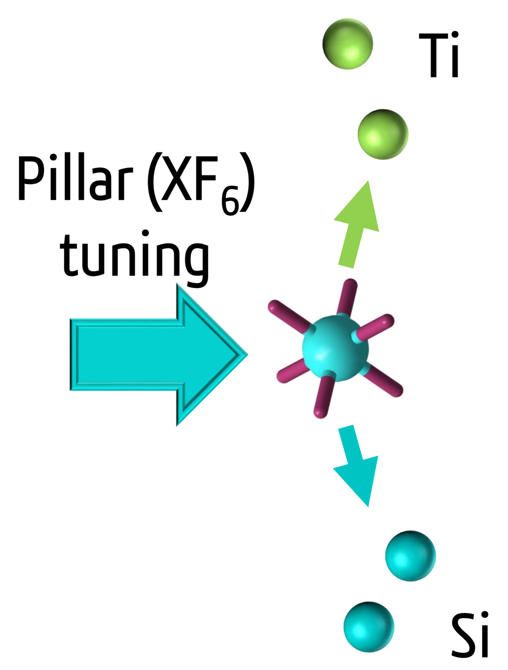
Reticular chemistry: varying the ligand's length

Besides varying the metal (Co, Cu, Zn), we demonstrate that the SD technology is adapted to rationally synthesize isoreticular MOFs. We successfully achieved the synthesis of an expanded analogue, **SIFSIX-1-Zn**, by replacing the pyrazine ligand by the longer 4,4'-bipyridine.





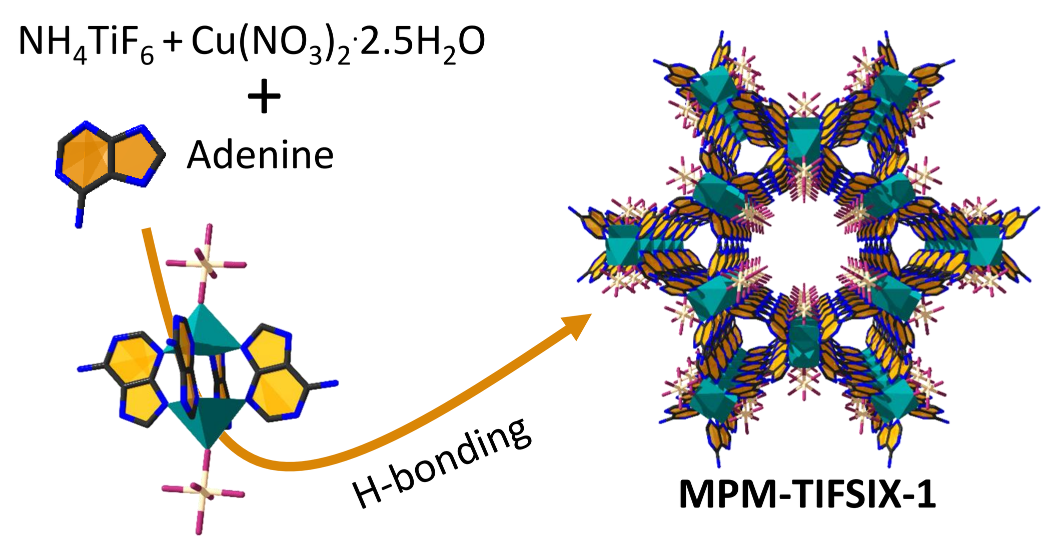
Reticular chemistry: pillar substitution



The tunability of the **M-XF_6** platform is not limited to varying the metal and the ligand.

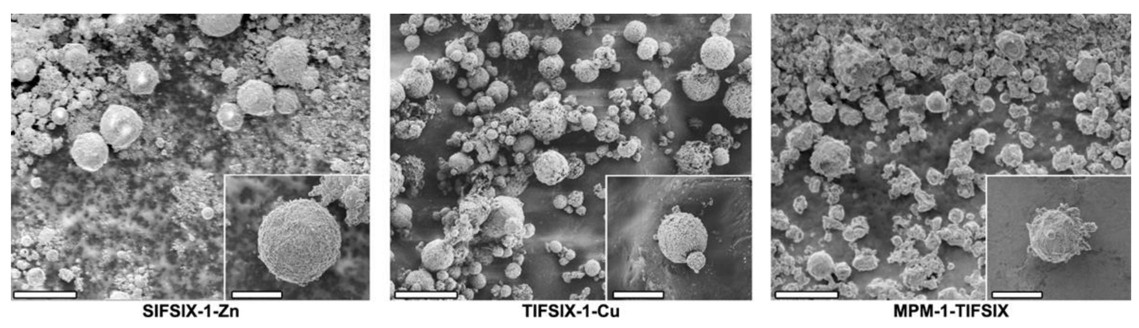
Indeed, it is also possible to achieve the replacement of the pillaring $[SiF_6]^{2-}$ anion by $[TiF_6]^{2-}$,[5] and once again the SD technology was found to be suitable to achieve the synthesis of superstructures of the highly porous **TIFSIX-1-Cu**.

We can also spray H-bonded porous materials!

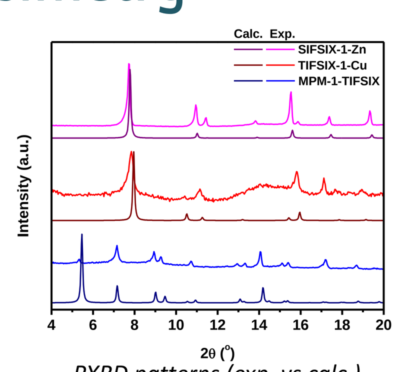


After successfully synthesizing various **M-XF_6** based MOFs by SD technology, we selected another porous material, **MPM-1-TIFSIX**,[6] based on the supramolecular assembly of $[Cu_2(adenine)_4(TiF_6)_2]$ paddlewheels. In the present case, the selected material to be synthesized by SD is not a MOF but a supramolecular hydrogen-bonded network.

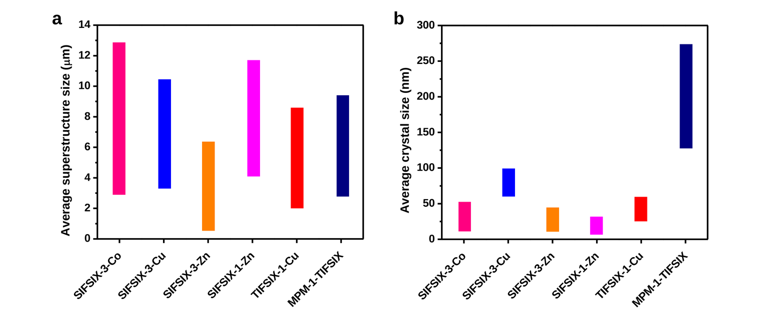
Microscopy, powder X-ray diffraction & porosimetry



*FE-SEM images of **SIFSIX-1-Zn, TIFSIX-1-Cu** and **MPM-1-TIFSIX**. Scale bars: 20 μm and 5 μm (insets)*



PXRD patterns (exp. vs calc.)



*Average superstructure size (**a**) and crystal size (**b**) of the sprayed materials*

MOF	A_{BET} ($m^2.g^{-1}$)	V_{micro} ($cm^3.g^{-1}$) at $P/P_0 = 0.3$	V_t ($cm^3.g^{-1}$) at $P/P_0 = 0.95$	Theo V_t ($cm^3.g^{-1}$)
SIFSIX-1-Zn	1300	0.53	0.58	0.68
TIFSIX-1-Cu	1650	0.66	0.88	0.70
MPM-1-TIFSIX	805	0.32	0.32	0.39

BET areas and pore volumes

References

1 • V. Guillerm *et al., Chem. Eur. J.*, **2017**, 23 (28), 6829-6835
2 • A. Carne-Sanchez *et al., Nat. Chem.* 2013, 5, 203-211
3 • V. Guillerm *et al., Chem. Soc. Rev.*, 2014, 43, 6141-6172
4 • P. Nugent *et al., Nature* 2013, *495*, 80-84; O. Shekhah *et al., Nat. Commun.* 2014, *5*, 4228; O. Shekhah *et al., Chem. Commun.* 2015, *51*, 13595-13598
5 • P. Nugent *et al., Chem. Commun.* 2013, *49*, 1606-1608
6 • P. Nugent *et al., J. Am. Chem. Soc.* 2013, *135*, 10950-10953

Conclusions and Perspectives

-Possibility to synthesize a new type of useful, highly efficient CO_2 sorbents by spray-drying technology: **On the way to pilot scale system**

-Proof of concept for the compatibility of spray-drying method with reticular chemistry: **Many metals, ligands and pillars to be explored**

-First example of H-bonded porous material synthesized by spray-dryer: **A new path has just been opened**

ICN2 Institut Català de Nanociència i Nanotecnologia
Excelencia Severo Ochoa
Supramolecular NanoChemistry & Materials
BEATRIU DE PINÓS PROGRAMME