



A critical step change has been accomplished in the manufacturing of MOFs that will significantly advance their commercialisation.

In 2018, a group of EU project partners (ProDIA) have successfully developed synthesis processes enabling the manufacture of metal organic framework (MOFs) materials at an industrial scale. These innovative methods have significantly reduced production costs permitting MOFs to be priced competitively against many current market leading materials. With this ability to offer these advanced porous materials at an economically viable price, the projected benefits from their superior performance can now be realised. This places MOFs perfectly to meet tomorrow's big challenges in energy, environmental and health application areas

What is a MOF?

Metal organic frameworks (MOFs) are some of the most exciting materials to have emerged in science in the last two decades. They are powdered solids comprised of metals or metal clusters linked by organic ligands into extended networks, which often have very high porosity in the nanopore range (1 nanometre = 10^{-9} m). It is these small pores or cavities that make these MOF materials ideally suited for the storage of gases such as CH₄, H₂O, CO₂, NH₃ and NO to name but a few. Indeed, coupled with their chemical flexibility it has been shown that MOFs have great potential in a diverse range of sectors covering energy, environmental and biological application areas. To date, the number (several 1000's) and rate of scientific publications relating to the synthesis, characterisation and application of MOF materials has broken all previous records. The momentum gained in these academic studies however, has not yet been translated to industrial use until now!

Who is ProDIA?

In the framework of the European collaborative research project ProDIA, 12 partners from industry, R&D organisations and universities joined forces with the aim of accelerating the industrialisation of nanoporous materials¹. Within the three year timescale, the ambitious plan was to link experts in synthesis, shaping and formulation with end application users to create scalable processes that enable manufacture of application ready MOF articles. The ProDIA consortium was awarded 7 million Euros from the EU Horizon 2020 program amounting to a global effort of 760 person months.

What has ProDIA achieved?

The consortium has successfully achieved significant advances in two areas critical to MOF industrialisation/manufacture and shaping/formulation. Several manufacturing processes were explored, developed and validated to enable the multi-kilo scale production of a structurally and chemically diverse range of MOF materials. Suitably shaped bodies and formulations comprising the manufactured MOF powders were fabricated, characterised and tested for use in the key application areas of gas storage for clean mobile energy, waste heat-based cooling solutions for data centres, air purification, and prevention of

¹ ProDIA has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 685727. Partners: CNRS (FR), Institute of Nanoscience and Nanotechnology (ES), Axel'One, ENGIE, IFP Energies nouvelles (FR), Fraunhofer IKTS (DE), Johnson Matthey, MOF technologies, University of St Andrews (GB), MOFapps, SINTEF and University of Oslo (NO).

medical device acquired infections. Data collected in side-by-side testing with industry benchmarks prove the superior performance achievable from the manufactured materials, confirming their immense future potential.

UiO-66: from discovery at CNRS to innovation at MOFapps

MOFs of the UiO-66 family are among the most stable hybrid materials at the thermal, chemical, hydrothermal and mechanical levels². These zirconium-based solids also pose no problem in terms of toxicity. The crystal structure of UiO-66, which has a unique Zr_6O_6 cornerstone cluster, was jointly discovered in 2008 at CNRS and University of Oslo³. Since then, UiO-66 type solids have become featured materials and account today for more than 1.100 citations in the literature⁴. CNRS accounts over 30 patent classes on MOF synthesis and applications. In 2014 a license was given to the start-up MOFapps for the production and use of UiO-66 type MOFs.

In the framework of the European project ProDIA, pilot production processes for the manufacture of MOFs at pre-industrial scale and for their shaping have been successfully demonstrated.

An innovative aqueous manufacture process for UiO-66 was jointly developed by CNRS (IRCELYON), Axel'One and MOFapps⁵. The innovations concern "green", safe and scalable synthesis procedures that function without the organic solvents or the salts that up to now had been required to obtain high-purity MOF materials, enabling production to be cost competitive with current adsorbents. A demonstration a 130 kg pilot batch was successfully produced in a single batch on a 650L vessel (Figure 1).

Developed by Fraunhofer IKTS, the crystalline powder has been extruded in the form of small pellets with no loss of adsorption properties for ammonia air purification filters



Figure 1: Photography of the 650L vessel for the demonstration of UiO-66 manufacture (left), photography of UiO-66 extrudates of 1mm in diameter for ammonia air purification filters⁹.

The MOFapps start-up company will thus offer zirconium-based MOF pellets for air purification, notably for personal and collective ammonia protection cartridges. The lifetime of these cartridges is doubled compared to that of the cartridges currently on the market, which use active carbon based adsorbents.

² Kandiah, M.; et al. *Chemistry of Materials*, **2010**, Vol.22(24) 6632-6640

³ WO2009GB01087

⁴ Cavka JH, Jakobsen S, Olsbye U, Guillou N, Lillerud KP. et al. *J. Am. Chem. Soc.*, **2008**, 130(42), 13850

⁵ Khabzina Y., Dhainaut J., Farrusseng D. et al. *Industrial & Engineering Chemistry Research*, **2018**, 57 (24), 8200

Future Outlook?

Prof S. Kitagawa (Kyoto University), pioneer and most cited MOF researcher, explains: "The ProDIA project is a real success in the innovation field. Prodia partners and their scale-up results made a major contribution. Today, the availability of MOFs at the pilot scale makes it possible to foresee their future use in large-scale applications"

Without any doubt, the fate of MOF is *crystalline*.



Figure 2 : 130kg of UiO-66 – from left to right: T. Michon (Axel'One), D. Farrusseng (CNRS), M. Bessaa (CNRS)

About MOFapps

MOFapps were founded in 2013 on the assumption that metal organic frame works are a class of materials, so powerful in their capacity and so versatile in their application that it is a pity that to date there was practically no industrial application after more than 10 years of research. Materials were apparently up to this point not stable enough, not mechanically robust, too expensive and production methods for larger quantities were environmentally unfriendly. At MOFapps we believe that MOFs can change the world: our individual mobility, the ways we deliver medication, treat wounds, store toxic gas or cool computer servers. What it takes to make this happen is to bring MOF science experts together and create an environment which allows industry partners to define their technical applications. It requires chemical engineering to design MOFs and production processes robust enough for everyday life and the spirit of entrepreneurship to make it all happen. Today we are proud to partner with institutes and companies who offer environmentally friendly production methods, we have licenses to market and produce a full range of Zirconium based high performance MOFs (UiO-66 and family) as well as very positive feedback from industrial feasibility tests. <http://www.mofapps.com/company/>

About CNRS/IRCELYON

The Centre National de la Recherche Scientifique (French National Center for Scientific Research) is a public organisation for scientific and technological research and is under the authority of the French Ministry for Research. The **CNRS** is also the largest fundamental research organisation in Europe. IRCELYON (Research Institute for Catalysis and Environment of Lyon) is a department of CNRS and was founded in 2007. It is the largest national department devoted to the development of catalytic and environmental remediation processes. **Dr. David Farrusseng** is heading a group of 8 permanent staffs which scopes deal with i) the development of new porous materials, and ii) applications in adsorption and catalytic processes. His contribution for the application of MOF to adsorption and catalysis is acknowledged at the international level. He is co-author of more than 160 papers on related subjects and was awarded by the DivCat 2008 price and the prestigious IAC award in 2016. He has participated to numbers of European collaborative research projects such as FP6 TOPCOMBI, FP7 OCMOL and NanoMOF in which MOFs have been developed for gas separation and catalytic applications. He is the scientific coordinator of PRoDia. http://www.ircelyon.univ-lyon1.fr/en/research/research_teams

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