Alexandre Legrand received his PhD degree in physicla-chemistry in 2012 from Lille1 University. After postdoctoral research at the Institute of Researches on Catalysis and Environment in Lyon (IRCELYON, France) and at Catalan Institute of Nanoscience and Nanochemistry (ICN2, Spain) to develop (i) catalytic and sensing applications using Metal-Organic Frameworks (MOFs) and (ii) up-scale MOFs synthesis, he joined Kyoto University in 2016 as JSPS fellow. In 2018, he moved to the Furukawa group as postdoctoral researcher in an international colaboration (LIA) between the IRCELYON (CNRS, France) and the Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University. His main research interests are focused on the tailor-made design and applications of porous materials and in particular exploring the fundamental chemistry of Metal-Organic Polyhedrons (MOPs), mainly their supramolecular polymerization for the fabrication of soft and flexible materials with permanent porosity.

Towards the creation of complex hierarchical structures starting from metal-organic frameworks (MOFs) or metal-organic polyhedra (MOPs) as initial buildingblocks

Presentation Abstract:

Porous materials are ubiquitous and indispensable in daily life. The discovery of a new microporous material with unique properties arising from intrinsic nanosized space is scientifically and technologically topical. In particular, the creation of a more complex porous system with multicomponent, hierarchical architectures, or disordered structures, over the multiple length scales is current scientific challenge. Over the last two decades, a new class of microporous materials known as metal–organic frameworks (MOFs) have attracted much attention because they have displayed surprising and unprecedented phenomena. In order to emerge advanced functions beyond simple crystalline MOFs, a greater focus is needed on the question of how these materials can be used to create higher complex system.

One approach is to use the suitable nanopores of MOFs for polymerization of accommodated monomers to control the structure of resulting polymers. In addition, transferring the shape pattern from MOF host materials is a simple yet powerful method to control the morphology of polymer guest particles because size and shape of the initial porous building block can be easily tune using capping additive. We have recently demonstrated that the orientation of unsubstituted polythiophene (PTh) chains was not disturbed during the isolation process from the host, resulting in the PTh particles with ordered chain alignment and increased electron conductivity compared to bulk PTh (Fig. 1A). In addition, control on the orientation and alignment of the resulting polymer particles could be achieved through (i) the tuning of particle aspect ratio or (ii) a vortex-flow-induced alignment method. This could lead to various materials with macroscopic anisotropic properties with possible application in optoelectronic devices.

Another approach will be to take advantage of the flexibility of metal-organic polyhedra (MOPs), as one of the smallest porous building unit, in order to reach more complex hierarchical structures thanks to their solubility and processability. Recently, we have reported a synthetic approach that lead to the fabrication of soft, flexible gel materials with permanent porosity. Using robust MOPs as molecular building unit (monomer), we were able to designed micro- and mesoporosity in an amorphous coordination material via a supramolecular approach. Time-resolved dynamic light scattering has revealed the dynamic of gel formation and bring better understanding on the mechanism of gelation and architecture of gelling clusters (Fig. 1B). The effect of MOP concentration on the gel kinetic and its mechanical properties were investigated as well as different trigger for the gelation to occurs (temperature, pH, light…). Furthermore, we take advantages of such hierarchical nature of colloidal gels to generate spatial heterogeneity and gradients within the porous materials that could lead to advanced materials function such as separation, catalysis or energy storage.

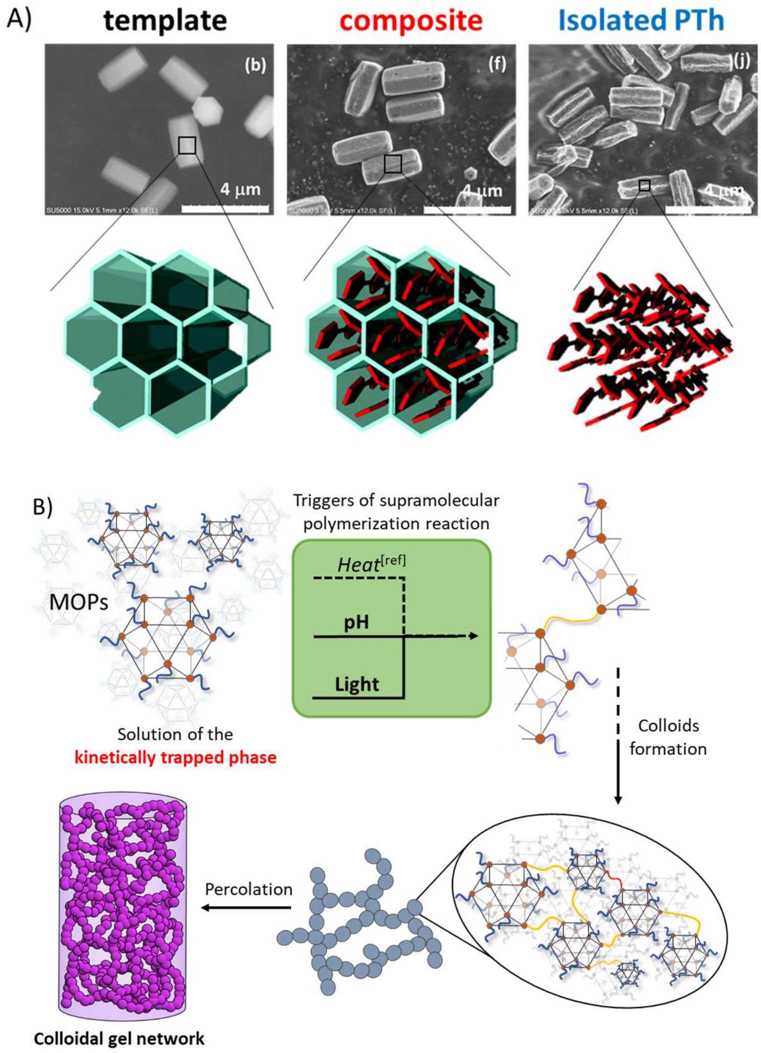

Figure 1. Two different approaches to create hierarchical structure starting from (A) MOFs as template for controlled polymerization reaction and shape transfer to the resulting polymers and (B) MOPs as building block for the formation of colloidal gel networks through supramolecular polymerization

Recent Publications:

1. "Hysteresis in the gas sorption isotherms of metal-organic cages accompanied by subtle changes in molecular packing" G. A. Craig, P. Larpent, H. Urabe, M. Bonneau, A. Legrand, S. Kusaka, S. Furukawa, *Chem. Comm.* accepted
2. "Understanding of the multiscale self-assembly of metal-organic polyhedra towards functionally graded porous gels" A. Legrand, G. A. Craig, M. Bonneau, S. Minami, K. Urayama, S. Furukawa, *Chem. Sci.* **2019**, 10, 10833-10842
3. "Aqueous production of spherical Zr-MOF beads via continuous-flow spray-drying" C. Avci-Camur, J. Troyano, J. Perez-Carvajal, A. Legrand, D. Farrusseng, I. Imaz, D. Maspoch, *Green Chem.* **2018**, 20, 873-878.
4. "Sensitive Photoacoustic IR-Spectroscopy for the Characterization of Amino/Azido Mixed-Linker Metal-Organic Frameworks" J. Canivet, V. Lysenko, J. Lehtinen, A. Legrand, F. M. Wisser, E. A. Quadrelli, D. Farrusseng, *ChemPhysChem* **2017**, 18, 2855.

5. “Enhanced Ligand-Based Luminescence in Metal-Organic Framework Sensor” A. Legrand, A. Pastushenko, V. Lysenko, A. Geloen, E. A. Quadrelli, J. Canivet, D. Farrusseng, *Chem. Nano. Mat.* **2016**, 9, 866.
6. “Enantiopure Peptide-Functionalized Metal–Organic Frameworks” J. Bonnefoy, A. Legrand, E. A. Quadrelli, J. Canivet, D. Farrusseng, *J. Am. Chem. Soc.* **2015**, 137, 9409.