**DASZIF -** Rational Design and Synthesis of Zeolitic Imidazolate Frameworks (ZIFs): an experimental and statistical approach

Institute for Materials and Processes, School of Engineering, The University of Edinburgh, United Kingdom

The principal aim of this project was the study of novel porous materials for the adsorption of energy-related gases. The research carried out by Dr. David Fairen-Jimenez (DFJ) focused on the study of a specific family of metal-organic frameworks (MOFs), which are one of the most exciting developments in recent porous-materials science, called zeolitic imidazolate frameworks (ZIFs). MOFs and ZIFs are synthesized in a self-assembly process from metal corner units bridged by organic linkers (Figure 1). Over the last years, ZIFs have emerged as a very promising family of nanoporous materials with large pore volumes and surface areas (+2000 $m^2/g$), high stability and framework diversity. Their adsorption properties can be tuned through chemical modification of the organic molecules used in the synthesis. Furthermore, many ZIFs exhibit large cavities interconnected by small windows which allows in principle for shape- and size- selective separations. Although the project focused on ZIFs, DFJ also studied adsorption behaviour in a number of other MOFs.

Over the duration of this project, DFJ received a wide variety of interdisciplinary research training in both computational methods (grand canonical Monte Carlo, GCMC) and experimental techniques (synthesis, characterisation, and adsorption performance) to study adsorption processes in nanoporous materials. He was thus able to work in a number of different areas and disciplines (chemistry, statistical physics, chemical engineering and materials science) to produce advances in the field that are of both fundamental scientific interest and of engineering relevance in industrial applications. He addressed three ***general objectives***: ***i)*** the identification of optimal ZIFs structures through the simulation of their adsorption performance, ***ii)*** the synthesis and characterisation of pre-selected ZIFs using different experimental and computational techniques, ***iii)*** the assessment of their performance for industrial applications by simulations and experiments. More specifically, the ***target applications*** were: ***a)*** gas separation of $CO_2/CH_4$; ***b)*** $CH_4$ and $H_2$ storage; ***c)*** $CO_2$ capture. A wide variety of different ZIF structures exist and DFJ used a molecular simulation approach to screen existing and hypothetical ZIFs in order to identify promising structures for the specific applications outlined above. In the next step, DFJ synthesised these ZIFs and studied their adsorption performance which allowed validating the molecular simulation results under realistic conditions. The highlights of his scientific discoveries include:

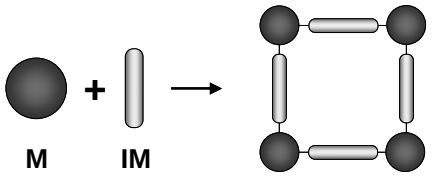


**Figure 1:** *Schematic representation of the self-assembly process from metals **(M)** and organic bridging units **(IM).***

- **Identifying optimal ZIFs structures using molecular simulation:** DFJ classified ZIFs in terms of pore volume, surface area, and size of windows between cavities to find structures with improved adsorption performance. Using molecular simulations, he identified three different topologies and seven specific materials: sod (ZIF-8, ZIF-65 and ZIF-90), rho (ZIF-11 and ZIF-71) and lta (ZIF-20 and ZIF-76). He localised the different adsorption sites for these materials and studied multi-component adsorption related to the purification of $CH_4$, $H_2$ and the capture of $CO_2$ in these ZIFs.
- **Synthesis and characterisation of optimal ZIFs.** In collaboration with Prof. Paul Wright, University of St. Andrews, UK, DFJ was able to synthesise five different ZIFs identified as promising materials: ZIF-8, ZIF-20, ZIF-65, ZIF-90 and ZIF-71, changing the reaction conditions by using new solvents, precursors or higher pH to activate the imidazolate rings. He obtained experimental adsorption data for the $N_2$, $CO_2$, $CH_4$, Ar and $H_2$ for these materials, adapting and validating the simulation model for ZIFs. The match of the maximum uptake between experimental and simulated values at low temperature showed the good quality and complete activation of the samples.
- **Understanding the occurrence of Type V isotherms in microporous MOFs.** DFJ used grand canonical Monte Carlo simulation to investigate why certain MOFs show unusual Type V-sigmoidal adsorption isotherms in contrast to the expected Type I (Langmuir) isotherms. He found that the presence of Type V adsorption is caused by a fine balance between the strength of the fluid-fluid and fluid-solid interactions, which in turn is a strong function of type of fluid and the length of the linker and therefore the pore size of the material.
- **Flexibility in the ZIF framework caused by adsorption:** One of the most exciting findings of this project was the discovery of framework flexibility in ZIFs. It has been previously observed that gas molecules with larger size than the windows between cavities are taken up in these materials. We were able to use for the first time a diamond anvil-cell experiment, used to put a material under extremely high pressures (i.e.

14,700 bar), to obtain structural models for the molecular simulation which then showed very good agreement with experimental adsorption measurements. Using *in-situ* synchrotron experiments at Diamond Light Source, UK, DFJ showed that the ZIF-8 structure was modified by gas adsorption uptake in the same way as it is at a very high pressure due to a swing effect in the imidazolate linkers, enlarging the pore window and giving access to the porosity and thus explaining the adsorption of large molecules. The transition between configurations not only increases the adsorption capacity but also increases the size of the narrow channels that connect these pores, with implications in the mobility of the molecules trough the porous network for selectivity purposes. Our results have shown the impact of flexibility in other MOFs, such as ScBDC (collaboration with Prof. Paul Wright), and the necessity to develop structural models for the molecular simulations in order to reproduce this effect.

- **ZIFs on industrial applications.** DFJ assessed the impact of flexibility on the adsorption of different energy-related gases on ZIF-8, such as alkanes, $CO_2$ and $H_2$. He achieved excellent agreement between simulated and experimental results by solely adapting the UFF generic force field reducing the Lennard-Jones interaction parameter ε. The results show that two different structural configurations of ZIF-8 were needed to properly describe its adsorption performance, demonstrating that ZIF-8 is undergoing a structural change during gas adsorption.

**Potential impact**

Understanding the role of the interactions in adsorption phenomena leads to interesting possibilities in the design of MOF adsorbents for use in gas separation and gas storage applications. Specifically, the shape of Type V isotherms makes these porous materials much easier to regenerate and therefore can potentially make adsorption processes much more energy effective. Second, the accurate prediction of adsorption processes in ZIFs using molecular simulation, together with the new finding of ZIF flexibility opens a new direction in the design of porous solids for gas separation. The possibility of keeping the same topology (i.e. big cavities interconnected by narrow windows) while introducing new functional groups in the framework gives a new dimension in the performance of these materials. The understanding of the role of the different functional groups on the flexibility phenomenon is of fundamental importance. Tuning this effect and so the opening of the windows between cavities by changing the functional groups in the imidazolate linker will directly affect the diffusivity of fluids through the porous network, which has a fundamental impact on the performance of ZIFs as advanced molecular sieving membrane materials in applications such as $H_2$ purification and $CO_2$ capture.

**Additional Training Activities**

Dr. David Fairen-Jimenez received research training in a number of areas: the use of molecular simulation (grand canonical Monte Carlo), quantum simulations, synthesis of ZIFs using solvothermal and conventional methods, study of high pressure adsorption processes through experimental techniques and the use of *in-situ* X-Ray diffraction techniques using synchrotron radiation. This research training for which the most significant outcomes are outlined above provided him with a unique skills set in both simulation and experimental methods and covering the synthesis of materials and their characterisation to measuring their adsorption performance. His combination of experimental expertise in both adsorption and materials synthesis, and his expertise in molecular simulation is, in my experience, almost unique in this area of research.

In addition, he attended different workshops and courses from to improve his complementary skills in higher-education and research management (e.g. Supervising postgraduate research students; Funding opportunities; Enhancing presentation skills; Team work and leadership; Introduction to project management for researchers). He also attended the Postgraduate Course in University Teaching and gained hands-on experience in teaching at university level by being a guest lecturer and demonstrator in classes of up to 60 students for the chemical engineering course at the University of Edinburgh. He contributed to the course design; developed his own lecture materials and laboratory manuals and was responsible of marking the assignments. He has supervised two final year MEng projects and co-supervised, with Dr. Tina Düren, one PhD student. Besides this experience, he has been responsible for introducing a broad number of visitors and PhD students to adsorption experiments and molecular simulation, creating a innovative educational systems such as the design of a Wiki website for online learning. This experience allowed him to link his responsabilities at The University of Edinburgh with different conferences and workshop in education, where he acted as member of the scientific comitees (Learning Technology for Education in Cloud LTEC'12, Salamanca, Spain; and the 1st and 2nd International Conference on European Transnational Education ICEUTE 2010 and 2011, Burgos, Spain). He also participated in the organisation of the 34th Annual British Zeolite Association Conference.