

METAL-ORGANIC FRAMEWORKS: A DYNAMIC PLAYGROUND FOR WATER AND ENERGY HARVESTING

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Metal-organic frameworks are 3-D crystalline nanoporous materials build as frameworks from metal ions or inorganic clusters connected via organic linkers. They have been explored for a wide range of applications including adsorptive separations, sensing, catalysis, water harvesting, and so forth.

MOF structures are literally dynamic. Rotational dynamics of linkers and guest-induced deformations are very prevalent, and impact their behaviour in gas sorption, sensing and as stimuli-responsive materials. In rotor-MOFs ultrafast rotation can be engineering by decreasing the rotation energy barrier via molecular design.[1] Yet, MOFs have, in fact, the potential of displaying much more intricate dynamics, similar to other dynamic materials containing closely interacting molecules, such as crowded movement of proteins in lipid bilayers, or concerted molecular motion in liquid crystals. MOFs in fact provide an exceptional playing ground, as they offer a regular arrangement of rotors with defined intermolecular distances that can be tuned through the choice of building blocks. This means that the free pore space and inter-rotor distance can be tuned to a desired level of “crowdedness” of the rotors for cooperative motion. Here I will present how we achieved the emergence of correlated motions in the MIL-53 family,[2] and how we uncovered the progression of these rotational motions along a series of neighbouring linkers. Such understanding of correlated dynamics is highly relevant for the design of ferroelectric MOFs.

Another way to explore the structural dynamics of MOFs is via the piezoelectric effect, which means that electrical fields can induce structural changes in non-centrosymmetric MOFs. The low dielectric permittivity, due to their porosity, means that MOFs potentially could be very efficient for piezoelectric harvesting of mechanical energy. Yet, studies of the piezoelectric response of MOFs are very scarce.[3] Via high throughput DFT calculations we found several types of MOFs with ‘e’ values up to $1.55 \mu\text{C}/\text{m}^2$, making them very competitive. The most striking group among these high ‘e’ structures are Mo-MOFs with a polar ordering due ...-Mo-O-Mo-... chains that have long-short-long-short-.... coordinating bond lengths. Very akin to ferroelectric oxides. Indeed, our preliminary experimental results indicate a ferroelectric-paraelectric phase transition. And this makes these materials particularly exciting, as ferroelectricity means that these materials are easily processable into energy harvesting devices.

Apart from the dynamic nature of MOFs, it is paramount to consider that in many applications, e.g. direct air capture of CO_2 and sensing, humidity will be prevalent. This is often seen as a hassle due to the competitive adsorption of water. Yet water may also present an opportunity: in some cases humidity might actually lead to water-assisted adsorption of CO_2 [4]. The combination of water and microporous materials can even be a match made in heaven: some of them, especially certain MOFs are capable of harvesting water in the desert [5]. I will present an understanding of the structure-property relationships leading to such behaviour.[6]

To conclude, metal-organic frameworks provide a dynamic playground, literally and figuratively with potential of solving exciting challenges like those of water and mechanical energy harvesting.

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