

Towards a molecular level understanding of metal-organic frameworks

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Metal Organic Frameworks have received enormous attention the last two decades due to their versatility and potential to tune the materials towards high-tech applications. A huge amount of materials has been synthesized so far, but the true challenge consists in tuning the materials towards proper applications. Molecular modeling with its diversity in methods has now reached the point that it may give complementary insight to the experiment and can even predict properties which are hardly accessible from the experiment.

In this contribution we showcase by a set of examples how an ingenious combination of molecular modeling tools may be used to obtain molecular level insight into the structural, electronic, spectroscopic and thermodynamic properties of MOFs. The methods encompass atomistic models based on in-house developed force fields, quantum mechanical based methods and thermodynamic models. To describe transformations between various phases of MOFs, advanced molecular dynamics tools are used to sample the relevant parts of the free energy surface.

A variety of framework materials will be highlighted ranging from rigid to flexible materials. The Zirconium based UiO-66 material belonging to the class of rigid materials, is an ideal starting point to illustrate some concepts related to mechanical stability, defect engineering, electronic properties. The UiO-66 material has become a very attractive material for various applications due to its exceptional stability under various conditions.

In a next step we will illustrate how theoretical modeling tools may give a molecular level understanding of the observed flexible behavior in some Metal Organic Frameworks. Some materials show large volume changes upon exposure to external stimuli, such as temperature, pressure, guest molecules. By using an ingenious combination of force field based procedures, advanced molecular dynamics sampling methods and Density Functional theory based calculations, we are able to give a deep molecular understanding of this flexibility.