

Implementing highly selective sorption sites in metal-organic frameworks – a force field study

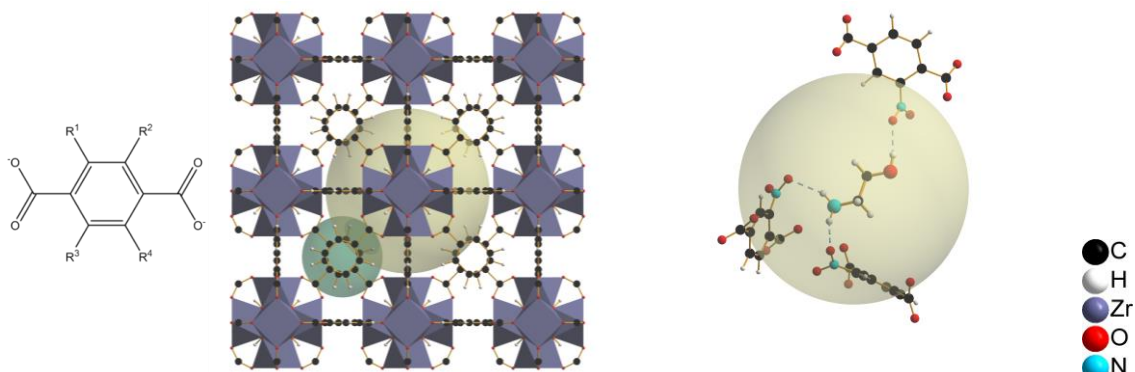
Malte Schäfer, Andreas M. Schneider, Peter Behrens

Institut für Anorganische Chemie, Leibniz Universität Hannover

Enzymes play an essential role in biology. Due to active pockets, which are formed by certain functionalities at defined positions, these macromolecules can perform specific reactions with high selectivity. Many attempts have been made to transfer such capability to applicable devices. E.g., aptamers can be deposited on a substrate, potentially retaining their high selectivity, to create a highly selective sensing device. [1] Another example is the design of a metal-organic framework containing such active pockets, by using different substituted linker molecules. [2]

Metal-organic frameworks (MOFs) are one class of microporous coordination polymers. In general, these material exhibit large pore volumes and a high surface area. Amongst others, these properties lead to a high application potential in gas storage and separation. Especially the latter depends not only on volume and surface but on the so-called host-guest interactions between the framework and the sorbate. Due to the fact, that MOFs can be constructed using various linker molecules, these interactions can be tuned. For example, UiO-66 analogue MOFs can be synthesized by using derivatives of the linker molecule. Applying this approach, substituents can be introduced within the porous system of the MOF, which show a big impact on the adsorption of CO₂. [3] Using the structure of UiO-66 as a starting point, different substituents can be introduced at the linker molecules and a specific arrangement of the functionalities within the pores can be achieved (construction principle and linker with positions indicated carrying substituents are shown in the figure (left)). [4] This design targets the generation of an enzyme-like pocket and a sensing device employing such a MOF may enzyme-like selectivity as well. Here, we present a force field study as basis for the experiments.

For this investigation, a suitable force field needs to be identified first. Once this force field meets the requirements, different derivatives of the UiO-66 can be modelled. The interaction between the MOFs and the target analyte ethanolamine is investigated by means of molecular mechanics and dynamics. Monte Carlo simulated annealing is supported by energy minimisation procedures to find the most preferred sorption sites within the MOF structures. The resulting structures are evaluated in detail by the calculation of the interaction energy, the individual energy contributions, and the examination of the analytes' conformation as well as the inter- and intramolecular hydrogen bonds formed. An example of an ethanolamine molecule at the preferred sorption site is shown in the figure, dashed lines indicate hydrogen bonds.



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