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Towards porous 3D covalent organic framework films

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Abstract

Porous materials are of great scientific interest because they are able to interact with guests, such as ions, atoms and molecules throughout their entire volume. One big subgroup of organic porous materials are covalent organic frameworks (COFs), which are mainly synthesized as powders with an uncontrolled grain size. In order to broaden the application range for those materials towards utilizations, which require mechanical strength, such as membranes and electronics, it would be beneficial to synthesize COFs also as continuous films.

This dissertation aims for developing a method to grow 3D COF films and overcome this powder limitation. The used approach is based on a continuous flow setup and the involvement of a quartz crystal microbalance (QCM), which enables real time monitoring of the film growth by mass deposition. During the performance of these surface reactions, two reactions are kinetically competing with each other. The kinetic promotion of the desired surface reaction over the bulk reaction was achieved by using low concentrations. This led to an increased smoothness of the framework material, compared to its growth under batch conditions. The modular strategy allows full control over the reaction conditions at any time and makes the approach versatile, meaning it can be used for the assembly of different networks. Three different amorphous or crystalline films were synthesized and characterized via EDX-SEM, XPS, GIWAXS, AFM, as well as IR and Raman spectroscopy. The synthesized framework materials use a C-C linkage, making them to one of the first examples for carbon-carbon linked COFs. It could be demonstrated that both networks can be grown on each other, forming a layered COF film. Those findings confirm a successful assembly of a covalently connected layered 3D COF.

The findings presented in this thesis contribute to an increased method variety for the formation of porous materials. This will enable the synthesis of more rigid and stable COF materials, as well as the possibility to introduce a certain functionality only locally into a framework in the future. Additionally, the strategy enables the formation of rigid films on a variety of substrates. Consequently, the results will expand the design and application range for porous materials

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