Integrated Research Training Group 2D Materials

Thesis Advisory Meeting – Annual Progress Report

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Introduction

Covalent-organic frameworks (COFs) are organic framework materials that can be described as crystalline organic polymers. COFs are often polymerized from core monomers that are linked together with linking monomers (although COFs with only one type of monomers exist as well). Due to their ordered and porous structure and the vast variety of possible combinations of core and linker molecules, they have been a topic of high interest since their first synthesis by Yaghi et. al. in 2005. [1]
COFs either have a 3D structure or a layered 2D structure, depending on the symmetry of the cores and linkers. Since the discovery of graphene, the quest for other monolayer 2D materials has gained traction and it has been shown that COFs can be synthesized as such 2D monolayer. However, controlling defects, stacking and crystallite size still is a challenge up to this day.

Understanding 2D COF polymerization at interfaces

A promising approach was introduced by Feng et. al. in 2019 with the SMAIS (surfactant-monolayer-assisted interfacial synthesis) method where surfactants (organic molecules with apolar tails and polar heads) are used to facilitate the ordered synthesis of monolayer 2D COFs on a water interface. [2] The surfactants float on the surface with the negatively charged head on the water surface and attract the positively charged monomers to the surface. This results in a preordering of the monomers and hence higher crystallinity and domain size of the 2D COFs. There are, however, many possible other reasons that could affect the polymerization and are not clear from the experimental characterization. Here, molecular dynamics (MD) simulations can help to understand the dynamics of the surfactants at the surface and how the monomers behave in the water phase and the interface.

Hofstadter's Butterfly in 2D COFs

2D COFs can be classified by their topology, like a square or a honeycomb topology. When we look at other simpler materials with the same topologies (for example graphene), we might be able to find similarities between them. The Hofstadter's Butterfly is a well-known phenomenon in solid-state physics which is interaction of a magnetic field with the electronic states. [3] The Butterfly has been experimentally measured for graphene and theoretically described for many other systems. [4] The main difficulty for the experimental validation is that very high magnetic fields are necessary to measure this effect. However, the larger the pores, the lower the magnetic field needed to measure it. Hence, COFs are promising candidates with their larger pores and their often large delocalized electronic systems to measure a Butterfly structure without highly specialized equipment.

Calculation of Energy Profiles for the HWE-Reaction

One of the challenges in creating COFs of high crystallinity is that due to their strong covalent bonds, bond formation is irreversible which means that no error correction is possible when defects form. Hence, it is the goal to increase the reversibility of reactions and through this obtain highly crystalline COFs. Recently, it was shown that a two-dimensional conjugated polymer could be synthesized with the HWE reaction. [5] In the case of the HWE reaction, one way of tuning reversibility is to lower the energy of the transition state. The idea is to use similar reactants but with different electron pulling or donating groups to see how this affects the reversibility.

OBJECTIVES AND CHALLENGES

Understanding COF polymerization at interfaces

In the world of 2D crystalline polymers, it is a challenge to understand the precise mechanisms of formation, especially if the synthesis is not carried out on a solid interface. From the experimental side, it is challenging to get insights because these processes are difficult to measure. From a theoretical point of view, it is difficult because usually the systems are very large or the processes take place on very long length scales which means that normal ab-initio methods or even classical molecular dynamics simulations are not feasible. Therefore, the challenge is to find ways to model these processes and the resulting structures with approximations that are accurate enough but computationally still cheap.

One way to address this is in the case of the SMAIS method, to not look at the actual polymerizations but at the surfactant system itself to gain more insights on how the surfactant monolayer behaves on the water surface. By doing this, we can infer which surfactants or synthesis conditions are optimal.

Another way to do this is to use so called cross-linking molecular dynamics simulations where monomers are linked purely on a distance criterion. This will be discussed more in detail in the Outlook section.

Hofstadter’s Butterfly

With simple systems like graphene where there is one pore of one size and few electronic states, beautiful and symmetric butterfly patterns arise. However, a system with more and asymmetric electronic states results in a more complicated butterfly structure. Hence, we now want to simplify our model to break down the structure of a 2D COF to its bare topology to better see the main features of the COF-Butterfly.

Calculation of Energy Profiles for the HWE-Reaction

The goal is to see which substitutions lead to a lower energy barrier of the backreaction. However, it can be computationally very demanding to calculate the actual transition state ensemble, since a lot of different configurations of the transition state must be sampled. Therefore, we only use the configurations which by intuition seem to be of lowest energy and relax these.

RESEARCH PROGRESS

Understanding 2D COF polymerization at interfaces

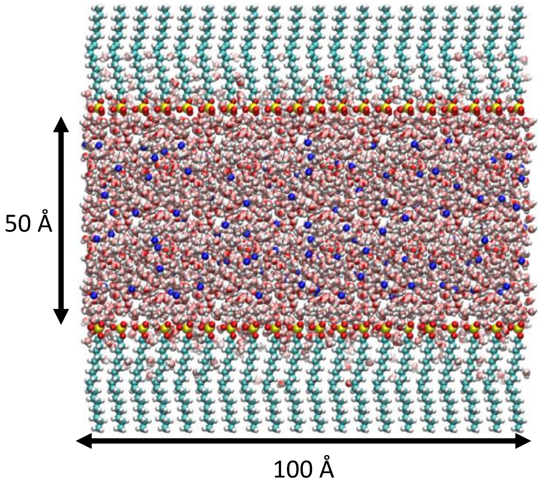

Figure 2: MD Simulation setup.

In order to understand the influence of the surfactants for the reaction, it is crucial to first understand how the surfactant monolayer itself behaves. This is done by using Molecular Dynamics (MD) simulations with the simulation code GROMACS, where a two monolayers setup of surfactants with a vacuum layer was used to achieve a better efficiency for the simulation (see Fig. 1). As surfactant, sodium oleyl sulfate (SOS) was used. The radial distribution function, which was averaged over 10 ns, was calculated (see Fig. 2) and the surface packing studied. As expected, the tails of the surfactant pack hexagonally since it is the densest circle packing in 2D. However, the surfactant heads (represented by the sulfur atom) pack in a square fashion. To validate that this is not an artefact of the initial setup, initial square, hexagonal and random packing was compared, but in all variants the same qualitative result was obtained. While it is not yet clear why exactly this happens, a possible explanation is that it is caused by the interaction of the sodium counterion and the surfactant head which leads to an energetically more stable square packing.

Furthermore, the effect of another counterion was studied. The same simulations were now performed with calcium as counterion. Because calcium has a higher charge, the surfactant heads cluster around the ions, making the surfactant monolayer very irregular and creating holes. Additionally, the ion mobility is significantly reduced to a point where Ca^{2+}-ions stay at the surface and not enter the water phase at all. (see Fig. 3)

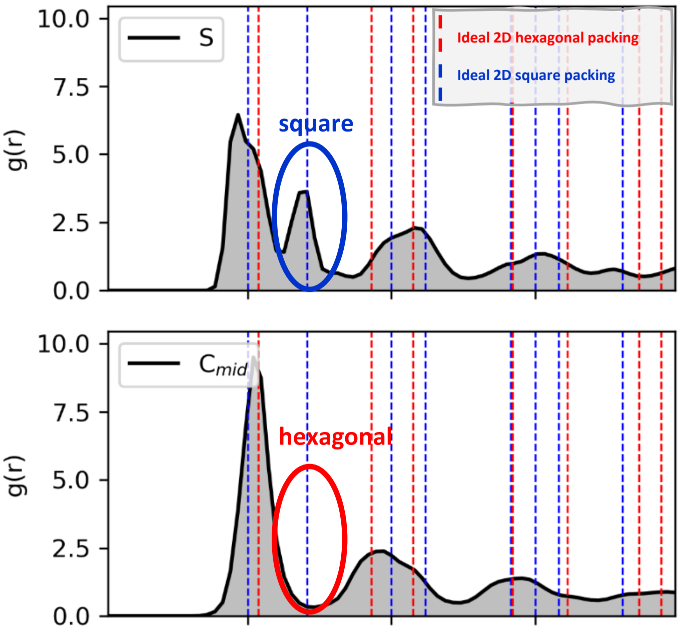

Figure 1: Radial distribution function of the sulfur atom and a carbon atom in the middle of the surfactant tail. Red and blue lines indicate distances of an ideal square

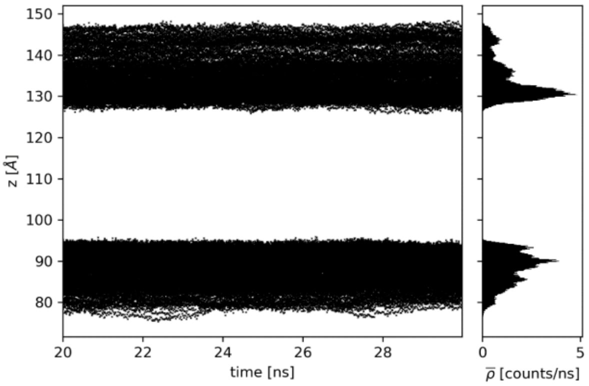

Figure 3: Calcium ion position over time. At each time frame, the z-position of a calcium is represented as a black dot. On the right: the averaged density.

Finally, the stability of the surfactant was investigated by calculating the free energy that is necessary for one or several surfactant molecules to enter from the surfactant monolayer into the water phase. Potential mean force calculations with umbrella sampling were performed for a different number of surfactants. As seen in Fig. 4, the energy barrier of a single surfactant entering the water phase is very high. This might be because of the attraction of the sodium ions at the surface that provide an energetic barrier. However, if two neighboring surfactants enter the water phase, the free energy barrier reduces. This leads to the conclusion that several surfactants exhibit a cooperative energy barrier reduction. However, calculations with more surfactants must be performed in the future.

In summary, surfactant heads pack in a square, the tails in a hexagonal fashion in the case of SOS. If calcium is used as counterions, the surfactant monolayer becomes irregular and the calcium cations have a very low mobility and hence should not be used for the synthesis as these features might increase defects. The surfactant monolayer seems to be quite stable at room temperature which means that this can be ruled out as significant influence of creating defects in the crystalline polymers.

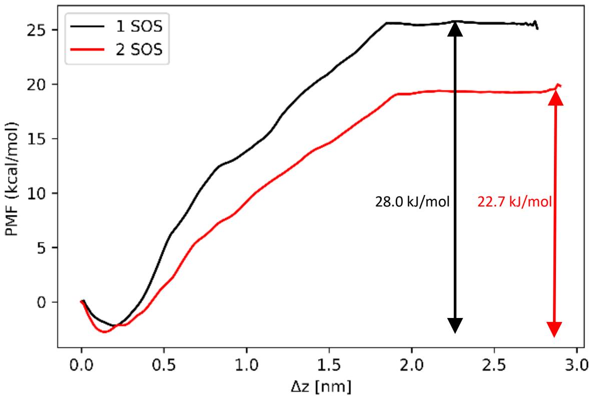

Figure 4: Potential Mean Force calculations which represent the barrier of 1 or 2 neighboring SOS moleculues entering the water phase.

Hofstadter's Butterfly for 2D Covalent-Organic Frameworks

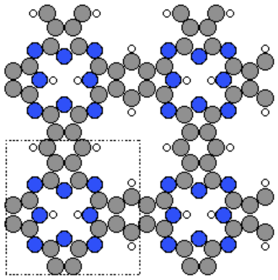

Figure 5: Structure that was used to create the Butterfly structure.

A Hamiltonian for a with DFTB optimized COF structure (see Fig. 5) was constructed by using π-orbital energy values of p_z-orbitals from Slater-Koster parameters. Then, using the Peierls-substitution, the hopping parameters were altered according to the applied perpendicular magnetic field and the density of states for a specific magnetic field could be calculated and by this the butterfly-structure. However, as seen in Fig. 6, the resulting pattern is very complicated. This is due to the complexity of the COF structure compared to graphene. There might be several underlying periodicities that are created by the different rings in the COF. Since there are many energy levels in the system, we need to simplify the Hamiltonian to get more insight and to create a clearer the Butterfly. This will be discussed in the Outlook section.

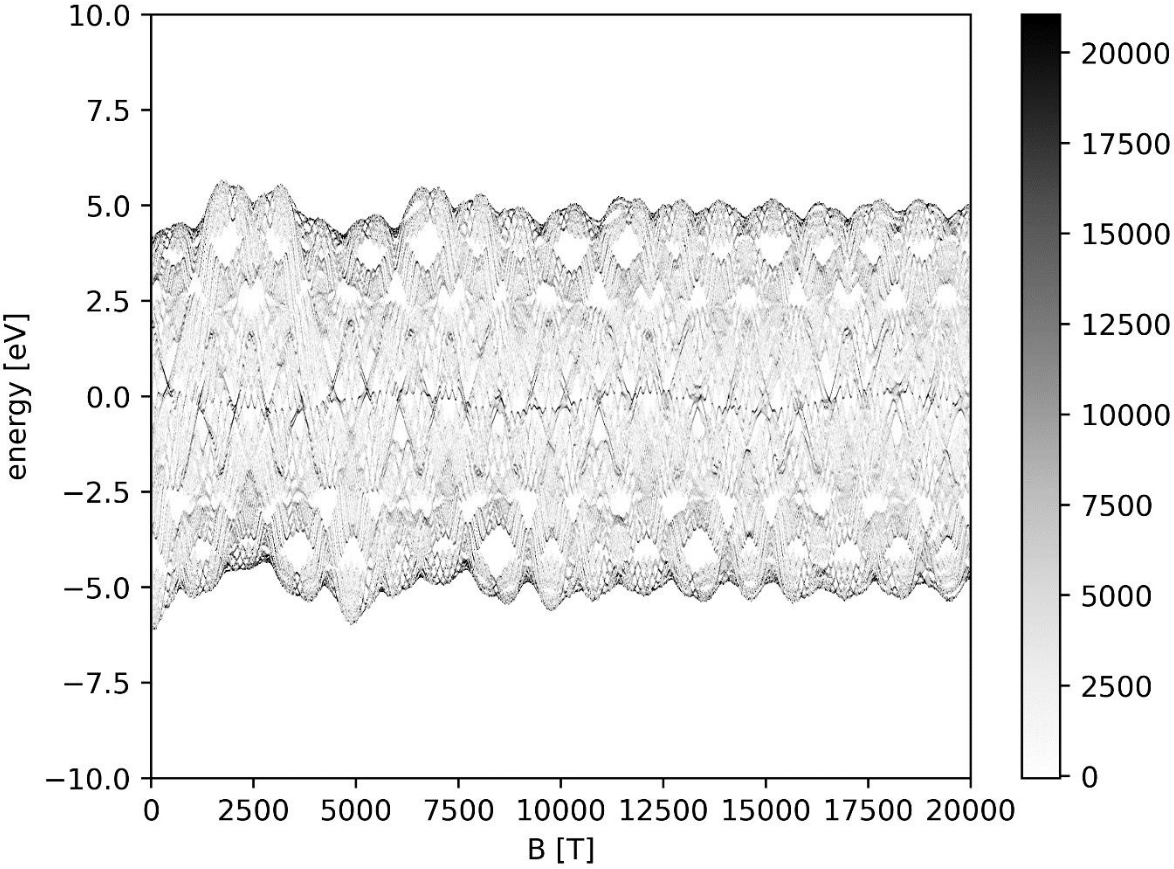

Figure 6: Density of states with respect to applied magnetic field vertically to the COF. The grayscale indicates the intensity of the underlying density of states.

Calculation of Energy Profiles for the HWE-Reaction

No meaningful results could be obtained because we found out that there exist many local minima for different substitutions. This means that it is very difficult to compare two different HWE reactions with different substitutions with each other because the local minima might differ a lot.

COLLABORATION WITHIN THE CRC

Primary cooperations

Project	Collaborator	Description
A09	**Rehnao Dong**	Investigation of the SMAIS method

Secondary cooperations

Project	Collaborator	Description
A1	**Xinliang Feng** Dr. Markus Richter Dominik Pastötter	Calculation of Energy Profiles for HWE-Reactions

OUTLOOK

Understanding 2D COF polymerization at interfaces

The next steps will be to see how different surfactants behave compared to SOS. Also, actual monomers will be included in the simulation to see how they interact with the surfactant monolayer and eventually get more insights into the preassembly.
A big challenge is to investigate actual reactions because usually MD simulations are not capable of that. For this, we are planning to use a crosslinking approach. Here, monomers that should react with each other are introduced in a simulation box and a MD simulation is started. As soon as two feasible monomers are close enough to each other, they will be connected. This will yield a polymer network which we can analyze in terms of crystallinity and defects to better understand which synthesis parameters are best suitable.
More potential mean force calculations will be performed for more surfactant molecules in different configurations.
Furthermore, an option might be to connect results from the surfactant simulations with the crosslinking simulations to obtain a more accurate model.

Hofstadter's Butterfly for 2D COFs

In future work, many other COFs of different topologies will be studied. We will try to find patterns that are characteristic for specific topologies. Furthermore, we will try to simplify our models as far as possible by generating simpler effective hamiltonians that represent the respective topology of the COFs to understand the features of the resulting butterflies.

Calculation of Energy Profiles for the HWE-Reaction

In the future we have to take into account many other configurations to get a feeling and a good sampling of the actual transition state. This will however require a substantial number of calculations.

References

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