Computational study of building blocks of 2D polymers confined on the surface of water

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Since the discovery of graphene, two-dimensional materials (2DMs) have become a primary target to study. A promising route in the synthesis of novel 2DMs is given by forming conjugated 2D polymers (2DPs) based on organic building-blocks (monomers) at an air/water interface through the Langmuir-Blodgett method [1]. It is important for the design of the 2DPs to understand the "adsorption" process of the monomers at the water surface and to control their structure on an atomic scale [2].

This work presents a computational study of two different molecules (polycyclic aromatic hydrocarbons) as suitable building blocks for 2DPs using classical Molecular Dynamics (MD) simulations and Density Functional Tight Binding (DFTB) calculations. The MD simulations reveal the preference of the monomers to stay at the air/water surface (Figure 1). Umbrella sampling simulations were conducted to obtain the potential mean force of pulling the molecule out from the water. The latter calculations show an energy minimum at the air/water interface, which is on the order of *-24* kJ/mol. Using the stable monomer geometries from the MD simulations, the formation of dimers at the air/water interface was investigated using the DFTB approach. It is found that the interface stabilizes a flat conformation of the dimer (Figure 2). Constructing ring geometries from the dimers we find different candidates for unit cells, which can realize crystals of the target 2DP. Finally, the stability and electronic structure of the crystals is investigated.

References

[1] H. Sahabudeen et al. Nature Communications **7**, 13461 (2016).

[2] R. Koitz, M. Iannuzzi, and J. Hutter. The Journal of Physical Chemistry C **119**, 4023 (2015).

Figures

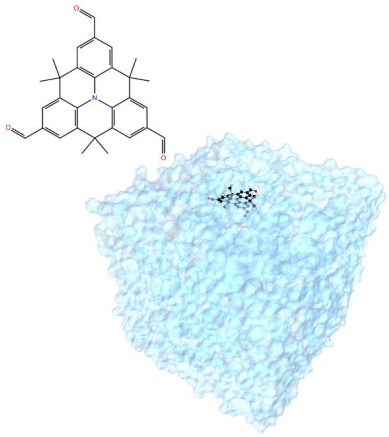

Figure 1. Sketch of the simulation cell consisting of the water slab and the monomer at the vacuum/water interface.

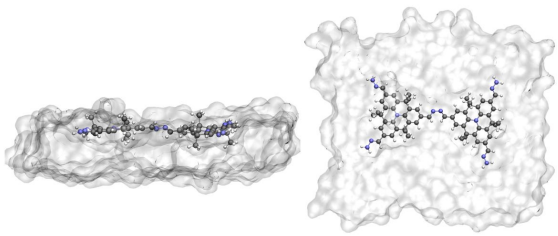

Figure 2. DFTB-MD simulations of the dimer placed on the water surface at *295.15* K.