Monolayers of molecules can be formed at a variety of interfaces, and over the years many techniques have been developed to construct them and to study the resulting organisation of the molecules. At a liquid-solid interface, 2D assemblies can be created by depositing a solution of the compound of interest on top of the substrate. Depending on the nature of the solvent, the substrate, and the dissolved molecules, the latter might form an ordered monolayer or multilayer at the liquid-solid interface. When the interactions remain relatively weak, the process is called physisorption. Advanced interface specific methods such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) are needed to study the interface at the nanoscopic level.

We focus on several aspects of self-assembly at the liquid-solid interface, ranging from the fundamentals to applications. We will discuss the concept of 2D crystal engineering and the effect of solvent, solute concentration and temperature, bringing insight into thermodynamic and kinetics aspects of the self-assembly process at the liquid-solid interface. Based on these insights, we demonstrate the self-assembly of several molecular systems at the liquid-solid interface for the formation of functional (nanoporous) networks and the functionalization of surfaces, including graphene. Applications range from surface-assisted enantioselective adsorption and separation of enantiomers, to tunable doping of graphene based field effect transistors.