Electronic states of Porphyrins at surfaces: The signature of supramolecular network formation

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Porphyrins are a family of aromatic molecules that gathers a strong community interest due to highly promising and successful surface applications, such as surface catalysis, lighting and energy harvesting. In applications, organic-inorganic structures with a few to several monolayer thick porphyrins films are utilized. Successful functionalization depends on the alignment of the porphyrin levels with the substrate. Investigation by state of the art spectroscopy techniques [1] reveal porphyrin-related HOMO and LUMO peaks and a HUMO-LUMO gap that cannot be satisfactorily explained by the common model of a standalone or adsorbed porphyrin. In order to unravel the nature of these features, we investigate supramolecular networks and film formation, and its influence on electronic and photophysical properties. The thickness of such films allows models based on e.g. experimentally reported crystal phase. Here we focus on H2TPP and MgTPP. Since these porphyrins possess large macrocycle and aromatic character, strong dispersive interactions arise. We use VdW-DFT for obtaining the structural properties, and many-body perturbation theory within the sc-qpGW-approach (calibrated against NIST data) for calculating the electronic spectra. The film formation involves a competition between the solvent energy and energy of formation [2]. Our *ab initio* calculations, and other work in the literature [3] suggest that the surface adsorption energy tends to be very close to film formation energy, thus, depending on the substrate, film formation or agglomeration of porphyrins are likely. A thick film leads to a considerable decrease in the HOMO-LUMO gap compared to the standalone molecule and also a non-symmetric peak broadening distinct from thermal broadening due to dispersion of the bands. The calculated HOMO-LUMO gap and the level-position agrees with the features seen UPS/2PPE spectra [1]. Our findings underline that the formation of films or supra molecular networks has important influence on the electronic levels.

References:

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