Investigation of Charge Transfer at Interfaces Involving Transition-Metal Phthalocyanines

***Naidel Caturello, Daria Gorelova**, Brandenburg University of Technology Cottbus-Senftenberg*

In Short

- Explicitly quantifying how excited states depend on the thickness of the substrate.
- Deliver ΔSCF-level calculations on these large-scale heterostructures, enabling direct comparison with time-resolved X-ray photoemission spectroscopy (XPS) experiments.
- Gain site-specific information about charge separation through the evaluation of partial charges and molecular orbitals.

Interfaces composed of molecular films host a plethora of phenomena related to electronic level alignment[1, 2], charge transfer states emergence[3, 4], and hybridization at the interfaces[5]. Beyond that, the adsorption of molecules onto a substrate can reconstruct the topmost layer of the substrate, changing its symmetry, while allowing the appearance of emergent phases, e.g., metallic[6, 7] or insulating[8, 9]. In particular, recent developments have highlighted that ultrafast excitation is capable of promoting collective structural rearrangements [7, 10], symmetry breaking [1, 11], and even transient chiral organization [12, 2].

Specifically, this class of materials presents efficient charge transfer that defines their emergent properties. The substrate layer thickness controls the electronic screening as the interfaces form[13, 14], while the change of the metallic center in the phthalocyanine defines the frontier orbitals, which in turn define the binding energies and the interaction between the electronic levels interaction of the molecule and the substrate. Optically-induced changes can be monitored by photoelectron momentum microscopy and x-ray photoemission spectroscopy (XPS) spectra intensities [10].

We intend to use ΔSCF method to describe their excited-states. The application of the ΔSCF method offers the description of excited-states using constrained occupation numbers in the self-consistent field approach combined with DFT [15]. It is a reasonable alternative to other ab initio techniques for excited states that can be computationally unfeasible for very large unit cells.

We anticipate to achieve the microscopic understanding of orbital-driven control of interfacial charge transfer establishing predictive design principles. Analyzing how electronic properties change depending on the substrate composition and thickness, we are going to gain physical insights about charge-transfer processes in these systems. In particular, we will analyze how charge density in the ground and excited states changes in different compositions. We also intend to calculate the partial charges of this class of interfaces in the ground and excited states in order to connect their variation to changes in XPS spectra due to varying binding energies.

Hence, to address these systems in details, the main objective of this project is to understand how (i) substrate thickness and (ii) its composition, and (iii) distinct transition-metals modulate the excited-states properties of MPc_2 having as substrates molecular films of C_{60} and $TiSe_2$, where M = Cu, Mn, and Pc = phthalocyanine. Experiments in these donor-acceptor systems have shown an efficient charge transfer at interfaces following a photo excitation. These systems are going to be investigated under the following aspects: (a) explicitly quantifying how excited states depend on the thickness of the substrate in these structures, (b) delivering ΔSCF-level calculations on these large-scale heterostructures, enabling a comparison with time-resolved X-ray photoemission spectroscopy (XPS) experiments, and (c) gaining a site-specific information about charge separation through the evaluation of partial charges and molecular orbitals. Within this theoretical approach, we intend to unify structural and electronic phenomena within one predictive framework which allows design principles for these interfaces.

WWW

`https://www.b-tu.de/en/fg-comp-materials`

More Information

More information can be found at the group's webpage (WWW Section) and in the following references:

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Project Partners

Dr. Markus Scholz, FLASH, DESY, Hamburg
Fahimeh Norouzi, University of Hamburg

DFG Subject Area

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