Optical studies of crystalline organic semiconductor films

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Organic-inorganic semiconductor hybrid systems are key components of dye-sensitized solar cells and have also been utilized on the basis of ZnO in combination with the p-type organic semiconductor pentacene for the fabrication of p-n junction diodes. To achieve a better understanding of the electronic coupling between molecular films and inorganic substrates, especially the relaxation dynamics and charge separation of excitonic excitations, well defined model interfaces with known molecular structure and orientation are desirable. At the example of structurally well defined crystalline organic thin films deposited on inorganic semiconductors of insulators the excitonic properties of the molecular films will be discussed. In combination with micro-spot spectroscopy it has been possible to perform azimuthally and polarization resolved absorption measurements on single crystalline domains.

In the case of pentacene on ZnO this allows to unambiguously identify both Davydov components of the exciton. Moreover, accompanied temperature dependent measurements reveal a reversible shift of the exciton energy which depend on the actual films thickness and can be attributed to a tensile strain at the organic/inorganic interface due to large differences in the thermal expansion of the organic film and the inorganic substrate [1]. Comparing pentacene films that were grown on both polar ZnO(0001) and ZnO(000-1) as well as on the mixed-terminated ZnO(10-10) surface yields for all substrates a uniform upright orientation which reflects the weak, essentially van der Waals type molecule-substrate interaction, hence making this a structurally robust system. Upon cooling, however, a slightly different relaxation behavior of the exciton energies was found for pentacene on the polar ZnO surfaces compared to the mixed-terminated surface which can be related to the anisotropic thermal expansion within the substrates [2].

In a more general context it would be preferable to also access optical excitations with transition dipole moments oriented along other molecular axes. This has been possible for the case of perfluoropentacene (PFP) because of a peculiar epitaxial growth relation on alkali halides. This yields azimuthally well aligned PFP crystallites with exclusive upright molecular orientation on NaF(100) and recumbent orientation on KCl(100), hence allows polarization resolved absorption measurements along different crystalline and molecular axis. In that way the orientation of the transition dipole moments of the various optical excitations were experimentally determined and a directional anisotropic exciton coupling was observed, which is attributed to the asymmetric molecular packing motif within the (100) plane of the PFP crystal lattice [3]. Time resolved pump-probe measurements on these films exhibit a pronounced polarization dependent response which can be attributed to the anisotropic packing within the (bc)-planes of PFP yielding additional evidence for a quasi-one dimensional electronic band structure.

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ZnO-based inorganic/organic systems from first principles

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The properties of hybrid inorganic/organic systems (HIOS) can be tuned by inserting dipolar layers at the interface between the two materials. To study the interface between ZnO and molecular dipole layers we use quantum mechanical first-principles approaches. To take the bulk doping concentration of ZnO into account, I here present an approach that introduces excess charge in the unit cell by means of the virtual crystal approximation with fractionally charged nuclei [1] and that includes the energy contribution of space-charge layers and the associated band bending explicitly. For the bulk terminated ZnO($000\bar{1}$) surface covered with half a monolayer of hydrogen (2x1-H), I demonstrate that electrons from bulk dopants can stabilize deviations from this half monolayer coverage at low hydrogen pressures [2]. Ambient hydrogen background pressures are therefore more conducive than ultra high vacuum conditions to form the defect free 2x1-H surface, which would be a more controlled substrate in HIOS [2]. For the interface between ZnO($000\bar{1}$) 2x1-H and tetrafluoro-tetracyanoquinodimethane (F4TCNQ) monolayers, I show that the adsorption energy and the charge transfer to the molecules depend strongly on the bulk dopant concentration. While the build-up of a space-charge layer is not unexpected, the magnitude of its effect is astounding: the adsorption energy of F4TCNQ changes by more than 2 eV and more than doubles from low to high doping. In the limit of low bulk doping concentrations, charge transfer becomes vanishingly small in agreement with photoemission data [3], while the F4TCNQ induced work function increase remains unaffected and large. The bulk doping concentration and the associated build-up of a space-charge layer therefore provide an additional way to tune the interface properties in HIOS. For the mixed terminated ZnO($10\bar{1}0$) surface, I show that pyridine monolayers lead to large work-function reductions [4]. Based on simple alignment considerations, I illustrate that even larger work function modifications should be achievable using molecules with negative electron affinity [4].

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