Electrostatic-Field Driven Alignment of Organic Oligomers on ZnO Surface

The physisorption of organic oligomers on the strongly ionic ZnO(1010) surface has been studied by Fabio della Sala (NNL, Lecce), Sylke Blumstengel, and Fritz Henneberger (both **IRIS Adlershof** and Department of Physics HU Berlin). In previous experiments (see S. Blumstengel et al., Phys. Chem. Chem. Phys. 12, (2010) 11642), it has been found that sexiphenyl adsorbs on this surface in a well-defined orientation where the long axis of the flat-lying molecules is aligned perpendicular to the c-direction of the ZnO crystal. Using first-principles density-functional theory and non-empirical embedding methods, it could be demonstrated that this observation is representative of a generic scenario related to the strong dipolar electrostatic field created by the ZnO surface dimers. The electrostatic molecule-substrate coupling is characterized by a linear relation between the in-plane variation of the interaction energy and the molecular dipole moment induced in vertical direction. Long oligomers with a highly axial π-electron system are aligned along rows of positive electric field. The energies required for reorientation reach some 100 meV. These findings define a new route towards the realization of highly ordered self-assembled arrays of oligomers/polymers on inorganic semiconductors as well as for the interfacial energy level adjustment.

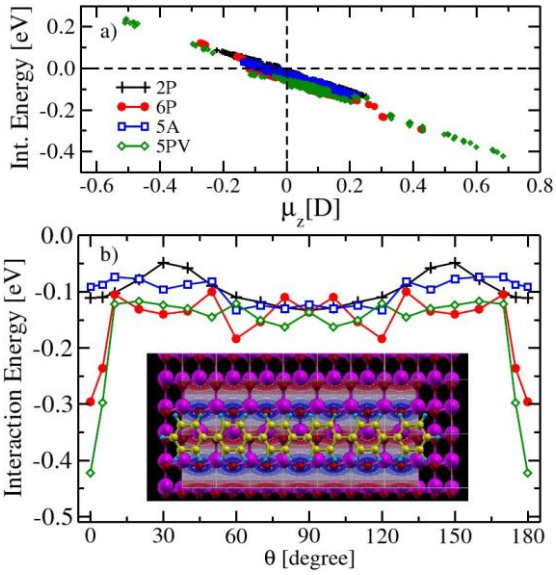

Fig.: Electrostatic molecule-substrate interaction energy for biphenyle (2P), sexiphenyl (6P), pentacene (5A), and penta-phenylene-vinylene(5PV) on ZnO(1010). a) Linear relation between the interaction energy and the molecular dipole moment μz induced in vertical direction. The points are obtained by sampling 1470 different molecular configurations.
b) Interaction energy versus rotation angle Θ defining the orientation of the long molecular axis relative to the direction perpendicular to the (1010) axis. Inset: Orientation of 6P at the global minimum shown on a colormap of the vertical component Fz of the dipolar electrostatic field generated by the ZnO(1010) surface. Vertical distance from surface is 3.5 Å.

This work was carried out in the framework of the CRC 951 and published on: 30 September 2011 in: Phys. Rev. Lett. 107 (2011) 146401 DOI: 10.1103/PhysRevLett.107.146401