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Energy-level alignment in donor-acceptor monolayers and bilayer blends on metals

The development of organic hetero-junction devices, such as photovoltaic cells and organic light emitting diodes demands the ability of tailoring physical/chemical properties at both metal-organic and organic-organic interfaces. One possible strategy to steer the structural and electronic properties at interfaces is to use molecular mixtures such as donor-acceptor molecular pairs. Through a powerful combination of surface sensitive techniques, we determine the structure, the energy level alignment and interfacial charge transfer of two-dimensional donor-acceptor monolayers in direct contact with noble metal (111) surfaces. The formation of an ordered mixed layer with a maximized donor-acceptor contact area leads to a characteristic energy level alignment at the molecule/metal interface regardless of the particular molecules and substrate. By appropriate design of the supramolecular environment, charge transfer into empty molecular levels can be triggered across the metal-organic interface without the need to intercalate substrate-functionalizing buffer layers.

This study is also extended to molecular bilayers made of variable donor-acceptor blends. Core-level and valence band photo emission reveals that upon capping, electronic states of both contact and capping layers “realign” with respect to the monolayer and the multilayer references. Such rigid, donor/acceptor shifts are explained assuming a variable, local electrostatic potential that molecules sense upon mixing or capping with other species.

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