

# Near- and Far-Field Effects on Excited States at Organic Semiconductor / Metal Interfaces

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We present an investigation of the evolution of highly excited states at the interface of the dipolar organic semiconductor vanadyl naphthalocyanine on highly oriented pyrolytic graphite. Using two-photon photoemission we observe several image states at sub-monolayer to few-monolayer coverages: The first image state evolves seamlessly out of the graphite image state, with *increased* binding energy between zero and one monolayer, while the second image state appears at coverages of just below one monolayer and is pinned to the vacuum level. These findings can be understood in the context of a simple electrostatic model [1] that considers how molecular levels and vacuum level are influenced differentially by the the strong electrostatic fields present at the interface with dipolar molecules: While the vacuum level rises continuously with coverage, the molecular states are significantly depolarized as a function of electric fields in the near-field regime. This depolarization, while originally generating a hybrid molecular anion / graphite image state whose binding energy increases with coverage, ultimately diminishes the coupling of the image state to the molecular affinity level by driving the affinity level out of resonance with the image state. Interfacial electrostatic fields may therefore be used to manipulate in a concrete fashion interfacial charge transfer processes such as indirect photoinduced interfacial electron transfer.

[1] Michael L. Blumenfeld, Mary P. Steele, Oliver L.A. Monti, *J. Phys. Chem. Let.* **1**, 145 (2010)