



## Mechanism of the Fermi level pinning at organic donor–acceptor heterojunction interfaces

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### ABSTRACT

We investigate the energy level alignment and the Fermi level pinning mechanism at organic donor–acceptor heterojunctions interfaces by using the model organic–organic heterojunctions (OOHs) with well-defined molecular orientation of the standing copper (II) phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc) films on the standing copper-hexadecafluoro-phthalocyanine (F<sub>16</sub>CuPc) thin films on SiO<sub>2</sub>. We identify two distinct regions for the energy level alignment by *in situ* ultraviolet photoelectron spectroscopy investigation. In region (I) where the work function (WF) of the underlying substrate is larger than the ionization potential (IP) of the top organic layers, the substrate Fermi level is pinned at the leading edge of the HOMO peak accompanied by a decreasing of the WF; in region (II) where the WF is smaller than the IP of the top organic layers, a downward shift of both the HOMO and vacuum level is observed. In connection with the defect induced gap states, we provide a detailed explanation for this thickness dependent energy level alignment and Fermi level pinning mechanism at the organic donor–acceptor OOH interface.

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### 1. Introduction

Understanding the energy level alignment at organic–organic heterojunction (OOH) interfaces is crucial for organic electronic devices, such as OOH-based organic photovoltaic cells (OPVs), organic photodiodes and organic light-emitting diodes (OLEDs). It is of key importance for determining the electron and hole injection barriers in OLEDs or open circuit voltages and charge collection in OPVs [1–6]. Intensive research efforts have been devoted to establishing a general mechanism that governs the energy level alignment at these interfaces with limited success [4–14]. Various models, including the integer charge transfer (ICT) [10] model and the induced density of

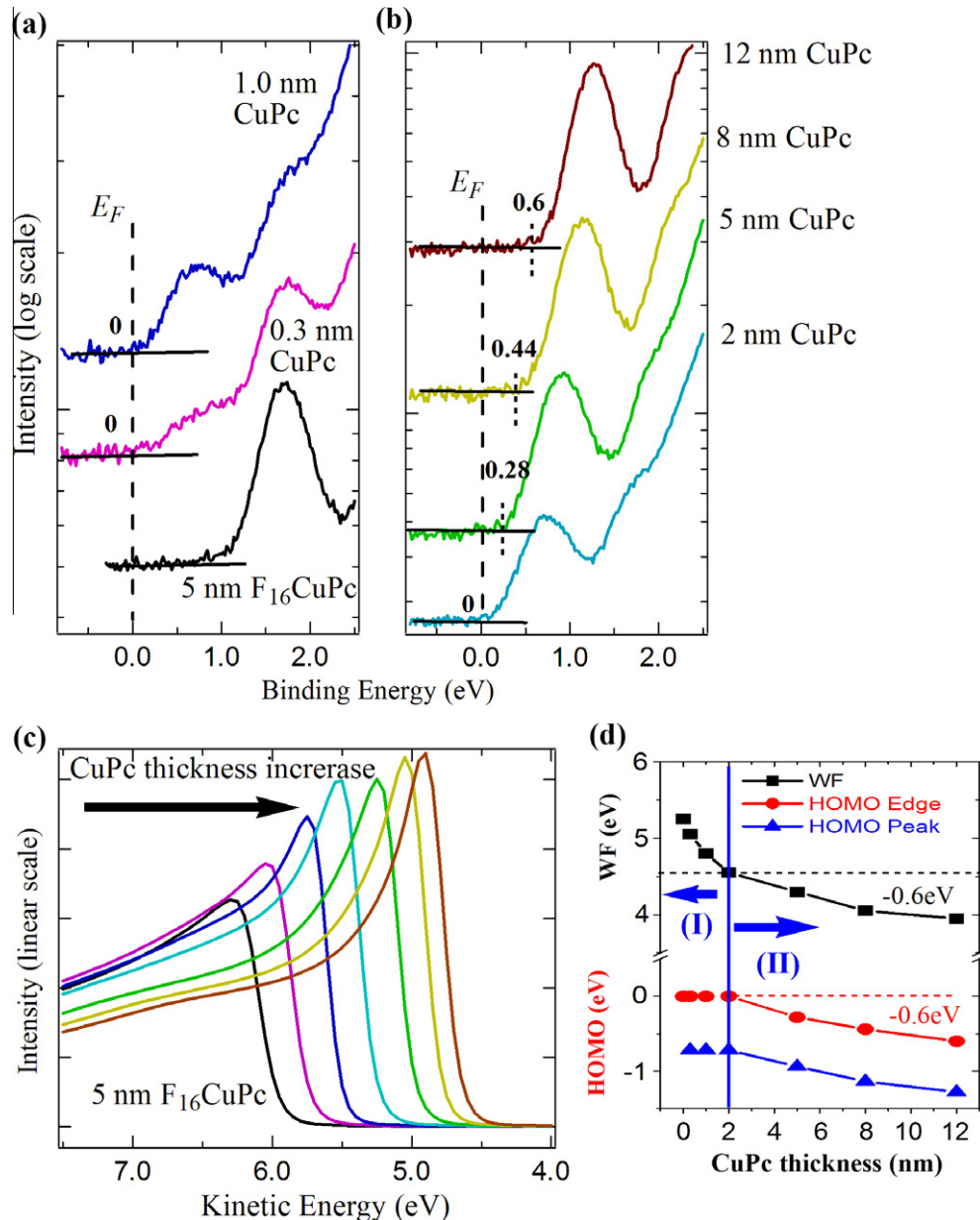
interface states (IDIS) [8,15] model, have been proposed. It is also argued that the tiny density of gap states, which is induced by defects and/or disorder in the molecular packing structure, determine the interfacial energy level alignment as well as the position of the highest-occupied-molecular-orbital (HOMO) with respect to the Fermi level [8,12,16,17]. Moreover, the highly anisotropic nature of  $\pi$ -conjugated organic molecules leads to the orientation dependent charge transport, as well as the electronic structures of highly ordered organic thin films, such as ionization potential (IP) of organic films and the interfacial dipole formation at the donor–acceptor OOH interfaces [18–22]. These can further complicate the understanding of the energy level alignment at the OOH interfaces. Therefore, it is necessary to carry out detailed investigation to understand the energy level alignment mechanism at the OOHs with well-defined supramolecular arrangement or molecular orientation.

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Using well-oriented polar phthalocyanine (Pc) monolayers on graphite surface to control the substrate work function, Fukagawa et al. [12] have demonstrated the role of the IP in vacuum-level alignment at organic semiconductor interfaces. When work function of substrate is smaller than the IP of the standing pentacene films, the vacuum-level alignment can be observed; whereas for substrate work functions exceed the IP of the pentacene films, the Fermi level of the substrate is pinned with the HOMO of the pentacene films due to spontaneous electron

transfer under thermodynamic equilibrium. Similar pinning effect relative to the substrate Fermi level was also observed by Koch et al. [23] for pentacene on several polymer substrates with different work functions, due to a charge transfer reaction between neutral pentacene molecules and poly(3,4-ethylenedioxythiophene)/poly(styrene-sulfonic acid) (PEDT/PSS) substrate cations in the presence of sulfonate moieties. However, in both cases the thickness of the pentacene thin films is no more than 2.0 nm corresponding to one or two monolayer of the standing



**Fig. 1.** Synchrotron-based UPS spectra for the deposition of CuPc on F<sub>16</sub>CuPc film on SiO<sub>2</sub> at (a and b) the low-binding energy part near the  $E_F$  region (the intensity is on a log scale) and (c) at the low-kinetic energy region (secondary electron cut-off and the intensity is in linear scale) with a sample bias of  $-5$  V. (d) Plot showing the change of the work function, CuPc HOMO edge and HOMO peak maximum as a function of CuPc thickness. All spectra are measured with photon energy of 60 eV. All binding energy are relative to the Fermi level position of the electron analyzer.

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