



The importance of gap states for energy level alignment at hybrid interfaces



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ABSTRACT

Energy level alignment and electronic structure at organic semiconductor interfaces must be controlled to ensure efficient carrier harvesting or injection in next-generation organic optoelectronic technologies. In this context, hybrid organic/inorganic semiconductor interfaces exhibit particularly rich physics. Here, we show that states in the band gap of the inorganic layered van der Waals dichalcogenide SnS_2 play an important role in determining energy level alignment at the hybrid interface with copper phthalocyanine (CuPc). By taking advantage of the closely related CuPc film growth on SnS_2 and the well-studied interface of CuPc/HOPG, we are able to trace spectroscopic differences to the fundamentally different electronic interactions across the two interfaces. We provide a detailed picture of the role of gap states at the hybrid interface and shed light on the electronic properties of inorganic semiconductors in general and metal dichalcogenides in particular.

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1. Introduction

The energy level alignment at organic semiconductor interfaces is a critical factor in determining the performance of organic optoelectronic devices. There are many elements that establish this alignment [1–4], and a predictive and quantitative understanding of these interfaces has remained elusive, despite a great deal of progress in elucidating and modeling the electronic structure of organic thin films. In particular, molecular states with energies in the band gap of the organic semiconductor have recently drawn significant attention as an important factor in determining charge-injection or -extraction barriers [3–6]. Here, we extend this growing understanding to the hybrid heterointerface between organic and inorganic semiconductors. We show how gap states in the *inorganic* semiconductor also develop a significant influence on the interfacial energy level alignment, in ways that are not expected from current models for organic semiconductor interfaces.

We compare the interfaces developed by the prototypical organic semiconductor copper phthalocyanine (CuPc) on the quasi-2D layered materials tin disulfide (SnS_2) and highly ordered pyrolytic graphite (HOPG). These substrates are structurally related but exhibit fundamentally different electronic properties near the Fermi level, ideally suited to highlight the influence of substrate gap states on energy level alignment. Comparison between CuPc/ SnS_2

and CuPc/HOPG is facilitated by seminal work on CuPc/HOPG and related systems by the group of Ueno [5–12], enabling us to reveal the different physics that emerge at organic/inorganic *hybrid* interfaces.

In the spirit of a *festschrift* article, and to honor these contributions, we start by briefly reviewing salient features of interfaces of phthalocyanines on layered surfaces. For a more general description of molecular behavior at interfaces, we refer to several recent publications [4,13,14]. Taking advantage of the atomically flat surface of layered materials such as HOPG and the transition metal dichalcogenides (TMDs), considerable effort has been spent on establishing the growth and structure of the molecular film. Dispersion interactions are typically much weaker across this type of interface than *e.g.* on coinage metal surfaces [15,16]; as a result, the molecular film structures on different layered van der Waals materials resemble each other strongly. Indeed, the thin film structure of various phthalocyanines has been compared on molybdenum disulfide (MoS_2) and tin disulfide (SnS_2) using techniques such as angle-resolved ultraviolet photoemission spectroscopy (ARUPS) and low-energy electron diffraction (LEED) [7,9,17–19]. Such structural understanding is essential for a correct interpretation of the interfacial electronic structure as revealed *e.g.* by photoelectron spectroscopies [20,21].

Large workfunction drops observed at the interface of phthalocyanines and TMDs reflect a strongly perturbed electronic structure and may in fact obscure some of the more subtle interactions [10,22]. HOPG provides however a highly suitable structural analog to TMDs, promoting nearly identical film growth while

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providing an electronically more inert surface. As a result, the interfacial electronic structure developed at organic/HOPG interfaces reveals a wide range of phenomena previously concealed in the initial investigations on TMDs. Very narrow ultraviolet photoemission peak widths were observed for CuPc/HOPG. If interpreted as homogeneous linewidths, these measured peak widths enable the calculation of photohole lifetimes, providing a first principles estimate of carrier mobilities at the interface [8]. Growth of an ordered layer of dipolar titanyl phthalocyanine (TiOPc) was shown to create a uniform electrostatic field at the interface [11], which enables extrinsic control of the surface electronic structure [11,23]. This theme has since then been picked up more generally and extended to a broad class of self-assembled monolayers [24–27].

The exquisite spectroscopic resolution available for interfaces of organic semiconductors with HOPG has been instrumental in uncovering the importance of gap states in determining interfacial energy level alignment. First indications in this direction were obtained from the discovery of a reversible phase transition for CuPc at 130 K on HOPG, which alters the electronic structure at the interface [28]. Further details regarding the role of gap states were revealed by using layered van der Waals materials, such as MoS₂, as a template for ultraflat metallic substrates, as e.g. achieved by growing a thin layer of indium [29]. Metastable atom electron spectroscopy (MAES) of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on such a structure revealed strong interfacial interactions due to gap states induced in PTCDA [29], also observed for other molecule/metal systems [30,31]. Strikingly, defects in molecular packing of pentacene on HOPG were demonstrated to control the energy level alignment, explained by a perturbation of the pentacene highest occupied molecular orbital (HOMO) and consequently a change of the conditions for Fermi level pinning [32]. The importance of gap states in the organic thin film was made explicit with their reversible creation by exposure to inert gas, suggested to penetrate and alter the thin film structure [5,6,33]. These experiments demonstrate that the energy level alignment may be controlled by a relatively low density of states (DOS) in the organic thin film. This density of gap states (DOGS) pins the molecular states at the Fermi energy and thus limits the extent to which carrier injection barriers can be minimized. The DOGS is typically quite small and hence still rather challenging to detect [5,6,32,33], thus obscuring more detailed insight into the origins of energy level alignment at organic/metal interfaces.

Therefore, an understanding of the electronic structure of organic semiconductor interfaces that incorporates the influence of a DOGS provides a powerful basis for predicting energy level alignment. Some essential ideas in this context were recently summarized by Oehzelt et al. [3]. One of the primary conclusions from this body of work is that the charge injection/extraction barrier can be minimized by reducing the DOGS in the organic semiconductor film, which reduces the propensity for Fermi level pinning. In addition to minimizing the organic semiconductor gap states arising from e.g. structural packing/defects [5,6,32,33], the DOGS can also be reduced by attenuating electronic coupling to metallic electrodes [3].

Assuming for the sake of simplicity similar interfacial electronic coupling matrix elements between substrate and organic semiconductor, replacing the metallic substrate with an inorganic semiconductor might therefore be expected to result in improved energy level alignment. This stems from a typically much reduced substrate DOS vis-à-vis clean metal surfaces. This prediction is however not born out experimentally, even for the quasi-2D transition metal dichalcogenides (TMDs) that present atomically flat and inert surfaces and generally substantial bandgaps in the range of 1–2 eV. Hydrogen and lead phthalocyanine (H₂Pc and PbPc) each establish significant interface dipoles when deposited on MoS₂ [10,22], despite the fact that the ionization energy of these

molecules is in excess of the substrate workfunction. This implies the existence of strong interfacial interactions despite the presumed low DOS in the MoS₂ bandgap. Furthermore, the interfacial electronic structure of MoS₂ was observed to depend significantly on the surface preparation [10], demonstrating that the electronic character of the TMD surface is rather sensitive to structural effects. Based on previous work in a related system, these observed interfacial interactions may in fact arise predominately from a finite DOGS in the *inorganic semiconductor substrate* rather than in the organic thin film [34]. Indeed, ground-state interfacial charge transfer between CuPc and substrate defects has previously been demonstrated to control energy level alignment at the hybrid CuPc/indium phosphide (InP) interface [35]. Although the relevance of this mechanism for the inert TMD surfaces is somewhat surprising, it is also supported by the observation of defect-induced carrier scattering and trapping near the TMD surface [36,37], dynamic shifts in energy level alignment at TMD interfaces [34], and electronic coupling between different stacked van der Waals materials [38].

To explore this phenomenon and elucidate the role of these gap states on the interfacial energy level alignment, we compare here the interfacial electronic structure of CuPc on the two related layered materials HOPG and SnS₂. HOPG is a layered semimetal, and the CuPc/HOPG interface has been studied extensively as a model of a nonreactive organic semiconductor interface [8,11,28,39,40]. We therefore use this system as a reference for the more electronically active surface of the layered semiconductor SnS₂. Since film structure can play an important role in the electronic structure at organic semiconductor interfaces, we have deliberately chosen these substrates to provide as similar growth modes as possible while varying the *electronic* nature of the substrate. Previous research has already established the high degree of similarity of molecular growth on SnS₂ and HOPG for several different organics, showing that both surfaces support Stranski–Krastanov growth [41,42]. This is consistent with our spectroscopic observations presented below as well. Moreover, this conclusion is further supported by STM studies of CuPc monolayers on MoS₂ and HOPG, which indicate similar packing structures and unit cells for both interfaces [43,44]. Therefore, one may anticipate that significant differences observed between CuPc/HOPG and CuPc/SnS₂ should be attributed to changes in the interfacial electronic interactions, rather than to trivial differences in the organic thin film growth. We will revisit this proposition at several points in the remainder of our report, demonstrating how differences in film structure are insufficient to explain the observed phenomena.

After a brief summary of experimental details, we compare the interfacial energy level alignment for CuPc/HOPG and CuPc/SnS₂. We observe that HOPG provides an inert substrate with virtually no vacuum level offset and thus a rather low DOGS. In contrast, the CuPc/SnS₂ interface displays interactions that can only be fully explained by a finite DOGS *in the substrate*. Finally, we discuss the nature and identity of these observed gap states for SnS₂.

2. Materials and methods

All photoelectron spectra were collected at room temperature in a VG EscaLab MK II photoelectron spectrometer, base pressure 2×10^{-10} Torr, with a He(I) lamp (Specs UVS 10/35, 30° angle of incidence from normal) as an excitation source. Spectra were referenced to the Fermi energy of the analyzer, which was calibrated using a sputter-cleaned Au foil. The sample workfunction was measured from the baseline intercept with the spectral slope at the inflection point of the secondary electron cutoff (SECO); a –5 V bias was applied for workfunction measurements to obtain a clear SECO. Spectra were recorded with a takeoff angle of 0° with respect to

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