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Interfacial electronic structure of vanadyl naphthalocyanine on highly ordered pyrolytic graphite

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ABSTRACT

We present a core and valence region spectroscopic analysis of the interfacial electronic structure of thin films of vanadyl naphthalocyanine (VONc) deposited onto highly oriented pyrolytic graphite (HOPG). X-ray photoelectron spectroscopy indicates the predominantly ionic character of the vanadyl metal center coordinated by the heterocycle and affords the bandgap in the thin VONc films. Valence band photoelectron spectroscopy points to the existence of three different adsorption geometries of VONc on the HOPG surface. The distribution of the different geometries can be systematically influenced in a simple post-deposition processing step, with an immediate effect on the interfacial electronic environment. We find spectroscopic evidence in the valence levels that VONc grows on HOPG most likely in a 2D-gas fashion rather than by nucleation and growth of islands. These data allow us to predict accurately the interface dipole in the case of a broad class of dipolar organic semiconductors, based simply on molecular dipole moment, polarizability and molecular diameter. This ability provides an important step towards rational optimization of energy level alignment in organic electronics.

1. Introduction

The process of interfacial charge transfer plays a critical role in determining the efficiency of organic photovoltaic cells. Consequently, a fundamental understanding of the interfacial electronic structure is necessary in order to optimize device design. In particular, the formation of interfacial dipoles has drawn significant attention, with the majority of studies concentrating on the organic/electrode interface [1–7]. The source of this dipole appears to depend strongly on the specifics of the interfaces involved. Its magnitude, reflected in the position of the vacuum level, can be measured sensitively using UPS. While still the subject of intense debate, possible origins of the interface dipole include "push-back" of the surface electron density [8], an induced density of states [9,10], charge transfer across the interface [11], chemisorptive interactions [12] and fields induced by dipolar molecules [13]. The notion of an interface dipole implies a change in the electrostatic potential across the interface while leaving the molecular electronic structure unaffected: The molecular IP stays constant and the binding energies of electrons originating from molecular levels such as the HOMO shift rigidly by an amount identical to the shift in the vacuum level [14]. This assumption is however not necessarily correct, as shown in cases where image potential, molecular polarization energy, orientation on the surface, molecular packing and strong interfacial fields can cause significant changes in the IP [15–19]. The interplay between molecular and interfacial electronic structure is therefore far from clear and depends sensitively on the thin film organization, making predictive control of interfacial energy level alignment still a challenge.

Systematic investigations of single systems are therefore important in order to assess the evolution of the electronic structure and molecular organization at the interface. Here we focus on VONc whose properties are well-suited to this purpose: Like Pcs, VONc can be vacuum-deposited, allowing the growth of well-defined interfaces from sub-ML to many ML coverage [20]. The molecule is near-planar with a permanent dipole moment of 2.7(4) D in the thin film phase [15]. VONc is structurally related to the phthalocyanines [21–23], with a considerably larger polarizability providing high sensitivity to the local electrostatic environment [15]. VONc interacts weakly with HOPG or other van der Waals surfaces, permitting high resolution spectroscopic band analysis and revealing thus subtle changes to the electronic structure [15]. In addition, VONc has a large absorption cross-section in the near-infrared and an optical gap of 1.5 eV [24], making it suitable for photovoltaic applications.

We use core and valence band photoelectron spectroscopy to study interfacial thin film structure and growth. We find that VONc organizes in different orientations on the surface, providing a range of local electronic environments. We show that these populations can be controlled by annealing at modest temperatures, with a profound influence on the electronic structure. Importantly, the interface dipole

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Abbreviations: UPS, Ultraviolet photoelectron spectroscopy; ML, Monolayer; MLE, Monolayer equivalent; HOMO, Highest occupied molecular orbital; Nc, Naphthalocyanine; Pc, Phthalocyanine; IP, Ionization potential; SECO, Secondary electron cut-off; HOPG, Highly oriented pyrolytic graphite; DFT, Density functional theory; FWHM, Full-width-half-maximum; DOS, Density of states.

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is predominantly controlled by molecular packing density, polarizability and dipole moment, representative of weak intermolecular electrostatic coupling [13,15]. This allows a predictive comparison of the interface dipole across a class of dipolar organic semiconductors, offering an avenue towards determining energy level alignment at interfaces that is potentially applicable to a wide range of systems. The detailed knowledge of the interfacial electronic structure can also be used to assess the growth mode of VONc on HOPG.

The paper is organized as follows: We start with a brief discussion of the experimental procedure, followed by photoelectron spectroscopy results of thin VONc layers in both the core and valence region. We then discuss the origin of the interface dipole in dipolar phthalo- and naphthalocyanines on HOPG and use the spectroscopic evidence to investigate growth of thin VONc films on HOPG.

2. Materials and methods

VONc was purchased from Sigma-Aldrich and used without further purification by sublimation from a home-built shuttered Knudsen cell. For degassing, the cell was slowly ramped from 100 °C to 450 °C over 3 h and kept at this temperature for approximately 20 min to establish a consistent evaporation rate. This procedure was found to minimize the risk of thermal decomposition of VONc prior to and during evaporation at 450 °C. HOPG was purchased from SPI (grade SPI-1, similar to ZYA), freshly cleaved and annealed in UHV for 12 h at 450 °C on a VG-style heater stub. Sample deposition occurred at 1 Å/min in a custom-built deposition chamber, with a base pressure of less than $8 \cdot 10^{-10}$ Torr. Film thicknesses were determined using a quartz crystal microbalance calibrated by XPS and the vacuum level shift in the annealed film [15], with 1 MLE corresponding to 5 Å for a complete monolayer of oriented VONc. The sample was introduced into the photoelectron spectrometer (VG EscaLab MK II, base pressure $5 \cdot 10^{-10}$ Torr) equipped with an integrated sample heater. All UPS spectra were referenced to the Fermi energy E_F and collected at room temperature using a He(I) lamp (SPECS UVS 10/35, 30° angle of incidence from normal) with a take-off angle of 22° with respect to normal, -5 V sample bias and 10 eV pass energy. The off-normal take-off angle did not affect the spectral peak positions, in agreement with recent findings for TiOPc on HOPG [25]. The vacuum level was measured from the baseline intercept with the spectral slope at the inflection point in the low kinetic energy region. From deconvolution of the Au Fermi edge a spectral resolution of 96(8) meV was determined. Note that the precision with which a spectral peak position can be determined is however much higher and determined by both experimental repeatability and the quality of spectral peak fits (centroid determination). For peaks near E_F we found this uncertainty to be less than 10 meV. Core level spectroscopy of VONc on sputter-cleaned Au foil and freshly cleaved and annealed HOPG was performed in a Kratos Axis XPS/UPS system using the monochromatized Al Kα anode with a pass energy of 20 eV. Peak positions were determined in accordance with the NIST XPS calibration protocol and based on nearby photoemission lines such as the Au 4f line where possible. A Shirley background was subtracted from all XPS spectra.

Computations and geometry optimizations for isolated VONc molecules were carried out using NWChem [26] by DFT at the unrestricted PBEh level, using a 6–31 g** basis set for C, H, N and O and an extended SDD (Stuttgart RSC 1997 ECP) basis set for V [27–30]. This level of theory has been demonstrated to give a reliable DOS, ground state structure and reasonable optical gap for CuPc and other metal-containing systems [31,32].

3. Results

3.1. Molecular structure

Fig. 1a shows a calculated molecular gas phase structure of VONc. The molecule is slightly puckered with a C_{4v} symmetry induced by the VO-group located above the molecular plane. The molecule has a calculated dipole moment of 2.8 D, in excellent agreement with experiment [15].

The molecular structure and Kohn–Sham orbitals strongly resemble those of the related Pcs such as *e.g.* VOPc or TiOPc [21,25]. Fig. 1b shows the VONc HOMO with the characteristic node at the metal center found also in all Pcs. This suggests that the ground state electronic structure should be comparable across a set of Pcs and Ncs with different metal centers. The calculations reproduce the molecular density of states reasonably well when compared to the UP-spectrum of a 10 MLE VONc film (Fig. 1c). They show clearly that the HOMO is separated noticeably from the lower-lying MOs, with a large electronic DOS only appearing below 2 eV relative to the Fermi energy.

3.2. Core level spectra

The elevated sublimation temperatures require evidence of successful deposition without molecular decomposition. To this end and in order to characterize the electronic structure of VONc/HOPG completely as necessary for a comparison with the Pc systems, we performed XPS measurements. In order to be able to observe the C 1s bands free from interference by HOPG, we acquired Al Kα XP-spectra of a 5 nm thick VONc film on polycrystalline Au. Aside from obtaining electronic structure information, this also helps with verifying intact deposition in the face of the required elevated sublimation temperatures. Fig. 2a shows the C 1s region, where the solid line represents a non-linear least-squares fit of the spectrum using a series of Voigt profiles. The two principal features, located at 284.4 eV and 285.5 eV with widths of 0.95 eV and 0.90 eV, are assigned to the two chemically distinct types of carbon atoms present, *i.e.* the naphthalene and pyrrole carbons. The integrated intensity ratio of 5.2:1 is in good

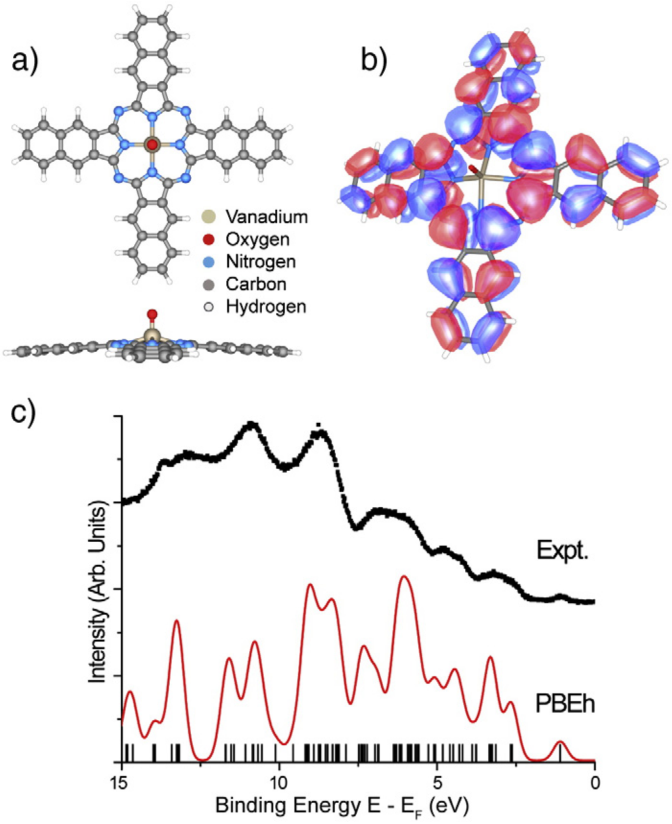

Fig. 1. a) Molecular structure of VONc obtained by DFT at the PBEh level. b) VONc HOMO. c) Comparison of experimental UP-spectrum of 10 MLE VONc on HOPG, unannealed, and DOS from DFT, convoluted with a Gaussian of 0.4 eV width.