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Integer Charge Transfer and Hybridization at an Organic Semiconductor / Conductive Oxide Interface

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ABSTRACT

We investigate the prototypical hybrid interface formed between PTCDA and conductive n-doped ZnO films by means of complementary optical and electronic spectroscopic techniques. We demonstrate that shallow donors in the vicinity of the ZnO surface cause an *integer* charge transfer to PTCDA, which is clearly restricted to the first monolayer. By means of DFT calculations, we show that the experimental signatures of the anionic PTCDA species can be understood in terms of strong hybridization with localized states (the shallow donors) in the substrate and charge back-donation, resulting in an effectively integer charge transfer across the interface. Charge transfer is thus not merely a question of locating the Fermi level above the PTCDA electron-transport level, but requires rather an atomistic understanding of the interfacial interactions. The study reveals that defect sites and dopants can have a significant influence on the specifics of interfacial coupling and thus on carrier injection or extraction.

INTRODUCTION

The interface between organic semiconductors and electrodes plays a central role in organic-based optoelectronics and next-generation energy conversion technologies, since they control charge collection and charge injection. Specifically, the organic / metal interface has been the subject of intense study: Exchange correlation effects, chemisorption vs. physisorption, local electric fields and gap states, among others, are considered to be key factors in establishing energy-level alignment and ultimately carrier dynamics.¹⁻⁶ In contrast, interfaces between organic semiconductors and transparent conductive oxides (TCOs) have received less attention. Compatible with the properties of organic semiconductors, TCOs function as low-temperature processable semiconductors and are used as charge-selective interlayers or transparent electrodes.⁷⁻⁹ In comparison to metal surfaces, the complex surface chemistry of TCOs, much reduced screening, and the presence of a bandgap, alter interfacial coupling pathways and mechanisms. However, a molecular level understanding of the interfacial electronic structure at such hybrid interfaces is still far from being complete.¹⁰

Due to its abundance and facile solution processing, ZnO films have received renewed attention in hybrid organic / inorganic electronics.¹¹⁻¹⁴ Several studies have also investigated specific organic / ZnO interfaces, both theoretically and experimentally.¹⁵⁻¹⁸ Winget *et al.* previously reported the formation of interface states at an organic / ZnO interface, attributed to the presence of specific gap states in highly conductive ZnO films.¹⁹ Indeed, electronic coupling between molecules and the ZnO surface has also been shown to determine excited-state dynamics at these interfaces.²⁰⁻²² The precise nature of these newly formed interface states is generally difficult to establish, making rational control of such interfaces still a significant

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challenge.²³ Indeed, seemingly different conceptual models are frequently involved in discussing the formation of interfacial states, and the distinction between hybridization and other forms of coupling at the interface are usually not clear. This is not least due to the limited ability of photoelectron spectroscopies to distinguish easily between different interfacial interactions.

Here, we present a detailed study that combines differential reflectance spectroscopy (DRS), ultraviolet and x-ray photoemission spectroscopies, and first-principles electronic-structure calculations of the hybrid interface between the prototypical organic acceptor perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and conductive n-type ZnO thin films. With this combined approach, we are able to identify unambiguously the origin of the observed interface state and discuss the mechanism for its formation in relation to reports of charge transfer states observed at organic / metal interfaces. Our results point to an *integer* charge transfer mechanism from the ZnO surface to the first PTCDA monolayer. Further, we find that contributions from back-donation have to be taken into account as well to understand the charge redistribution.

EXPERIMENTAL METHODS

Materials: Two different types of ZnO thin films were grown in order to meet the specific requirements of the different analysis techniques. The thin films used for photoelectron spectroscopy have been described in detail elsewhere.¹⁹ Briefly, atomic layer deposition (ALD) on ITO or pulsed laser deposition on c- and r-plane sapphire was used to prepare n-doped films with an estimated defect concentration of 10^{19} - 10^{20} cm⁻³. On ITO and c-plane sapphire, the resulting polycrystalline films were oriented towards the (0002) surface, while (11 $\bar{2}$ 0) was preferred on r-plane sapphire. For PTCDA and all other systems investigated,^{19,23} both x-ray and ultraviolet photoelectron spectra were found to be insensitive to preferred crystalline orientation

or growth method. For DRS, it was necessary to remove interlayers in order to prevent strong optical interference effects that precluded spectroscopic analysis. Therefore, 30 nm ZnO was sputter-deposited on quartz glass at room temperature, with a deposition rate of 5 nm/min and using an argon flow at 6 sccm. During deposition, the pressure was kept at approx. $3 \cdot 10^{-3}$ mbar. After introduction into the respective ultrahigh vacuum chambers, all ZnO films were gently sputtered with Ar^+ (1 kV, 100 nA, 15 min). As detailed elsewhere,²³ this treatment primarily removes adventitious adsorbates with mild enrichment for Zn in the near surface region, and no indication of Zn segregation or surface metallization could be observed in the ultraviolet photoelectron spectra.²⁴ PTCDA was evaporated from a Knudsen cell at 0.2 monolayer equivalents (MLE) / min, with 3.2 Å corresponding to 1 MLE.

DRS: The experimental set-up for DRS has been described already elsewhere.^{25–27} Briefly, the photon energy- and film thickness-dependent reflectance was measured *in situ* in ultrahigh vacuum. The optical functions of the glass substrate and the bare ZnO film were determined separately by transmission and reflectance measurements in an *ex situ* Varian Cary 5000 spectrophotometer. Subsequently, the contribution of PTCDA to the DR spectra and the complex dielectric function was extracted using a numerical algorithm introduced detailed previously.^{25,28}

Photoelectron spectroscopy: As already described elsewhere, valence band ultraviolet photoemission spectra (UPS) were obtained with a He(I) lamp in ultrahigh vacuum (base pressure $2 \cdot 10^{-10}$ mbar), with photoelectrons collected normal to the surface with an acceptance angle of $\pm 12.5^\circ$ and an applied sample bias of -5 V. The workfunction is obtained from the secondary electron cut-off in UPS. Binding energies for the molecular features are reported as peak onset, determined by the intercept of the slope at the inflection point of the peak and the baseline. This reflects most accurately the relevant transport level by diminishing dispersion

effects, incomplete screening of the photohole and peak asymmetries introduced by inelastic scattering.²⁹ All results presented here are insensitive to the specific ZnO film growth protocol.

Computational: Electronic structure calculations were performed using the Vienna ab initio simulation package (VASP)³⁰ at the generalized gradient approximation level, using PBE and including a Hubbard U correction ($U = 8.5$ eV). This approach has been detailed and validated extensively already, and as discussed previously yields qualitatively similar results as the computationally more involved approaches using range-separated functionals despite non-trivial issues of error-cancellation.^{10,19,23,31} Both polar and non-polar surfaces were investigated computationally; in agreement with experiment, the conclusions do not differ substantially in response to the specific surface orientation,^{19,23} allowing us to concentrate here mainly on the prototypical (10 $\bar{1}$ 0) surface to elaborate the salient features of the PTCDA / ZnO interface. We computed the electronic structure for an orthogonal unit cell of ten ZnO layers with dimensions of 19.50 Å $\times$ 10.41 Å in the [11 $\bar{2}$ 0] and [0001] directions and 36.00 Å in the [10 $\bar{1}$ 0] direction, with PTCDA molecules adsorbed in rows at a resulting monolayer density of 4.92×10^{13} molecules cm $^{-2}$. Stoichiometric surfaces lead to qualitatively wrong workfunctions and energy-level alignment, as already reported for the bare surfaces and interfaces with perylene bisimides.^{19,31} Instead, shallow donor levels such as Zn $_i$ are necessary to obtain good qualitative and reasonable quantitative agreement between experiment and theory. Zn $_i$ shift the chemical potential and may couple directly to the molecular adsorbate if in close proximity to the surface.¹⁹ For this reason, a concentration of 1 Zn $_i$ out of 120 Zn atoms was introduced near the surface in the calculations, leading to a free electron density in the near-surface region of $1 \cdot 10^{14}$ electrons cm $^{-2}$, in agreement with the level of n-doping found in the thin films and relevant for potential direct coupling pathways with the adsorbate.

RESULTS

In order to investigate the molecular interactions at the interface with n-doped conductive ZnO films, we employed DRS that provides access to the wavelength-dependent and coverage-dependent complex dielectric function of PTCDA. DRS is defined as:

$$DRS(E, d) \equiv \frac{\Delta R}{R} := \frac{R(E, d) - R(E, d=0)}{R(E, d=0)} \quad (1)$$

where $R(E, d)$ denotes in our case the reflectivity of the sample stack consisting of the quartz glass substrate, 30 nm ZnO, and a thin PTCDA layer of varying thickness. Consequently, the DRS signal depends on the photon energy E and the PTCDA film thickness d . The raw DR spectra are shown in the Supplementary Figure 1, for coverages ranging from 0 to 7 MLE of PTCDA on ZnO on glass, with increments of 0.2 MLE in the range of 0 – 1 MLE. In Figure 1(a) we present the imaginary component of the dielectric function ϵ'' of the *adsorbate* film extracted from the DRS data, which represents the absorption behavior, following the numerical procedure outlined previously.²⁵

Figure 1 a) Imaginary part ε'' of the dielectric function of PTCDA on 30 nm ZnO on quartz glass for nominal thicknesses ranging from submonolayers up to 7 MLE extracted from the DRS shown in Supplementary Figure 1. For comparison ε'' spectra of 1 MLE PTCDA on inert mica,²⁷ 1 MLE of PTCDA partially potassium-doped providing pronounced new features of PTCDA radical anions at low photon energies (investigated in detail previously³²), polycrystalline (pc) PTCDA³³ and the dramatically broadened spectra of 1 MLE of PTCDA on Au(111) and Ag(111)^{34,35} are shown in the bottom panel. **b)** Δ DRS of PTCDA on quartz glass for nominal thicknesses ranging from submonolayers up to 1 MLE. The graphs are labeled according to the scheme $(m + 1) - m$ referring to eq. (2).

At $\hbar\omega \geq 2.1$ eV, the spectra display the typical PTCDA $S_0 \rightarrow S_1$ absorption for all coverages. For the thinnest films the vibronic progression typical of monomeric PTCDA molecules is visible, and is consistent with what is observed in solution and thin films on mica, although somewhat affected by inhomogeneous broadening and/or weak hybridization with the surface (cf. discussion section); this observation indicates that there are no appreciable interactions among the molecular transition dipoles.^{32,36} At higher coverages, the formation of PTCDA molecular stacks (or at least piles) is expected. The interactions among molecular

transition dipoles in such stacks changes the spectral shape noticeably, and the bulk spectrum of PTCDA emerges.³⁶ It is worthwhile to note that the convergence towards the bulk spectrum takes as much as seven MLEs due to the growth of three-dimensional clusters of disordered PTCDA on ZnO, in contrast to the case on mica where four MLEs are sufficient.

The most striking feature in the DR spectra appears, however, at an energy of 1.86 eV, well below the absorption bands of neutral PTCDA monomers and the spectral features observed in bulk PTCDA.³⁷ A comparison with DR spectra of thin films of PTCDA on mica, as deposited and potassium-doped, is shown in the bottom panel of Figure 1(a), and identifies this feature unequivocally as originating from PTCDA radical anions (PTCDA^{•-}). Exposure of robust molecules such as PTCDA to a potassium vapor induces *integer* ground-state charge transfer to form K⁺ and PTCDA^{•-}, where the latter exhibits an absorption band at 1.86 eV with a peak shape similar to that observed on ZnO. We conclude therefore that the growth of PTCDA on ZnO leads directly to the formation of PTCDA^{•-}, carrying a full additional electron, without any need for doping. This is in contrast to PTCDA adsorbed on mica where intentional doping with K is required to produce the PTCDA anion.³²

In order to investigate the origin of the PTCDA radical anion in more detail, we plot the ΔDRS spectra obtained by subtracting pairs of reflectance spectra R_m and R_{m+1} representing two sequential coverages:

$$\Delta DRS_{(m+1)-m} := \frac{R_{m+1} - R_m}{R_m}, \quad (2)$$

In contrast to *DRS* itself, where *all* absorbing species in the layer at a specific total thickness d contribute to the signal, ΔDRS allows one to clearly determine which absorbing species are emerging or vanishing in the small thickness increment from d_m to d_{m+1} .

The ΔDR spectra obtained for the data in Figure 1(a) are shown in Figure 1(b). Strikingly, the anion band is most prominent at coverages of ≤ 1 MLE, weakening already below 1 MLE, and is essentially absent above that coverage. Indeed, close inspection of these spectra reveals that anion formation is restricted to coverages of ≤ 0.5 MLE, after which additional PTCDA molecules grow as neutral molecules on the surface. These spectra demonstrate that the strong acceptor PTCDA undergoes ground state charge transfer *at the interface* with conductive n-ZnO thin films: already below 1 MLE, the PTCDA $^{\bullet-}$ absorption has saturated and no further increase is observed, identifying the PTCDA anion as a strictly interfacial species.

We note that the observed ground-state charge transfer is not to be confused with conventional band doping: In PTCDA layers with a coverage below 1 MLE, no bands are formed. Consequently, one has to understand the charge transfer as charging of single quantum objects, i.e., single molecules, by an additional full electron rather than as doping of a (3-dimensional) solid where a fractional charge per building block is the usual case.

The DR spectra can be separated into two regions: below (above) a threshold energy of *ca.* 2.1 eV, the absorption features stem from the PTCDA radical anions (neutral PTCDA molecules). This situation is similar to the K-doping of PTCDA on mica,³² where the K-doping of a monolayer of neutral PTCDA initially follows the reaction $K + PTCDA \rightarrow K^+ + PTCDA^{\bullet-}$. Hence, for every radical anion formed, a neutral molecule disappears. Consequently, the absorbance below (above) 2.1 eV increases (decreases). Given that the same number of charged or uncharged molecules are responsible for the changes in both spectral regions, the ratio of the oscillator strengths between PTCDA radical anions and neutral molecules can be estimated as the ratio of the change in spectral area below and above this threshold energy for consecutive spectra during K-doping. Similar arguments apply for the absorbance spectra in solution, as

discussed in previously.³² There, discharging of dissolved PTCDA anions causes the low-energy spectral features (property of the PTCDA anions) to decrease while the high-energy absorbance (property of the neutral PTCDA) simultaneously increased. We decompose therefore the spectra in terms of their relative molecular oscillator strengths:

$$OS = \int_{\text{absorption band}} \epsilon''(E) \cdot E \, dE \quad (3)$$

The ratio of oscillator strengths of these two species calculated for the absorption bands in the energy interval considered here has been previously determined to be $\frac{OS_{\text{anions}}}{OS_{\text{neutral}}} \approx 0.6$.³² Consequently, we estimate the fraction of charged molecules with respect to the total number of molecules within the first MLE (cf. Fig 1(a), thick red line) to be 30-40 %.

Further evidence for our interpretation of charge transfer at the interface can be obtained from investigating the electronic structure. Coverage-dependent valence band photoemission spectra for PTCDA on ZnO are shown in Figure 2. While the spectra generally show the emergence of PTCDA features (*e.g.*, the first ionization feature, “HOMO” at -2.1(1) eV (peak onset), see SI) and the suppression of the O 2p bands associated with ZnO, the most striking changes are (*i*) the rapid increase of the workfunction (Figure 2(a)) and (*ii*) the emergence of a new spectroscopic feature at -0.3(1) eV (peak onset), located in the bandgaps of both PTCDA and ZnO (Figure 2(b)).

Figure 2 **a)** Secondary electron cut-off and work function of bare atomic layer deposited ZnO and thin layers of PTCDA subsequently deposited onto the ZnO surface. **b)** Close-up of the interface state peak as a function of coverage. Full spectra are shown in the Supplementary Information.

The workfunction increase indicates a build-up of electron density at the interface, in agreement with ground-state interfacial charge transfer from ZnO to PTCDA. Remarkably, the workfunction saturates at 0.6 MLE PTCDA already, which is consistent with the observed anion formation at coverages ≤ 0.5 MLE in DRS. The new feature at $-0.3(1)$ eV also increases up to a nominal coverage of 0.6 MLE, before weakening at higher coverages and finally completely disappearing in films with thicknesses in considerable excess of 1 MLE. Due to the finite escape depth of photoelectrons with kinetic energies around 16 eV,³⁸ a species formed only at the PTCDA / ZnO interface is expected to weaken in UPS at coverages significantly above 1 MLE, identifying this peak as originating from an interfacial process. The binding energy for this state is close to the Fermi energy, E_F , and located in the bandgap of both ZnO and neutral PTCDA, indicating charge transfer and formation of $\text{PTCDA}^{\bullet-}$. This is consistent with (i) the observed workfunction increase, (ii) the anion spectrum in DRS, and (iii) a new peak arising in the C 1s x-

ray photoelectron emission spectrum (XPS, see Supplementary Information). The interfacial electronic structure obtained from UPS and the chemical identification of thin film molecular species in DRS show together in an unambiguous fashion that many of the PTCDA molecules in the first monolayer couple electronically strongly to the conductive n-ZnO substrate, resulting in an *integer* charge transfer to form the PTCDA radical anion.

Remarkably, our observations are independent of the specific ZnO film growth protocols for these highly n-doped ZnO films and any variations of the associated preferential crystallographic orientation. This indicates that the interfacial interactions are not caused by a surface – molecule interaction specific to a particular surface termination, but rather by a more general mechanism. This suggests further that our observations are likely more general and extend beyond the particular molecular system and the specific oxide investigated here.

We now turn to electronic-structure calculations in order to uncover a more detailed molecular-level mechanism of this charge transfer. Using a recently established and validated methodology for highly conductive n-type ZnO films,^{19,23,31} we modeled the bare ZnO surface and the interface with PTCDA for three different limiting cases: (i) A stoichiometric and thus idealized ZnO surface, (ii) ZnO including deep donor oxygen vacancies (O_v) often claimed to be responsible for the n-character of ZnO,^{39,40} and (iii) ZnO containing shallow donors modeled here by zinc interstitials (Zn_i) contributing each two electrons, resulting in a free-electron density of 10^{14} electrons cm^{-2} . Table 1 shows the workfunction change for these different surfaces upon adsorption of a PTCDA monolayer.

Table 1 Individual contributions ΔV_{SAM} , ΔV_{id} and ΔV_{gr} to computed workfunction changes $\Delta\Phi$ and amount of charge transfer q at the interface of 1 monolayer PTCDA with stoichiometric ZnO, ZnO with oxygen vacancies O_v and ZnO with zinc interstitials (Zn_i). The values shown here pertain to ZnO ($10\bar{1}0$). For an explanation of $\Delta\Phi$, ΔV_{SAM} , ΔV_{id} , ΔV_{gr} and q see text.

	$\Delta\Phi$ (eV)	ΔV_{SAM} (eV)	ΔV_{id} (eV)	ΔV_{gr} (eV)	q (e)
PTCDA on ZnO (stoich.)	-0.76	-0.30	-0.37	-0.06	0.02
PTCDA on ZnO (O_v)	-0.24	-0.33	0.31	-0.25	-0.35
PTCDA on ZnO (Zn_i)	+1.18	-0.39	1.59	-0.24	-0.98

For these ideal monolayer interfaces with ZnO, workfunction changes for the stoichiometric and O_v surfaces are both qualitatively and quantitatively different from the rapid workfunction *increase* of 1.0(1) eV observed experimentally. In contrast, the inclusion of shallow donors such as Zn_i results in good agreement between theory and experiment which is consistent with the findings for perylene bisimide on ZnO.¹⁹ We note that this agreement also extends to the bare ZnO surfaces, where Zn_i species are necessary for agreement with the experimentally observed low workfunction, regardless of the specific surface orientation modeled.¹⁹ ZnO thin films that are useful as carrier-selective interlayers in hybrid organic/inorganic electronics include a considerable concentration of shallow donors in order to exhibit the desirable high conductivity levels. Indeed, some of the films used in the experiments are nearly degenerately doped with a carrier concentration of $10^{19} - 10^{20} \text{ cm}^{-3}$.

The workfunction change arises from several separate contributions that provide further insight into the interfacial interactions:⁴¹

$$\Delta\Phi = \Delta V_{SAM} + \Delta V_{id} + \Delta V_{gr} \quad (4)$$

where ΔV_{SAM} is the electrostatic potential drop across the molecular layer suspended in vacuum while maintaining the geometry of the thin film on the surface, ΔV_{id} is the charge rearrangement-

induced interface dipole arising from adsorption of PTCDA on ZnO, and ΔV_{gr} captures the potential change due to geometric rearrangement upon molecular adsorption. Table 1 lists these values for all three variants of the $(10\bar{1}0)$ surface. Clearly, structural relaxations upon adsorption and the electrostatic potential arising from the PTCDA layer contribute minimally to the calculated workfunction change, particularly for the defect containing surface. This effect is dwarfed by the interface dipole contribution ΔV_{id} which dominates the workfunction change and is responsible for the observed workfunction increase upon adsorption of a PTCDA monolayer. This interface dipole originates from charge reorganization at this interface and results in a net charge transfer q across the interface, tabulated in the last column of Table 1. Strikingly, for the ZnO surface with shallow donors (Zn_i), almost a full electron is transferred from ZnO to PTCDA at monolayer coverage. We note that these conclusions remain unaltered even in the event of adsorption to a hydrated surface, albeit to a somewhat smaller extent (-0.44 e). This finding supports the observation of an anionic interface state of PTCDA on ZnO as observed with both DRS and UPS.

Figure 3 **a)** Projected density of states for ZnO $(10\bar{1}0)$ containing Zn_i (blue dotted line) and for PTCDA (red solid line). **b)** Electron density plot of interface state located near E_F , comprised of a LUMO-like wavefunction and weakly hybridized with the Zn_i . C atoms are black, H atoms grey, O atoms red and Zn atoms silver.

The effect of electron transfer to PTCDA is also clearly visible in the projected density of states (pDOS), shown for the Zn_i surface in Figure 3(a). We recall that despite the underestimation of the bandgaps of both ZnO and PTCDA, our computational approach represents the relative energy-level alignment at this interface well as detailed elsewhere.^{19,23} With Zn_i present, the HOMO is located inside the ZnO bandgap as observed experimentally, and a new state appears close to E_F . This state corresponds to the interface state observed in UPS. A plot of the calculated electron density of this state readily reveals its identity (Figure 3(b)) as containing strong PTCDA LUMO (lowest unoccupied molecular orbital) character, as expected for charge transfer from ZnO to PTCDA. Interestingly, there is as well a contribution from Zn_i highlighting the hybridized character of this state.

DISCUSSION

Before analyzing our findings further and in order to connect our work to the gamut of other interacting adsorbate systems, it is important to differentiate clearly between two different limiting cases of surface / molecule interactions. In particular, we highlight the difference between *i*) strong hybridization with *delocalized* substrate states and *ii*) weak molecule substrate interaction, i.e., no hybridization, presented here as two well-known and widely appreciated extreme cases of coupling to the substrate. The basic schemes are sketched in Figure 4. In cases where there is no hybridization, the molecule remains almost unchanged with regard to its orbital structure (Fig. 4(a)). Due to the essentially two-dimensional nature of the interface and poor intermolecular coupling, no new bands electronic develop. As a consequence, the molecules retain their character as individual nano objects, and only integer charge transfer is feasible in

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3 this limit. This leads to distinct charge-states and different orbital filling schemes of the charged
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5 single nano objects, and in turn to strongly altered optical absorption spectra.
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9 In contrast, the charge transfer mechanism upon strong hybridization with *delocalized*
10 substrate states like on metals is entirely different (Fig. 4(b)): Here, the strong hybridization
11 leads to a substantial broadening of molecular states.^{42,43} Further, the intermolecular interaction
12 is mediated by the substrate such that new electronic bands can be formed even in a two-
13 dimensional film with otherwise weak intermolecular coupling.⁴⁴ Accordingly, the molecules
14 lose their individual character. From a simplified point of view, this can be regarded as formation
15 of a new system at the interface consisting of the original molecules and a certain number of
16 strongly coupled substrate atoms. This situation leads to rather broad and unstructured optical
17 absorption bands usually combined with a strong spectral shift.^{34,35,45} Consequently, the resulting
18 spectra bear no resemblance to the monomer spectra (cf. Fig. 1(a), lower panel). Note that the
19 apparent spectral width depends on the strength of molecule- metal interaction and is therefore a
20 fingerprint of the degree of chemisorption vs. physisorption.³⁵
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38 Yet another general consequence of strong hybridization is the effect of charge back-
39 donation from the molecule toward the substrate, frequently observed in strong hybridization at
40 metal / organic interfaces: Due to broadening of the molecular states, certain deep lying orbitals
41 extend energetically above the Fermi level, such that the charge density on the molecule is
42 lowered, as was explicitly shown for the case of PTCDA on Ag(111).⁴⁶ All these effects (spatial
43 extension of the molecular wave function into the substrate, charge back-donation, formation of
44 two-dimensional bands at the interface due to the substrate-mediated intermolecular interaction)
45 result in a fractional net charge transfer, usually well below 1 electron charge and e.g., in the
46 case of PTCDA on Ag(111) as low as 0.3 e.⁴⁶
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Figure 4: Sketch of two different charge transfer mechanisms upon adsorption in the case of no hybridization (a) and strong hybridization with delocalized substrate states (b). In the first case, the molecular wave functions extend largely over the molecules only and the single molecules retain their character as individual nano objects. Only integer charge transfer is feasible. In contrast, for strong hybridization with delocalized states the wavefunctions extend into the substrate and/or to neighboring molecules. This leads to charge back-donation, and the net charge transfer is effectively fractional.

These two limiting cases permit us to shed more light into the specific interactions at the PTCDA / ZnO interface. Investigating small contributions of hybridization by our optical spectroscopic method presents a challenge, since hybridized interface states may not be easily interpreted by comparison with simple chemical species in bulk or solution. As a general trend, however, we observed in previous DRS experiments for molecules on metal substrates a broadening of the spectra depending on the strength of electronic interaction (see lower panel of Fig. 1(a)), characteristic of strong hybridization with delocalized states as delineated above.³⁵ Therefore, the slight broadening of the anion peaks in the DRS spectra in Figure 1(a) at higher deposition levels may be partially attributed to only a weak hybridization of the PTCDA

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3 molecules on ZnO. On the scale of electronic interaction strength, the adsorption regime can be
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5 however clearly regarded as physisorption, comparable to PTCDA on top of 1 ML PTCDA /
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7 Ag(111), where a slight broadening of the optical spectra is also observed.³⁵ In that case, the 1st
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9 ML PTCDA, in direct contact with the silver substrate, is strongly hybridized and functions as
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11 decoupling interlayer for the subsequent PTCDA layer, which is consequently only slightly
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13 hybridized. This suggests initially that PTCDA on ZnO falls into the limit of weak hybridization
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15 and expected integer charge transfer, as borne out by an initial analysis of the computational
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17 results (0.98 e transferred to PTCDA).
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23 There is however a notable discrepancy between the computational results and the DRS data
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25 regarding the extent of charge transfer: By analyzing the oscillator strengths of both anion and
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27 neutral PTCDA transitions in DRS, we obtain an average charge transfer of approximately 1
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29 electron per 3 molecules for 1 MLE, and even more for submonolayers of PTCDA, where we
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31 find an average of up to 1 electron per 2 molecules at 0.5 MLE and where the anion signature in
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33 UPS also reaches its maximum. In contrast, DFT predicts transfer of almost a full electron per
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35 molecule at one monolayer coverage for the PTCDA / Zn_i / ZnO system. We stress, however,
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37 that the DRS clearly indicates *integer* charge transfer to the molecule, *i.e.*, the charged molecules
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39 exhibit spectra that appear like anions, consistent with carrying a full charge of one electron per
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41 charged molecule and as expected for the weak hybridization limit.
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48 The quantitative discrepancy between experiment and theory can be understood by
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50 considering that, contrary to the ideal epitaxial PTCDA growth on ZnO considered in the DFT
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52 calculations, the film structure is likely disordered on the polycrystalline ZnO films used in our
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54 experiments (see atomic force microscopy image, Figure 4 in SI), an assumption consistent with
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56 the broadened DR spectra for the S₀ → S₁ absorption of neutral PTCDA. This has two
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consequences: First, the measured coverages do not reflect the actual number of molecules in direct contact with the ZnO surface, nor are all surface sites that can participate in charge transfer necessarily accessed by PTCDA. As a result, the observed *average* extent of charge transfer across this interface is lower than estimated for the calculated idealized system, and ~ 0.33 electrons per molecule may simply indicate that every 3rd molecule has experienced a full one-electron reduction by ZnO, as predicted by DFT. Second, the DFT calculations show that the charge transfer is not site specific but orientation-dependent, with the amount of charge transferred reduced when the molecules are rotated (e.g. by 45°) in-plane on the surface. A mixture of orientations would be expected on a disordered surface. In both scenarios the observed charge transfer is *integer*, giving rise to a fully negatively charged molecule in accordance with our interpretation of the DR spectral signature, while the inhomogeneous experimental PTCDA film structure and polycrystalline nature of the ZnO film does not match the idealized case considered in the computational model. The observed UP and DR spectra can consequently be understood to represent the electronic structure of a supramolecular entity consisting of an ionized shallow donor site such as Zn_i and a reduced PTCDA molecule.

Charge transfer from an oxide surface to a strong acceptor such as PTCDA is however not merely a question of locating the Fermi level above PTCDA electron-transport levels. In fact, it also involves a measure of rather strong interface hybridization leading to charge back-donation. This can be seen by closer inspection of the UPS and DFT results: By integrating the charge density for the LUMO-like state near the Fermi level (Fig. 3) and assigning the charge based on the Bader volumes for that state, we find a charge of ~ 2 e residing in this LUMO-like state of PTCDA. Of these ~ 2 e, ~ 0.6 e are in fact located well within the ZnO slab, leaving ~ 1.4 e on PTCDA (see Fig. 3(b)). This is still larger than the total charge of 0.98 e transferred to PTCDA

(see Table 1). This apparent contradiction can be readily understood by taking charge back-donation into account: While the PTCDA LUMO is filled due to the high ZnO Fermi level in the presence of shallow donors, charge (~ 0.4 e) flows back from PTCDA to ZnO out of a set of lower lying occupied molecular orbitals. Such back-donation is characteristic of strong hybridization and reminiscent of the case of PTCDA adsorbed on the (111) surfaces of coinage metals,^{46–48} as well as, e.g., F₄-TCNQ on Cu(111) and Ag(111).^{49,50}

This interpretation is also fully consistent with the photoelectron spectra: The interface state is not located at exactly E_F , as would be expected for a simple integer charge transfer / weak hybridization scenario. It is rather bound by 0.3(1) eV, in agreement with a more complex interfacial charge-rearrangement and a component of strong hybridization. This interpretation highlights the failure of the one-electron interpretation of photoemission data to capture electron correlation and many-body effects at the interface.

Naturally the question arises why our DR spectra do *not* indicate strong but rather weak hybridization, seemingly contradicting our conclusions above. However, it is necessary to distinguish not merely the strength of the hybridization but also the nature of the states involved. In case of metal substrates, hybridization occurs with strongly delocalized states which gives rise to the observation of broad and structureless absorption spectra. This results in part from coupling to broad bands with substantially delocalized electrons such as *e.g.* the sp-bands in coinage metal surfaces. In contrast, hybridization in the case of PTCDA on ZnO involves strongly *localized* states in rather narrow bands, such as *e.g.* the shallow donors (cf. Fig. 3(b)). While the interaction strength in terms of charge transfer and back-donation is strong, this type of hybridization does therefore not lead to a significant spectral broadening.

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The proposed charge transfer mechanism at the hybrid organic/inorganic interface is thus rather more subtle than what might be expected from merely comparing the molecular electron affinity and the Fermi level. Indeed, even any one spectroscopic approach delivers an incomplete understanding of such interfaces. Instead, we show in our combined experimental and computational study that a hybrid organic/inorganic interface such as PTCDA/ZnO does not fall neatly into either of the two limiting cases: While the net result is one of nearly integer charge transfer and apparent weak hybridization, this appearance is in fact caused in part by a strong hybridization and a back-donation. This is rather different from previous reports of ground state charge transfer, e.g., at metal surfaces, and highlights the need for detailed investigations of the electronic structure of hybrid organic/inorganic interfaces. We suggest that this has important consequences for charge transfer dynamics across this interface.

CONCLUSION

Taken together, the combination of *in situ* optical spectroscopy with measurements of the interfacial electronic structure and computational modeling of the defective ZnO surface yields a comprehensive understanding of the prototypical hybrid interface formed between PTCDA and conductive n-doped ZnO films. Our data show unambiguously that shallow donors cause *integer* charge transfer to PTCDA, manifesting itself as a new feature in DRS with an absorption band similar to that of PTCDA radical anions, and as a strong workfunction increase in the first monolayer together with the emergence of new features in UPS and XPS. The DFT results indicate that charge transfer arises from the formation of a hybrid interface state between PTCDA and shallow donor levels, here modeled as Zn_i . Charge transfer from a defective oxide surface to a strong acceptor such as PTCDA is therefore not merely a question of locating the Fermi level above the PTCDA electron-transport levels but also involves a measure of interface

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3 hybridization. Furthermore, back-donation of electrons through occupied molecular orbitals
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6 lying below the Fermi energy needs to be taken into account for understanding the charge
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8 redistribution at the interface. Our data highlight the important differences between the case of
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10 strong hybridization with delocalized states, involving the loss of molecular identity and
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12 typically fractional charge transfer, and other forms of interfacial coupling that may
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14 accommodate transfer of a full elementary charge and yet also involve strong hybridization,
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17 albeit with localized states.
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21 This study opens new avenues to understanding the interfacial electronic structure in the limit
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23 of weak screening and suggests that defect sites and dopants can have a significant influence on
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25 the specifics of interfacial coupling and thus carrier injection at hybrid interfaces.
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27 28 29 ACKNOWLEDGMENT

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51 52 53 SUPPORTING INFORMATION AVAILABLE

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Complete DR, UP and XP spectra together with an atomic force microscopy image of the ZnO surface and computational values for the hydrated defective surfaces are presented in the Supplementary Information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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