Energy-Level Alignment of a Hole-Transport Organic Layer and ITO:
Toward Applications for Organic Electronic Devices

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Supporting Information

ABSTRACT: 2,2′,6,6′-Tetraphenyl-4,4′-dipyranylidene (DIPO-Ph₄) was grown by vacuum deposition on an indium tin oxide (ITO) substrate. The films were characterized by atomic force microscopy as well as synchrotron radiation UV and X-ray photoelectron spectroscopy to gain an insight into the material growth and to better understand the electronic properties of the ITO/DIPO-Ph₄ interface. To interpret our spectroscopic data, we consider the formation of cationic DIPO-Ph₄ at the ITO interface owing to a charge transfer from the organic layer to the substrate. Ionization energy DFT calculations of the neutral and cationic species substantiate this hypothesis. Finally, we present the energetic diagram of the ITO/DIPO-Ph₄ system, and we discuss the application of this interface in various technologically relevant systems, as a hole-injector in OLEDs or as a hole-collector interfacial layer adjacent to the prototypical OPV layer P3HT:PCBM.

KEYWORDS: organic solar cells, interfacial layer, hole-transport layer, metal/organic interface, photoemission spectroscopy, charge transfer

INTRODUCTION

The materials of the transparent electrodes (anodes) of the organic photovoltaic (OPV) devices are mainly oxides,1−3 although a replacement with alternative materials, for instance, polymers4 and graphene,5−7 is recently being explored. Among the oxides, Sn-doped In₂O₃ (indium tin oxide, ITO) still remains the dominant material, despite its high cost, in front of alternative oxides like aluminum-doped zinc oxides, mainly because of a better resistance to degradation in outdoor environments.8 In fact, those types of oxides present detrimental effect on the power conversion efficiency of organic solar cells because of their sensitivity to acidic condition, or because they may induce the degradation of the active layer.

To improve the durability and the efficiency of the OPV, interfacial layers (IFLs) are used to bridge morphologically and electronically the electrode and the active layer. The IFL is made of organic materials (polymers, small molecules), of graphene oxide9 or even of inorganic material like NiO.10 It is systematically deposited between the ITO electrode and the standard photovoltaic active layers (often a P3HT:PCBM blend).11 The most widely used IFL is the PEDOT:PSS polymer because of its high conductivity and easy processability, but its high acidity can lead to ITO deterioration.11 To circumvent this difficulty, some of the present authors have explored the benefit of depositing a hole-transport molecular solid of the dipyranylidene (DIP) family (2,2′,6,6′-tetraphenyl-4,4′-dithiapryylanilene, DIPS-Ph₄) on ITO to finally form an ITO/DIPS-Ph₄/P3HT:PCBM/LiF/Al cell in which the short-circuit density...
The present study examines the growth of a molecular solid $2,2',6,6'$-tetraphenyl-4,4'-dipryanilidene (DIPO-Ph$_4$, Figure 1) on ITO substrates. Indeed, DIPO-Ph$_4$ is a promising molecule to create an effective hole-conducting IFL at the transparent anode in OPV.

$$J_{sc}$$ is efficiently increased. Current-sensing contact-mode atomic force microscopy (CS-AFM) shows that there is a considerable increase in the total number of hole-carrying pathways with respect to a PEDOT:PSS IFL.

The reason for the hole-collection efficiency lies, besides interface morphological aspects, in the favorable alignment of the energy levels of the molecular solid with the ITO band structure. However, it is worth noticing that the formation of the interface between ITO and a molecular film is often oversimplified in the literature on OPV, and this occurs because of two reasons.

First, the electronic levels of the conductive oxide and of the molecular materials are most often placed against each other by aligning the vacuum levels (the so-called Schottky–Mott limit). A vast literature on metal/organic or on inorganic semiconductor/organic interfaces shows that it is not the case. Various models were proposed. In the integer charge-transfer model, according to the respective energies of the metal work function and of donor/acceptor polaronic levels related to, but not confounded with, the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) level, charge can be transferred across the interface or not. When charge transfer occurs, the energy levels are pinned by the acceptor/donor polaronic levels. A change in the work function is seen, and the Schottky–Mott alignment is not observed. The concept of the polaronic level, on which the integer charge-transfer model was based, was recently challenged by the electrostatic model of Oehzelt and co-workers who considered the polaronic energy as almost negligible. Relying heavily on the density of state (DOS) of the organic layer was calculated via the density of state (DOS) of the organic layer. A change in the work function is seen, and the Schottky–Mott alignment is not observed.

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1.2. Sample Preparation at TEMPO Beamline. All DIPO-Ph₄ deposits are prepared on commercial ITO substrate (SOLEMS) having a sheet resistance of 25 Ω·sq⁻¹. After DECON 90 treatment, the ITO substrates were cleaned ultrasonically in baths of dichloromethane and propan-2-ol (10 min each) without any further treatment before DIPO-Ph₄ deposition. After its introduction into the ultrahigh vacuum (≈10⁻¹⁰ mbar) preparation chamber, the ITO substrate was exposed to a molecular beam of DIPO-Ph₄ using a Knudsen cell positioned at 4 cm from it. The molecular beam was slightly tilted. A quartz balance (QB) monitor allows us to follow the deposition rate. The substrate is kept at room temperature. Several deposits are made, characterized by the average number of molecules per cm²: 1 × 10¹⁵, 2 × 10¹⁵, 3 × 10¹⁵, and 8 × 10¹⁵ molecule·cm⁻². The DIPO-Ph₄ covered substrates are then introduced in the XPS analysis chamber of TEMPO beamline in a pressure better than ≈10⁻¹⁰ mbar.

1.3. Photoemission Spectroscopies. Most of the photoemission data were collected at TEMPO beamline, SOLEIL synchrotron, France. The synchrotron light spot of the TEMPO beamline is defocused to 1 mm × 2 mm purposely to decrease the photon flux, and to avoid beam damage, without losing photoelectron count rate. The electron analyzer is a modified SCIENTA200 machine fitted with a delay line detector. All photoemission spectra are taken with a takeoff angle of 0° with respect to the surface normal. Valence-band spectra and shallow core-levels (Sn 4d, In 4d) are recorded at hν = 60 eV in surface sensitive conditions. The In 4d and Sn 4d spectra are also recorded in more bulk sensitive conditions at 825 eV to profile out the Sn distribution in the material. In 3d core-levels were measured at 600 eV. C 1s, O 1s core-level XPS spectra were respectively recorded at hν = 340 eV and hν = 600 eV with an overall experimental resolution better than 100 meV. After subtraction of a Shirley background, the spectra are reconstructed with sums of Voigt functions, with respectively a 340, 380, 80, 150, 199, and 210 meV Lorentzian full widths at half-maximum (fwhm, corresponding to the core-hole lifetime) for Sn 3d, In 3d, C 1s, O 1s, In 4d, and Sn 4d, respectively, according to the literature. The Gaussian contribution, which may change according to the chemical environment, is indicated in the text. It is worth to notice that the value of core/valence level width σ can be determined according to Hwang et al. work:

\[
\sigma_i = \sqrt{\sigma_{XPS/UPS}^2 - \sigma_{\text{inst}}^2 - \sigma_{\text{surf}}^2 - \sigma_{\text{br}}^2}
\]
Surface relaxation processes ($\sigma_{\text{rel}}$) and vibrational coupling ($\sigma_{\text{vib}}$) are estimated to be both in the range of 0.05–0.2 eV. The instrumental resolution ($\sigma_{\text{inst}}$) is measured at the Fermi edge of a clean metal sample ($\sigma_{\text{inst}}$(Au) = 0.08 eV). $\sigma_{\text{vib}}$ can be then used as a key value for the determination of the effective injection barrier.\(^{35}\)

The variation curve of the inelastic mean free path versus the kinetic energy of the photoelectron was calculated for ITO using TPP-2 M method.\(^{39,40}\) It is given as Figure S2 in the Supporting Information. Binding energies (BE) are referenced with respect to the Fermi level ($E_F$), that is determined thanks to root-mean-square method (RMS).\(^{36}\)

Binding energies ($\nu$) determined for ITO using TPP-2 M method, were referenced with respect to the Fermi level ($E_F$) determined from a scrapped area of the copper sample holder in electrical contact with the ITO substrate. The work function was determined by measuring the kinetic energy ($KE_{\text{FL}}$) of the secondary electron cutoff ($KE_{\text{CO}}$) measured on the metallic contact, and the precise determination of the photon energy $h\nu$ (using first- and second-order core level peaks), enables the determination of the work function $\Phi$ of the sample as $\Phi = h\nu - (KE_{\text{FL}} - KE_{\text{CO}})$.\(^{37}\)

Complementary XPS characterization of the bare ITO surface were also carried at ALOISA beamline out using synchrotron light (ELETTRA synchrotron Facility, Trieste, Italy) and at Laboratoire de Chimie Physique Matière et Rayonnement (LCPMR, Paris), where a standard laboratory setup was used (a PHOIBOS 150 analyzer from SPECS and a nonmonochromatized Al Kα source).\(^{38}\)

1.4. Atomic Force Microscopy (AFM). The surface morphology of the DIPO-Ph4 films deposited in the TEMPO beamline preparation chamber is investigated ex situ via Atomic Force Microscopy (AFM) at CEA (IRAMIS group). The AFM used is a Molecular Imaging from Agilent, PicoLE, used in contact mode using a conductive Pt/Ir tip of radius 20 nm. The spring constant of the cantilever is 0.2 N/m. The vertical resolution in contact mode is 0.5 nm. The sample roughness is determined thanks to root-mean-square method (RMS).\(^{39}\)

2. RESULTS AND DISCUSSION

2.1. DIPO-Ph4 Layer Morphology Studied via AFM. Atomic force microscopy (AFM) is used to examine those samples that were previously examined by photoelectron spectroscopies. As the knowledge of the morphology of the deposited layer is instrumental to interpret correctly our XPS/UPS data, the AFM images (shown in Figure 2) are discussed first.

The chemical cleaning is efficient as the bare ITO surface appears without particle contamination. Yet, after the chemical cleaning process, ring-shaped structures remain on ITO surface. They are characterized by an average height of 2 nm and an average diameter of 100 nm (Figure 2a). They cover 20% of the surface. Away from these "craters", the roughness remains low ($\pm0.65$ nm).

The DIPO-Ph4 coverage is monitored during the evaporation in the preparation chamber of TEMPO beamline via a quartz balance (QB-coverage). The weight increase per surface unit is converted into a molecular surface density using the density given by Chasseau et al.\(^{31}\) After the deposition of $10^{15}$ molecule-cm$^{-2}$, the AFM image (Figure 2b) shows that 3D clusters ("mounds") cover 25% of ITO surface. The average height of the clusters is 30 nm with an average diameter of 150 nm. Given the cluster density, an average volume of DIPO-Ph4 per surface unit is obtained, leading to a molecular surface density of $0.94 \times 10^{15}$ molecule-cm$^{-2}$ (using the density of ref 31) in excellent agreement with the QB-coverage. These clusters grow from nucleation points situated at the side of the ring-shaped features. For the $3 \times 10^{15}$ molecule-cm$^{-2}$ deposit (QB-coverage), the DIPO-Ph4 layer covers now 60% of the ITO surface. The 3D growth of circular mounds switches to that of recumbent, elongated (needle-like) mounds. Their average height remains $\sim30$ nm, as for the $10^{15}$ molecule-cm$^{-2}$ deposit, with typical lateral and longitudinal dimensions of $\sim150$ and $\sim400$ nm. The molecular coverage deduced from the AFM image is $2.80 \times 10^{15}$ molecule-cm$^{-2}$, also in accord with the QB measurement. Finally, we show the AFM image (Figure 2d) and profile (Figure 2d) of the "thick" layer, corresponding to a deposit of $8 \times 10^{15}$ molecule-cm$^{-2}$. The film covers now more than 95% of the ITO surface, and its average thickness is $\sim43$ nm.

When layers are deposited over homogeneous substrates, like single crystals, two types of growth are classically considered. In a Volmer–Weber\(^{41}\) growth, the organic molecules cluster in islands, leaving bare substrate areas. This arises from the fact that the interaction between molecules (π-stacking) is much stronger than the interaction between the DIPO-Ph4 molecule and the ITO substrate. Alternately, in a Stranski–Krstanov growth,\(^{41}\)
the molecule–molecule interaction competes with molecule–substrate interactions. A thin wetting layer covers all the substrate, on top of which the 3D island growth mode takes place. If a Stranski–Krastanov mode stands, then given that the crater-like defects of the ITO substrate remain visible (Figure 2b2), the wetting layer, if present, should not exceed \(\sim 2\) nm.

In the present case, the growth mode may be more complicated as numerous, 10 to 100 nm size defects (the calderas) are found on the surface, that serve as starting point for the mound growth. The flanks of the mounds themselves cannot be abrupt, and a significant “aureole” may surround the mounds, with a thickness comparable to the XPS probing depths (\(\leq 1\) nm).

### 2.2. Core-Level XPS Spectroscopy

The In 3d\(5/2\) spectra of the bare, chemically cleaned surface are given in Figure S3 and Table S2. The value of the first plasmon component energy (\(\hbar \omega_p \sim 0.75\) eV) measured in surface sensitive conditions (\(h \nu = 600\) eV, kinetic energy of 155 eV, \(\lambda_{ITO} \sim 0.56\) nm) enables an estimate of the carrier density, about \(4 \times 10^{20}\) cm\(^{-3}\).

<table>
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<tr>
<th>samples</th>
<th>phot. energy</th>
<th>G-fwhm</th>
<th>peak C1 (eV)</th>
<th>peak C2 (eV)</th>
<th>(\tau_{C1+C2})</th>
<th>C 1s/In 3d(5/2) ratio</th>
</tr>
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<tbody>
<tr>
<td>chemically cleaned ITO</td>
<td>825 eV</td>
<td>1.657 eV</td>
<td>284.91</td>
<td>–</td>
<td>–</td>
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<td>284.92</td>
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<td>–</td>
<td>16%</td>
</tr>
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</tr>
<tr>
<td>8 (\times 10^{15}) molecule·cm(^{-2})</td>
<td>600 eV</td>
<td>1.156 eV</td>
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<td>79%</td>
</tr>
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<td>285.08</td>
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<td>0.09</td>
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</tr>
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<td>285.06</td>
<td>286.00</td>
<td>0.11</td>
<td>2364%</td>
</tr>
</tbody>
</table>

The core-hole lifetime Lorentzian fwhm (L-fwhm) is 80 meV for C 1s. DIPO-Ph\(_4\) coverages (in molecule·cm\(^{-2}\)) are deduced from QB measurements. The C 1s to In 3d\(5/2\) intensity ratio is also given.

**Figure 4.** (a) O 1s spectra of the chemically cleaned ITO substrate, bare and covered with increasing QB-coverages of DIPO-Ph\(_4\) (1 \(\times 10^{15}\), 2 \(\times 10^{15}\) and 3 \(\times 10^{15}\) molecule·cm\(^{-2}\)). The molecular solid contribution comprises two new components O1 and O2 added to the “synthesized” bare ITO spectrum. The spectra shown in (b) are obtained by subtraction of the ITO substrate contribution to the spectra shown in (a), emphasizing the contribution of DIPO-Ph\(_4\). Coverages are obtained from QB measurements. (c) The O 1s spectrum of the thickest deposit measured at photon energy of 650 eV. The gray shaded component arises from the ITO substrate.
excitation energies, see Figure S4 and Table S3, SI Section S5) suggest an accumulation of Sn dopants in the near surface region (Sn/In equal to 0.13 at the surface, and 0.10 more in the bulk), in agreement with previous observations.20

The deposition of the DIPO-Ph4 molecule affects the In 3d_{3/2} BE. The first deposit (10^{15} molecule·cm^{-2}, see Figure S3), the In 3d_{3/2} peak (hν = 600 eV) moves to higher binding energy by 100 meV. This indicates that the energy difference between the Fermi level and the conduction band minimum increases. According to the AFM images, DIPO-Ph4 is in the form of mounds, of thickness ~30 nm, separated by intermound areas. Thus, given the IMFP (~0.56 nm), most of the In 3d signal comes from the intermound areas (75% of the surface) and from thin aureoles around the mounds. The observed BE shift means that molecules interacting with ITO surface change slightly the surface charge density: an electronic transfer from the molecule to the substrate could explain the motion of the Fermi with respect to conduction band minimum. For subsequent depositions (for which the intermound area recedes down to 40%), the position of the In 3d_{3/2} peak does not change any more, showing that the Fermi level remains anchored at the position reached after the first deposit.

The C 1s XPS spectra of the ITO surface, bare and covered by the molecule are shown in Figure 3 and Table 1. The C 1s of the bare sample is due to contamination. It presents the characteristic peak of an aliphatic carbon at ~284.9 eV.44 The C 1s/In 3d_{3/2} intensity ratio, measured at hν = 600 eV (KE C 1s ~ 315 eV, λ_{DIPO-Ph4} ~ 1.19 nm), is 16% for the chemical cleaned ITO. Then it increases to 65, 79, 139, and 2364% for the QB coverages of 1 × 10^{15}, 2 × 10^{15}, 3 × 10^{15}, and 8 × 10^{15} molecule·cm^{-2}, respectively. These ratio values indicate that the C 1s spectra are characteristic of the deposited film.

The C 1s spectra does not exhibit any BE shift, from 1 × 10^{15} to 3 × 10^{15} molecule·cm^{-2}, indicating that the position of the Fermi level remains constant in the organic material while the mounds are laterally growing. The C 1s spectra are fitted with three Voigt components: one main component labeled C1 at ~285 eV, with a fwhm of ~1.2 eV and two weaker peaks, one labeled C2 at ~286 eV and one labeled C3 at 287.5 eV. Peak C1 has the typical BE expected for aryl carbons. A more thorough examination of the BEs will be made after the discussion of the O 1s spectra, here below. C2 peak is attributed to C bonded to oxygen atoms and C3 one at ~1.5 eV higher BE that is likely a shakeup. The spectral weight of the C–O component is 0.15, 0.13, 0.09, and 0.11 for the 1 × 10^{15}, 2 × 10^{15}, 3 × 10^{15}, and 8 × 10^{15} molecule·cm^{-2} respectively. Note that the aryl carbons and core carbons not bonded to O atoms represent 70.5% and 17.6% of the carbon atoms (88% in all), while the carbons in ether bonds amount to 12%.

The O 1s core-level spectra of the chemically cleaned bare ITO surface (Figure 4 and Table 2) are measured at hν = 825 eV (KE O 1s ~ 295 eV, λ_{ITO} ~ 0.79 nm) and at hν = 600 eV (KE O 1s ~ 70 eV, λ_{ITO} ~ 0.47 nm). In both cases, the spectra are fitted with four components of equal widths. In more bulk sensitive conditions (hν = 825 eV) the BE of peak I (42% of the spectra weight), II (31%), III (22%), and IV (6%) are 530.17, 530.81, 531.78, and 532.89 eV, respectively. Peak II (0.6 eV from peak I) can be attributed to a plasmon loss, as also observed in the In 3d_{3/2} spectra (Figure S3). Peak III (1.6 eV from peak I) could correspond to the second plasmon or to organic contamination.45 Finally peak IV may be attributable to surface hydroxyls, that are expected in the range 532.5–532.9 eV.35,46

In more surface-sensitive conditions (hν = 600 eV), peaks I (51%), II (31%), III (15%), and IV (3%) are found at 530.30, 531.38, 532.37, 533.48, respectively. The second observation is the increased BE shift (1.07 eV instead of 0.75 eV) between peak I and peak II. This is reminiscent of what is observed for the plasmon loss energy in the In 3d_{3/2} spectra that is greater at the surface than in the bulk. However, 1.07 eV is an excessive value for the plasmon energy. It is likely that peak II encompasses both the plasmon peak and a component due to defects (e.g., suboxides45), the latter being more abundant at the surface. Surface contamination by oxygenated species can be estimated from the atomic ratio r_{O/In} = (λ_{ITO} ∼ 0.47–0.56 nm). The latter is calculated from O 1s intensity and In 3d at hν = 600 eV, corrected from cross-sectional variations. r_{O/In} = 1.8, very close to 1.7, the value expected for the In2O3 stoichiometry. This indicates that the contribution of the oxygen contamination is small.

We consider now the changes induced on the O 1s spectrum by the deposition of DIPO-Ph4. The O 1s spectrum measured at hν = 600 eV in “surface-sensitive conditions” (KE O 1s ~ 70 eV, λ_{ITO} ~ 0.47 nm and λ_{DIPO-Ph4} ~ 0.55 nm) are given in Figure 4a. As the substrate contains oxygen, the spectra of the DIPO-Ph4 covered ITO surface are fitted by a sum of Voigt components that reproduces the bare ITO spectral shape, to which two new components, due to the DIPO-Ph4 molecule are added. As shown in Figure 4, the O1 and O2 components appear at ~322 and ~353 eV, respectively. We have also verified that the appearance of O2 is not trivially due to beam damage (see Figure S5) during the XPS measurements.

The subtraction of the bare ITO contribution emphasizes the molecular solid contribution. In Figure 4b, we give the difference spectra obtained in surface sensitive condition (KE ~ 70 eV, λ_{DIPO-Ph4} ~ 0.55 nm) in bulk sensitive ones (KE ~ 293 eV, 

<table>
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<th>samples</th>
<th>phot. energy</th>
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<th>peak I (eV)</th>
<th>peak O1 (eV)</th>
<th>peak O2 (eV)</th>
<th>r_{O2}/(O1-O2)</th>
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<td>1.370 eV</td>
<td>530.17</td>
<td>--</td>
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<td>--</td>
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<td>8 × 10^{15} molecule·cm^{-2}</td>
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<td>0.56</td>
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<td>532.84</td>
<td>534.27</td>
<td>0.16</td>
</tr>
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</table>

“The Lorentzian width (L-fwhm) is 150 meV for the O 1s peaks. r_{O2}/(O1-O2) measures the O2 (BE ~ 533.6 ± 0.1 eV) contribution weight in the molecule-related spectral intensity. Coverages are obtained from QB measurements.”
\( \lambda_{\text{DIPO-Ph}} \sim 1.14 \text{ nm}, \) the original spectra are given in Figure S6). In fact, in DIPO-Ph, the two oxygen atoms are chemically equivalent (see Figure 1), and thus, one single O 1s contribution should be observed. Indeed, peak O1 is found at the typical BE of the C–O–C ether bond, in the range of 531.5–532 eV, according to the literature.47 The O 1s spectrum (\( h\nu = 650 \text{ eV}, \lambda_{\text{DIPO-Ph}} \sim 0.6 \text{ nm} \)) of thick DIPO-Ph deposit (\( 8 \times 10^{15} \text{ molecule-cm}^{-2} \)) is the one for which the contribution of the substrate (the gray shaded component) is the least, see Figure 4c. It exhibits the O1 and the O2 components at $34.27 \text{ eV}$ (with $\rho_{\text{O2}}/\rho_{\text{O1}} = 0.16$, see Table 2).

The observation of two oxygen components can find various explanations. Let us examine the more trivial explanations. First, the used material introduced in the crucible may contain a high proportion of oxygen containing molecules coevaporated with DIPO-Ph. This must be discarded as the purity of the material was checked by NMR and elementary analysis (see experimental details in Table S1, Section S2). Second, the presence of background impurities coadsorbed with DIPO-Ph is not realistic as the evaporation was carried out in a UHV system. Therefore, we must consider that the molecule is present in two different forms: one corresponding to the unaltered molecule, with an ether O 1s component labeled O1, and one corresponding to an altered form, characterized by the O2 component. Any interpretation of the O2 component should be consistent with the fitting of the C 1s spectrum into two components (attributed to ester carbons and carbons not bonded to oxygen) that corresponds to the DIPO-Ph stoichiometry.

The molecule can be altered by a chemical reaction with species released by the ITO substrate. Indeed, aggressive oxygenated species on the ITO substrate (e.g., generated by UV ozone treatments) can break the bonds of organic molecules and oxidize them.45 The C–O bond of the ether moiety may break leading to the insertion of further oxygen. Indeed, BEs of 532.2 and 533.7 eV are found for the carbonyl and ether type oxygens in ester groups of polymers, respectively.47 Against this view, there is no indication for a carboxylic/carboxylate peak at \( \sim 289 \text{ eV} \) in the C 1s spectrum as shown in Figure 3, and $\rho_{\text{O2}}/\rho_{\text{O1}}$ is not fixed at 0.5. Other species could diffuse away from the substrate. For instance indium atoms are reported to penetrate deeply into molecular solids such as PTCDA when an iodine metal layer is deposited upon it.48 Tin atoms are less prone to diffuse into PTCDA.49 The presence of indium in the molecular solid should be noticed by new components appearing away from the substrate. For instance indium atoms are reported to penetrate deeply into molecular solids such as PTCDA when an indium metal layer is deposited upon it.49 Tin atoms are less prone to diffuse into PTCDA.49

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This hypothesis is further explored by calculating the O 1s BE shift between the cationic and the neutral molecule in the gas phase (we consider a single molecule) using DFT (Table 3). Details on the method are given in the SI, Section S9 and in previous papers by our group.51–53 Calculations of C, N, and O 1s ionization potentials of a series of molecules were shown to be precise, within 0.1 eV, when compared to the experimental gas-phase values.51,53–55 The calculated O 1s ionization energy (IEcore, i.e. the BE referenced to the vacuum level) of the neutral molecule (IEcore,neutral,gas) is $537.64 \text{ eV}$, while that of the molecular cation (IEcore,cation,gas) in the triplet state is $541.42 \text{ eV}$. Via a Hartree–Fock (HF) calculation, we have checked that the singlet state IEcore,cation,gas that contributes to 1/3 of the spectra weight is very close in energy to the triplet state, i.e. only 0.08 eV higher in energy, see Table S4, SI Section S9. Therefore, the triplet and singlet states should be merged into one in the experimental spectra, given the resolution.

The difference of \( \sim 3.8 \text{ eV} \) between the cationic (triplet) and neutral-state DFT ionization energies is much larger than the O2–O1 BE difference of 1.5 eV we measure for the molecular solid. In fact, as shown in the SI, Section S10, a simple dielectric response model describes the relaxation energy effects via the polarization energy $P$ of a unit charge. Then the cationic-neutral BE shift is reduced in the solid state with respect to the gas phase due to core-hole screening by the dielectric medium in the final state. This relationship is represented by

\[
BE_{\text{cation,solid}} - BE_{\text{neutral,solid}} = (IE_{\text{cation,gas}} - IE_{\text{neutral,gas}}) - 2P
\]

where $IE_{\text{cation,solid}}$ and $IE_{\text{neutral,solid}}$ are the ionization energies (measured from the vacuum level) in the solid of the cation and of the neutral species, respectively, and where $BE_{\text{cation,solid}}$ and $BE_{\text{neutral,solid}}$ are the binding energies (measured from the Fermi level) in the solid of the cation and of the neutral species, respectively.

A polarization energy $P$ of \( \sim 1.2 \text{ eV} \) explains why the calculated energy difference of \( 3.8 \text{ eV} \) between the cationic and neutral species calculated in the gas phase can be reduced to 1.5 eV in the solid state. Therefore, the charge-transfer hypothesis must be regarded as likely. Nevertheless, we must check the consistency of two “charge state” model for the C 1s spectra.

In the DFT framework, we also calculate theoretically the C 1s IEcore,neutral,gas and triplet-state IEcore,cation,gas of selected atoms in the molecule. We distinguish three atoms: one labeled Carb1 pertains to the phenyl ring, and the two others pertain to the dipyranylidene core, Carb2 (central atoms) and Carb3 (ether bond), see Figure 1. The calculated energies are reported in Table 3. Via the HF approach, we have obtained that the singlet-state IEcore,cation,gas is higher in energy than the triplet-state one by 0.2 eV.

Table 3. Calculated DFT IEcore,neutral,gas and IEcore,cation,gas Values for the Neutral and Cationic DIPO-Ph$_4$ Molecule$^a$

<table>
<thead>
<tr>
<th>core/valence level energy (eV)</th>
<th>O 1s</th>
<th>C 1s Carb1 (phenyl)</th>
<th>C 1s Carb2 (ether)</th>
<th>C 1s Carb3 (central)</th>
<th>HOMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>IEcore,neutral,gas</td>
<td>537.67</td>
<td>289.25</td>
<td>290.70</td>
<td>289.14</td>
<td>5.14</td>
</tr>
<tr>
<td>IEcore,cation,gas</td>
<td>541.47</td>
<td>292.00</td>
<td>294.27</td>
<td>293.02</td>
<td>8.49</td>
</tr>
<tr>
<td>IEcore,neutral,solid</td>
<td>3.80</td>
<td>2.75</td>
<td>3.57</td>
<td>3.88</td>
<td>3.35</td>
</tr>
<tr>
<td>IEcore,cation,solid</td>
<td>1.40</td>
<td>0.35</td>
<td>1.2</td>
<td>1.5</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$For the cationic form, core-ionized energies are calculated for the triplet final state. In the estimation of $BE_{\text{cation,solid}} - BE_{\text{neutral,solid}}$, the polarization energy $P$ is taken as 1.2 eV (see eq 2).
and 0.4 eV for the dipyranylidene carbons, Carb2 and Carb3, respectively (see SI, Section S9). Considering that the singlet state contributes to only 1/3 of the spectra weight and the rather small triplet-singlet energy shifts indicated by the HF calculation, the spectra curve is mainly due to triplet-state.

For the neutral molecule, the triplet-state DFT IE of the central atoms is slightly shifted with respect to that of the phenyl carbons (by \(-0.1\) eV), while that of the ether carbon is 1.5 eV higher, as experimentally observed. In contrast, for the cationic species, the IE of the central atoms is distinct from that of the phenyl by +1 eV. Physically, this means that the central carbons have lost charge, as can be determined from a representation of the HOMO (Figure 1). The ether carbon is found to be +2.3 eV higher than the phenyl, a sizable increase when one considers the neutral molecule case.

Considering a polarization energy of \(\sim 1.2\) eV that accounts for the solid effects, the energy difference \(E_{\text{BE,core, solid}} - E_{\text{BE,neutral, solid}}\) is reduced to \(\sim 0.35\) eV for the phenyl carbon. Consequently, peak C1 in Figure 3 can correspond to the phenyl carbons of both the neutral and cationic species. Component C2 at \(\sim 1.2\) eV from C1 can be attributed to the ether carbons of the neutral molecule and to the central carbons of the molecular cation, as \(E_{\text{BE,neutral, solid}} - E_{\text{BE,core}}\) is worth \(\sim 1.5\) eV for the latter ones. Component C3 at 2.5 eV from C1 can be attributed to the ether carbons of the cation given that \(E_{\text{BE,neutral, solid}} - E_{\text{BE,core}}\) is worth \(\sim 1.2\) eV. Consequently, the hypothesis of a mixture of neutral and cationic species in similar proportions consistently explains both the O 1s and C 1s spectra. Note that the O1/O2 proportions do not depend on the sample coverage as the island aureoles probed via XPS have the same area for the different sample from \(1 \times 10^{15}\) to \(3 \times 10^{15}\) molecule·cm\(^{-2}\). Between the islands, no DIPO-Ph\(_4\) material is thus deposited. Therefore, the DIPO-Ph\(_4\) growth follows a Volmer–Weber mode.

### 2.3. Valence-Band Energy Levels

The valence-band spectra of the chemically cleaned ITO substrate measured at a photon energy of 60 eV is presented in Figure 5a, corresponding to a short IMFP (\(\lambda_{\text{ITO}}\) of \(\sim 0.5\) nm). From the valence-band edge, at a binding about 3 eV, a “tail” extends into the oxide gap. The origin of these gap states, which we observe up to about \(\sim 1.2\) eV, see Figure 5a2, is yet unclear: mixed 5s/5p states of surface In\(^+\) lone pairs, on the one hand, bulk oxygen vacancies and oxygen interstitials, on the other hand.\(^{22,56,57}\) The valence-band maximum energy (\(E_{\text{VBM}}\)) can be determined by fitting the valence-band with two broad Gaussians, one representing the O 2p valence-band edge and one the gap states,\(^{20}\) see Figure 5a1. Then a value of \(\sim 3.14\) eV for the O 2p \(E_{\text{VBM}}\) is determined. A comparison with the UPS and XPS measurements made by Gassenbauer et al. is relevant for the discussion on the band level scheme. The \(E_{\text{VBM}}\) value we find is bracketed between an \(E_{\text{VBM}}\) of \(\sim 3.54\) eV for a magnetron-deposited reduced film (spattering in argon, emission at Fermi level) and an \(E_{\text{VBM}}\) of \(\sim 2.94\) eV for a
film grown in more oxidative conditions (sputtering in 1% O₂/Ar no emission at Fermi level).²⁰ With an E_C value of ~2.9 eV, the E_F – E_BM in the range of 3.0–3.2 eV points to a Fermi level in the conduction band. This is consistent with the In 3d₄/₅ peak maximum at 444.63 eV that falls between that of the film sputtered in pure Ar (444.93 eV, emission at Fermi level) and the one sputtered in the 1% O₂/Ar mixture (444.63 eV, no emission at Fermi level). Therefore, the In 5s states forming the conduction band should be occupied, considering the small E_C value that is now adopted. They do not appear clearly at hν = 60 eV. However, they clearly show up using a much higher excitation energy of 850 eV (Figure 5b). Indeed, the conditions of their observation is optimized in the XPS regime, as the photoionization cross-sectional ratio of σ_{O 1s}/σ_{O 2p} is 1.5 at a photon energy of 850 eV while it is only 3.1 × 10⁻² at 60 eV.

We focus now on changes in the electronic structure due to DIPO-Ph₄ deposition. With respect to the substrate spectrum prior to deposition, the valence-band spectra measured at hν = 60 eV (Figure 5a) exhibit new features (red, blue-, green-, and violet-shifted components) related to the occupied molecular orbitals of DIPO-Ph₄ superimposed onto the ITO valence-band structure. Note that the valence-band photoelectrons measured at this energy and the O 1s photoelectrons measured at hν = 600 eV correspond to the same probing depth, as their KE (~60 eV and ~70 eV, respectively) are very close. Therefore, the two chemical states associated with the O1 and O2 components in the O 1s spectrum contribute in nearly equal weights to the molecular valence-band spectrum.

For deposits ≤3 × 10¹⁵ molecule·cm⁻², a gray-shaded synthetic spectrum represents the ITO contribution. This is the major one in the valence spectra. At hν = 60 eV, the IMFP λ_{DIPO-Ph₄}, of the photoelectron in the molecular solid is only ~0.55 nm. Considering the morphology of the deposit, the photo-emission signal comes from the top of the molecular mounds and from the intermound areas, which still represents 40% of the surface for a deposit of 3 × 10¹⁵ molecule·cm⁻². The probed ITO still shows its metallic character (there is a weak Fermi level emission for the 3 × 10¹⁵ molecule·cm⁻² deposit). The valence-band spectrum of the thickest deposit (8 × 10¹⁵ molecule·cm⁻²) is more characteristic of the organic material as the ITO contribution in the O 1s spectrum (Figure 4c) is minimal, and the neutral state corresponds to 70% of the molecular spectral weight. We observe the growth of six strong components, labeled A to F, that show up at BE 14.06, 10.97, 9.36, 6.99, 4.30, and 3.29 eV, respectively, plus two molecular states that appear in the ITO gap centered at 2.5 and 1.4 eV, which we denote H(+) and H, respectively.

As the measured spectrum results from the combination of two different chemical states (neutral versus cationic) of the molecule, the respective molecular levels are mixed up in the experimental spectrum. Let us now start with the two molecular levels with lower BE, H(+) and H that appear in the gap of ITO. Using DFT, we have calculated the vertical valence ionization energy of the highest occupied molecular orbital (HOMO, neutral) and singly occupied molecular orbital (SOMO, cationic), IE_{neutral, gas} and IE_{cation, gas} respectively. We find IE_{neutral, gas} = 5.14 eV and IE_{cation, gas} = 8.49 eV. The DFT energy difference IE_{cation, gas} – IE_{neutral, gas} (Table 3) is close to that calculated for the (triplet state) C 1s core-levels of atoms in the dipyrindylene core. The estimated BE energy difference in the solid state B_{cation, solid} – B_{neutral, solid} is reduced ~1 eV with P equal to ~1.2 eV (Equation 2). Therefore, the components H(+) and H, whose measured BE difference is also ~1 eV, are attributed to the SOMO level of the cationic species and to the HOMO of the neutral molecule, respectively.

We have tried to calculate the DFT ionization energy of molecular orbitals (neutral and cationic state) that are essentially localized on phenyls. The calculation of the doubly ionized states does not converge, because the phenyl localized orbitals pertain to a manifold of levels with very close energies. Nevertheless, the difference in the ionization energies between the neutral state and the cationic state may be expected to be lower than in the case of the highest energy levels (HOMO and SOMO), since the charge appearing on the phenyl is spatially remote from the electron vacancy localized on the core of the molecule. The latter point is clearly demonstrated by the valence-band spectra of films of 2,2’,6,6’-tetraphenyl-4,4’-dithiadiipyramiendine (DIPS-Ph₄) we present in Figure S9 of the SI, Section S11. In DIPS-Ph₄ the two oxygen atoms of DIPO-Ph₄ (see Figure 1) are substituted by two sulfur atoms, and the molecular orbitals are very similar. We have successfully prepared a very thick layer (13 × 10¹⁵ molecule·cm⁻²), for which only the neutral state is seen, as proved by a single spin–orbit split doublet in the S 2p spectra. We label the molecular components A−F and H, as for the DIPO-Ph₄ molecule. We observe a clear narrow HOMO level well isolated from the A−F series.

2.4. Electron-Energy-Level Scheme of the ITO/DIPO-Ph₄ Interface. To complete the electronic level scheme of the ITO/DIPO-Ph₄ interface, work function (Φ) measurements are determined via the measurement of the cutoff of secondary electron energy distribution curves (SEEDC). We find Φ equal to 4.20 eV for the bare substrate (see Figure S10). The SEEDC of the deposits 1 × 10¹⁵, 2 × 10¹⁵, and 3 × 10¹⁵ molecule·cm⁻² give a Φ value of 3.90 eV, independent of coverage (in the thick limit). The slight decrease in work-function associated with molecular adsorption can be attributed to the formation of cationic species at the ITO/DIPO-Ph₄ interface.¹⁶

We present in Figure 6, the electron-energy-level scheme of the ITO/DIPO-Ph₄ interface. The important parameters are the E_F – HOMO (neutral) energy offset of 0.7 eV (leading edge)/1.4 eV (centroid), the molecular solid work function Φ (3.90 eV), and the valence ionization energy of DIPO-Ph₄ is obtained by adding Φ to the HOMO binding energy measured from the Fermi level to give 4.6 eV (HOMO leading edge)/5.3 eV (centroid). The SOMO level of the cationic species H(+) has a higher binding energy (referenced to the Fermi level) and thus a higher ionization energy (referenced to the vacuum level) than that of the neutral HOMO level, as demonstrated by the DFT calculation of the isolated molecule (see section 2.3). As emphasized in ref 58, UPS generates photoemitted electrons that carry away with them the relaxation energies (electronic polarization and structural relaxation) of the valence ionized molecule. This is entirely true for molecules in the neutral ground state, and therefore, the measured HOMO binding energies are relevant to discuss transport properties, in particular the transport gap of molecular solids, when inverse photoemission spectroscopy data about the lowest unoccupied molecular orbital (LUMO) energy are also available. However, as E_F approaches the HOMO, this molecular level is partly emptied due to a charge transfer to the substrate, but the spectroscopic level H(+) (a doubly ionized final state) will appear below the HOMO due to the strong hole−hole interaction. This is a common observation in UPS spectroscopy, when SOMOs are concerned (a good example is the valence-band spectroscopy of copper phthalocyanine⁵⁸⁵).
The work function of P3HT is 3.9 eV\(^61\) and of P3HT:PCBM blends of hole-transport P3HT and electron transport PCBM are favorable interfacial layers for hole collection in organic photovoltaics. The BHJ are competitive with other organic hole-transport materials such as TPD and α-NPD deposited on ITO.\(^60\)

The Fermi levels in metallic ITO, P3HT, and PCBM\(^61\) are both equal to 3.9 eV (and coincidently the vacuum levels are aligned). The HOMO energy versus \(E_v\) (vacuum level) in P3HT is from ref \(^62\). The Fermi levels in metallic ITO, P3HT, and PCBM\(^61\) are assumed to be aligned. \(\Delta\) is the energy offset. The LUMO/HOMO energies versus vacuum are from ref \(^62\). As the LUMO – HOMO gap in DIPO-Ph4 is greater than 2 eV (Figure S1), the minimum electron blocking barrier \(B_{\text{min}}\) is 0.8 eV. \(E_F\) and \(E_{\text{vac}}\) are the Fermi and vacuum level, respectively (\(E_v\) is the zero of energies).

Now, could the DIPO-Ph4 layer be an efficient interfacial hole collecting layer per se in the context of the state-of-the-art bulk heterojunctions (BHJ) of organic photovoltaics? The BHJ are blends of hole-transport P3HT and electron transport PCBM. Some work functions can be made from the present data and from already published UPS\(^61,62\) and inverse photoemission spectroscopy (IPES) works.\(^62\). The expected energy-level schemes of the interfaces are given in Figure 6.

Vacuum-level alignment should be obeyed at the DIPO-Ph4/P3HT interface. Indeed, the work function of P3HT is 3.9 eV\(^61\) (identical to that of DIPO-Ph4) and its ionization energy (HOMO edge) is 4.65 eV.\(^62\) As the ionization energy (HOMO edge) of DIPO-Ph4 is 4.6 eV, then the HOMOs of the two materials are practically coincident. Therefore, the injection of holes from P3HT to ITO via the DIPO-Ph4 interfacial layer remains barrierless.

The interfacial DIPO-Ph4 may also come into contact with PCBM. Figure 6 shows the expected energy-level scheme at the DIPO-Ph4/PCBM interface. The work function of DIPO-Ph4 donor (3.9 eV) is smaller than that of the PCBM acceptor, 4.3 eV.\(^61\) Therefore, electron charge should be transferred from DIPO-Ph4 to PCBM, and after level alignment, an energy offset \(\Delta\) of \(\sim 0.4\) eV appears.\(^61,62\) This offset (generally ignored in most depictions of the energy schemes of these photovoltaic materials) will bring up the PCBM LUMO in energy and make it closer to that of DIPO-Ph4. Considering that transport gap in DIPO-Ph4 is greater than 2 eV (the value of the optical gap, see Figure S1), and considering that the PCBM LUMO is 3.8 eV below the vacuum level,\(^62\) then the LUMO (DIPO-Ph4)/LUMO (PCBM) energy difference is greater than 0.8 eV. Therefore, DIPO-Ph4 should remain an efficient blocking barrier (\(B_e\)) to electrons coming from PCBM despite the positive value of \(\Delta\).

In summary, the DIPO-Ph4 interfacial layer presents a favorable energy-level scheme to collect holes from P3HT and to block electrons from PCBM. However, if this condition is necessary, it is not sufficient for the material to behave as an efficient hole collector and to improve the performances of the BHJ cells. The conductivity of the DIPO-Ph4 material and the number of good “contact” points with the ITO substrate (per surface unit) must be also high. In the case of the parent molecule DIPS-Ph4, CS-AFM points to a sizable increase in hole-carrying pathways with respect to PEDOT:PSS.\(^12\)

Given the UVH deposition conditions, DIPO-Ph4 should be undoped and moderately conductive. It is only when it meets the substrate that it can transfer electronic charge and become a cation. This is a particular case of doping different from the classical molecular doping,\(^63\) where acceptor or donor molecules are inserted into the organic semiconductor host. A significant difference with molecular doping is the absence of negatively charged recombination centers in the film itself. Thin layers in contact with the substrate may have a high hole conductivity.

CONCLUSIONS

We combine AFM and synchrotron radiation XPS/UPS to elucidate the formation the ITO/DIPO-Ph4 interface, DIPO-Ph4 has appeared as a very promising interfacial layer for hole collection in organic photovoltaics. The ITO/DIPO-Ph4 morphology of the deposits otherwise characterized by XPS/UPS, is examined by AFM. For coverages in the \(1 \times 10^{15} \sim 8 \times 10^{15}\) molecule-cm\(^{-2}\) range, we do not observe a layer-by-layer growth mode. Molecular mounds are formed, starting from ITO macroscopic surface defects. In the \(1 \times 10^{15} \sim 3 \times 10^{15}\) molecule-cm\(^{-2}\) range the height of the mounds is typically 30 nm, leaving intermound area bare or covered by an ultrathin layer that remains unobservable by AFM. Only at \(8 \times 10^{15}\) molecule-cm\(^{-2}\) do the mounds tend to coalesce, and their height reaches an average value of 50 nm.

Synchrotron radiation XPS and UPS give unique information on the electronic properties of both the substrate and the film. The fact that the film thickness is not uniform, as shown by AFM, is crucial to interpret the photoemission spectra. Indeed, for coverages \(\leq 3 \times 10^{15}\) molecule-cm\(^{-2}\), a sizable ITO contribution is always observed in the O 1s and valence-band spectra, even in highly surface-sensitive conditions. The ITO-related signal originates from the intermound areas (and the aureoles of the mounds) where the deposit thickness is very thin. All substrate related components (e.g. In 3d) increase their binding energies when the molecule is deposited, indicating that the Fermi level moves up in energy due to the interaction with the molecule. This may be interpreted as a filling of the conduction band by electrons coming from the deposited molecules.

For all the deposits studied, we detect the presence of two components in the O 1s spectra, indicating that the molecule is in two different states. One state corresponds to an ether oxygen of an otherwise unaltered molecule. The second one at higher binding energy originates from an altered molecule interacting with the substrate. These two molecular states are in comparable amounts until the DIPO-Ph4 mounds almost coalesce. Then the...
The authors declare no competing financial interest.

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