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Electronic Properties of Interfaces between PCPDTBT and Prototypical Electrodes Studied by Photoemission Spectroscopy**

Umut Aygül,*[a] Heiko Peisert,[a] Johannes Frisch,[b] Antje Vollmer,[c] Norbert Koch,[b] and Thomas Chassé[a]

We report on the electronic structure of poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT), a promising low-band-gap donor material for efficient bulk heterojunction organic solar cells. Electronic properties of interfaces formed between PCPDTBT and prototypical electrodes [Au, indium-tin-oxide and poly(ethylene-dioxythiophene): poly(styrenesulfonate)], ob-tained from X-ray photoemission spectroscopy and ultraviolet photoemission spectroscopy, are evaluated. The formation of interface dipoles is observed, and their consequences for device performance are discussed. For the system PCPDTBT/Au chemical interactions occur, which may affect in particular the charge extraction at the corresponding interface.

1. Introduction

Organic photovoltaic cells based on donor–acceptor blends posses a significant market potential for low-cost energy generation, although their efficiency today is still low compared to a number of inorganic-based photovoltaic devices. Fundamental research on the electronic properties at interfaces (between electrodes and photovoltaic organic materials) is still at an early stage. In polymer-based bulk heterojunction solar cells low-band-gap materials are promising donor components in active layers. Conjugated polymers with low optical band gaps may improve the efficiency of organic photovoltaic devices by increasing the absorption in the visible and near-infrared region of the solar spectrum and by improving the offset of the frontier energy levels of the donor and acceptor.[1,2] A promising candidate in this context is poly[2,6-(4,4-bis-(2-ethyl-hexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7(2,1,3-ben-zothiadiazole)] (PCPDTBT),[3–5] (Figure 1) with an optical gap of only 1.46 eV.[5] The low band gap of PCPDTBT can be explained by the hybridization of electron-rich thiophene- and electron-deficient benzothiadiazole units leading to a reduction of the bond-length alternation.[6]

The transport of charges through the device and charge extraction is controlled considerably by the structural and electronic properties of the related interfaces. In particular, the relative position of frontier energy levels, that is, the charge carrier transport states, is an important issue for the optimization of the device performance. However, the energy level alignment cannot be reliably estimated from properties determined for individual materials, since interface dipoles often occur upon contact between different materials. The mechanisms

that determine electronic interface properties depend, for example, on the reactivity of the materials, on preparation conditions and on fundamental electronic parameters of the materials.[7–11]

Although there has been considerable progress in recent years in the understanding of the mechanism that lead to interface dipoles, only in a few exceptional cases their magnitude and sign may be predicted.[12,13]

Herein, the electronic structure of the polymer PCPDTBT and its interfaces to Au, indium–tin–oxide (ITO), and poly(ethylene-dioxythiophene):poly(styrenesulfonate) (PEDT:PSS) are investigated. These substrates were chosen because of their technical relevance as electrodes in organic photovoltaic cells.

2. Results and Discussion

2.1. Material Characterization with X-Ray Photoemission Spectroscopy

We first discuss core-level photoemission spectra of a 12 nm thick PCPDTBT film on ITO (Figure 2). The two chemically dif-
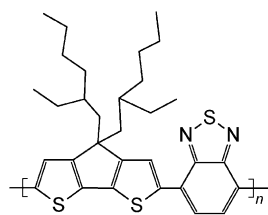

Figure 1. Chemical structure of PCPDTBT.

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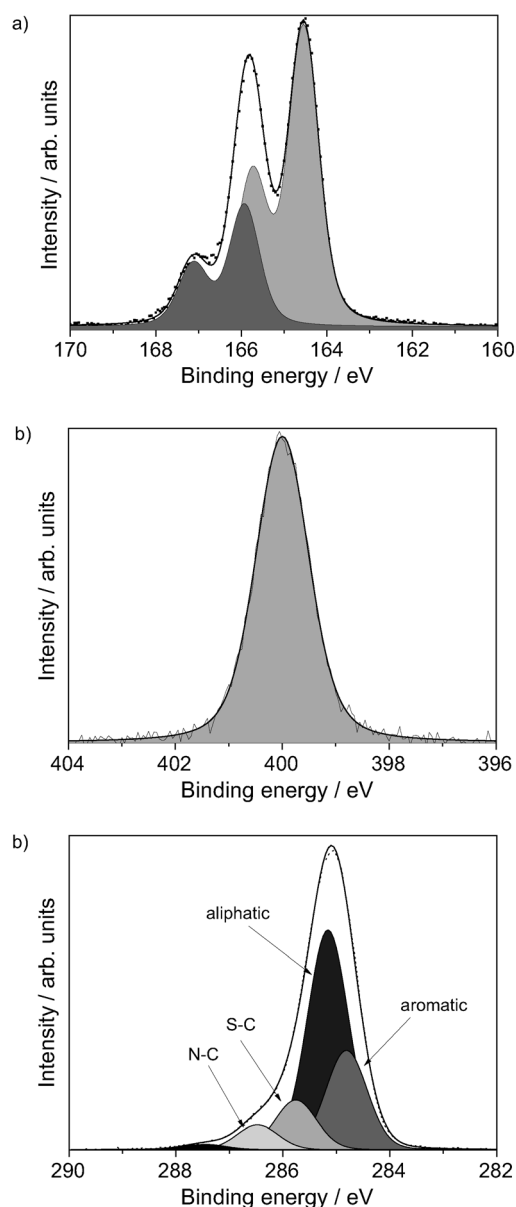Speicherring BESSY II, 12489 Berlin (Germany)

a)

b)

b)

Figure 2. a) S 2p, b) N 1s and c) C 1s core-level photoemission spectra of PCPDTBT on ITO with a film thickness if 12 nm. Analysis of the XPS signals was done by a peak-fitting routine. Four different components contribute to the C 1s signal: carbon bonded to sulfur, carbon bonded to nitrogen, aromatic carbon and aliphatic carbon. Two chemically different sulfur atoms contribute to the S 2p signal. For the two chemically equivalent nitrogen atoms we obtain a single component in the N 1s XPS spectrum.

ferent sulfur atoms in the electron-rich thiophene- and electron-deficient benzothiadiazole units can be clearly separated in the corresponding S 2p spectra. Detailed analysis of the signal by a peak-fitting routine can be performed using two components with the same Voigt profile and a spin–orbit splitting of 1.20 eV (Figure 2 a). The spin–orbit doublet with the lower S $2p_{3/2}$ binding energy (E_B) at 164.4 eV corresponds to sulfur bonded to carbon (S—C, thiophene unit). The S 2p peak with the higher binding energy at 165.8 eV can be assigned to the nitrogen-bonded sulfur (S—N, benzothiadiazole unit) due to the high electronegativity of the nitrogen atom. The intensi-

ty ratio of both components is in good agreement with the expected stoichiometry (2:1). For the two chemically equivalent nitrogen atoms we obtain a single component in the N 1s (X-ray photoemission spectroscopy) XPS spectrum (Figure 2 b). The binding energy of 399.9 eV is typical for N 1s in organic compounds.[15, 16]

Several species contribute to the C 1s signal and we observe an asymmetric peak with a tail to higher binding energies. For thiophenes we expect two components, corresponding to C—S and C=C bonding configurations.[17] In addition, we expect two additional components for PCPDTBT: carbon bonded to nitrogen (C—N) and aliphatic carbon (C—C). The aromatic carbon of the benzothiadiazole units might be expected at the same position as C=C of the thiophene units. Thus, we expect a C 1s intensity ratio for PCPDTBT of 4:2:8:18 (C—S:C—N:C=C:C—C). With these assumptions the C 1s spectrum of PCPDTBT can be well described and the result of the peak fitting[14] is shown in Figure 2 c. Both the number of peaks and the intensity ratio were constrained. The peak with the lowest binding energy at 284.8 eV corresponds to aromatic carbon. The binding energy for the sulfur-bonded carbon component is about 285.7 eV. The difference of ca. 0.9 eV between these two components is in good agreement with other thiophenes.[17] The peak for the aliphatic carbon component is observed between the S—C and the aromatic component at 285.2 eV. Due to the higher electronegativity of nitrogen compared to sulfur, the energetic position of N—C is even higher than for the S—C component. The binding energy for the N—C singlet is at 286.5 eV. Overall, the binding energies of these four carbon components are in good agreement with the literature.

2.2. Energy-Level Alignment at Electrodes

From ultraviolet photoemission spectroscopy (UPS) valence-band spectra we obtain information on the electronic structure and interface properties, such as the position of the valence band onset (VB onset), interface dipole, work function (Φ), and ionization potential. The energetics of all electrode interfaces is discussed for ~10 nm thick films prepared by doctor-blade casting or spin-coating.

The UPS spectra for PCPDTBT on the three different substrates are shown in Figure 3. On the left-hand side the secondary electron cutoff (SECO) of PCPDTBT (——) and the corresponding substrate (-----) are compared. The difference between the photon energy and the width of the photoemission spectra gives Φ, so changes in the SECO position are related directly to changes in Φ upon PCPDTBT deposition, indicating the formation of interface dipoles.

For all three substrates changes in Φ are observed after deposition of PCPDTBT, pointing to the formation of interface dipoles (Δ) at the related polymer/substrate interfaces. We obtain values between −0.8 eV and +0.4 eV, depending on the substrate under consideration.

On the right-hand side of the figure pairs in Figure 3 the valence band region of PCPDTBT on different substrates are presented. The hole injection barrier is obtained as the energy difference between the Fermi level E_F and the VB onset. Figure 4
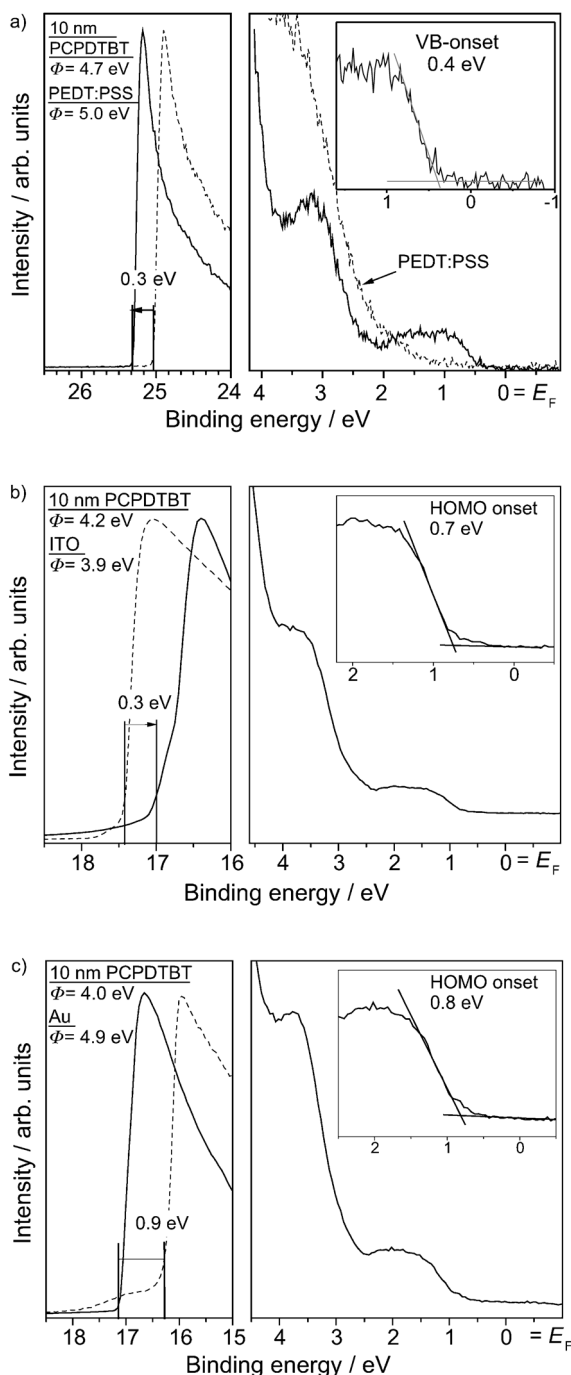
Figure 3. Valence-band photoemission spectra (UPS) of PCPDTBT on a) PEDT:PSS, b) ITO and c) Au. Left: An interface dipole is formed, which is indicated by the energetic shift of the secondary electron cutoff. Right: Binding energy of the VB onset of PCPDTBT.

Figure 4. Energy-level alignment for PCPDTBT on a) PEDT:PSS, b) ITO and c) Au.

summarizes the energy level alignment for PCPDTBT on different substrates.

Different models for the energy level alignment have been discussed so far for interfaces of organic semiconductors. For polymer/metal interfaces two limiting alignment regimes have been observed, namely vacuum-level alignment and Fermi-level pinning.[18,19] The Fermi-level alignment regime requires charge-transfer processes. An electron transfer from the mole-
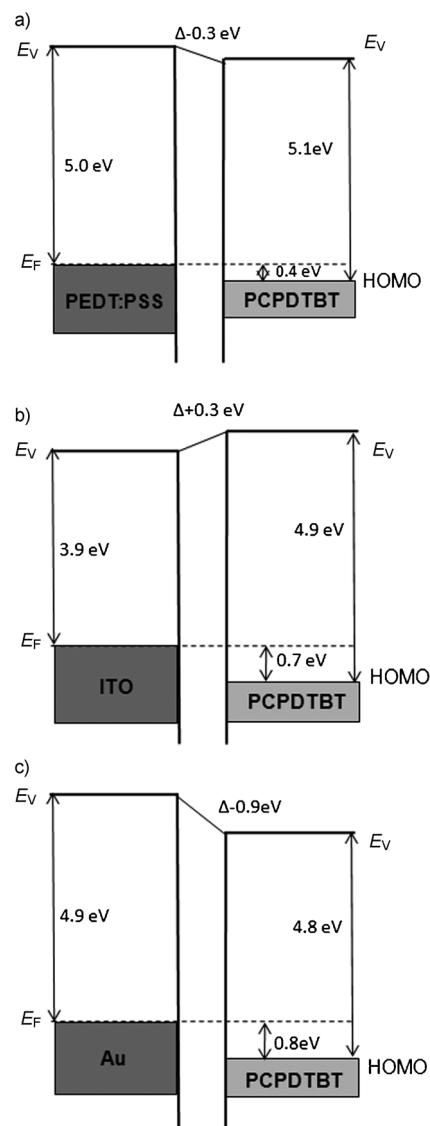
cule is expected whenever the Fermi level of the substrate exceeds the energy of the polymer charge carrier transport level (positive polaron/bipolaron formation energy). Within the integer charge-transfer model, it has been suggested[12,20] that for every organic material between an upper and a lower critical Φ value (of a conductive substrate) the energy levels essentially follow the Schottky–Mott limit (no interface dipoles). The energy of these upper and lower critical values are related to the negative and positive polaron energies, respectively. If the work function of the substrate is smaller than the negative or higher that the positive polaron energy, an (integer) charge transfer at the corresponding interface may occur resulting in a pinning at these levels, that is, the Fermi level and the positive or negative polaronic level of the polymer align.

First we consider the PCPDTBT/PEDT:PSS interface. Comparing the ionization energy of PCPDTBT (5.1 eV) with Φ of PEDT:PSS (5.0 eV), one may expect no significant charge trans-

fer because both values are fairly similar. However, due to relaxation processes in charged molecules, the polaron energy is not identical to the HOMO energy. For example, the vibronic relaxation in pentacene causes a lowering of the positive polaron energy (also denoted as polaron binding energy) by approximately 0.2 eV.[21] The occurrence of an interface dipole at the PCPDTBT/PEDT:PSS interface (Figure 4) hints strongly at such a pinning, and the critical Φ value for pinning at positive polarons of PCPDTBT is about 4.7 eV below the vacuum level, that is, 0.4 eV above the VB onset.

Interface dipoles are also present at PCPDTBT/Au and PCPDTBT/ITO interfaces (Figure 4). However, most apparently, the separation of the VB onset of PCPDTBT and the Fermi level of the substrate (i.e. the hole injection or extraction barrier in devices) is larger compared to PCPDTBT/PEDT:PSS. However, this is not expected for Fermi-level pinning at the polaron energy, since the polaron energy is a property of the semiconducting material. Rather, the pinning occurs near the mid-gap position (using the optical gap of 1.45 eV, as the charge-transport gap is not known). This is reminiscent of the behavior of several interfaces between small molecules and metals, where interface dipoles roughly following the Schottky–Mott scenario, that is, the size of the dipoles is proportional to the difference of the metal-organic work function Φ in the bulk (Φ_B),[22] often denoted as built-in potential. Thereby, the bulk Φ of the semiconducting polymer can be calculated according to $\Phi_B = IP - 1/2E(\text{gap})$, assuming a mid-gap position of E_F. In other words, for such systems an alignment of the Fermi levels (or more exactly of charge neutrality levels[23]) at the organic/metal interface occurs. For an interfacial charge transfer, an overlap of molecular orbitals of the organic with the metal is necessary, which was recently presumed for several organic interfaces.[23–25] In some cases such interactions result in the formation of gap states that can be directly observed in photoemission.[25]

We note that differences in the energy-level alignment were recently observed between contaminated and clean metal surfaces.[26] In this case, molecules of low molecular weight were evaporated in ultra-high vacuum (UHV) on contaminated metal surfaces. We think, however, that the interface formation on ex situ prepared substrates observed herein is in principle different, since the polymer is prepared from solution. The best-known example in this context is the behavior of self-assembled monolayers (SAMs) on different substrates. The adsorption of the SAM results in the removal of carbon contamination layers.[16,27] The chemical interaction between PCPDTBT and Au discussed below suggests that also for the system considered herein the contamination can be replaced by the polymer. Therefore, we use the work function of Au after preparation in UHV for the discussion of the electronic properties. For ITO the situation is somewhat more complicated, since a cleaning procedure in UHV, for example, by Ar-ion sputtering, also causes changes in the stoichiometry and may activate the corresponding surface.[28] However the change in the work function due to sputtering is small—an increase of 0.2 eV was observed. Therefore we assume that the energetic values discussed above describe the energetic situation at these interfaces well.

In summary, we are left with the conclusion that the pinning of the Fermi level depends on the substrate under consideration. The position of the pinning level seems to be not only characteristic for the positively or negatively charged molecule, local chemical interactions may also occur and/or different gap states may be induced, depending on the nature of the interface.

2.3. Chemical interaction between PCPDTBT and Au

For the investigation of possible interaction at the interfaces, photoemission is a valuable tool. Due to the typical elastic mean free path of photoemitted core electrons (about 2.5 nm at the kinetic energy used here) only ultrathin films in the nm range enable access to signals of interface components. For this reason, ultrathin PCPDTBT films were prepared by subsequent rinsing with chloroform. Although we do not assume that all substrates are homogeneously covered with the polymer after this procedure, this preparation method enables the access to interface species.

In Figure 5 we show C 1s, N 1s, and S 2p core-level photoemission spectra of thin and ultrathin PCPDTBT films on all three substrates. For both PEDT:PSS and ITO (Figures 5 a,b) we observe no differences in the shape of all XPS spectra between thin and ultrathin films. Minor energy shifts in the case of PCPDTBT/PEDT:PSS are most likely related to a change in the local environment of the relevant atom (e.g. due to conformation changes of slight intermixing with the conductive polymer substrate), resulting in a variation of the screening of the corresponding photoemission final state. Alternatively, the presumed charge transfer from the polymer to PEDT:PSS, which is associated with the formation of a positive polaron (see above), represents a p-doping of the polymer. The p-doping causes a lowering of the binding energy of all energy levels, which is most effective directly at the interface. Almost no energy shifts were observed for the other substrates, which may point to the absence of interface doping in these cases.

The situation is different for the PCPDTBT/Au interface, a system where the position of the pinning level is not conforming to the polaron level model (see above). For ultrathin films, the S 2p spectra of PCPDTBT on Au in Figure 5 c show an additional feature at a lower binding energy (162.0 eV). The appearance of this additional feature for ultrathin films is an indication of a chemical interaction at this interface. Because no solvent-related features in the XPS spectra can be found (e.g. absent Cl core-level signals) changes in the S 2p spectrum due to residual solvent/PCPDTBT interactions can be ruled out. Although this observation is reminiscent of the related oligomer MTBT [4,7-bis(5-methylthiophen-2-yl)benzo[c][1,2,5]thiadiazole], a model molecule for PCPDTBT,[29] the situation is generally different for both systems due to the different preparation methods. Even if PCPDTBT thin films were prepared ex situ from solution and MTBT was evaporated in situ on sputter-cleaned Au[29] a similar chemical interaction is found. A chemical interaction between sulfur and Au has already been investigated
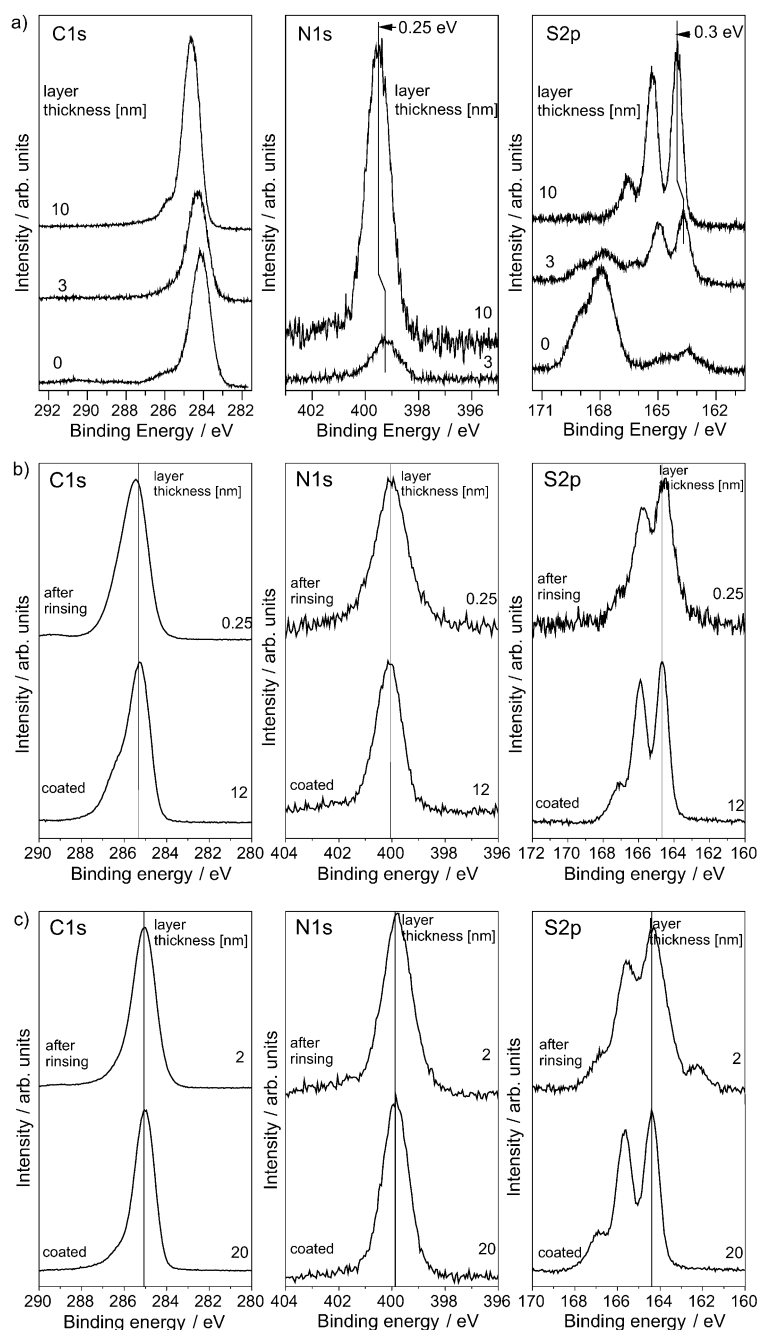
Figure 5. C 1s, N 1s, and S 2p core-level photoemission spectra of thin and ultrathin PCPDTBT films on a) PEDT:PSS b) ITO and c) Au. An additional feature appears only in the S 2p spectra of ultrathin PCPDTBT films on Au, pointing to a chemical interaction on this substrate.

doublet. For all fit components, the peak shape was kept constant. The peak fit of the S 2p signal results in three doublets with S $2p_{3/2}$ binding energies of 164.3 eV assigned for thiophene sulfur, 165.8 eV for benzothiadiazole sulfur and 162.3 eV for the interface component. The chemical interaction of sulfur with Au results in a lowering of the binding energy of the corresponding S 2p component due to the increase of the electron density at this site. From the comparison of the intensity ratio of the sulfur components, one can conclude which of the two chemically different sulfur atoms interacts with Au. The intensity ratio between benzothiadiazole sulfur and thiophene sulfur is about 1:3, that is, distinctly smaller than expected from the chemical composition (1:2). The relative decrease of the intensity of sulfur of the benzothiadiazole subunit reveals an energetic shift for a fraction of this species. Moreover, the ratio rises to the expected stoichiometric value if we add the intensity of the interface component to the benzothiadiazole component. Therefore, we conclude that a highly localized chemical interaction between Au and benzothiadiazole sulfur of PCPDTBT occurs and that the thiophene sulfur is not involved.

The chemical interaction at the PCPDTBT/Au interface may now explain the observed energy level alignment, as discussed above. The observed

for other systems such as thiols.[16, 27] On the other hand, for thiophenes, such interactions are not yet known. The appearance of an additional peak only in the S 2p spectra, reveal a local chemical interaction between Au and the sulfur atoms in PCPDTBT. A charge transfer from Au into the more delocalized molecular orbitals of the polymer is unlikely, since additional features are not found in the corresponding N 1s and C 1s spectra.

The S 2p spectrum for the ultrathin PCPDTBT film on Au is analyzed in detail in Figure 6 using a peak-fitting routine. The interface component can be described by an additional single

large interface dipole of −0.9 eV is a consequence of the charge rearrangement due to the Au–benzothiadiazole-sulfur interaction. Even if such clear evidence for chemical interactions were not found for PCPDTBT/ITO, weaker electronic interactions cannot be ruled out (e.g. the overlapping of molecular orbitals with substrate wavefunctions), resulting in a Fermi-level pinning close to the mid-gap position.

The formation of interface dipoles and their origin may now have consequences for performance of devices. For example, local chemical interactions as observed for PCPDTBT/Au have important consequences for the charge carrier transport across
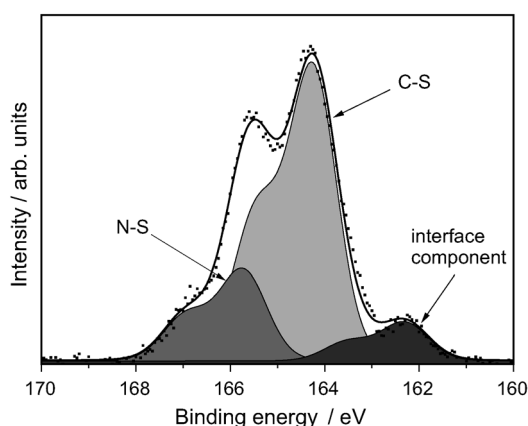
2·10⁻¹⁰ mbar), equipped with a SPECS Phoibos 150 cylindrical hemispherical analyzer, a monochromatic Al Kα source (Focus 500 monochromator, XR50 м X-ray source, Al K$_\alpha$ 1486.74 eV) and a UVS 300 He discharge lamp (21.22 eV excitation energy). The energetic resolution determined from the width of the Fermi edge for XPS and UPS were about 400 meV and 100 meV, respectively. The energy scale for XPS was calibrated to the binding energy (BE) of Au 4f$_{7/2}$ (84.00 eV) Ag 3d$_{5/2}$ (368.3 eV) and Cu 2p$_{3/2}$ (932.7 eV). In the case of UPS He I β and He I γ satellites were subtracted from the data. The polymer film thickness was estimated from the attenuation of XPS intensities of substrate features assuming homogeneous films. Peak fitting was performed using the program Unifit 2008.[14]

XPS and UPS measurements of the PCPDTBT/PEDT:PSS were carried out at the endstation SurlCat of beamline PM4 at the synchrotron light source BESSY II. The spectra were collected with a hemispherical electron analyzer Scienta SES 100 using an excitation energy of 30 eV for UPS and 600 eV for XPS. Peak fitting was done using the program WINSPEC.

Figure 6. Analysis of the S 2p spectrum for PCPDTBT on Au with a layer thickness of 2 nm. After rinsing, an additional feature appears at low binding energies (162 eV), which is related to a strong chemical interaction between benzothiadiazole sulfur and Au.

the interface as they are responsible for the formation of interface states and thus for energy levels that can trap the charge carriers.[30] On the other hand, interface doping (PCPDTBT/PEDT:PSS) may improve the device performance due to the optimization of interfacial barriers and the charge carrier mobility.

3. Conclusions

In summary, we have shown that interface dipoles in all cases affect the energy level alignment at technically relevant interfaces of the low-band-gap polymer PCPDTBT. The barrier heights depend on the substrate under consideration, that is, the position of the pinning level seems not to be the only characteristic for the positively or negatively charged molecule. Local chemical interactions are observed for PCPDTBT on Au in particular.

Experimental Section

Au substrates were prepared by evaporation in UHV on glass substrates (film thickness about 100 nm) for which commercial ITO-coated glass substrates were used (~ 13 Ω □⁻¹). Thin layers (nominal thickness 10–20 nm, determined from XPS spectra) of PCPDTBT (Konarka) were coated on Au or ITO substrates from chloroform solution (1 mg PCPDTBT/100 mg Chloroform) by doctor-blade casting at ambient conditions. Prior to the application of the thin film, ITO substrates were cleaned by ultrasonic treatment in acetone for 15 min. To achieve ultrathin films (1–2 nm), the doctor-bladed samples were rinsed with 0.5 mL chloroform. This procedure enables the investigation of the polymer–substrate interface.

PCPDTBT films on PEDT:PSS substrates were spin-coated from chloroform solution (1 mg mL⁻¹, rps 50) in a glovebox under N₂ atmosphere. This resulted in 10 nm thick PCPDTBT films, determined from calibration with UV/Vis absorption measurements. PEDT:PSS (H.C. Starck) was spin-coated under ambient conditions on UV/O₃-treated ITO substrates and subsequently annealed at 200 °C for 5 min.

XPS and UPS measurements of PCPDTBT/Au and PCPDTBT/ITO were carried out using a multi-chamber UHV-system (base pressure

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