Phenyl-Capped EDOT Trimer: Its Chemical and Electronic Structure and Its Interface with Aluminum

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The chemical and electronic properties of a phenyl-capped 3,4-(ethylenedioxy)thiophene trimer (EDOT trimer) and its interface formation with aluminum have been studied. Thin EDOT trimer films were prepared on clean gold substrates through in-situ vapor deposition. Aluminum was deposited stepwise on top of the EDOT trimer, and the initial stages of interface formation were investigated by photoelectron spectroscopy. The organic/metal interface formed was not completely abrupt; some degree of diffusion of aluminum into the EDOT trimer film occurred. The aluminum atoms preferentially react with the α-position of the trimer (C−S carbon atoms) forming covalent bonds. The formation of these covalent bonds causes a break in the π-conjugation of the system due to the introduction of sp³ defects. The charge density also is somewhat redistributed within the oligomer as a whole, mainly affecting the neighboring atoms: sulfur and β-position of the trimer (C=C−O carbon atoms). Once the C−S carbon sites are saturated, the aluminum instead reacts with the less favorable carbon atom of the ethylene bridge (C−O−C carbons). Worth noting is the decrease in work function from 5.2 eV for sputter cleaned gold to 4.1 eV upon deposition of the EDOT trimer. Our results have several implications for organic electronics. The sp³ defects introduced by the aluminum−EDOT contacting will influence the charge injection into the material across the EDOT trimer/aluminum interface negatively. The change in work function could potentially be used to modify gold contacts for electron injection into molecules with low electron affinity.

Introduction

The discovery of electrically conducting and semiconducting polymers in the mid 1970s[1] has led to intensive efforts aimed at developing electronic devices based on organic materials.[2−5] The application that perhaps so far has received the most interest is polymer-based light-emitting diodes,[6] but polymer/oligomer-based transistors[7] and photodiodes[8] are also being developed.

One of the more popular materials systems during the past few decades is thiophene-based oligomers and polymers. Polythiophene derivatives are and have been used widely in organic electronics.[7,9,10] The popularity of the thiophenes emancipates from the fact that they are relatively easy to synthesize, and their properties can easily be altered and designed to suit various purposes.[11] Hence, much effort has been invested in improving the environmental, thermal, and electro-chemical stability of this organic system and by using 3,4-ethylenedioxy substituents at the β-positions of the thiophene rings (see Figure 1) such improvements have been achieved.[12] The polymerized version, poly(3,4-(ethylenedioxy)thiophene),[12] PEDOT, is a good hole conductor that is highly transparent, sky blue in its p-doped state, and nontransparent, dark blue (band gap ∼1.6 eV) in its neutral state.[13] Conducting (p-doped) PEDOT and its derivatives are presently used in a wide variety of applications, including antistatic coatings, electrode material in inorganic electroluminescent lamps and capacitors, transistors,
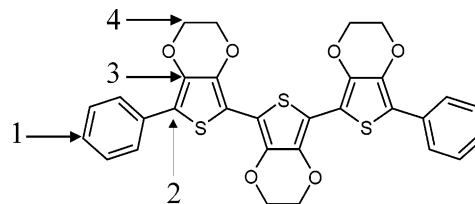

Figure 1. Molecular structure of phenyl-capped EDOT trimer.

photovoltaic devices, etc.; see ref 13 and references therein. Recently, the bistable switching between p-doped and neutral PEDOT has been utilized to realize both electrochemical transistor and display functions.[14]

In many of those applications, the PEDOT derivatives are typically contacted to metals for charge injecting purposes, though the metal films also may serve additional purposes such as forming mirrors for wave-guiding or reflectors in solar cell applications. Even though conducting PEDOT can and is used as electrode material, for applications where high current densities are required (and small loss), metals should be used due to their higher conductivities. The polymer/metal contacts can be created by depositing a metal layer onto the PEDOT film through thermal evaporation, sputtering, etc., in (ultra) high vacuum or by coating a metal surface with a PEDOT layer from solution. A very attractive approach is to use printing techniques such as ink-jet printing or off-set printing[2,4] for polymer patterning of metal substrates, and if the metal substrate is flexible such as metal-laminated plastic or paper, reel-to-reel printing of organic-based electronic components could be achieved. No matter what the application, the nature of the

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organic/metal contact greatly influences properties such as charge injection, device lifetime, efficiencies, etc.[5,15] Hence, careful study of organic/metal contacts is not only of pure basic science interest but also has a great technological importance.

In this paper we present a study on the surface properties of a phenyl-capped 3,4-(ethylenedioxy)thiophene oligomer: the EDOT trimer, see Figure 1, and its interface formation with aluminum. Its synthesis and general characteristics are described elsewhere.[16] There are two major reasons why EDOT oligomers are relevant to study. First of all, EDOT oligomers are potential candidates for inclusion in devices as, for example, organic field effect transistors and solar cells. Highly ordered oligo-EDOT films are expected to have good hole-mobility, since other thiophene oligomers such as sexithiophene (six-ringed oligomer of thiophene) have been successfully used in transistor applications.[17,18] Second, EDOT oligomers are good model systems for the popular and widely used conjugated polymer PEDOT, described previously.

Aluminum owes its wide use as an electrode material to the fact that it is a low work function metal, which is chemically stable under ambient conditions. Aluminum has therefore been widely used in organic electronics applications; many studies have been focused on organic/aluminum interfaces,[15,19–23] and there are many published works on the polythiophene/aluminum interface in particular.[24–28] However, substituent groups have been shown to sometimes strongly affect the interface formation between metals and organic molecules,[19,20] and in general, organic/metal interfaces are so complex that even small changes in molecular structure or choice of metals can dramatically change the properties of the contact.[15] Hence there is the need to study the PEDOT/aluminum interface separately, with the intent that understanding the nature of the interface between EDOT oligomers and aluminum will facilitate understanding/improving PEDOT-based devices contacted with aluminum, as well as oligo-EDOT-based transistors.

The EDOT trimer was selected because the conjugated part is long enough to act as a model molecule for neutral PEDOT, yet it could still be easily deposited by sublimation in ultrahigh vacuum. We have chosen to investigate the interface where aluminum is deposited onto the organic film, which gives rise to the least ideal interface (with diffusion). The other alternative would be to deposit a thin EDOT trimer layer (or even a monolayer) on top of an aluminum substrate, yielding a more ideal interface and thus less information.

XPS and UPS are very powerful tools to probe the chemical and electronic properties of organic/metal interfaces and are the two methods used in this work. The physical–chemical changes during the interface formation have been monitored during a stepwise evaporation of aluminum (the EDOT trimer film was previously deposited) with an information depth of a few tens of Å (given in the Experimental Section). The fact that the complete set of experiments was performed in-situ under ultrahigh vacuum conditions makes it possible to draw conclusions about the intrinsic interactions between the organic material and the metal.

Experimental Details

The experiments were carried out in a Scienta ESCA 200 spectrometer. The vacuum system consists of an analysis chamber and a preparation chamber. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) are performed in the analysis chamber at base pressure of 10^{-10} mbar, using monochromatized Al Kα X-rays, at $h\nu = 1486.6$ eV, and HeI, at $h\nu = 21.2$ eV, respectively. The

TABLE 1: (a) Elemental Ratios of Phenyl-Capped EDOT Trimer and (b) Elemental Composition of Phenyl-Capped EDOT Trimer

(a) Elemental Ratios			
	O/C	S/C	S/O
theoretical	0.2	0.1	0.5
EDOT film*	0.23	0.11	0.49

(b) Elemental Composition			
	C	O	S
theoretical	0.77	0.15	0.08
EDOT film*	0.75	0.17	0.08

experimental conditions were such that the full width at half maximum (fwhm) of the gold Au(4f$_{7/2}$) line was 0.65 eV. The binding energies are obtained with an error of ±0.05 eV.

The EDOT trimers were evaporated in-situ from powder inserted in the vacuum system in an evaporation device (a simple Knudsen cell). The crucible containing the EDOT trimer powder was heated to +400 °C, and the pressure during the sublimation was 4×10^{-8} mbar. The oligomers were deposited onto a sputtered gold substrate, which was cooled to −100 °C to increase the sticking of the oligomers on the substrate. An EDOT trimer film of thickness ~100 Å was obtained when depositing for 90 min, as was estimated from the complete suppression of the Au(4f) peaks[29] and the absence of sample charging.

The XPS and UPS spectra were taken directly after depositing the film. Subsequently, gradual aluminum deposition was performed in-situ on the film. An Omicron UHV evaporator was used. The settings for the aluminum evaporation source were calibrated such that deposition of aluminum on a sputtered clean gold surface was 1 Å/min. The deposition was done in steps of 5, 10, and 20 Å. XPS and UPS spectra were recorded after each deposition. The pressure during aluminum deposition was in the range $(3–6) \times 10^{-9}$ mbar.

Results

(i) Pristine Films on Gold. The molecular structure of phenyl-capped EDOT trimer can be seen in Figure 1. Apart from the elements present in the molecule (carbon, oxygen, and sulfur), no foreign elements were detected in XPS wide-scan spectra, which indicates that the films are contaminant free within the experimental limits (~0.1–1%).

The purity of the film obtained from vapor deposition of the EDOT trimer powder can be estimated by comparing the expected values of the elemental ratios (on the basis of the molecular structure) and the values obtained from XPS measurements. For the pristine films the stoichiometry is obtained experimentally with an error smaller than ±5% of the individual values. These numbers are given in Table 1a,b. The discrepancies between the two sets of values lie within the normal error margins of stoichiometry determination via XPS.[30] Thus, the XPS results confirm that the film obtained consists of the "true" oligomer.

There is only one type of oxygen, at ~533.4 eV binding energy, present in the film. (Note that binding energies are referenced to the Fermi level.) This corresponds to the oxygen in the C−O−C ethylene bridge in the oligomer. The binding energy lies within the range found in the literature for similar structures (532.7−533.7 eV, depending in part on the nature of the carbon atoms: aromatic or saturated). There is one sulfur species in the oligomer, a spin-split doublet S(2p), as expected for a pristine EDOT trimer film.

Phenyl-Capped EDOT Trimer

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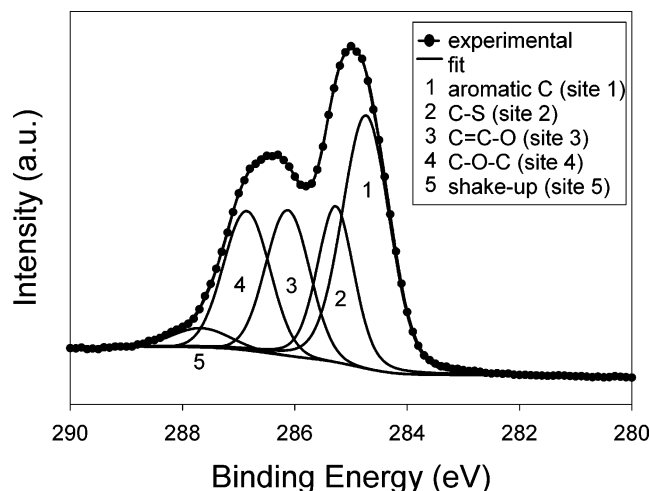
Figure 2. Peak deconvolution of C(1s) spectrum for pristine phenyl-capped EDOT trimer, referenced to the Fermi level.

TABLE 2: Data from Peak Deconvolution of the C(1s) Spectrum for Phenyl-Capped EDOT Trimer

peak	site	binding energy (eV)		area (%)
1	aromatic C	284.7		100
2	C−S	285.3	+0.5	50
3	C=C−O	286.1	+1.4	50
4	C−O−C	286.9	+2.2	50
5	shake-up	287.7	+2.9	8.5

There are four different carbon sites in the EDOT trimer as can be seen in Figure 1: site 1, *para*-position of the phenyl ring (aromatic carbon); site2, α-position of the EDOT unit (C−S carbon); site 3, β-position of the EDOT unit (C=C−O carbon); site 4, carbon atom of the ethylene bridge (C−O−C carbon). To assign peaks in the spectrum to the different sites a peak deconvolution was done. Figure 2 shows the C(1s) core level spectrum with the deconvolution. The four different carbon sites are all represented in the peak deconvolution as separate features due to binding energy shifts induced by the different chemical environments of the carbon atoms. There are 12 carbon atoms in site 1, and 6 of each of the others (site 2, 3 and 4) in each molecule; thus, peak 2−4 should have half of the intensity of peak 1 each, to match the stoichiometry of the molecule. In the peak deconvolution procedure the intensities of the peaks were initially locked to the ratios that they should have, i.e., 2:1:1:1. When a satisfactory peak deconvolution was obtained, the intensity ratio constraints were relieved. Continuation of the now free peaks did not lead to any change in the 2:1:1:1 intensity ratios or in the binding energy positions. The same procedure of initially fixed and then freed peaks were used for all peak deconvolutions in the paper.

The binding energies for the various sites, given in Table 2, correspond well to values found in the literature for similar sites in organic materials.[29,31] The extra peak 5 inserted in the peak deconvolution represents a shake-up effect and also compensates for residual background signal (background cannot be correctly accounted for by the Shirley method[32] if there are too many peaks involved). The "shake-up and background compensation" peak is ∼8.5% of the main carbon peak, which is a reasonable value according to reference literature.[31] This peak is broader than the others because of its double character. The values obtained from the peak deconvolution are summarized in Table 2. These data correspond very well to the structure of the molecule, and they provide a good fit of the experimentally obtained spectrum.
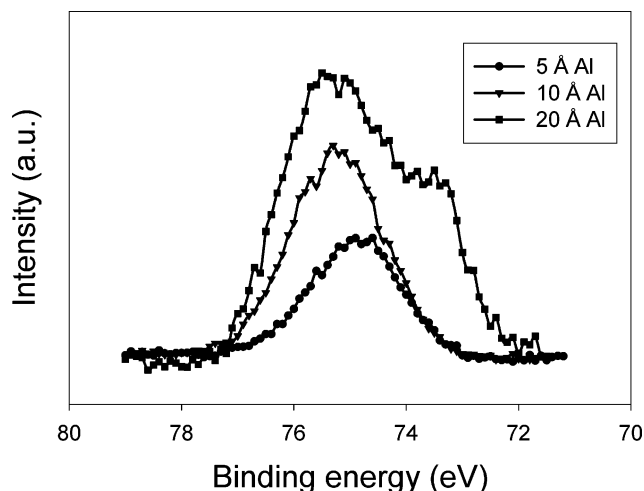
Figure 3. Al(2p) peak evolution as aluminum is deposited on the phenyl-capped EDOT trimer. The binding energy is referenced to the Fermi level, and the intensity is normalized to the number of scans taken for each spectrum.

The work function is measured to be 4.1 eV for EDOT trimer on sputtered gold substrate. This is in sharp contrast to the work function of the sputtered clean gold substrate, which is 5.2 eV. Shifts of work functions when organic films are deposited onto metal substrates can be explained by the following: (i) the modification of the metal surface dipole upon chemisorption; (ii) the metal polarization energy; (iii) the molecular contribution to the polarization energy within the monolayer.[33,34] Hence, the change in measured work function indicates that there is strong interaction between the sputtered clean gold substrate and EDOT trimer, likely chemisorption resulting in the formation of an interface dipole. An interface dipole could create a shift in the vacuum level at the interface and explain the decrease of the measured work function if the resulting dipole was oriented with the negative pole on the gold side. Given the electron-rich character of EDOT-based derivatives, meaning that they are easy to p-dope, charge transfer from the EDOT trimer to the gold substrate is reasonable to expect. Also, it has previously been shown that the EDOT monomer chemisorbs on sputtered clean gold substrates,[35,36] and as a consequence the work function changes from 5.2 eV for the gold surface to 4.0 eV for a monolayer of EDOT monomer. Hence, the change in work function observed in going from sputtered clean gold substrate to a (∼100 Å) thick EDOT trimer film is consistent with the changes observed by Birgerson et al. The ability to decrease the work function of the gold surface by over 1 eV by a relatively stable and processable molecule is quite intriguing for charge injection purposes. The modified gold (or another stable high work function metal) surface could then conceivably be used as an electron injecting contact.

The distinct features observed in the valence region (not shown) correspond well to previous valence band spectra of EDOT trimer films.[37] From the He I UPS spectrum the ionization potential (position of the highest occupied state) is estimated to be 4.9 eV. This is consistent with the value previously obtained (∼5.0 eV),[37] yet again confirming that clean, pristine EDOT trimer films are obtained.

(ii) Aluminum on EDOT Trimer Interface. The evolution of the Al(2p) core level is shown in Figure 3. At 5 and 10 Å there is a broad peak evolving at ∼75 eV binding energy (referenced to Fermi level). This corresponds to aluminum atoms that have donated charge. Not until 20 Å aluminum coverage is there a peak appearing at lower binding energies, ∼73.5 eV,

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TABLE 3: Peak Areas of Al(2p) Intensities/Areas with Increasing Aluminum Deposition under the Same Conditions for a Gold Substrate (No Diffusion) and an EDOT Trimer Film (Diffusion)

	on Au substrate	on EDOT film	EDOT/Au
5 min/5 Å Al	1138	1045	0.92
10 min/10 Å Al	2276	1980	0.87
20 min/20 Å Al	4552	4051	0.89

which corresponds to metallic aluminum. Previous studies of aluminum deposited onto conjugated organic systems indicate that clustering at the surface as well as diffusion in the near surface region of the organic material occurs.[38] The length scale of the diffusion was estimated to $\sim$20$-$30 Å (the order of an electron tunneling distance).[38] The data obtained in this work follow this trend. The same amount of deposited aluminum on gold substrates ($\sim$10 Å equivalent thickness) gives a metallic Al(2p) feature (not shown) whereas for aluminum on EDOT no metallic feature is visible in the Al(2p) spectrum; see Figure 3. This suggests that there must be some aluminum diffusion in the EDOT case, probably in combination with clustering. The amount of diffusion in the EDOT trimer film is determined by comparing the Al(2p) peaks for aluminum deposited onto a sputtered clean gold substrate and on a film of EDOT trimer. The values from these measurements are given in Table 3. The areas are based on wide scans (the only ones taken for Al/Au-series); thus, there are large error margins. Clustering will also introduce errors given that the substrate signal is enhanced and hence the overlayer thickeness will be underestimated.

We can conclude that there is clustering as well as some diffusion in the EDOT trimer material. This means that there is not an immediate overlayer formed, thus not a clean or ideal interface. There is instead an interfacial layer where there is a mixture of the EDOT trimer and aluminum more or less reacted with each other. Once there is an overlayer of aluminum formed, no more diffusion of aluminum into the organic film is expected, and the aluminum should be deposited as metallic aluminum on top of the interfacial layer in absence of oxygen in the vacuum chamber.

The stoichiometry data from the measurement series with increasing aluminum deposition are given in Table 4a$-$c. The uncertainty increases with the amount of aluminum deposited but remains below $\pm$10% of the individual values. The intensity of the Al(2p) peak increases as expected upon deposition. The intensities of the peaks O(1s), C(1s), and S(2p) decrease as more aluminum is deposited onto the film. This is assumed to merely be due to the overlayer caused by the aluminum deposition and not due to any degradation of the organic material. From Table 4a, S/C is constant while O/C increases and S/O decreases, though only significantly for the 20 Å aluminum thickness. Again, assuming that the molecule is intact, i.e., no part is broken or cut off and pumped away due to chemical interaction with aluminum, then the relative amount of carbon and sulfur should remain the same. This is clearly the case, as illustrated in Table 4c. Meanwhile, the relative amount of oxygen increases which shows that there is a trace surplus of oxygen in the film, which increases with the aluminum deposition and emancipates from oxygen from the chamber and/or water captured in the film during the film deposition process (less likely). This surplus of oxygen reacts with aluminum as it is deposited onto the film, producing some form of aluminum oxide. Given that the significant increase of the oxygen content occurs when going from 10 to 20 Å in aluminum thickness, it is likely that oxygen from the background pressure plays the major role. For the 5 and 10 Å aluminum thicknesses, no continuous aluminum

TABLE 4: (a) Elemental Ratios of Phenyl-Capped EDOT Trimer with Gradual Aluminum Deposition, (b) Elemental Composition of Phenyl-Capped EDOT Trimer upon Gradual Aluminum Deposition, and (c) Relative Elemental Change of Phenyl-Capped EDOT Trimer upon Gradual Aluminum Deposition

(a) Elemental Ratios						
	O/C	S/C	Al/C	S/O	Al/O	Al/S
theoretical	0.2	0.1		0.5		
EDOT film	0.23	0.11	0.00	0.49	0.00	0.00
5 Å Al	0.24	0.11	0.04	0.449	0.16	0.35
10 Å Al	0.25	0.10	0.07	0.40	0.29	0.73
20 Å Al	0.31	0.10	0.30	0.33	0.97	2.95

(b) Elemental Composition				
	C	O	S	Al
EDOT film	0.75	0.17	0.08	0.00
5 Å Al	0.72	0.17	0.08	0.03
10 Å Al	0.70	0.18	0.07	0.05
20 Å Al	0.58	0.18	0.06	0.18

(c) Relative Elemental Change				
	C/C$_{initial}$	O/O$_{initial}$	S/S$_{initial}$	Al/Al$_{initial}$
EDOT film	1.00	1.00	1.00	
5 Å Al	0.93	0.97	0.88	1.00
10 Å Al	0.88	0.97	0.78	1.83
20 Å Al	0.42	0.56	0.38	3.60

overlayer is formed, and thus, if it was excess oxygen in the film that reacted, the effect should be stronger here which is not the case. Also, the Al(2p) peak at low aluminum coverage (5 Å) is at slightly lower binding energy than the one at higher coverage, indicating a less oxidized version of aluminum at the organic/metal interface, i.e. Al$-$EDOT trimer bonds. Hence, the data indicate that aluminum reacts with the EDOT trimer film, and when the film interface region is saturated by reacted aluminum, metallic aluminum (and some aluminum oxide) is deposited onto this reacted EDOT trimer/aluminum layer.

To determine how aluminum reacts with the EDOT trimer, the different peaks in the XPS spectra corresponding to atom sites in the oligomer are studied as the amount of deposited aluminum increases. From the stoichiometry data in Table 4 it is shown that the oxygen signal decreases less than the carbon and sulfur, indicating that there is extra oxygen added to the film as discussed above.

In the O(1s) spectra evolution depicted in Figure 4, there is a new component evolving at the low binding energy side. This is the oxygen signal arising from the new oxygen species, aluminum oxide. The intensity of this new peak corresponds to the surplus of oxygen in the film. The binding energy position of the new feature corresponds to values for Al$_2$O$_3$ found in the literature (with the vacuum level shift of 1.1 eV taken into account). The EDOT trimer oxygen sites, however, are not noticeably affected by the deposition of aluminum atoms. This is in agreement with results on alkoxy-substituted poly(*p*-phenylenevinylene) derivatives.[19,20]

The evolution of the S(2p) spectra with increasing aluminum coverage is given in Figure 5. There is a new feature appearing at the lower binding energy side of the S(2p) spectra after aluminum deposition. Thus, the deposited aluminum affects the sulfur sites. Deconvolutions of the S(2p) core level feature are depicted in Figure 6a$-$d, and the relative intensities are presented in Table 5. The S(2p) core level is a spin-split doublet, S(2p$_{3/2}$) and S(2p$_{1/2}$), so a sulfur atom gives rise to two peaks in the S(2p) core level spectrum with an energy splitting of $\sim$1.2 eV and an intensity ratio of 1:2. The appearance of a new spin split doublet upon aluminum deposition at lower binding

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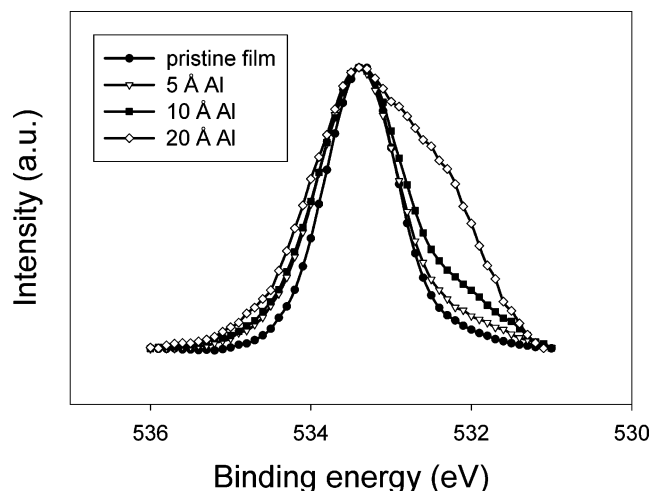
Figure 4. O(1s) peak evolution as aluminum is deposited on phenyl-capped EDOT trimer. The binding energy is referenced to the Fermi level, and the intensity is normalized to the number of scans taken for each spectrum.
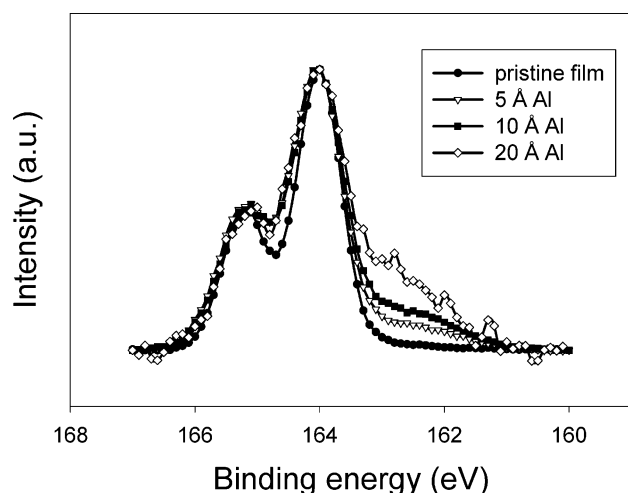
Figure 5. S(2p) peak evolution as aluminum is deposited on phenyl-capped EDOT trimer. The binding energy is referenced to the Fermi level, and the intensity is normalized to the number of scans taken for each spectrum.

TABLE 5: Pristine EDOT Trimer Sulfur (Peak 1) and New Sulfur Feature Appearing upon Aluminum Deposition (Peak 2)[a]

	binding energy (eV)		area (%)	
	peak 1 S(2p$_{3/2}$)	peak 2 S(2p$_{3/2}$)	peak 1	peak 2
EDOT	163.9	-	100	0
5 Å Al	164.1	162.3	92	8
10 Å Al	164.0	162.4	87.5	12.5
20 Å Al	164.0	162.6	75	25

[a] Only the main peak of each spin split doublet is listed.

energy suggests that some of the sulfur atoms have received charge (e⁻) or that the neighboring carbon atoms, site 2, have received charge. In either case, a core hole created on the sulfur atom during the photoemission event would then be better screened either by the remaining electrons on the sulfur atoms or by the neighboring carbons, resulting in the shift toward lower binding energy detected in the spectra.

As is depicted in Figure 7, the shape of the C(1s) spectrum changes significantly as compared to pristine EDOT trimer (Figure 2), which indicates that aluminum reacts with the carbon sites in the EDOT trimer. The main C(1s) line corresponding

TABLE 6: (a) C(1s) Peak Deconvolution Parameters for 5 Å Aluminum on the EDOT Film, (b) C(1s) Peak Deconvolution Parameters for 10 Å Aluminum on the EDOT Film, and (c) C(1s) Peak Deconvolution Parameters for 20 Å Aluminum on the EDOT Film, with Extra Peak

peak	posn (eV)	area (%)
	(a) C(1s) Parameters for 5 Å Al	
1	284.7	100
2	285.2	38
3	286.1	38
4	286.8	50
5	287.6	9.2
6	285.8	12
7	284.0	12
	(b) C(1s) Parameters for 10 Å Al	
1	284.7	100
2	285.2	36
3	286.1	36
4	286.8	50
5	287.6	7.3
6	285.8	14
7	284.0	14
	(c) C(1s) Parameters for 20 Å Al	
1	284.7	100
2	285.2	31
3	286.1	31
4	286.8	40
5	287.7	10.7
6	285.8	19
7	283.8	19
8	285.3	10

to aromatic carbon (phenyl rings) does not significantly change in binding energy position. This is agreement with literature, where previous studies showed that aliphatic and aromatic carbon do not tend to react.[19,20,39] However, through peak deconvolution of the C(1s) core level spectrum, it is evident that sites 2 (C−S) and 3 (C=C−O) are affected, and upon aluminum deposition peaks 6 and 7 have to be inserted to represent the site 2 and 3 carbons affected by the aluminum atoms to obtain a good fit. The amounts of altered sites 2 and 3 carbons should be the same, if the aluminum preferentially attacks the site 2 carbons. Bond formation between aluminum and a carbon on site 2 would break the π-conjugation and thus effect the charge distribution on its ring neighbors (sulfur and the site 3 carbon). No change was seen for site 4 (unaffected by the aluminum atoms as expected from literature) so its peak parameters were kept fixed.

For 5 Å aluminum deposition the best peak deconvolution was obtained for 24% of the sites 2 and 3 being altered, suggesting that aluminum preferentially bonds with the site 2 carbons, as stated above. If the aluminum atoms would bond to the site 3 carbons, we would expect a significant change in the O(1s) spectrum as well, which does not occur. Also, for a site 3 reaction we would not expect to see a change in the S(2p) spectrum. Correspondingly, if aluminum interacted directly with the sulfur, we would expect the site 2 carbons to be chemically shifted but not the site 3 carbons. Thus, we conclude that site 2 is the reaction site for aluminum at the 5 Å coverage. The outcome of the deconvolution can be seen in Figure 7a, where 24% of the C−S carbon atoms are attacked by the aluminum atoms leaving 76% unaffected, and the C=C−O carbon atoms are affected in the same amount by this attack as expected from the proposed reaction scheme. The best peak deconvolution is obtained when peaks 2 and 3 are affected by the same amount. Table 6a shows that the relative intensity of the site 2 and 3 carbons have gone from 50% to 38% of the main C(1s) peak (aromatic carbons from the phenyl end caps). The two new
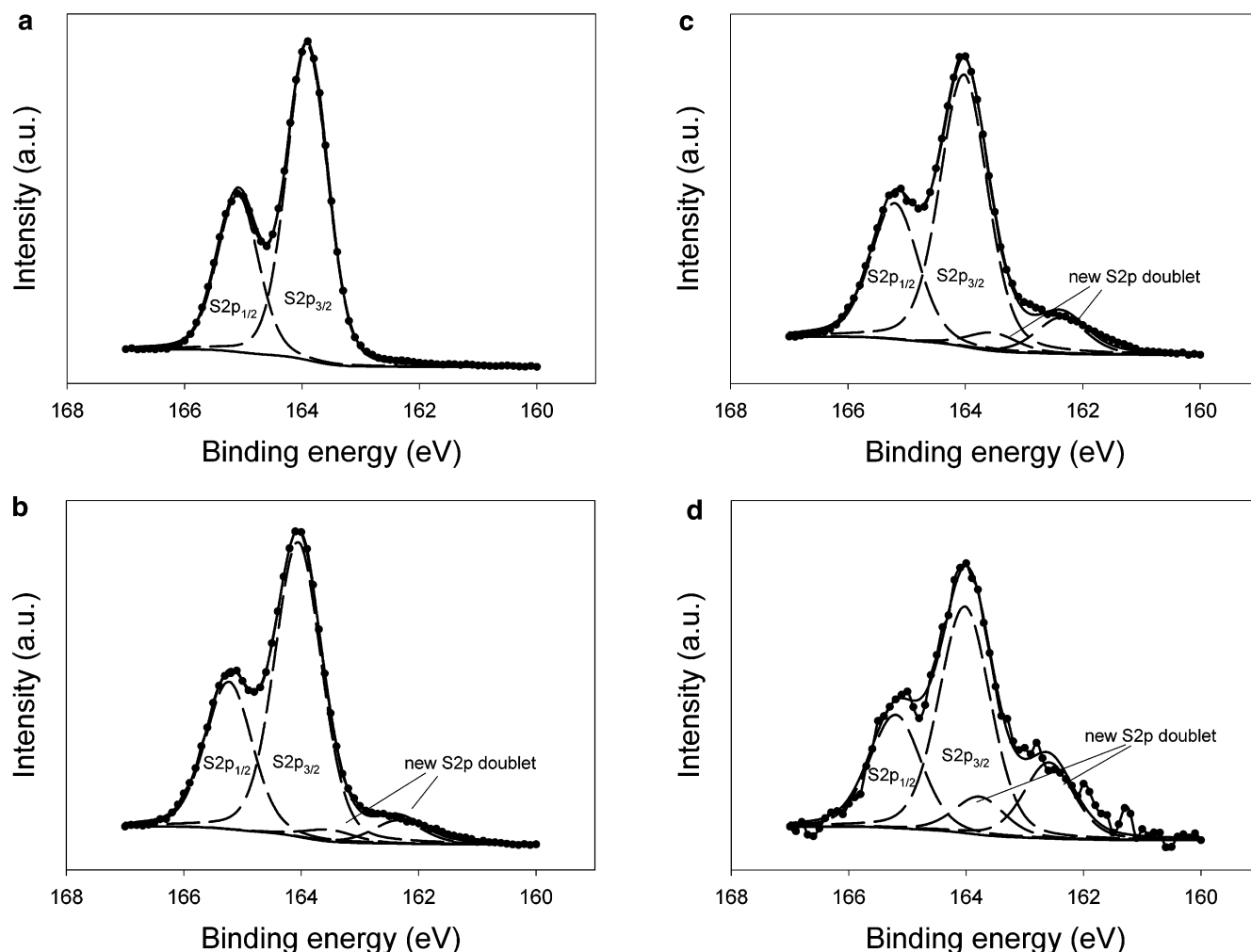
Figure 6. Peak deconvolution of the S(2p) spectrum for (a) pristine phenyl-capped EDOT trimer and (b) 5 Å, (c) 10 Å, and (d) 20 Å aluminum referenced to the Fermi level.

peaks, 6 and 7, corresponding to the modified C−S and C═C−O, respectively, have 12% relative intensity each, as expected if the total amount of carbons is conserved (no film degradation). To summarize, the altered site 2, Al−C−S, is represented by peak 7 and the altered site 3, C═C−O, is represented by site 6. Because aluminum is an electron donor, both of these altered sites have resulting lower binding energies than their respective unaffected sites.

For 10 Å aluminum deposition, 28% of the C−S and the C═C−O carbon sites are affected by the aluminum atoms; thus, 72% remain the same. The peak deconvolution is presented in Figure 7b. The relative intensities of sites 2 and 3 are now 36%, and the modified Al−C−S and C═C−O sites, peaks 6 and 7, have 14% relative intensity each (Table 6b), again suggesting a nondegrading film and the reaction scheme where the aluminum atoms react with the site 2 carbon.

For 20 Å aluminum deposition, the experimental spectrum can no longer be adequately fitted with the peaks previously used, implying that the reaction scheme above is not correct at high aluminum coverage. In fact, it is clear from the spectra that site 4 (C−O−C carbon) is affected at this coverage. Hence, we need to add an additional peak representing the Al-ethylenedioxy interaction, peak 8. The appearance of the new reaction site is probably due to that the preferential reaction sites (site 2) in the interface region become saturated, and the "excess" aluminum has to use less favorable sites. Peak deconvolution leads to 38% of the C−S and the C═C−O carbon

sites affected by the aluminum atoms; thus, 62% remain the same (Table 6c). This corresponds to 31% relative intensity for peaks 2 and 3 and 19% relative intensity for peaks 6 and 7. Peak 8 has a 10% relative intensity which is matched by the decrease in site 4 intensity from 50% to 40%, as is be expected from the proposed reaction scheme.

In the spectra deconvolution above there is always a peak 5, which represents the effect of shake-up and compensates for the complicated background due to the many different peaks, as mentioned previously. This peak varies between 7 and 10% of the main carbon line for the different peak deconvolutions, which is a reasonable value,[31] and does not affect our overall conclusions.
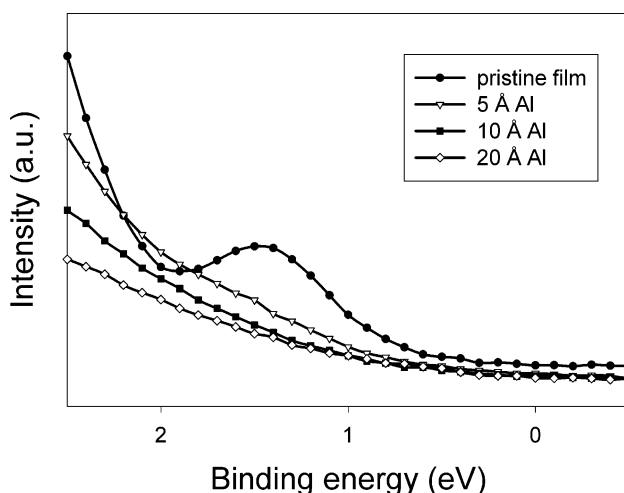
Further evidence of aluminum bonding with the EDOT trimer is obtained from He I UPS spectra. As aluminum is deposited onto the film, the work function drops slightly from 4.1 to 3.9 eV. The distinct peaks in the valence band region derived from the π-electronic states delocalized over the EDOT trimer, the HOMO peak in particular, are "smoothened" out upon the aluminum deposition, and the effect is significant even at the low coverage of 5 Å; see Figure 8. This suggests that the conjugation along the EDOT trimer is disrupted,[21] in agreement with our proposed reaction scheme. At 20 Å aluminum the HOMO peak is completely flat, though, at this coverage, an aluminum overlayer has begun to form (metallic aluminum seen in Al(2p) spectrum), so the Al−EDOT trimer signal also is partly dampened.

Phenyl-Capped EDOT Trimer

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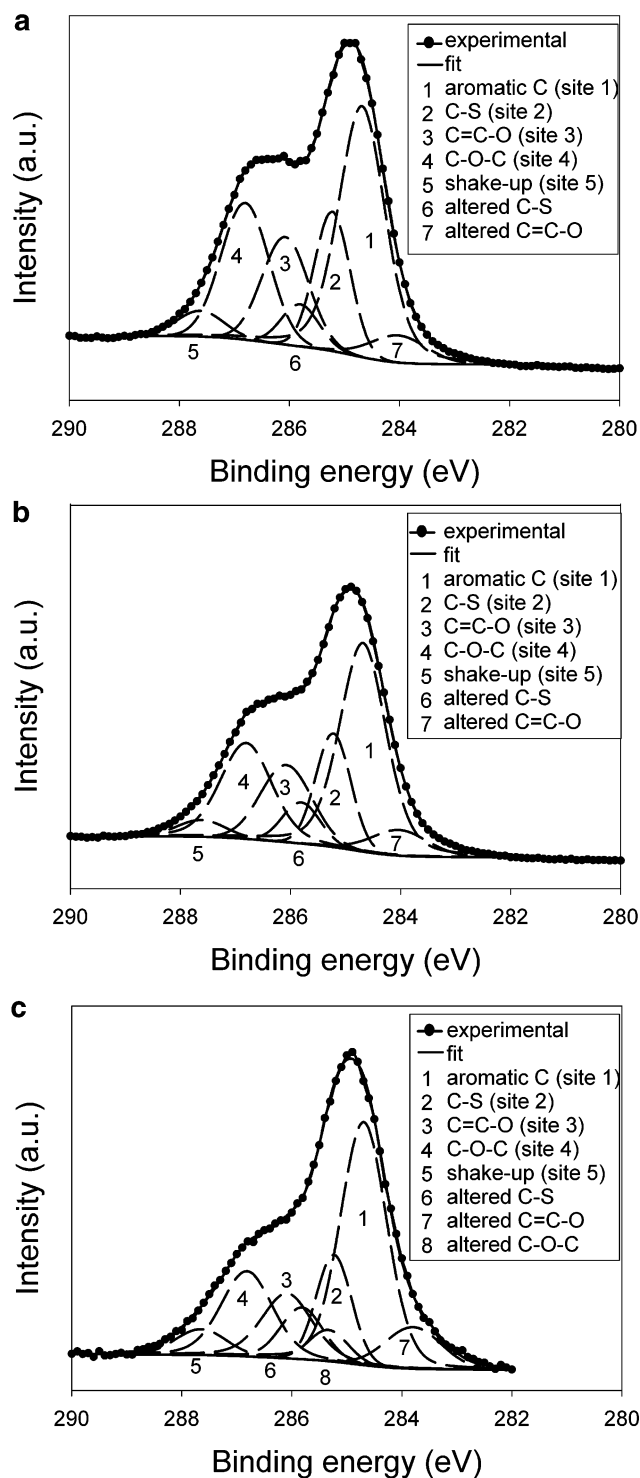
Figure 7. Peak deconvolution of the C(1s) spectrum for (a) 5 Å, (b) 10 Å, and (c) 20 Å aluminum on phenyl-capped EDOT trimer, referenced to the Fermi level.

Figure 8. UPS He I spectra of the HOMO peak as aluminum is deposited on phenyl-capped EDOT trimer.

Discussion

Due to the fact that EDOT trimer does not make up a "closed lattice structure", but is an organic soft material, the aluminum atoms are able to diffuse into the material upon deposition. Since the aluminum atoms react with the organic film, this could decrease the diffusion. Once an aluminum atom has reacted with a specific EDOT oligomer it will stick to this molecule and not diffuse further in the film. However, the question is if this also prohibits other aluminum atoms to diffuse or if it instead facilitates their diffusion (less sites available at the surface region to react with). Moreover, the creation of aluminum oxides due to (likely) background oxygen pressure further complicates the diffusion process, though we assume that an increased presence of oxygen at the surface would prevent diffusion resulting in Al−O−EDOT trimer complexes. The amount of aluminum atoms that diffuses is about 10% of the total amount in our experiments. The fact that the UPS valence band features are smoothened out so quickly indicates that the diffusion into the material is limited, supported by the fact that we still see unreacted EDOT trimers in the XPS spectra even at metallic aluminum coverage (20 Å) (UPS is more surface sensitive than XPS). The scale of the diffusion is thus roughly estimated to be at the most ∼20−30 Å.

The reaction scheme derived from our experiments, aluminum interacting preferentially with the site 2 carbon (forming covalent bonds), followed by interaction with the site 4 (ethylenedioxy) carbon, is in part supported by results on "pure" polythiophene. In those studies, the site 2 carbon was also the preferred reaction site for aluminum, and the adjacent sulfur atom received part of the charge transferred from the aluminum.[24,25,27] However, in contrast to our result, the site 3 carbon did not receive additional charge and was unaffected by the aluminum deposition. To explain this difference, we propose that the charge withdrawing nature of the ethylenedioxy substituent group cause the site 3 carbon to be electron deficient, as is supported by the shift toward higher binding energy in the C(1s) core level spectrum. This electron deficiency may then make the site 3 carbon more likely to accept some of the charge transferred to the site 2 carbon than is the case for pure polythiophene where the site 3 carbons are bonded to a hydrogen atom instead of the ethylenedioxy group.

The work function change, 0.2 eV, is almost within the experimental error, so it should not significantly affect charge injection properties. However, since the aluminum bonding to the site 2 carbons causes a disruption of the π-conjugation, the mobility of the interface region is expected to be substantially lower and could provide electron traps. Hence, it may be necessary to use a thin buffer layer such as LiF to prevent Al−EDOT trimer interaction[21] or change the oxygen background pressure to obtain a more abrupt interface in a device.[40] Depositing EDOT trimer on top of an existing aluminum film would likely reduce the diffusion problem as well, given that the perturbed interfacial layer should then only be one monolayer thick.

Conclusion

Aluminum interacts strongly with the phenyl-capped EDOT trimer preferentially forming covalent bonds with the site 2 carbons of the thiophene rings. Aluminum donates charge to the site 2 carbon, and some of that charge is further transferred to the site 3 carbon and the thiophene sulfur. When the site 2 reaction sites are saturated in the interface region (∼20−30 Å), aluminum bonds with the site 4 carbon of the ethylenedioxy groups, here too donating charge. The strong chemical interactions perturb the original bond structure and charge distribution of the oligomer, disrupting the π-conjugation along the EDOT trimer. This could have a negative impact on the charge transport across the interface, thus inhibiting the overall performance of an EDOT oligomer (and possibly PEDOT) device. Therefore, if EDOT oligomers were to be used with aluminum contact(s), the interaction of aluminum with the oligo-EDOT should probably be limited either by thin interfacial layers or by decreasing the Al−EDOT oligomer interfacial region.

References and Notes

(1) Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gua, S. C.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098.

(2) Gelinck, G. H.; Geuns, T. C. T.; de Leeuw, D. M. *Appl. Phys. Lett.* **2000**, *77*, 1487.

(3) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741.

(4) Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P. *Science* **2000**, *290*, 2123.

(5) Fahlman, M.; Salaneck, W. R. *Surf. Sci.* **2002**, *500*, 904.

(6) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(7) Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 684.

(8) Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498.

(9) Tsumura, A.; Koezuka, H.; Ando, T. *Appl. Phys. Lett.* **1986**, *49*, 1210.

(10) Li, X. C.; Sirringhaus, H.; Garnier, F.; Holmes, A. B.; Moratti, S. C.; Feeder, N.; Clegg, W.; Teat, S. J.; Friend, R. H. *J. Am. Soc.* **1998**, *120*, 2206.

(11) Berggren, M.; Inganas, O.; Gustafsson, C.; Rasmusson, J.; Andersson, M. R.; Hjertberg, T.; Wennerstrom, O. *Nature* **1994**, *372*, 444.

(12) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.

(13) Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.

(14) Nilsson, D.; Chen, M.; Kugler, T.; Remonen, T.; Armgarth, M.; Berggren, M. *Adv. Mater.* **2002**, *14*, 51.

(15) *Conjugated polymer and molecular interfaces: Science and technology for photonic and optoelectronic applications*; Salaneck, W. R., Seki, K., Kahn, A., Pireaux, J.-J., Eds.; Marcel Dekker: New York, 2002.

(16) Apperloo, J.; Groenendaal, L.; Verheyen, H.; Jayakannan, M.; Janssen, R.; Dkhissi, A.; Beljonne, D.; Lazzaroni, R.; Bredas, J.-L. *Chem.−Eur. J.* **2002**, *8*, 2384.

(17) Horowitz, G.; Garnier, F.; Yassar, A.; Hajaoui, R.; Kouki, F. *Adv. Mater.* **1996**, *8*, 52.

(18) Brown, A. R.; Jarrett, C. P.; de Leeuw, D. M.; Matters, M. *Synth. Met.* **1997**, *88*, 37.

(19) Lögdlund, M.; Brédas, J. L. *J. Chem. Phys.* **1994**, *101*, 4357.

(20) Fahlman, M.; Salaneck, W. R.; Moratti, S. C.; Holmes, A. B.; Brédas, J. L. *Chem.−Eur. J.* **1997**, *3*, 286.

(21) Greczynski, G.; Fahlman, M.; Salaneck, W. R. *J. Chem. Phys.* **2000**, *113*, 2407.

(22) Greczynski, G.; Salaneck, W. R.; Fahlman, M. *J. Chem. Phys.* **2001**, *114*, 8628.

(23) Hung, L. S.; Tang, C. W.; Mason, M. G. *Appl. Phys. Lett.* **1997**, *70*, 152.

(24) Boman, M.; Stafstrom, S.; Bredas, J. L. *J. Chem. Phys.* **1992**, *97*, 9144.

(25) Dannetum, P.; Boman, M.; Stafström, S.; Salaneck, W. R.; Lazzaroni, R.; Fredriksson, C.; Brédas, J. L.; Zamboni, R.; Taliani, C. *J. Chem. Phys.* **1993**, *99*, 664.

(26) Dannetun, P.; Lögdlund, M.; Fahlman, M.; Boman, M.; Stafström, S.; Salaneck, W. R.; Lazzaroni, R.; Fredriksson, C.; Bredas, J.-L.; Graham, S.; Friend, R. H.; Holmes, A. B.; Zamboni, R.; Taliani, C. *Synth. Met.* **1993**, *55*, 212.

(27) Lazzaroni, R.; Bredas, J.-L.; Dannetun, P.; Lögdlund, M.; Uvdal, K.; Salaneck, W. R. *Synth. Met.* **1991**, *41*, 3323.

(28) Lazzaroni, R.; Lögdlund, M.; Calderone, A.; Bredas, J.-L. *Synth. Met.* **1995**, *71*, 2159.

(29) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; 1992.

(30) Wagner, C. D.; Davis, L. E.; Zeller, M. V.; Taylor, J. A.; Raymond, R. H.; Gale, L. H. *Surf. Interface Anal.* **1981**, *3*, 211.

(31) Beamson, G.; Briggs, D. *High-resolution XPS of organic polymers-The Scienta ECSA300 Database*; J. W. S. Ltd.: 1993.

(32) Shirley, D. A. *Phys. Rev. B* **1972**, *5*, 4709.

(33) Crispin, X.; Lazzaroni, R.; Crispin, A.; Geskin, V. M.; Brédas, J. L.;

(34) Salaneck, W. R. *J. Electron Spectrosc. Relat. Phenom.* **2001**, *121*, 57.

(35) Crispin, X.; Geskin, V. M.; Crispin, A.; Cornil, J.; Lazzaroni, R.; Salaneck, W. R.; Brédas, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 8132.

(36) Birgerson, J.; Keil, M.; Denier van der Gon, A.; Crispin, X.; Lögdlund, M.; Salaneck, W. *Mater. Res. Soc. Symp. Proc.* **2001**, *660*, JJ5.29.

(37) Birgerson, J. *A study of materials and devices for polymer electronics*, in *Department of Physics and Measurement Technology*; Linköpings Universitet: Linköping, Sweden, 2002; pp 105−113.

(38) Osikowicz, W.; deJong, M. P.; Crispin, X.; Denier van der Gon, A.; Dkhissi, A.; Beljonne, D.; Apperloo, J.; Birgerson, J.; Fahlman, M.; Groenendaal, L.; Lazzaroni, R.; Bredas, J.-L.; Salaneck, W. Manuscript in preparation.

(39) Birgerson, J.; Fahlman, M.; Bröms, P.; Salaneck, W. R. *Synth. Met.* **1996**, *80*, 125.

(40) Koch, N.; Yu, L.-M.; Parente, V.; Lazzaroni, R.; Johnson, R. L.; Leising, G.; Pireaux, J.-J.; Bredas, J.-L. *Synth. Met.* **1999**, *101*, 438.

(41) Bröms, P.; Birgersson, J.; Johnsson, N.; Lögdlund, M.; Salaneck, W. R. *Synth. Met.* **1995**, *74*, 179.