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The electronic structure of *n*- and *p*-doped phenyl-capped 3,4-ethylenedioxythiophene trimer

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The phenyl-capped 3,4-ethylenedioxythiophene (EDOT) trimer is a well-defined oligomer of the related poly(3,4-ethylenedioxythiophene), the conjugated polymer that forms the basis of the commercialized conducting polymer “PEDOT-PSS.” EDOT-based oligomers are themselves potential candidates for applications in molecular electronics, such as organic field effect transistors and organic solar cells. Well controlled chemical doping is of importance in such applications, since it enables tuning of important properties such as the electrical conductivity, the position of the Fermi-level, the optical absorption edge, and the quantum efficiency for photovoltaic devices. The effects of chemical doping, both *p*-type doping with iodine, and *n*-type doping with lithium, on the electronic structure of condensed molecular solid films of EDOT trimer have been studied using ultraviolet photoelectron spectroscopy and x-ray photoelectron spectroscopy. The results are discussed in terms of parameters important for device applications. © 2003 American Institute of Physics. [DOI: 10.1063/1.1558037]

I. INTRODUCTION

Recently, a series of phenyl-capped 3,4-ethylenedioxythiophene (EDOT) oligomers was synthesized.¹ One of these, the trimer, is shown in Fig. 1. This molecule is of interest for two reasons. First, it is a candidate for application in molecular electronics in organic field effect transistors (OFETs) and organic solar cells. In such applications, tuning the charge carrier concentration and the conductivity by means of chemical doping can play a crucial role, as discussed below. Second, the EDOT trimer can be regarded as a model compound for the parent polymer poly(3,4-ethylenedioxythiophene) (PEDOT), for which well-controlled doping studies are difficult to perform.² In the present work, the effects of chemical doping on the chemical and electronic structure of condensed molecular solid films of the EDOT trimer have been studied using ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS).

Oligo- and polythiophenes have been studied extensively during the past decade, due largely to their suitable properties for the fabrication of OFETs^{3,4} and organic solar cells.^{5–8} Until now, EDOT-based oligomers have not received as much attention, probably because they are difficult to synthesize and, in case of the longer species, sensitive to air oxida-

tion. Recently published studies on oligomers of EDOT include bis 2-(3,4-ethylenedioxy)thienyl that can be electrochemically polymerized to form electrochromic conducting polymers,⁹ and α,ω -bis(mesitylthio)(3,4-ethylenedioxythiophene) for molecular scale electronics applications.¹⁰ The phenyl-capped EDOT trimer considered in this work is quite stable in air, is solution processable and can be deposited onto suitable substrates in vacuum by sublimation at moderate temperatures. The phenyl end-caps prevent irreversible coupling reactions upon doping. The ultrathin films studied here were prepared by vapor deposition in vacuum, which enables the growth of solid films with a high degree of molecular ordering.

With respect to β,β' -unsubstituted oligothiophenes, EDOT oligomers are more electron rich and, therefore, have a lower oxidation potential, due to the electron donating ethylenedioxy groups on the thiophene rings. Consequently, the optical absorption spectrum is redshifted,¹ which is beneficial for solar cell applications. This has recently been demonstrated for polythiophenes and oligothiophenes containing various electron-donating groups.^{5,6} Additionally, EDOT oligomers have a more rigid planar π -electron system compared to thiophene oligomers,¹ which is thought to be due to intrachain interactions between sulfur and oxygen atoms.^{1,11,12}

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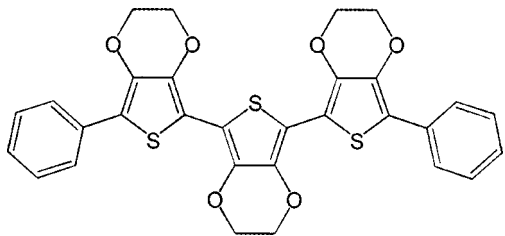


FIG. 1. Molecular structure of the phenyl-capped EDOT trimer.

II. MOTIVATION

In OFETs, much attention has been paid to the optimization of the charge carrier mobility, which is mainly determined by the degree of macroscopic ordering in the molecular solid.¹³ At present, pentacene based OFETs have been reported that show similar hole mobilities as amorphous silicon devices.^{14,15} The possibility of precisely controlling the electrical conductivity by means of chemical doping in organic semiconductors is also of great importance for (opto)-electronic devices. This has motivated several recent studies of the effects of chemical doping on the charge carrier concentration, trap density, electrical conductivity, and charge carrier mobility in molecular semiconductors.¹⁶ Iodine doping of ordered pentacene¹⁷ has been shown to control the conductivity over 10 orders of magnitude. In such crystalline molecular solids, highly ordered charge transfer complexes are formed with I_3^- ions incorporated between planes of π -stacked organic molecules.¹⁷ Chemical doping with iodine, therefore, seems to be a promising way to tune the electrical properties of organic semiconductors.

Recently, controlled *p*-doping of hole-transporting π -conjugated polymers has led to improved operation characteristics of organic light emitting diodes (OLEDs).^{18–20} In organic solar cells, tuning the doping level has also resulted in dramatically improved device performance.²¹ The improved photovoltaic properties as a result of doping are attributed to increased conductivity, a shift in the optical absorption edge, and improved quantum efficiency.

PEDOT is a π -conjugated polymer with a low oxidation potential and a narrow optical band gap, and has an exceptionally high environmental stability *in the oxidized state*.² By using poly(styrene sulfonic acid) (PSS) as a counter-ion to the positive charge on the PEDOT, a soluble and highly stable PEDOT-PSS complex is obtained. PEDOT-PSS is presently used in various applications where stability, good film forming properties, high electrical conductivity, and/or high transparency for visible light^{2,22} are important. In its neutral state, however, PEDOT is insoluble and easily oxidized. The electronic and optical properties of neutral PEDOT are therefore difficult to study, as is the evolution of these properties upon doping. To understand the doping induced changes in the electronic structure of PEDOT on a molecular level, studying oligomers as model compounds is, therefore, a good alternative.

The main advantage of PEDOT-PSS over other oxidized PEDOT complexes is its ability to form a stable dispersion in water, which allows for easy processing of the material. However, it is possible to obtain *ordered* doped PEDOT

films using thermally activated polymerization of EDOT-toluenesulfonate²³ or electrochemical polymerization of EDOT-(tetrabutylammonium hexafluorophosphate).²⁴ In both cases, x-ray diffraction data showed that paracrystalline material was obtained, with the PEDOT chains arranged in π -stacked planes and the dopants situated between those planes. This is a very similar structure to that observed for iodine doped pentacene crystalline films. Therefore, we expect iodine-doped EDOT trimer to be a suitable model system, in terms of electronic structure, for such ordered doped PEDOT films.

It has been recently shown that both *p*- and *n*-doping of PEDOT result in electrically conducting material.²⁵ Nevertheless, *n*-doped PEDOT proved to be unstable even in a dry oxygen-free environment, and its maximum conductivity was about 1% of that of *p*-doped PEDOT. It is therefore interesting to study the electronic structure of both *p*- and *n*-doped EDOT trimer.

III. EXPERIMENT

The EDOT trimer was synthesized as described recently in the literature.¹ Thin films of the EDOT-trimer were prepared by vapor deposition onto polycrystalline gold substrates inside the sample preparation chamber of an ultrahigh vacuum (UHV) UPS/XPS spectrometer of our own design and construction.²⁶ A glass crucible, a simple Knudsen cell, containing a few mg of the material was heated inside the preparation chamber (base pressure $\approx 10^{-9}$ mbar) to sublime the molecules, which were subsequently condensed on a substrate at -100°C . The sublimation temperature was adjusted such that the deposition rate was close to 1 Å per minute. The substrate was etched with Ne-ions and annealed prior to deposition in order to obtain a contaminant-free surface. The thickness of the as-deposited EDOT-trimer films varied between 5 and 10 nm, as was estimated from the attenuation of the Au(4*f*) photoelectron lines in XPS experiments.

Doping of the samples was carried out *in situ*, which enabled a study of the changes in the electronic structure while going from a pristine to a doped system in a precisely controlled way. *p*-type doping was achieved by exposing the sample to I_2 vapor, at room temperature, using an external gas handling system. The sample was kept at -50°C during the treatment, which proved to be an optimum trade-off between increasing the sticking coefficient of I_2 molecules on the surface of the film and stimulating subsequent I_2 diffusion, and doping of the EDOT trimer. For *n*-type doping, lithium vapor was used, from a Li-getter source in the sample preparation chamber. The doping rate could be controlled by varying the current through the getter source. The sample temperature was kept constant at -100°C during Li-doping, the same temperature at which the EDOT trimer was deposited.

Using a differentially pumped transfer shaft, the samples were transferred to the analysis chamber of the spectrometer (base pressure $< 10^{-9}$ mbar) for UPS and XPS analysis. UPS spectra were recorded using monochromatized He I (21.2 eV) irradiation from a He discharge lamp. XPS measurements were performed using an unfiltered Al(K_α) x-ray

source (1486.6 eV). In case of iodine doping, additional high-resolution XPS measurements were performed on some samples, using a state-of-the-art Scienta ESCA 200 spectrometer with a monochromated Al(K_{α}) x-ray source. For these measurements, separate, identical samples were prepared in the sample preparation chamber of the Scienta.

In UPS measurements, the binding energy of the photoelectrons is measured relative to the Fermi-level of the samples. The work function, i.e., the difference between the Fermi-level and the vacuum level, was determined from the secondary electron cut-off in the UPS spectra.²⁷ Doping induced shifts of the Fermi-level were assumed to be equal to the changes in work function.

The iodine and lithium doping concentrations were estimated from XPS measurements, using the intensity ratios of the I($3d_{5/2}$), C($1s$) lines and Li($1s$), C($1s$) lines, respectively. For doping levels below ≈ 1 Li atom per molecule, the Li($1s$) signal was too weak to be used as a measure for the concentration, and the precalibrated exposure time to the Li-getter source was used instead.

The uniformity of the iodine dopant (I_3^-) distribution was checked by angle-dependent XPS measurements. Other than a somewhat lower concentration of excess neutral iodine in the near surface region, no significant depth gradients were observed, indicating that the doped films were in thermodynamic equilibrium. For the low Li dopant concentrations that are relevant for this work, angle-dependent XPS measurements were hampered by the low Li($1s$) photoionization cross section. However, in view of the much smaller size of Li^+ ions compared to I_3^- clusters, diffusion of Li^+ can be expected to be fast in the EDOT-trimer films. Therefore, Li-doped films were also assumed to be in thermodynamic equilibrium.

NEXAFS measurements were carried out at beam line

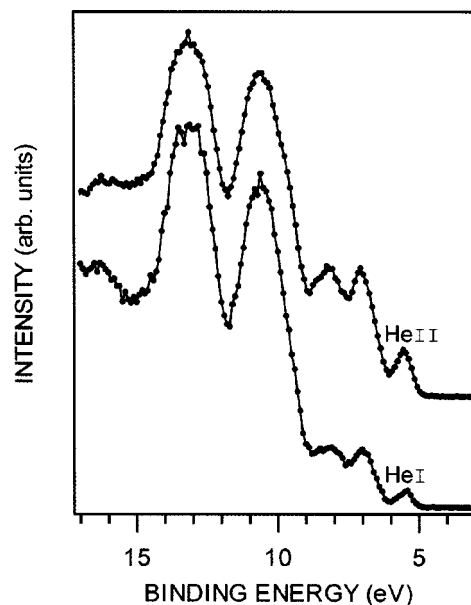


FIG. 2. He I and He II UPS spectra of a pristine vapor deposited EDOT-trimer film.

I411 of the MAX-laboratory for Synchrotron Radiation in Lund, Sweden, to study the unoccupied π^* structure of pristine EDOT-trimer films. The films were prepared in Linköping as described above, and were transported to Lund in an inert nitrogen atmosphere.

IV. RESULTS AND DISCUSSION

A. Pristine EDOT trimer

The UPS He I (21.2 eV photon energy) and He II (40.8 eV photon energy) valence band spectra of the phenyl-

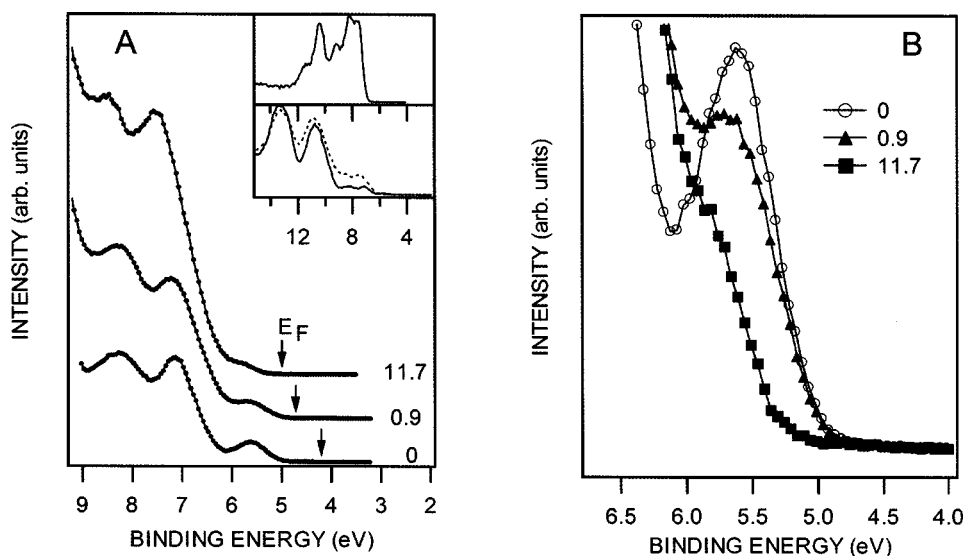


FIG. 3. He I (21.2 eV) UPS spectra of the EDOT trimer for various stages of I-doping. The numbers on the right hand side of the curves in (A) indicate the doping concentrations, in I atoms per molecule. Note that this iodine concentration includes both charged and neutral species. The upper inset in (A) shows the UPS spectrum of a solid iodine film, the lower inset shows wide range UPS spectra of the pristine EDOT-trimer (solid line) and I-doped EDOT-trimer with 11.7 I atoms per molecule (dotted line). The spectra are plotted relative to the vacuum level, the position of the Fermi level (E_F) is indicated with an arrow for each spectrum in (A). A close-up of the evolution of the HOMO feature upon doping is shown in (B), the numbers in the legend correspond to the number of I-atoms per molecule.

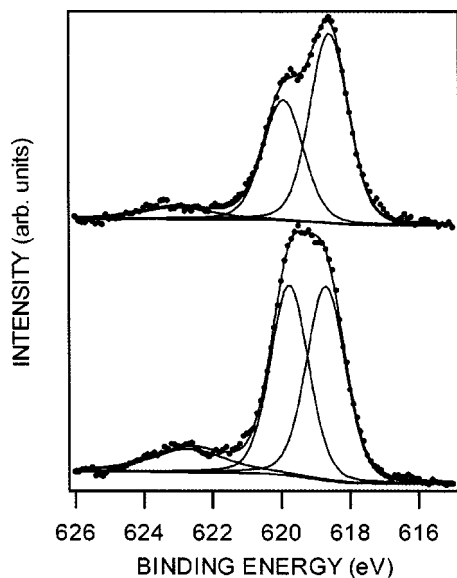


FIG. 4. High-resolution I($3d_{5/2}$) XPS spectra of an iodine-doped EDOT-trimer film, before (bottom) and after (top) removal of the majority of iodine by annealing at 100 °C. The dots represent the data points, the solid lines correspond to peak and background fits. The spectra are plotted relative to the Fermi level.

capped EDOT-trimer are shown in Fig. 2. The spectra are normalized to the integrated intensity between 9 and 15 eV. Above 9 eV, the spectra were dominated by two broad peaks centered at 10.5 and 13 eV, arising from a manifold of σ -states. Below 9 eV binding energy, the features in the UPS spectra corresponded solely to electron emission from delocalized π -orbitals.^{28,29} The increased intensity in this region of the He II spectrum compared to the He I spectrum was due to the increased photoionization cross sections for π -states versus σ -states, respectively, as the photon energy was changed from 21.2 to 40.8 eV. In general, π -orbitals are most sensitive to doping induced removal (or addition) of electrons, whereas deeper lying σ -orbitals are, in most cases, essentially unaffected by doping. In the following, changes in the π -electronic structure, upon doping, are addressed.

B. Iodine doping

Figure 3(A) shows the iodine-doping induced changes in the upper (π) region of the valence band of the EDOT trimer. In addition to the UPS spectrum of the pristine molecules, two spectra are shown that correspond to an intermediate (0.9 I molecule) and high (11.7 I molecule) doping level, respectively. The spectra are normalized to the area of the peak at ≈ 13 eV. At 13 eV, the emission intensity from iodine was low and did not significantly affect the normalization. This can be seen from the upper inset in Fig. 3(A), which shows a UPS spectrum of a solid iodine film (deposited on top of an EDOT-trimer film). Between 7 and 9 eV, a strong flat-topped feature in the iodine valence band spectrum resulted in the observed increase in intensity in this binding energy region of the UPS spectra of the iodine-doped EDOT trimer.

In the UPS spectra, the intensity of the highest occupied molecular orbital (HOMO)-related peak at 5.6 eV strongly

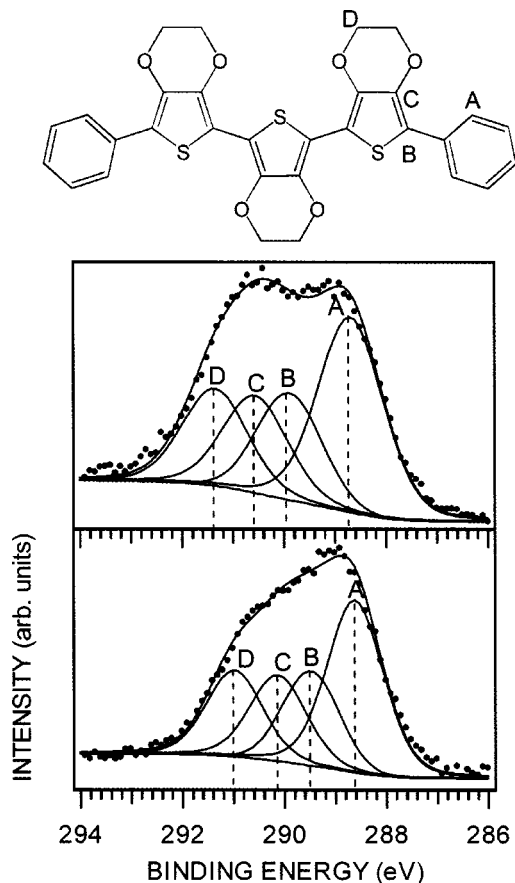


FIG. 5. C($1s$) XPS spectra of a pristine EDOT-trimer film (bottom) and an I-doped film with 11.7 I atoms per molecule (top). The spectra are plotted relative to the vacuum level. The dots represent the data points, the solid lines correspond to peak and background fits. The peaks labeled A, B, C, and D correspond to different carbon atoms in the EDOT-trimer, as shown in the picture of the molecular structure. The relative intensities A:B:C:D were fixed at 2:1:1:1, according to the abundance of the corresponding carbon atoms in the molecule.

decreased with increasing iodine concentration [Fig. 3(B)], which showed unambiguously that hole-doping of the EDOT trimer occurred by electron transfer from the HOMO to the iodine ligands. This was accompanied by a slight broadening of the valence band features at higher binding energies than 6 eV, due to small changes in the valence electronic levels upon removal of electrons from the HOMO. In addition, the Fermi-level shifted ~ 0.8 eV towards higher binding energy, to near the valence band edge, typical for doped semiconductors which display a higher conductivity. This nicely demonstrated the possibility of performing Fermi-level tuning in molecular semiconductors by means of controlled iodine doping. Accurate control of the Fermi-level is crucial for semiconductors devices; it was one of the key-issues in the development of inorganic semiconductors.

Iodine-doping-induced changes in the π -electronic structure of the EDOT trimer were subtle and could be solely attributed to transfer of HOMO-electrons to the iodine dopant species (in contrast to the Li-doping experiments discussed below). Moreover, the charge transfer process proved to be *fully reversible*. Iodine could be removed effectively from the film by heating the samples to 100 °C, which was still low enough to prevent substantial evaporation of the

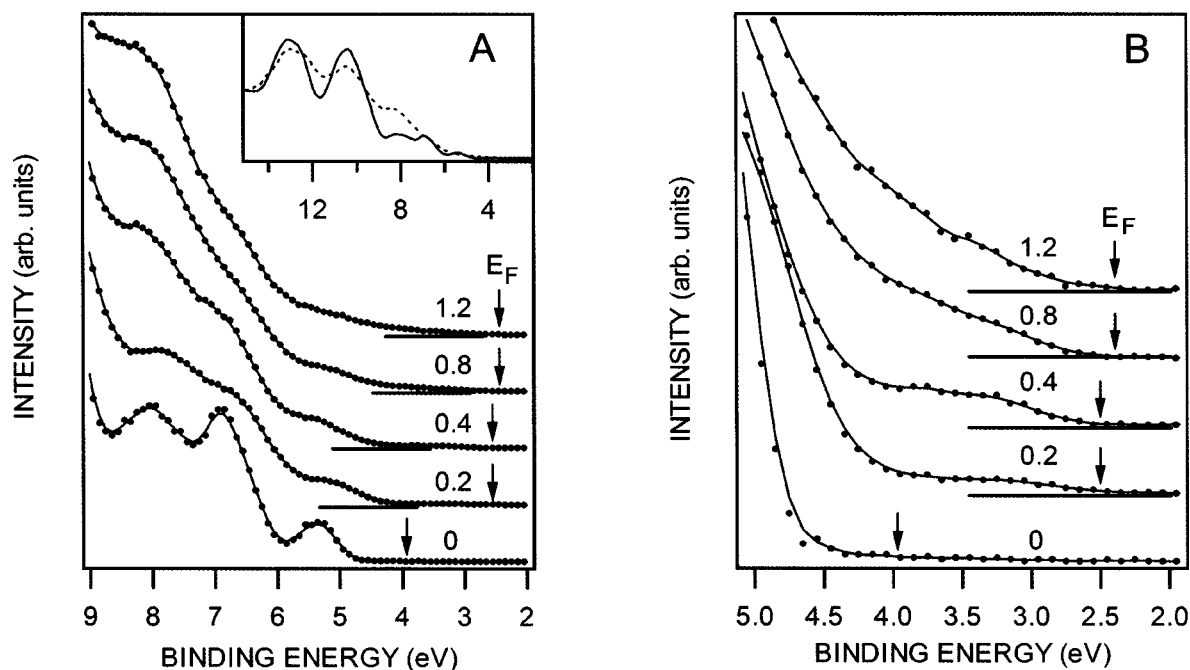


FIG. 6. He I (21.2 eV) UPS spectra of the EDOT trimer for various stages of Li doping. The doping concentration increases from undoped (bottom) to ≈ 1.2 Li atoms per molecule (top), as indicated above each spectrum. The dots represent the data points, the lines are shown as a guide to the eye. The spectra are plotted relative to the vacuum level, the position of the Fermi level (E_F) is indicated with an arrow for each doping level. (B) is a magnification of the low binding energy region in (A), in which the formation of new states in the former bandgap can be seen. The inset in (A) shows the UPS spectra between 15 and 2 eV binding energy of the undoped film (solid line) and for a doping level of 1.2 Li atoms per molecule (dotted line), respectively. All spectra are normalized on the integrated intensity between 9 and 14 eV binding energy.

EDOT trimer. The valence band features, including the HOMO, were *completely restored* by such a treatment, showing that the charge transfer equilibrium between iodine and the EDOT trimer could be easily shifted back towards the undoped system.

The high-resolution I($3d_{5/2}$) XPS spectra shown in Fig. 4 indicate that two different charge states of iodine were present in the doped EDOT trimer films. Following previously published results on the I($3d_{5/2}$) spectra of iodine-doped polyacetylene,³⁰ the peak at 619.9 eV was assigned to neutral I_2 , and the peak at 618.7 eV to I_3^- . This assignment was also supported by the dependence of the intensity ratio of the two peaks on the iodine concentration: For low doping levels, the 618.7 eV peak was larger than the 619.9 eV peak, while the situation was reversed for high doping levels, indicating the incorporation of excess neutral I_2 in the film as the doping level was increased. Annealing at 100 °C preferentially removed excess I_2 , as can be seen by comparing the two I($3d_{5/2}$) spectra in Fig. 4. These spectra correspond to an iodine-doped EDOT trimer film before (bottom) and after (top) cycling the temperature from -50 °C to 100 °C and to -50 °C again over several minutes. Longer annealing treatments resulted in complete removal of iodine, and a fully restored valence band, as discussed above.

The C(1s), O(1s), and S(2p) XPS spectra were only slightly affected by iodine doping, in agreement with a purely charge-transfer type interaction between iodine and the EDOT trimer. The O(1s) and S(2p) features (not shown) shifted by 0.3 and 0.5 eV, respectively, to a higher binding energy at a high doping level of 11.7 iodine atoms per molecule. This observation was consistent with the re-

moval of electrons from the molecules, resulting in reduced screening of the core holes. No significant changes in the peak-shapes were observed for the O(1s) and S(2p) core-levels. The C(1s) feature showed a different evolution upon doping: The low binding energy fraction of the feature stayed pinned at its original binding energy position, while the high binding energy fraction gained relative spectral weight and was shifted by about 0.3 eV to a higher binding energy (see Fig. 5). These observations were consistent with the removal of an electron from the HOMO, which is mainly distributed over the carbon atoms in the thiophene rings,²⁸ and has only a small overlap with the O and S atoms and with the phenyl rings. Therefore, the lowest binding energy fraction of the C(1s) feature (fitted peak A in Fig. 5), arising from the *phenyl rings*, was relatively unaffected by removal of an electron from the HOMO. The C(1s) binding energies of the carbon atoms in the *central part of the molecule* (fitted peaks B–D in Fig. 5) shifted by ≈ 0.3 eV, resulting in the observed changes in the shape of the C(1s) feature. The intensity ratios of the fitted peaks A:B:C:D were fixed at 2:1:1:1, in accordance with the molecular structure. Furthermore, as a starting point for the peak fits, the energy separation between the peaks was estimated from XPS measurements of the EDOT trimer in the gas phase.³¹

C. Lithium doping

The He I ($h\nu = 21.2$ eV) UPS spectra, below 9 eV binding energy, of the EDOT trimer in several stages of Li-doping, ranging from 0 to 1.2 Li atoms per molecule, are shown in Fig. 6. A wider range of the valence electronic

structure is also shown in the inset of Fig. 6(A), for both the pristine EDOT-trimer and a doping level of 1.2 Li atoms per molecule. Clearly, Li-doping of the EDOT-trimer resulted in dramatic changes in the electronic structure. Even above 9 eV, where the spectra were dominated by σ -states, the features were significantly broadened. This behavior deviated from the general trends observed in alkali metal doping of π -conjugated oligomers and polymers,^{29,32–36} indicating that chemical interactions other than those of charge-transfer type occurred between Li and the EDOT-trimer. In the following, the strong modifications of the π -system observed in the UPS spectra are discussed. Subsequently, XPS core-level measurements are presented to clarify the changes in the valence electronic structure.

From Fig. 6 it can be seen that the Fermi level E_F shifted by about 1.5 eV towards the vacuum level. This was consistent with the transfer of electrons from the Li atoms to previously unoccupied orbitals on the EDOT oligomers. A second indication of this charge transfer was the appearance of a broad feature extending towards the Fermi level [Fig. 6(B)], *albeit* with low intensity, corresponding to the formation of new states within the former energy gap. This is typical for the creation of polaronic or bipolaronic-type states, due to the significant geometrical deformation of the molecules that occurs upon addition of electrons.³⁷ So far, these results were in agreement with the general trends observed for n -doped π -conjugated oligomers.^{29,32–36} However, an anomalously large broadening of the valence band features was observed, even for doping concentrations as low as 0.2 Li atoms per molecule. It is well known that alkali metal doping results in significant destabilization of the molecular orbitals in thiophene oligomers²⁹ and in polythiophene,³⁴ resulting in peak-shifts and spreading of the features in the UPS spectra of such molecular solid films. In this case, however, the distortions in the valence band region were too large compared to the weak signal of the doping induced gap-states to be solely attributed to destabilization effects. Indeed, XPS data indicated that there were other reasons for the observed modifications in the valence electronic structure.

Figure 7 shows the evolution of the O(1s) and S(2p) core level peaks as a function of doping concentration. We consider higher Li-concentrations here (up to 3.2 Li atoms per EDOT trimer molecule) compared to the previously discussed UPS measurements (up to 1.2 Li atoms per EDOT trimer molecule), to show the changes in the core level features more clearly. The O(1s) binding energy, measured with respect to the *vacuum level*, of the initially single peak was decreased by about 0.7 eV as a result of Li-doping. Such a peak shift was in agreement with the addition of electrons to previously unoccupied orbitals of the molecules, which led to increased core-hole screening, and therefore, a lower energy of the final state. However, the appearance of a second peak at an ~ 2 eV lower binding energy showed that there were additional interactions between Li and the EDOT oligomers, which produced a chemical species in which the transferred electrons were localized on the oxygen sites. The formation of gap-states could not lead to this new feature, since the lowest unoccupied molecular orbital (LUMO)-derived wave functions of these states are distributed over

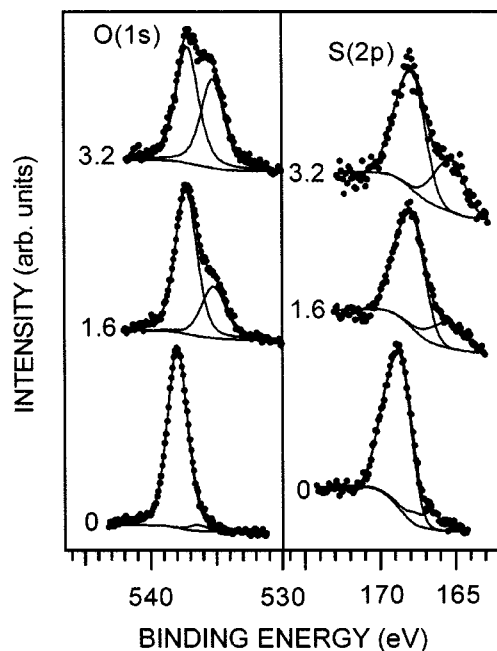


FIG. 7. Evolution of the O(1s) and S(2p) features upon Li-doping. The dots represent the data points, the solid lines correspond to peak and background fits. The S(2p) doublet, which could not be resolved in these measurements, was fitted by a single peak. The doping concentration increases from bottom to top, the number shown at the left hand side of the curves corresponds to the number Li atoms per molecule.

the conjugated thiophene rings and, therefore, have only very little overlap with the oxygen atoms. This can be seen from near edge x-ray absorption fine structure (NEXAFS) measurements taken at the C(1s) and O(1s) absorption edges, respectively, as shown in Fig. 8. The C(1s) NEXAFS spectrum shows a clear sharp resonance at the absorption edge (≈ 285 eV), due to C(1s)- π^* transitions. In the O(1s) NEXAFS spectrum, only a very weak feature appeared at the absorption edge (≈ 532 eV), which showed that the lowest

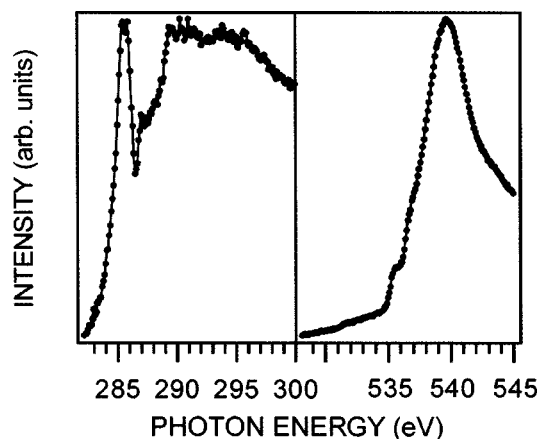


FIG. 8. C(1s) (left) and O(1s) (right) NEXAFS spectra of a thin EDOT trimer film on polycrystalline gold. The C(1s) NEXAFS spectrum shows an intense sharp resonance at the onset of absorption, at ≈ 285 eV photon energy, corresponding to C(1s)- π^* transitions. In contrast to this, the first O(1s)- π^* feature at ≈ 532 eV photon energy is very weak compared to the large O(1s)- σ^* resonance at ≈ 540 eV. This shows that the lowest unoccupied π^* states overlap only slightly with the O atoms in the molecule.

unoccupied π^* states have no significant overlap with the O atoms.

Li-doping caused a similar trend for the $S(2p)$ peaks (Fig. 7): In addition to a decrease of about 0.9 eV in the binding energy of the $S(2p)$ feature, a new feature again appeared at about 2 eV lower binding energy. This indicated the formation of yet another chemical species, with the transferred electrons strongly localized at the sulfur atoms. The intensity ratio of the new and initial $S(2p)$ features was low compared to that of the new and initial $O(1s)$ peaks, indicating that the reaction that produced an extra localized charge at the oxygen sites dominated. The $C(1s)$ peak (not shown) was shifted by about 0.8 eV and was broadened slightly as a result of Li-doping, but no new features were observed in the $C(1s)$ spectrum. These effects could be explained solely by electron transfer into gap-states, with the transferred charge distributed over many carbon atoms in the molecule.

The observations described above indicate that, in addition to charge-transfer into the LUMO, Li-doping resulted in the transfer of the electron locally to O and S atoms. More theoretical work is being performed to see to what extent these interactions are of a covalent character. These local interactions present a serious limitation for *n*-type doping of the EDOT-trimer. It can be concluded that well controlled *n*-type doping of the EDOT trimer is difficult to achieve, and the electrical properties of *n*-doped material are expected to be poor. This is in agreement with the results of previous studies of *n*-doped PEDOT,²⁵ which proved to have a much lower electrical conductivity than its *p*-doped counterpart, and was extremely unstable in air.

V. CONCLUSIONS

Phenyl-capped EDOT oligomers are potential candidates for molecular electronics applications and serve as model molecules for PEDOT. By combining UPS, XPS, and NEX-AFS, a clear picture of the doping induced changes in the electronic structure of phenyl-capped EDOT-trimer was obtained.

Upon *p*-doping with iodine, electrons were transferred from the HOMO of the EDOT-trimer to the iodine ligands, forming trimer- I_3^- charge transfer complexes. Deeper lying molecular orbitals were not significantly affected by this process, which proved to be fully reversible by shifting the $3I_2 + 2\text{trimer} \leftrightarrow 2I_3^- + 2\text{trimer}^+$ equilibrium by thermally stimulated desorption of iodine. Iodine-doping led to a transition from a semiconducting to a conducting hole-doped state. By varying the doping level, Fermi-level tuning over 0.8 eV could be realized. Iodine-doped EDOT trimer can thus be regarded as promising for molecular electronics applications that require a well-defined *p*-doped material. Extrapolating the results to PEDOT, hole-doping, as is the case in PEDOT-PSS, would involve only the uppermost π -band without modification of deeper lying electronic structure.

In the case of *n*-doping with lithium atoms, the formation of gap-states was accompanied by strong distortions in the π -system, due to local charge transfer from Li-atoms to O- and S-atoms in the molecules. This severely limits the

possibilities for well-controlled *n*-doping of the EDOT trimer.

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