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A joint theoretical and experimental study on the electronic properties of phenyl-capped 3,4-ethylenedioxythiophene oligomers

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The electronic structure of a series of phenyl-capped 3,4-ethylenedioxythiophene oligomers has been studied using ultraviolet photoelectron spectroscopy (UPS) in combination with theoretical calculations. The calculations were performed for isolated oligomers within the framework of density-functional theory, using the Becke–Lee–Yang–Parr exchange-correlation functional. Excellent agreement between the UPS spectra and the quantum-chemical calculations allowed for unambiguous interpretation of the results. We use the asymptotic extension of electronic properties of oligomers to discuss the electronic structure of neutral poly(3,4-ethylenedioxythiophene). In addition, experimentally determined ionization potentials for thin films prepared by vapor deposition and spin coating are reported, and are found to depend on the preparation method. The discrepancy is assigned to differences in the molecular packing.


INTRODUCTION

In recent years, a large effort has been devoted to the synthesis and characterization of \( \pi \)-conjugated oligomers of well-defined size and electronic properties. Several reasons explain this growing interest. First of all, oligomers usually arrange in crystalline phases displaying high charge carrier mobility,\(^1\) which is a necessary requirement for the fabrication of high quality organic field-effect transistors (OFET’S),\(^2\) and organic solar cells.\(^3\) The molecular orientation within the active organic layers in the devices is an important issue as well. As observed for oligothiophenes,\(^4\) oligophenylenes,\(^5\) and oligoacenes\(^6\) the crystallinity results in an anisotropy of the charge carrier mobilities that affects device properties. Since the spatial arrangement of individual molecules in crystals depends on their size, controlling the chain length of oligomers allows for optimization of the structural and electronic properties of molecular crystals. Second, the optical properties of oligomers can be tuned not only by controlling their size, but also by grafting electron donating or withdrawing groups. This is important for the development of efficient organic photovoltaic devices. Finally, oligomers represent well-defined model compounds for understanding the physical properties of the corresponding polymers.

In contrast to oligothiophenes, ethylenedioxythiophene (EDOT) oligomers have not received much attention yet, because they are difficult to synthesize and, in the case of the longer species, sensitive to oxidation in air. To date, the only EDOT oligomers that have been isolated and reported in the literature are 2,2’5’,2”-tris-EDOT,\(^7\) and 2,2’-bis-EDOT.\(^8\) Indeed, as compared to \( \beta,\beta’ \)-unsubstituted oligothiophenes, EDOT oligomers are more electron rich, due to the addition of electron donating ethylenedioxy groups and therefore have a lower oxidation potential. The substitution also causes the optical absorption spectrum to be red-shifted, which is promising for organic solar cell applications, for which the...
collection of the low-energy part of the solar spectrum is a major issue.\cite{9,10}

Phenyl-capped 3,4-ethylenedioxythiophene oligomers, Ph-(EDOT)$_n$-Ph, were recently synthesized\cite{11} (see Fig. 1). These oligomers are stable in air, because the phenyl groups block the α positions in the thiophene rings. The oligomers are expected to form crystalline condensed films, as is the case for oligothiophenes,\cite{12-14} which may result in high charge-carrier mobilities. Furthermore, EDOT-based oligomers have a more rigid planar π-electron system compared to oligothiophenes, due to intrachain interactions mediated by sulfur and oxygen atoms,\cite{11} and therefore may stack more efficiently. In addition, the phenyl-capped EDOT oligomers are solution processable.

Furthermore, EDOT oligomers can be regarded as model compounds for poly(3,4-ethylenedioxythiophene) (PEDOT), the conjugated polymer that forms the main ingredient for the commercial conducting polymer blend PEDOT:poly(styrenesulfonic acid) (PEDOT-PSS). The processable and highly stable PEDOT-PSS is obtained by adding PSS as charge-balancing counterion during the polymerization of EDOT. Due to its good film forming properties, high conductivity, visible-light transparency, and very high environmental stability, PEDOT-PSS is currently used for a wide range of applications.\cite{15} Neutral PEDOT on the other hand is highly unstable in air and insoluble, which makes it very difficult to characterize.\cite{16} Therefore studying the electronic structure of model compounds is a good alternative to the characterization of neutral PEDOT. Moreover, this approach is useful in understanding the doping processes in PEDOT on a molecular level, as it has been shown recently on example of Ph-EDOT$_3$-Ph oligomer in chemical $p$- and $n$-doping experiments.\cite{17}

Here, we report the results of joint theoretical and experimental investigations of the size-dependent electronic structure of phenyl-capped 3,4-ethylenedioxythiophene oligomers [Ph-(EDOT)$_n$-Ph; $n = 1$–4] by means of ultraviolet photoelectron spectroscopy (UPS) and quantum-chemical calculations. UPS is the method of choice for determining the valence density of electronic states for organic materials as thin films; the UPS spectra are best interpreted when compared with the results of quantum-chemical calculations of the molecular electronic structure, hence the joint approach followed in this study.

**THEORETICAL METHODOLOGY**

The quantum-chemical calculations for neutral phenyl-capped EDOT oligomers were carried out at either the density-functional theory (DFT) or the restricted Hartree–Fock (RHF) level. The DFT-based calculations were performed with the Becke+Lee–Yang–Parr (B3LYP) functional,\cite{23,24} which is a correlated functional including gradient corrections. Both DFT and RHF calculations were carried out with the standard 6-31G** basis set. The equilibrium geometries of the neutral oligomers were obtained using a full geometry optimization scheme.

The density-of-valence-states (DOVS) curves were used to facilitate the interpretation of the UPS spectra. The approach has been extensively described in connection with the
studies of conjugated molecules, where the DOVS curves were obtained by either \textit{ab initio} or semiempirical HF methods.\textsuperscript{25} Using Koopmans' approach, the peaks in the UPS spectra are associated to eigenenergies calculated for the electronic levels in the neutral molecule. The following steps were taken to facilitate comparison of the theoretical results with the experimental spectra. The DOVS curves derived from RHF calculations were scaled along the binding energy axis by a factor of 1.3 for RHF to correct for correlation and relaxation effects upon photoionization.\textsuperscript{25} In case of DFT calculated DOVS, the required scaling was negligible (0.97). Subsequently, the curves were rigidly shifted to match the experimental spectra, which compensate for solid-state relaxation effects. Finally, the DOVS were convoluted with Gaussian functions of 0.5 eV FWHM, to account for experimental and solid-state related inhomogeneous broadening.

All the quantum-chemical calculations were performed by means of the \textit{GAUSSIAN} 98 computational package.\textsuperscript{26} The results were interpreted with the aid of ZOA V2.0 software.\textsuperscript{27}

**RESULTS AND DISCUSSION**

**Influence of the oligomer size**

The experimental valence band spectra of the phenyl-capped EDOT oligomers are shown in Fig. 2. The measurements were recorded with monochromatized He-II (40.2 eV) radiation on vapor deposited films, kept at 170 K (i.e., the substrate temperature during deposition). The intensities in the spectra are normalized such that the peak corresponding to the highest occupied molecular orbital (HOMO) has similar intensity for all oligomers.

There are several common spectral features present in each spectrum, which can be observed in the binding energy region from 5 to 15 eV. The positions of features labeled B, C, D, E, and F are the same, while their relative intensities differ significantly. Analogous to oligothiopenes,\textsuperscript{28,29} peaks E and F are attributed mainly to \(\sigma\) orbitals. Peaks B, C, and D originate from \(\pi\)-type orbitals formed along the backbone of the oligomers. Peak A, corresponding to the HOMO of the oligomers, moves towards lower binding energies, as the molecule length increases. This is consistent with previous studies where the extension of the \(\pi\)-conjugated backbone has been shown to affect strongly the binding energy of the HOMO.\textsuperscript{28,30} As a consequence, the ionization potential (IP), determined as the onset of peak A, monotonically decreases with the extension of the conjugation length. This trend is shown in Fig. 3, where the evolution of the IP versus the oligomer size is shown. To first approximation, IP evolves linearly with the reciprocal number of double bonds (NDB's),\textsuperscript{31} for a one-dimensional system. Here, the following estimate of the bulk IP of neutral oligomers is found from a linear regression fit to the experimental points: \(\text{IP}[\text{eV}] = 9.8/\text{NDB} + 4.2\). Consequently, the IP of the infinite neutral PEDOT chain in solid films can be estimated to be \(\approx 4.2\) eV. It should be stressed that the estimate is based on a linear fit to the IP values measured for vapor deposited films kept at 170 K. The choice of this particular set of IP's is motivated by the following two reasons: First, the loose molecular packing in these films, as discussed below, most likely resembles the polymer case. Second, the influence of the phenyl caps on the HOMO of oligomers (and thus on IP) decreases with the increased numbers of EDOT units, as derived from the HOMO's molecular wave functions. The contributions from the phenyl groups are significant for Ph-EDOT-Ph, but steadily decrease with the oligomer size and essentially vanish already in the Ph-EDOT\(_3\)-Ph oligomer. Therefore the set of IP's for the three largest oligomers has been used to estimate the IP of even larger species.

**Influence of the preparation technique**

Differences in the IP have been observed for films prepared by spin coating versus vapor deposition. As shown in Fig. 3, spin coating always provides films with lower IP's than vapor deposition. Moreover, the difference increases with the size of the oligomers. The secondary electron cutoff...
in the UPS spectra of both vapor-deposited and spin-coated films falls at the same position (within the error bars) on the binding energy scale. Therefore the rigid shift of the remaining spectral features, corresponding to differences in the IP’s, is likely caused by different intermolecular polarization energies, $P^+$, upon ionization. The value of $P^+$ is well known to depend on the degree of order or the crystal structure of the film. A possible origin for this difference lies in temperature induced changes in the molecular arrangement, since the IP’s of the spin-coated films were measured at room temperature, as compared to 170 K for the vapor deposited films. In order to verify this hypothesis, the vapor deposited films were warmed up in the vacuum chamber. Indeed, a systematic decrease of the IP’s was observed upon heating and the resulting IP values were found to match those of the spin-coated films (within the errorbars). Note that the changes are not reversible upon decreasing the temperature. Therefore the molecular rearrangement most probably relates to temperature-induced changes in the degree of disorder, in other words annealinglike behavior. The results point out the importance of the molecular packing in determining the IP, an essential material property derived from the UPS measurements.

**Theory/experiment comparison**

Figure 4 shows the UPS spectra of the Ph-EDOT-Ph molecule, as measured in the gas and the solid phase. The spectra are compared with DOVS curves, simulated on the basis of B3LYP and RHF one-electron eigenvalues. The gas phase spectrum is shifted by $P^+ = 1.2$ eV towards the low binding energy side, in order to align it with the UPS spectrum of the solid. This rigid shift accounts for solid-state polarization effects. The polarization energy of 1.2 eV for Ph-EDOT-Ph is similar to what is typically found for organic molecules.

Note that when comparing UPS spectra with simulated DOVS, the calculated peak intensities are related to DOVS only, while intensities in the UPS spectra include also the cross sections for photoionization, as well as a background of inelastic scattered photoelectrons (for solid phase measurements).

The spectral features above 9 eV binding energy are fairly well represented in the RHF based DOVS simulation. In contrast, the RHF-calculated DOVS in the region of $\pi$-orbitals from 9 eV towards lower binding energies are not consistent with the UPS spectra: four distinct features are present in the experimental spectra, while the RHF calculations only yield three peaks. The disagreement between the HF eigenvalues and the UPS data is unexpected since it has been shown that such an HF theoretical scheme is successful in simulating the electronic structure of other conjugated oligomers.

As shown in Fig. 4, there is a one-to-one correspondence between the spectral features recorded in the gas and solid phase. This rules out possible solid-state modifications of the valence structure, which could be induced by $\pi$-stack formation. Although not fully understood, the disagreement between the RHF based DOVS and the experimental spectra is most likely related to electron correlation phenomena, which are not taken into account in the *ab initio* HF calculations. To address this problem, a DFT-based method, which includes electron-correlation phenomena, was applied. The agreement between the B3LYP based DOVS curve and the experimental spectra is excellent. That allows for an unambiguous assignment of the measured valence electronic structure of the phenyl-capped EDOT oligomers to UPS spectra simulated on the basis of B3LYP eigenvalues.

In Fig. 5, the valence spectra of vapor deposited films of phenyl-capped EDOT oligomers are compared to the DFT-calculated DOVS. Two strong features, previously labeled E and F, are found between 9 and 15 eV of binding energy, which are largely due to photoelectron emission from $\sigma$ orbitals (with only a small contribution from $\pi$ orbitals). Below 9 eV, all features are related to $\pi$-electronic states, as was concluded from the analysis of the corresponding wave functions. The spectral feature D is related to $\pi$ orbitals characterized by bonding overlaps between $\pi$-electronic states of EDOT and phenyl rings. Peaks C correspond largely to molecular orbitals localized on the phenyl rings, which are known to appear at about 8.1 eV (see also Ref. 39). The relative intensity of peak C decreases as the number of EDOT units in the molecules increases, since the phenyl endcaps contribution to the overall photoelectron emission signal diminishes with oligomer size. The two spectral features at lowest binding energies, peaks A and B, originate primarily from orbitals that are localized on the EDOT units. Peak B is derived from a number of molecular orbitals mainly related to the HOMO of EDOT [see Fig. 6(a)], while peak A corresponds to a single electronic state involving the HOMO-1 of EDOT [see Fig. 6(a)]. This state, which constitutes the HOMO of Ph-EDOT$_n$-Ph oligomers results from antibonding overlaps of the HOMO-1 molecular orbitals of the EDOT units [see Fig. 6(b)]. In addition, as pointed out earlier, there is also a finite contribution from phenyl-derived
states. The contribution decreases with the size of the oligomers, however, and essentially vanishes already for the Ph-EDOT$_3$-Ph oligomer.

When extrapolating these results to the polymer case, the frontier valence band structure of neutral PEDOT is expected to be composed of two distinct bands corresponding to spectral features A and B of the phenyl-capped EDOT oligomers. Similar to polythiophene, the highest occupied band in PEDOT arises from the overlap of the molecular orbitals of EDOT units, that have a strong contribution on the C$_a$ carbon atoms, but none on the sulfur atom $\sim$ see Fig. 6, HOMO-1. The significant overlap between these orbitals on adjacent units leads to a dispersed band. On the contrary, the overlap of the EDOT orbitals with negligible amplitude on the carbon atoms in C$_a$ position (see Fig. 6, HOMO) is weak. Therefore those orbitals yield a localized band, which energetically appears within the bandwidth of the dispersed one.

**SUMMARY AND CONCLUSIONS**

The electronic structure of a series of phenyl-capped EDOT oligomers has been studied using ultraviolet photoelectron spectroscopy, in combination with quantum-chemical methods.

First of all it was demonstrated that theoretical results based on RHF calculations are not adequate, when used to simulate the UPS spectra. Calculations were then performed for isolated oligomers within the DFT framework, using the B3LYP functional. Excellent agreement between the experimental data and UPS spectra simulated on the basis of DFT results was obtain. This points to the role of electron correlation effects and allows for an unambiguous interpretation of the experimental data.

We report a monotonical decrease of the IP’s with respect to the increased number of double bonds in the oligomers. This allows for an estimation of the IP of even larger oligomers, according to: IP[eV] = 9.8/NDB + 4.2. Differences in the IP for spin coated versus vapor deposited films were observed. A systematic decrease of the IP’s for vapor deposited films was observed upon heating, with resulting values similar to those measured in spin coated films at high temperature. The temperature induced modifications of the IP were related to changes in the molecular packing.

Based on the data for the oligomers, we estimated the bulk IP of the neutral PEDOT polymer to be 4.2 eV. The frontier band structure can be predicted from the evolution of the spectral features in the investigated series of oligomers. Similarly to polythiophene, the highest occupied and dispersed band arises from the overlap of EDOT orbitals that have a strong contribution on the C$_a$ carbon atoms, but none on the sulfur atom, whereas the formation of a localized band involves overlap of orbitals with negligible amplitude on the carbon atoms in C$_a$ position.

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