Site-specific electronic structure of an oligo-ethylenedioxythiophene derivative probed by resonant photoemission

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Abstract. A combination of conventional and resonant photoemission spectroscopy, x-ray absorption spectroscopy and ground-state quantum-chemical calculations has been used to study the valence electronic structure of a phenyl-capped 3,4-ethylenedioxythiophene oligomer, in polycrystalline thin films. The photon energy-dependent intensities of specific resonant decay channels are interpreted in terms of the spatial overlap of the excitation site and the ground-state molecular orbital involved in the decay. By making use of chemical shifts, excitations on different atomic sites are distinguished. It is demonstrated that site-specific information on the electronic structure of relatively large and complex organic systems may be obtained experimentally from non-radiative resonant decay spectra. In addition, these spectra provide relevant insight into the interpretation of near-edge x-ray absorption fine structure spectra.

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1. Introduction

The discovery of the photoelectric effect by Hertz [1], and later rationalized by Einstein [2], led over the years to the development of a variety of photoelectron spectroscopic techniques [3]. Today, many of these techniques are used to provide important information on the electronic properties of $\pi$-conjugated organic materials, which form the basis of the rapidly growing field of organic (opto) electronics. ‘Conventional’ x-ray and ultraviolet photoemission spectroscopy (XPS and UPS) probe occupied electronic states through direct photoionization (see figure 1). The latter is the method of choice regarding the integral density of valence electronic states for organic materials [4, 5]. UPS spectra are best interpreted when complemented with the results of quantum-chemical calculations of molecular electronic structure. Near-edge x-ray absorption fine structure (NEXAFS) studies provide information on unoccupied states in the presence of the core hole [6]. Core-excited states have a relatively short lifetime (on the fs scale) and decay by either radiative x-ray emission or non-radiative Auger-like electron emission [7]–[9]. The latter dominates for the lighter elements, which are the main components of organic materials. The non-radiative decay occurs by two qualitatively different processes schematically shown in figure 1: participator Auger decay, resulting in single-valence-hole final states, and spectator Auger decay, leading to two-hole/one-particle final states. The electronic final states in the former process are equal to those in direct photoemission. The study of participator decay channels is therefore usually referred to as resonant photoemission (RPE). In spite of the fact that the final states in the non-resonant and resonant photoelectron emission processes are equal, the transition matrix elements in these two processes are different: dipole versus Coulomb-type, respectively. Additionally, each has its own molecular dynamics. These differences often result in altered intensity ratios of the spectral features [10, 11], different relative population of vibrational states, leading to e.g. vibrational collapse [10, 12] or line narrowing [13] demonstrating the importance of the intermediate state in resonant processes. Such dynamic effects require a one-step model description, i.e., in terms of transitions from a neutral initial state to an ionized final state. Most importantly, since for different elements or chemically shifted atoms, core excitations are site-specific [6] with well-defined and separated absorption edges, RPE may supply information on the local electronic structure [14]–[16].
Figure 1. Schematic representation of electronic excitation and decay processes. The final states probed in various spectroscopic techniques are denoted by the corresponding acronym.

A detailed interpretation of RPE spectra requires, in general, sophisticated theoretical treatments and complex simulations, which for large-size and low-symmetry systems are still unavailable. $\pi$-Conjugated oligomers often fall into that category, such as the recently synthesized phenyl-capped oligomers of 3,4-ethylenedioxythiophene (EDOT) [17] considered in this work. The chemical structure of the phenyl-capped EDOT trimer, or Ph-EDOT$_3$-Ph, is illustrated in figure 2. This oligomer appears as a relevant and well-characterized material for exploring the possibilities and limitations of the RPE studies on extended $\pi$-conjugated systems. In general, the oligomers are of current interest in the context of modern molecular opto-electronic applications, largely because of their suitable electronic properties and the methods by which the molecules may be processed into thin films. Many oligomers readily form crystalline phases, facilitating high carrier mobilities [18]. Additionally, oligomers may be synthesized...
The chemical structure of phenyl-capped tri(3,4-ethylenedioxythiophene), Ph-EDOT$_3$-Ph. The four main chemically shifted carbon sites 1–4 are indicated.

with a well-defined number of monomer repeat units. Therefore, both electronic and optical properties may, in principle, be tailored to specific requirements for field effect transistors [19] and solar cells [20]. Furthermore, oligomers represent convenient, well-defined model molecules for helping to understand the electronic and optical properties of the corresponding polymer materials [21].

The phenyl-end caps, present in Ph-EDOT$_x$-Ph derivatives of EDOT, limit spontaneous oxidation of longer species and enable solution processing. In general, EDOT oligomers are electron-rich due to the presence of the electron donating ethylenedioxy substituents. This electron donation results in a lower oxidation potential for the EDOT oligomers relative to that of the corresponding thiophene-based oligomers [22]. In addition, this substitution leads to a red shift in the optical absorption, which should facilitate the collection of more of the lower-energy portion of the solar spectrum in organic solar cell applications [23, 24]. EDOT oligomers are model molecules for poly(3,4-ethylenedioxythiophene), or PEDOT, the conjugated polymer component in the well-known electrically conducting polymer blend, PEDOT-PSS, which is currently widely used in commercial and developing polymer electronic applications [22].

Here, we report the results of a study of Ph-EDOT$_3$-Ph molecules in the condensed solid state using RPE, UPS, XPS and NEXAFS. It is demonstrated that even without complex simulations, useful experimental information on the site-dependent electronic structure of relatively large-size and low-symmetry molecular systems can be obtained from the evaluation of resonant decay channels, aided by relatively simple ground state quantum-chemical calculations.

2. Experimental

The Ph-EDOT$_3$-Ph was synthesized as described previously [17]. Thin films of the oligomer were prepared by vapour deposition in ultra high vacuum (UHV). The molecules were condensed onto polycrystalline gold substrates at room temperature, which had been cleaned by Ar$^+$ ion etching prior to the deposition of the molecules. During the vapour deposition, the pressure never exceeded $8 \times 10^{-8}$ mbar. Such preparation conditions result in polycrystalline films [25] of a thickness varying between 5 and 10 nm, as estimated from the attenuation of the XPS Au(4f$_{7/2}$) line.

RPE and NEXAFS measurements were carried out at beamline I311 of the Swedish National Laboratory for Synchrotron Radiation, MAX-lab in Lund, Sweden [26]. The RPE spectra were recorded with the Scienta SES-200 electron spectrometer, with the energy resolution set to
60 meV. The spectral width of the incident radiation was matched with the energy resolution of the analyser. The partial yield of the NEXAFS spectrum was derived by integrating the RPE spectra within a kinetic energy window ranging from 267 to 278 eV. The photon energies and the binding energy scale were calibrated using the position of the Au(4f7/2) photoelectric line excited by first- and second-order light.\(^5\) The long-term beam stability was of the order of 50 meV, as estimated from the position of the C(1s) line excited by second-order radiation. The intensities of the spectra were normalized to the total incoming photon flux measured with a gold grid. All spectra are plotted relative to the Fermi level of the spectrometer.

Degradation of the organic film during the long-time exposure to high-energy photons was inspected by monitoring the valence band spectrum. The damage rate was sufficiently low to allow a series of RPE measurements within the first resonance at one irradiated spot.

3. Theoretical

Quantum-chemical calculations for neutral Ph-EDOT\(_3\)-Ph were carried out at the Density Functional Theory (DFT) level. The calculations were performed with the Becke + Lee-Yang-Parr (B3LYP) functional [27, 28] and the standard 6-31G** basis set. The equilibrium geometry of the neutral oligomer was obtained using a full geometry optimization scheme. The calculated density-of-valence-states (DOVS) used here to facilitate the interpretation of the photoemission spectra was derived as described elsewhere [25]. The quantum-chemical calculations were performed by means of the Gaussian 98 computational package [29]. The results were interpreted with the aid of the Molekel v4.3 software [30].

4. Results and discussion

4.1. Valence band structure

The low binding energy portion of the conventional UPS spectrum of the Ph-EDOT\(_3\)-Ph films is shown in figure 3. As revealed by the electronic structure calculation, photoemission within this binding energy region originates solely from electrons in \(\pi\)-type molecular orbitals (MOs) [25]. There are several distinct features in the spectrum, which are related to particular MOs. Peak A corresponds to the highest occupied molecular orbital (HOMO) delocalized along the oligomer (see lower panel of figure 2). Peak B is derived from three MOs: HOMO-2, HOMO-3 and HOMO-4, confined exclusively to the EDOT units. The shoulder (feature B') on the low binding energy side of peak B is related to emission from the HOMO-1, a delocalized MO with strong contributions from the phenyl rings. Peak C is related to two degenerate electronic states localized on the phenyl rings (HOMO-6 and HOMO-7) and to the HOMO-5, which is delocalized along the conjugated molecule. Finally, electronic states HOMO-8 and HOMO-9 extend throughout the oligomer and contribute to spectral feature C'. In addition, the molecular wave functions of the two lowest unoccupied MOs, LUMO and LUMO+1, are presented in figure 3. Both MOs are strongly delocalized. Their energies are separated by 0.8 eV.

\(^5\) The binding energy of that line was set at 83.9 eV.
4.2. X-ray photoemission and x-ray absorption spectra

The bottom part of figure 4 shows the XPS profile of the C(1s) core level spectrum, obtained with $h\nu = 350$ eV photons. Although the experimental spectrum displays only three distinct
features, four peaks were used in the fitting procedure of the XPS C(1s) spectrum. This takes into account the four main chemically shifted carbon sites (we neglect the small second-order effects), as highlighted in figure 2. The peak displacements, measured relative to the position of the phenyl C(1s) core level line, site 1, are in reasonable agreement with the values obtained previously in [31] and equal 0.4 eV for site 2, 1.2 eV for site 3 and 2.0 eV for site 4.

The onset region of the C K-edge NEXAFS spectrum recorded in the partial-yield mode is displayed in the upper part of figure 4. The first $\pi^*$ resonance is composed of two spectral features as seen previously [32]. The absorption starts at about 284.6 eV and exhibits a peak at 285.1 eV and a shoulder at approximately 285.5 eV. The frontier part of the NEXAFS spectrum is purely due to transitions from C(1s) core levels to the LUMO, whereas excitations to the LUMO + 1 might also take place at higher photon energies. Recall that the LUMO and LUMO + 1 are separated by about 0.8 eV in the ground state. Note, however, that particular transitions are suppressed (i) if the unoccupied valence orbital has a small overlap with the core orbital of the excited atomic site [33], (ii) in case of negligible Frank–Condon amplitudes of the transition.

Several constraints were imposed on the peaks in the deconvolution scheme. The parameters of the peaks, defining shape and position were not allowed to go outside physically reasonable limits (see [31]). In addition, the intensities of peaks 2, 3 and 4 were kept the same, without relating them to the intensity of peak 1. This takes account of the molecular stoichiometry. The non-stoichiometric ratio (1 : 1 : 1 : 9 ) appears to be a consequence of the predominant presence of phenyl groups at the surface ($h\nu = 350$ eV results in photoelectrons with a low kinetic energy of 50–60 eV, probing predominantly surface properties).

Figure 4. (a) The C K-edge NEXAFS spectrum and (b) the XPS spectrum of the C(1s) core level ($h\nu = 350$ eV) of polycrystalline Ph-EDOT$_3$-Ph film. The numbers assigned to deconvoluted peaks correspond to the carbon sites denoted in figure 2.
In the vicinity of the absorption threshold, excitations can occur only at site 1, which is exclusively at the carbon atoms situated in the phenyl rings. As the photon energy increases, sites 2 located at the EDOT units become accessible as well. Increasing the photon energy above 285.8 eV would enable absorption at sites 3. At these energies, however, the intensity of x-ray absorption (within the first C(1s)→π* resonance) decreases strongly. Therefore, core-excitations occur only at sites 1 and 2, when the photon energy is swept across the first π* resonance.

4.3. RPE spectra

Figure 5 shows a series of RPE spectra for excitation energies in the region of the first π* resonance. In addition, a spectrum recorded at \( h\nu = 274.9 \) eV, i.e., far below the resonance, is presented in the bottom of the figure. At resonance, an enhancement of particular valence band spectral features is observed. This behaviour arises from participator decay processes, which in a molecular solid are a major contribution to the resonant spectra in the low binding energy region as long as the excited electron remains localized on the molecule probed [9]. These relatively sharp features reside on top of an unstructured background consisting mostly of spectator decay processes. In addition, a well-pronounced peak, visible at low binding energy, appears to move linearly in energy as the x-ray photon energy is swept. This peak corresponds to C(1s) core.
levels photoionized by second-order light. Even though this C(1s) peak partly overlaps with the resonant features, it may be clearly identified by its dispersion with the photon energy. Therefore, the profile as obtained from the spectrum at $h\nu = 286.9$ eV can be directly subtracted from the spectra. Within the frontier valence $\pi$ band region, the non-resonant spectra are dominated by peak B. As the photon energy increases, the intensities of features A and C are enhanced by about one order of magnitude, whereas the intensity of feature B remains essentially constant. Feature C’ overlaps with the high binding energy shoulder of feature C. Thus, relative intensity changes between C and C’ are difficult to assess.

Although direct and RPE channels are known to interfere because they lead to the same electronic final state, it is instructive to subtract the direct valence band photoemission profile, as obtained from a non-resonant spectrum measured at an energy just below the resonance threshold, at $h\nu = 284.3$ eV. This is reasonable because for the Ph-EDOT$_3$-Ph system, the resonant processes have much larger cross-sections than the direct process, and because the interference effects are relatively weak whenever one type of process dominates [36]. The resulting set of RPE spectra is plotted along with experimentally and theoretically derived electronic structures in figure 6. Right above the x-ray absorption threshold, at $h\nu = 284.6$ eV, a clear resonant enhancement is seen for features A and C. As the photon energy increases, peak C amplifies and becomes the dominant spectral feature in the valence band region. The peak reaches its maximum intensity at about $h\nu = 285.1$ eV, as summarized in figure 7. Furthermore, peak C
broadens and disperses by about 0.5 eV towards higher binding energy when the photon energy is increased by 1 eV. Such a behaviour deviates from a linear (Raman) dispersion and might be expected as a result of the interplay between lifetime vibrational interference and degree of electronic localization [11, 37, 38]. In other words, the overlap between vibrational densities in the ground, core-excited and one-hole final states is affected by the displacement of the corresponding electronic potential surfaces [39]. In addition, the high binding energy shoulder of peak C might contain contributions from feature C’, which are more evident at elevated excitation energies. Resonant enhancement of the intensity is also observed for peak A. Although less pronounced than peak C, peak A clearly reaches its maximum intensity at photon energies slightly higher than C, between 285.5 and 285.7 eV (see figure 7). Interestingly, electronic states contributing to peak B do not take part in resonant deexcitation processes, even though peak B evidently dominates the valence band spectra below and again above the resonance.

4.4. Discussion

Although an accurate description of the RPE process requires complex many-body theory [16], a qualitative interpretation of the spectra might be possible from the present experimental data, supported by an MO-picture derived from ground state quantum-chemical calculations alone. The chemical shifts observed in the C(1s) core level spectrum confine x-ray absorption events to excitations to the LUMO and possibly to the LUMO + 1 at sites 1 and 2, as analysed in the previous section. For a given x-ray absorption channel, the rate of resonant Auger emission is governed by the overlap of the electronic wave functions of the core-excited intermediate state and the ionized final state, as well as by the Frank–Condon amplitudes of the transition [8, 40]. Consequently, for photon energies up to about 286 eV, resonant participator-type emission can only occur at atomic sites 1 and 2, the sites at which the intermediate, core-excited states are localized. Large decay rates are expected for valence states that have high electronic densities at these sites. The RPE spectra of the Ph-EDOT3-Ph reflect exactly this correlation, and the enhancement of features A and C can be understood as follows: peak A is due to participator-type Auger electron emission from a single delocalized orbital, the HOMO. This MO has high electronic densities at both 1 and

Figure 7. Intensity changes of feature A (●) and feature C (○) within the first $\pi^*$ resonance. Additionally, the NEXAFS spectrum (▲) is displayed in the figure. Unless specifically noted, the error bars correspond to the vertical size of the symbols.
2 carbon atom sites. Peak C corresponds to two localized phenyl states (HOMO-6 and HOMO-7) and a delocalized state (HOMO-5). For all of these states, high partial electronic densities effectively match the location of the core hole at site 1. An analogous interpretation might also explain a minor intensity increase observed at a binding energy of about 2.4 eV, which would correspond to resonant emission from the HOMO-1. As a result, spectral feature B' is resolved in the RPE spectra while this is not the case in the direct photoelectron emission spectra. Similarly, more pronounced resonant emission from states HOMO-8 and HOMO-9 (feature C') might occur at elevated photon energies, corresponding to an enhanced excitation probability at site 2 and diminished excitation probability at site 1. In contrast, MOs related to peak B (HOMO-2, HOMO-3 and HOMO-4) are exclusively confined to the EDOT units without any significant overlap with the carbon sites either at the phenyl ring (1), or at the α position of the EDOT units (2). Therefore, the intensity of feature B is not enhanced in the resonance. Clearly, using resonant processes, local ground state electronic properties are probed, demonstrating the usefulness of RPE to study the role of electronic subsystems or functional groups of large organic molecules.

Note that, in resonant x-ray scattering experiments, interference of resonant channels leading to the same final state might occur. It is well known that radiative decay processes in x-ray scattering experiments on systems with sub-eV chemically shifted atomic sites interfere strongly [15]. Due to the large momentum of the emitted (Auger-like or participator) electron, the situation can be, however, much different for non-radiative decay processes. Coherence of electron waves originating from different atomic sites within the same molecule is strongly quenched if the individual molecules are randomly oriented [41], as is the case in polycrystalline films with randomly oriented crystallites. Interference of non-radiative scattering channels at different atomic sites is then strongly suppressed. Other dephasing mechanisms like vibrational and librational motions, and scattering of the emitted electron by the surrounding matter contributes to the destruction of coherence as well [41]. Therefore, a quantitative analysis of the decay channels related to sub-eV shifted sites 1 and 2, interpreted as if they were independent, is legitimate in this case. Consequently, the fact that the intensity of peak A is maximal at about 0.5 eV higher excitation energies than peak C can be interpreted as follows: the HOMO (corresponding to peak A) has a strong overlap with site 2. Thus, since excitations at site 2 are enabled at about 0.4 eV higher photon energies than at site 1, the intensity of peak A is amplified for elevated photon energies. Hence, the experiments demonstrate the usefulness of RPE spectra for obtaining site-dependent information on the electronic structure, not only for substantially shifted atomic sites (e.g. 1.0 eV) but also in the cases of sub-eV chemical shifts.

Besides providing insight into local ground state properties, RPE spectra might also allow an otherwise uncertain interpretation of NEXAFS spectra [11]. For the phenyl-capped EDOT system, an understanding of substructures of the first π* resonance emerges: recall that the estimated chemical core level shift between carbon atom sites 1 and 2 equals 0.4 eV. Similarly, a 0.4 eV energy separation is observed between the two distinct features that comprise the first π* resonance, i.e., the peak at 285.1 eV and the shoulder at approximately 285.5 eV. This suggests that the increased x-ray absorption signal constituting the shoulder arises from the C(1s)→LUMO excitation at sites 2, in addition to diminished absorption at sites 1. Indeed, as revealed by the RPE spectra, excitations with 285.1 eV photons result in maximal intensities of the decay channels related to site 1, in particular peak C (see discussion above). On the other hand, the absorption of x-rays in the range 285.5–285.7 eV maximizes the intensities of the decay channels corresponding to atomic site 2, e.g. peak A. Thus, RPE provides compelling evidence that the shoulder identified...
In the NEXAFS spectrum is a consequence of an excitation to the LUMO at sites 2, rather than a C(1s)→LUMO + 1 transition at carbon atom sites 1. Hence, in general, C(1s)→LUMO + 1 transitions in the phenyl-capped EDOT trimer appear to be suppressed for excitation at sites 1 and 2. Note, however, that for the EDOT monomer, C(1s)→LUMO + 1 excitations at site 2 are not negligible [42].

Vibrational degrees of freedom expressed as the Franck–Condon amplitudes of the photoabsorption and decay processes influence the intensity and shape of the resonating features as well. However, it is demonstrated that binary-like criteria based on the overlap of electronic wave functions can be applied in this system, and justified and valuable arguments for an at least qualitative interpretation of the RPE spectra of large molecules, in terms of the site-dependent electronic structure can be provided.

5. Conclusions

RPE spectroscopy has been used to study the valence electronic structure of Ph-EDOT$_3$-Ph condensed into polycrystalline thin films. By tuning the photon energy for soft x-ray absorption, strong changes in intensities of the RPE peaks corresponding to participator decay events have been observed. Since interference between direct and RPE channels, as well as interference between the non-radiative resonant channels themselves, is negligible for such molecular systems, the intensity variations can be interpreted in terms of the spatial overlap of the electronic wave functions of initial, intermediate and final states. Because of chemical shifts between core levels at different atomic sites, soft x-ray excitations are confined to specific parts of the molecule. Exploiting these chemical shifts, we have demonstrated that site-specific information on the electronic structure of relatively large and complex organic molecules may be obtained experimentally from non-radiative resonant decay spectra. This provides more detailed experimental information on the ground state valence electronic structure of such large molecules and allows understanding of the fine structure of x-ray absorption spectra from RPE, without sophisticated excited state calculations. For this approach, systems with sufficiently separated energies of core-level lines are favoured, because different sites can be distinguished in the absorption of soft x-rays. But also for small chemical shifts, experimental information can still be extracted provided that the molecular film is globally disordered. The study of non-radiative resonant decay processes might therefore evolve as a powerful tool for the evaluation of the ground and excited state electronic structure of organic molecular materials.

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