

Resonant X-ray emission spectroscopy of thin organic films on ITO: PTCDA, TPD, and TPD/PTCDA

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INTRODUCTION

The investigation of the electronic structure of large organic molecules and their chemical interaction with substrate surfaces is one of the primary tasks in understanding the growth of highly-ordered thin organic films. Resonant X-ray emission spectroscopy (XES) is an outstanding tool for such investigations, because it is atom-specific and can hence distinguish between the electronic structure of the adsorbate molecule and the substrate. Due to its bulk sensitivity it can thus elucidate the chemical and electronic properties of buried layers, e.g., underneath an electrical contact. Furthermore, resonant excitation into well-defined intermediate states (i.e., NEXAFS resonances) can distinguish between different functional groups of the molecule, which opens the door to a wealth of information which can not be obtained by any other spectroscopic method.

There is, however, an experimental downside to this approach: high resolution XES – and even more so resonantly excited XES – needs a bright light source with large excitation photon flux due to the low fluorescence yield of the involved atoms (typically C, N, O). With the design of third-generation synchrotron sources (such as the ALS) and high-flux beamlines (such as beamline 8.0), fortunately, the experimental set-up has reached a high flux level which is sufficient for many (but not all !) investigations. With regards to organic molecules, this poses a new challenge, namely the radiation damage induced by the excitation beam. In order to show the general viability of such investigations, we have performed a resonant XES study of thin films and bilayers of two different organic molecules (TPD and PTCDA). We will show that spectra with sufficient spectral quality and clearly distinguishable signatures of the molecular functional groups can be taken in measurement times shorter than the relevant beam damage period, and that the investigation of very thin bilayer structures poses a challenge to optimize the detection efficiency of the current experimental set-up.

MATERIAL SYSTEMS

In this study, we have focused on organic and substrate materials that are of relevance for the preparation of organic light emitting diodes (OLEDs), namely TPD (N,N'-di-(3-methyl-phenyl)-N,N'-diphenyl-4,4'-diaminobiphenyl) and PTCDA (3,4,9,10 perylenetetracarboxylic dianhydride) on ITO (InSnO) substrates. TPD is widely used as a hole-injecting material for OLEDs, and PTCDA is of interest because it exhibits either electron transport (in the direction along molecular planes) or mainly hole transport (in the direction normal to molecular planes). In a recent publication [1], we were able to show that a very thin (2 nm) chemisorbed interlayer of PTCDA can substantially improve the electronic structure for hole injection from the ITO substrate into the TPD layer of OLEDs. Hence it is of interest to study (a) the electronic structure of thin films of the individual molecules (here: 110 nm TPD/ITO and 80 nm PTCDA/ITO) and (b) the interaction in thin bilayer systems (here: 6 nm TPD/2 nm PTCDA/ITO and 12 nm TPD/3 nm PTCDA/ITO). The experiments were performed at beamline 8.0 using the SXF endstation.

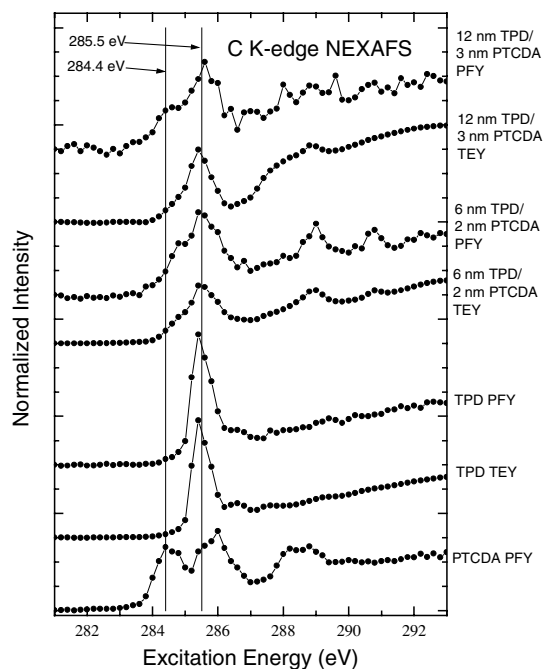


Figure 1. Carbon K-edge NEXAFS spectra of different organic thin film samples. Spectra were recorded in total electron yield (TEY) mode and/or partial fluorescence yield (PFY) mode. All spectra were normalized to give the same edge jump at 300 eV.

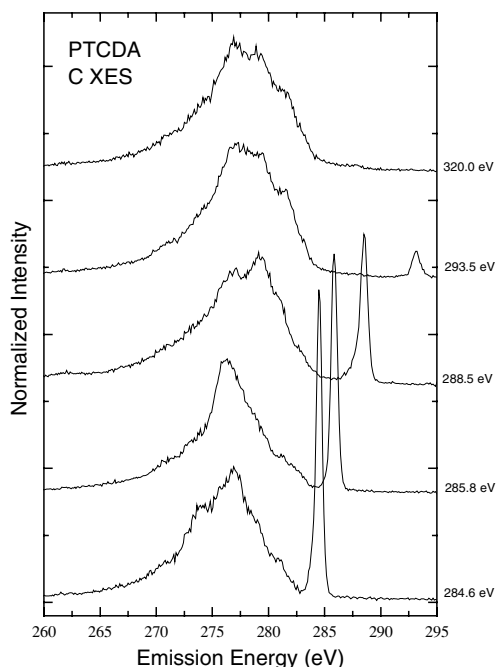


Figure 2. Resonant XES spectra of a 80 nm PTCDA film on ITO. Excitation energies are given on the right, and all spectra are normalized to give the same maximum intensity. Sharp peaks represent the elastically scattered spectral component.

RESULTS

NEXAFS spectra of various organic thin film samples are shown in Fig. 1, recorded by monitoring the sample current (TEY) and/or the integrated fluorescence intensity between emission energies of 260 and 300 eV (PFY). The PTCDA spectrum is dominated by three resonances (at 284.4 eV, 285.8 eV and 288.5 eV). Based on earlier experiments, the first two peaks are associated with the π^* resonances of C atoms in the PTCDA ring system, while the third resonance is associated with C atoms in the anhydride groups and in C-H bonds. TPD, on the other hand, shows one pronounced resonance at 285.5 eV (C atoms bound to hydrogen and/or other C atoms [2]) and a weak resonance at 286.6 eV (C atoms bound to nitrogen atoms [2]). Most spectral features of the bilayer films can be explained by a combination of the TPD and PTCDA resonances. In particular, we observe a PTCDA-derived shoulder at 284.4 eV and a TPD-derived resonance at 285.5 eV in all bilayer spectra. The latter is mixed with the contribution from the second π^* resonance of PTCDA (at 285.8 eV). Note that due to the increased information depth, the PTCDA-related shoulder at 284.4 eV in the bilayer spectra is more pronounced in the PFY mode, since the PTCDA layer is buried underneath the TPD top layer.

Resonant X-ray emission spectra at relevant excitation energies are shown in Fig. 2 for PTCDA and Fig. 3 for TPD (left graph), as well as 6 nm TPD on 2 nm PTCDA on ITO (right graph in Fig. 3). In all three cases, we observe a clear dependence of the spectral lineshape on the excitation photon energy, which is interpreted as a different partial contribution of the various occupied molecular orbitals (HOMO, HOMO-1, etc.) to the electronic structure of the excited molecular functional group. Note that in particular the PTCDA and TPD spectra clearly exhibit individual peaks corresponding to the different occupied molecular orbitals. A more rigorous lineshape

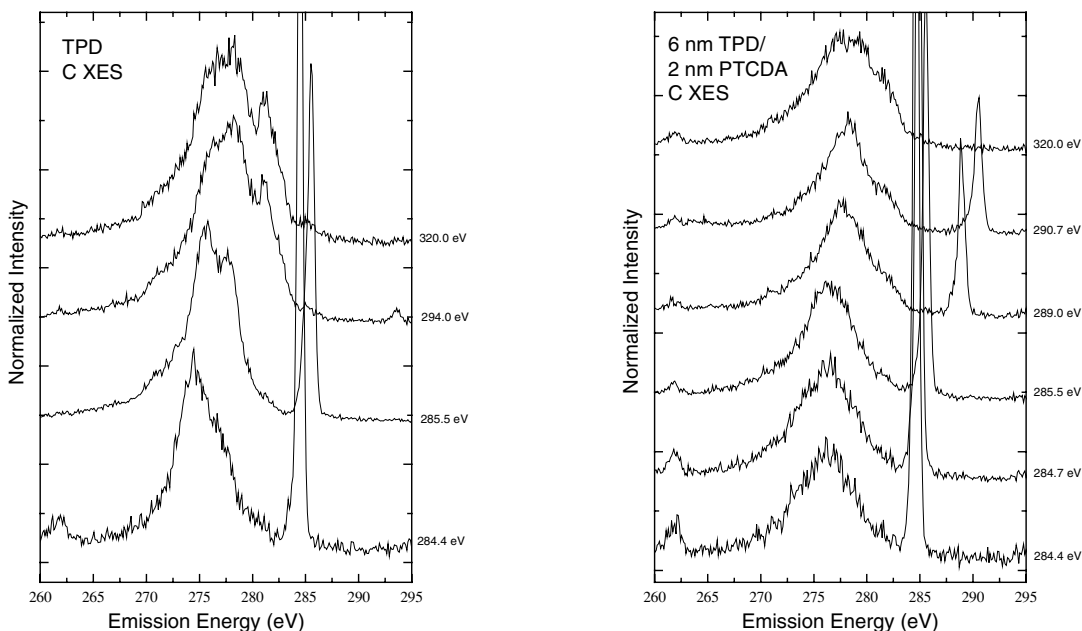


Figure 3. Resonant XES spectra of a 110 nm TPD film on ITO (left graph) and 6 nm TPD on 2 nm PTCDA on ITO (right graph). Excitation energies are given on the right, and all spectra are normalized to give approx. the same maximum intensity. Sharp peaks represent the elastically scattered spectral component.

analysis should then give a fairly detailed picture of the distribution of these states in the two molecules. It should be pointed out that the PTCDA and TPD spectra are a sum of up to 4 individual 2-minute spectra, each taken at previously unexposed regions of the film. Since in a careful study we were able to observe first (small) beam-induced spectral changes only after 10 minutes and more (at approx. 300 mA ring current), we can conclude that this approach can yield resonant XES spectra of sufficient quality without beam damage problems. In the case of the thin bilayer structure, also longer measurement times (up to 10 min) were included in the spectral summation in order to obtain a sufficient spectral quality. The spectrum of particular interest is the one with an excitation energy of 284.4 eV (lowest spectrum). In principle, this spectrum should be excited in and emitted from the PTCDA layer *underneath* the TPD layer. In fact, the observed spectral lineshape more closely resembles that of PTCDA rather than that of TPD in the relevant energy regime, but a detailed analysis of the lineshape is obscured by the low signal-to-noise ratio (note that the intensity of the 284.4 eV spectrum of TPD is very low (compare Fig. 1), and is shown on a strongly magnified scale in Fig. 3). Hence, an analysis of the difference in electronic structure between the buried chemisorbed PTCDA monolayer and the PTCDA multilayer calls for an optimization in detection efficiency.

In summary, we were able to show that resonantly excited XES spectra of high spectral quality can be obtained for thin films of large organic molecules with negligible impact of beam damage effects. The resolution of the XES spectra suffices to discern the occupied molecular orbitals and show a clear variation with excitation energy due to the creation of core holes in different functional groups of the molecules.

REFERENCES

1. L. Chkoda, C. Heske, M. Sokolowski, and E. Umbach, *Appl. Phys. Lett.* **77**, 1093 (2000).
2. R. Treusch et al., *J. Appl. Phys.* **86**, 88 (1999).

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