Evidence of hybridization states at the donor/acceptor interface: case of m-MTDATA/PPT

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Abstract

We performed a spectroscopic study on the *m*-MTDATA (donor) and PPT (acceptor) molecular vertical heterostructure. The electronic properties of the donor/acceptor interface have been comprehensively characterized by synchrotron radiation-based photoelectron spectroscopy and near-edge x-ray absorption fine structure. The spectroscopic results reveal the existence of new hybridization states in the original molecular energy gap, likely attributed to the interaction between the donor and the acceptor molecules at the interface. Such hybridized states can have a significant impact on the charge transport in organic electronic devices based on donor–acceptor molecules and can explain the increased efficiency of device using such molecules.

1. Introduction

Charge transfer/separation occurring at the interface plays a key role in organic optoelectronic devices, such as organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), as well as the solid dye-sensitized solar cell developed recently [1–5]. Blends of electron-donating and electron-accepting molecules constitute the active layer of OPVs and their use in OLEDs has been shown to improve the performance [6–10]. Therefore, understanding the electronic structure at the donor/acceptor heterostructure is the focus of intense research interest for developing efficient optoelectronic devices [11–15]. Fundamental studies focused on modifications of the electronic structure of the donor/acceptor components due to the interface are crucial to understand the charge separation processes at organic/inorganic and organic/organic heterojunctions for new developments and device optimizations [16]. We focus the present study on *in situ* samples grown under controlled ultra-high vacuum conditions to define a model system for studying these processes.

m-MTDATA (4,4',4"-Tris (N-3-methylphenyl-N-phenyl-amino) triphenylamine, $C_{57}H_{48}N_4$, shown in figure 1(a)) belongs to a group of molecules called 'starburst π-conjugated molecules', widely used in organic optoelectronic devices, like OLEDs and OPVs. The good electron-donating and charge-transport properties of *m*-MTDATA are largely given by its building block triphenylamine (TPA), involving the lone pair electrons of the N atom [17, 18]. Compared to TPA, *m*-MTDATA is a better electron donor and has higher thermal stability. The molecular plane of *m*-MTDATA can be defined by the four N atoms, i.e. $(N)_4$-plane [17]. PPT (2,8-bis-(diphenyl-phosphoryl)-dibenzo[b,d]thiophene, $C_{36}H_{26}O_2P_2S$, shown in figure 1(b)) is an ambipolar acceptor material, used in combination with electron-donating materials to enhance the electroluminescence efficiency [19, 20]. In this study, using Au(111) as substrate, we deposited *m*-MTDATA (donor) on top of a thick film (approx. four layers) of PPT (acceptor) and constructed a donor–acceptor molecular vertical heterostructure, used to shed light on the interfacial electronic structure modifications of *m*-MTDATA. An illustration of how this interface might look like is provided in figure 1(c). The comparison between different *m*-MTDATA depositions (i.e., monolayer-ML and submonolayer-subML) on PPT reveals, at subML coverage, a strong modification of the *m*-MTDATA molecular electronic structure, ascribed to a donor–acceptor hybridization due to the interaction within the resulting *m*-MTDATA/PPT heterostructure.

2. Methods

The synchrotron radiation-based photoelectron spectroscopy (PES) and near-edge x-ray absorption fine structure (NEXAFS) measurements were carried out at the materials science beamline of the Elettra synchrotron [21]. The PE spectra were recorded by the Specs Phoibos 150 hemispherical electron analyzer mounted at the end station. During the measurements, the base pressure of the analysis chamber was in the 10^{-10} mbar range. All the samples were prepared with a base pressure of a high 10^{-10} mbar range. The Au(111) substrate was cleaned by repeated Ar^+ sputtering and annealing cycles until no contaminants were observed by the PE measurements.

The PPT/Au(111) heterostructure was prepared by thermal evaporation of PPT (Lumtec, purity > 99%) at 205 °C from a quartz crucible, heated by a tantalum wire, onto the clean Au(111). The thickness of the PPT thick film was controlled by the evaporation time and was estimated at about 11.3 Å (i.e., approximately 4 ML) by the attenuation of the PES Au 4f lines [22]. Then the *m*-MTDATA/PPT/Au(111) heterostructure was prepared by depositing *m*-MTDATA (Sigma Aldrich, purity 98%) onto the PPT film via thermal evaporation at 190 °C from a similar Knudsen type evaporator as used for the PPT evaporation. Two thicknesses of *m*-MTDATA were prepared, corresponding to subML (approx. 0.5 ML) and 1 ML, respectively.

The C 1s and N 1s core level PE spectra were measured at normal emission (NE) to the electron analyzer using photon energies of 392 and 495 eV, respectively. The resolutions were about 330, 430, and 150 meV for C 1s, N 1s and VB measurements, respectively. The NEXAFS spectra at the C and N K-edges of the deposited molecules were recorded using partial Auger yield. The measurements were performed at different scattering geometries: normal incidence (NI, 90° between the incident light and the surface plane), normal emission (NE, 90° between the analyzer and the surface plane, or 60° between the incident light and

the surface plane) and grazing incidence (GI, 10°, between the incident light and the surface plane). The photon energy scales of the NEXAFS were calibrated measuring the Au 4f PES lines by the 1st and 2nd order light. The energy resolution for the C and N K-edge NEXAFS spectra was estimated to be about 250 and 400 meV, respectively. Other experiment details can be found in reference [23].

3. Results and discussions

The C 1s PES results of *m*-MTDATA/PPT/Au(111) are shown in figure 2(a). The PPT/Au(111) spectrum shows a symmetric peak centered at 285.15 eV binding energy (BE) with FWHM about 0.68 eV. The C 1s peak becomes slightly asymmetric and shifted toward higher BE with subML *m*-MTDATA coverage (285.30 eV, FWHM = 0.75 eV). The C1s peak shifts further at 1 ML *m*-MTDATA coverage (main peak at about 285.40 eV), and a shoulder appears at the higher BE side (286.40 eV, indicated by the blue arrow in figure 1(a)). Comparing to the gas phase *m*-MTDATA results [17], the shoulder feature at 1 ML *m*-MTDATA coverage can be attributed to the contribution from *ipso* (–C–N–) and methyl ($-CH_3$) type carbon of *m*-MTDATA. Since nitrogen is only present in *m*-MTDATA, we can visualize and confirm the *m*-MTDATA growth process by the N 1s PES measurements, shown in figure 2(b). The PPT/Au(111) substrate shows no N contribution and we find a broad N 1s peak centered at about 400.20 eV with FWHM = 1.20 eV of subML *m*-MTDATA/PPT. When the thickness of *m*-MTDATA reaches 1 ML the N 1s peak also shifts to higher BE (at 400.40 eV) with a FWHM of 1.20 eV. A similar shift to higher BE was also observed for *m*-MTDATA on Au(111), without PPT [23]. We note that similar shifts (for example C 1s and N 1s) toward higher BE with increasing thickness are quite common in organic films [24]. This kind of shift is usually ascribed to the decreased surface screening of the core hole in PES. The same trend of the shift toward higher BE can still be observed in very thick films (up to 100 Å) [25].

The valence band (VB) PES results of *m*-MTDATA/PPT are shown in figure 2(c), measured with 100 eV photon energy. At subML *m*-MTDATA coverage on PPT, only little changes can be observed, whereas at 1 ML *m*-MTDATA coverage, although the VB PES is still dominated by the PPT electronic states, we observe the appearance of the HOMO features and of another small feature (at 12.00 eV BE), indicated by the blue arrows in the figure.

For increasing the surface sensitivity of the valence measurements and then better resolve the *m*-MTDATA spectroscopic features, we used a photon energy of 40 eV (figure 1(d)). To easily locate the *m*-MTDATA electronic states, we also show the gas phase *m*-MTDATA valence PES measured at the same photon energy (green markers, shifted −4.6 eV) [17]. From this comparison, we clearly see the HOMO contribution from the *m*-MTDATA in the *m*-MTDATA/PPT/Au(111) structure, reasonable since *m*-MTDATA is a donor molecule. Although the characteristic three-peak outermost valence feature of *m*-MTDATA is not resolved due to the solid-state effect [23, 26], with the help of the gas phase result we can still identify the HOMO at about 1.55 eV. Moreover, the small feature at 11.90 eV is also a contribution by the *m*-MTDATA.

To understand the molecular arrangement of *m*-MTDATA when adsorbed onto PPT, we carried out polarization-dependent NEXAFS measurements for each *m*-MTDATA coverage (subML and 1 ML, respectively). This method consists of making NEXAFS measurements at different orientations of the sample with respect to the incident light. The molecular orientation can be extracted from the absorption spectra as a function of the angle θ formed by the surface plane with respect to the linearly polarized electric field of the photon beam [25]. Therefore, in general, the resonances are expected to be enhanced when the light polarization vector (*E* vector) is aligned along the direction of maximum amplitude of the final state orbital. Considering the N K-edge of *m*-MTDATA, the π^* resonance intensity is expected to be most intensive when the *E* vector is perpendicular to the molecular plane, i.e. $(N)_4$-plane, and to vanish when the polarization is parallel to the molecular plane [24]. Details of the discussions and illustrations of the deposited *m*-MTDATA molecular plane can be found in our recent *m*-MTDATA/Au(111) study [23].

The polarization-dependent C K-edge NEXAFS results are shown in figure 3, measured at GI and NI angles. It is no surprise to see that there is no evident polarization dependency in *m*-MTDATA/PPT/Au(111). With increasing *m*-MTDATA thickness, the C K-edge NEXAFS results still show no polarization dependency. In fact, all of the carbon atoms (in total 93 C atoms) from PPT and *m*-MTDATA (both of quite complex molecular structure), contribute to the C K-edge signal. We, therefore, cannot draw any conclusion about the molecular orientation and we just suggest that the molecules can have a quite complex/disordered arrangement.

To look closer at the modifications of the absorption spectra for increasing *m*-MTDATA coverage onto PPT, we zoom into the photon energy region of the main absorption resonance of the C K-edge NEXAFS (figure 3(b)). The main absorption peak of the C K-edge NEXAFS is found at about 285.00 eV for both subML *m*-MTDATA and 1 ML *m*-MTDATA coverage and also for PPT/Au(111). For increasing *m*-MTDATA coverage, the intensity of the peak at about 286.20 eV (i.e., about 1 eV from the main resonance) is enhanced. This peak is absent in C K-edge results of PPT in gas phase [19] and of the PPT thick film. By comparing to the gas phase and calculated *m*-MTDATA C K-edge NEXAFS results [17], the peak at about 286.20 eV is ascribed to the *ipso*-kind C atoms of the *m*-MTDATA molecule.

The N K-edge NEXAFS results of *m*-MTDATA/PPT are shown in figure 4. Unlike the C K-edge NEXAFS spectra that are the result from all C atoms from both *m*-MTDATA and PPT, only the four N atoms of the *m*-MTDATA molecule contribute to the N K-edge NEXAFS. Considering the molecular structure with the planes defined by the N atoms and the *ipso* carbons bonded to the nitrogens, we could be able to determine the arrangement of *m*-MTDATA from the N K-edge NEXAFS results. The analysis was focused on the prominent π^* structure, which corresponds to a transition into an empty N state oriented out of the molecular plane at 402.45 eV photon energy for the subML and 402.50 eV for the 1 ML *m*-MTDATA/PPT, respectively. From figure 4 we can find that, at the subML *m*-MTDATA/PPT coverage, the π^* resonance at 402.45 eV is enhanced at GI angle. Its intensity becomes much less sensitive to the polarization for increased molecular coverage (figure 4 upper panel). The results suggest that, at subML *m*-MTDATA/PPT, the N planes (formed by the four nitrogen atoms) of the *m*-MTDATA molecule would prefer to stay quite parallel to the substrate. However, it is important to consider the results as only indicating a trend, because the molecules are adsorbed on a PPT film and not on a flat substrate which can of course imply quite complex and diverse molecular arrangements. At 1 ML *m*-MTDATA/PPT, there is no polarization variation of the π^* resonance intensity for the diffferent experimental set-ups, indicating that the arrangement of *m*-MTDATA molecules becomes more disordered.

Another important finding is that at subML *m*-MTDATA/PPT, there is a new pre-edge feature starting at 399 eV photon energy, quite similar to the pre-edge at the interface of *m*-MTDATA/Au(111) attributed to the *m*-MTDATA-Au hybridization state [23]. However, in our case, the *m*-MTDATA molecules are adsorbed on a thick PPT film that breaks the interaction between *m*-MTDATA and Au(111). This is confirmed by figures 2(c) and (d) where the Au substrate photoemission lines are not visible in the PPT film spectra, indicating that the PPT thickness is larger than the escape depth of the Au photoelectron. Then we can regard these new states as formed by the interaction at the interface between the organic donor *m*-MTDATA and the organic acceptor PPT. On the other hand, there is no pre-edge feature at the 1 ML *m*-MTDATA/PPT/Au(111) supporting that these states are the results of the interaction at the organic donor–acceptor interface. In view of the molecular arrangement, changing from a quite defined orientation trend to a more disordered adsorption from subML to 1 ML *m*-MTDATA/PPT/Au(111), we can speculate that this pre-edge feature (and then the interface interaction) could be related to the molecular arrangement between *m*-MTDATA and PPT, i.e. the interaction could promote the adsorbate arrangement, and/or vice versa.

The energy position of the pre-edge feature, indicates, as already investigated for *m*-MTDATA/Au(111) that new hybrid states are available in the original molecular gap [23]. This is a crucial modification of the electronic structure at such an interface, because it can represent a new channel for delocalization of the excited electrons from the donor to the acceptor molecule. This new hybrid state provides an important insight to the D–A charge-transfer dynamics. Further ongoing investigations by means of resonance photoelectron spectroscopy and core-hole clock method will complete our spectroscopic results.

4. Conclusion

We successfully prepared *m*-MTDATA/PPT/Au(111) donor–acceptor vertical heterostructures. N K-edge NEXAFS shows that, at subML *m*-MTDATA/PPT/Au(111), the N-planes of the *m*-MTDATA molecules seem to prefer to arrange quite parallel to the surface. The molecular adsorbate becomes more disordered at 1 ML *m*-MTDATA/PPT/Au(111). The electronic structure of *m*-MTDATA in the subML *m*-MTDATA/PPT/Au sample undergoes important modifications as evidenced by the appearance of a pre-edge feature in the N K-edge spectrum. This pre-edge feature is ascribed to new hybrid states formed at the donor–acceptor interface, i.e. between *m*-MTDATA and PPT film. These findings and our previous study of *m*-MTDATA/Au(111) prove that *m*-MTDATA can form hybridization states between both organic-metal and organic–organic interfaces, with a consequent impact in donor–acceptor electronic devices. We believe that the new hybridized states at the organic–organic interface could promote/facilitate the charge transfer process and further electron dynamics studies are planned to fully elucidate this question.

Acknowledgments

TZ thanks the financial support from the National Natural Science Foundation of China (Nos. 61901038, 61971035, 61725107, 92163206), Beijing Natural Science Foundation (Nos. Z190006, 4192054), National Key Research and Development Program of China (2020YFA0308800, 2019YFA0308000), the support from the Beijing Institute of Technology Research Fund Program for Young Scholars and the Vice-Chancellor of Uppsala University for financial support through the U4 collaboration. BB acknowledges the Swedish Research Council for research Grant (VR 2014-3776). FOLJ acknowledges support from the Swedish Research Council (Grants VR 2014-6463 and 2020-06409). The authors acknowledge the EU CERIC-ERIC Consortium for the access to experimental facilities and financial support. We thank the staffs at Materials Science beam line, at Elettra, for all the help provided during the beamtimes. We thank G Bortoletto and C Pedersini of the User Support Lab at Elettra.

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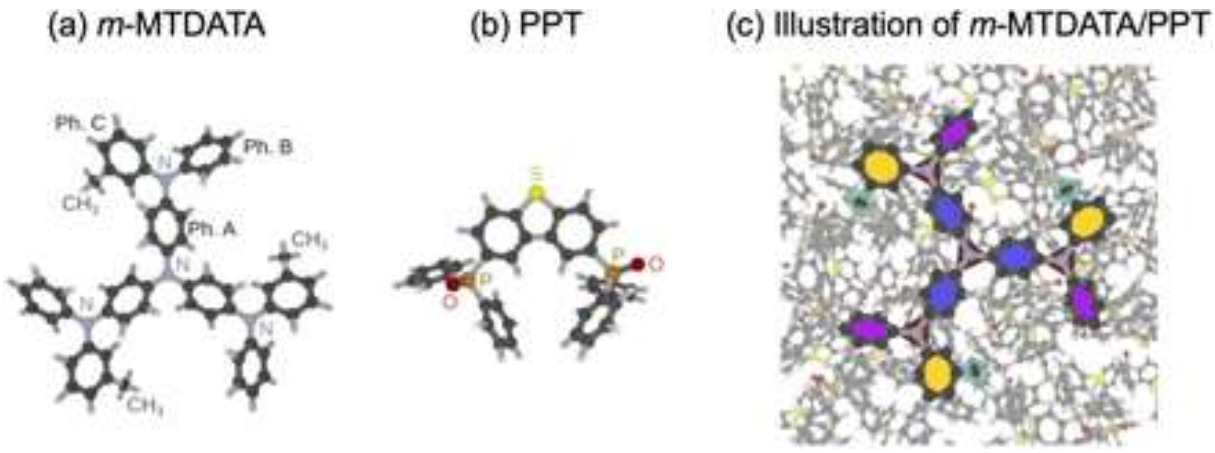

Figure 1. Structure of (a) *m*-MTDATA and (b) PPT. An illustration of a possible *m*-MTDATA/PPT interface is shown in (c).

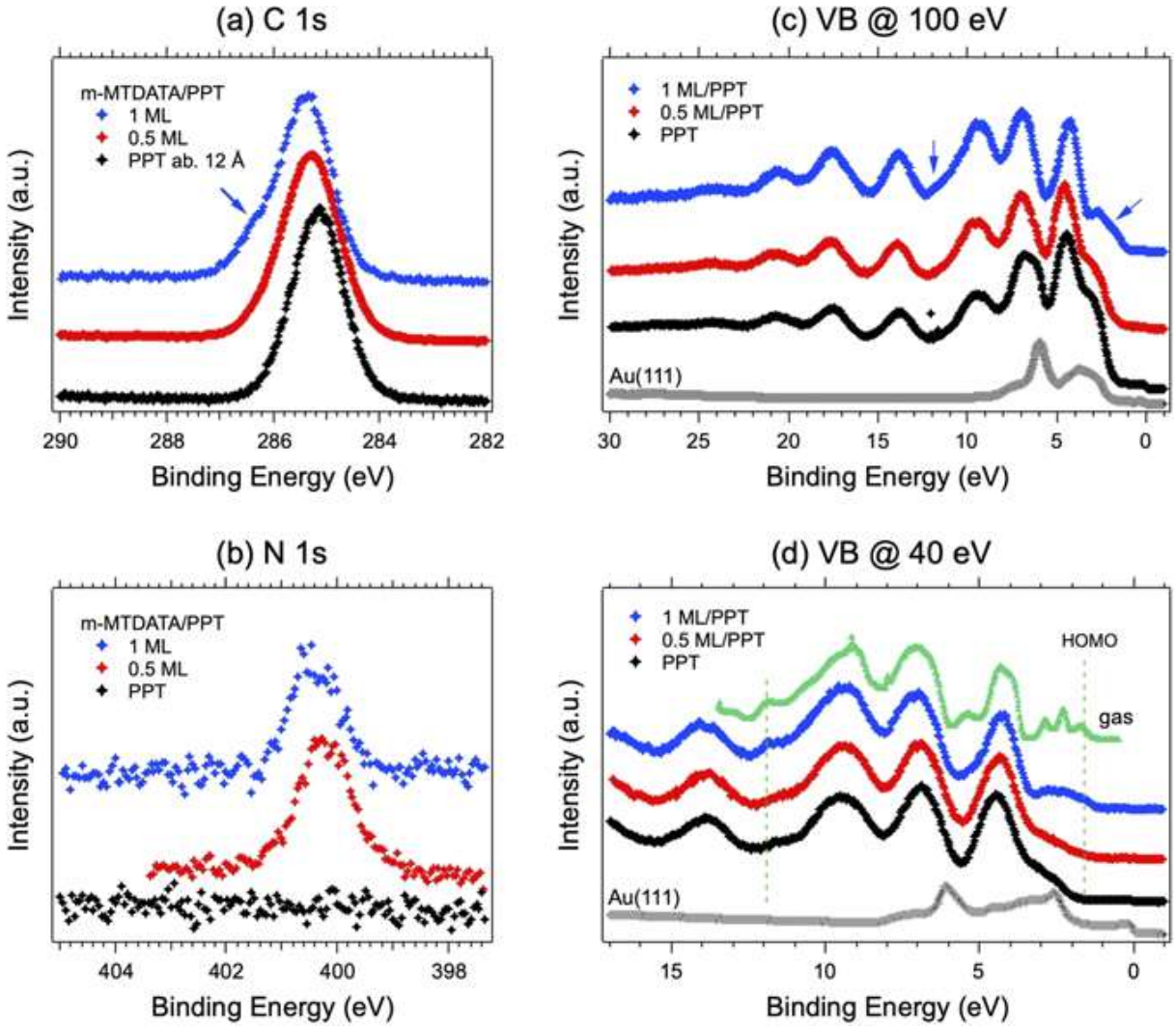

Figure 2. PES results of (a) C 1s core level, (b) N 1s core level, (c) VB measured at 100 eV photon energy and (d) VB measured at 40 eV, comparing different thicknesses of *m*-MTDATA on PPT/Au(111).

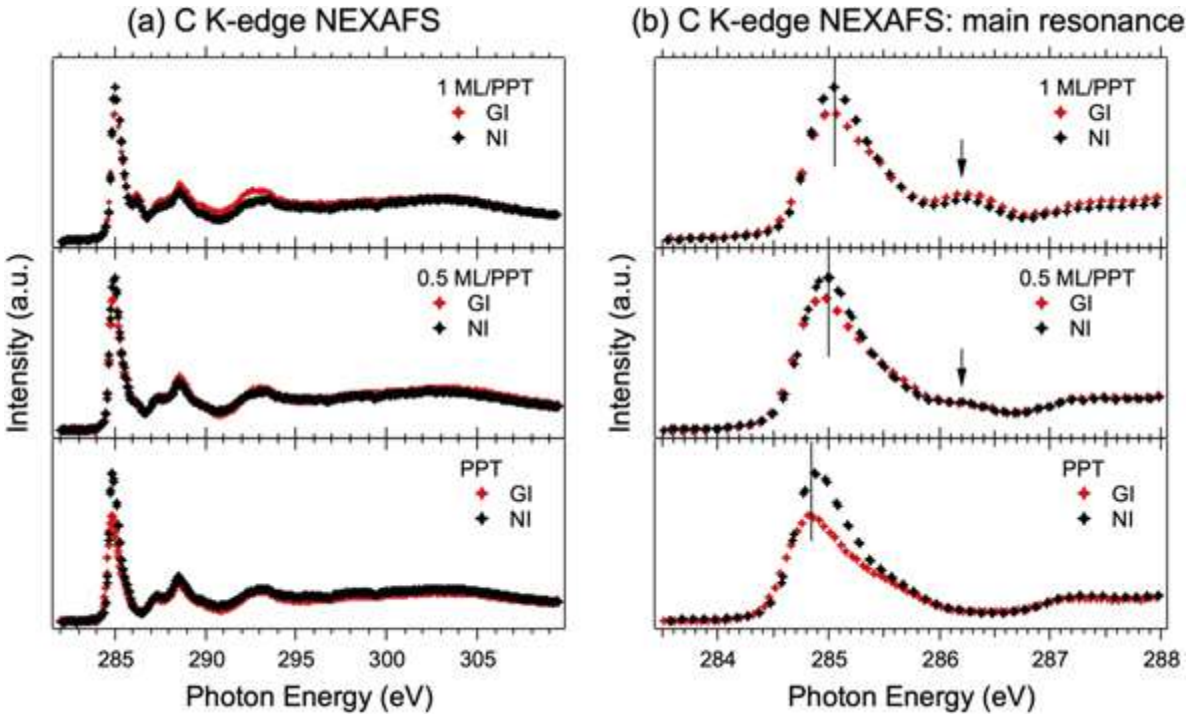

Figure 3. (a) Polarization dependent C K-edge NEXAFS results of *m*-MTDATA/PPT/Au(111) for different coverage from PPT thick film, subML to 1 ML. (b) Zoom-in of (a) to enlarge the main resonance energy region. The black bars indicate the position of the main resonance. The arrows point to the contribution from *ipso*-kind C atoms from *m*-MTDATA molecule.

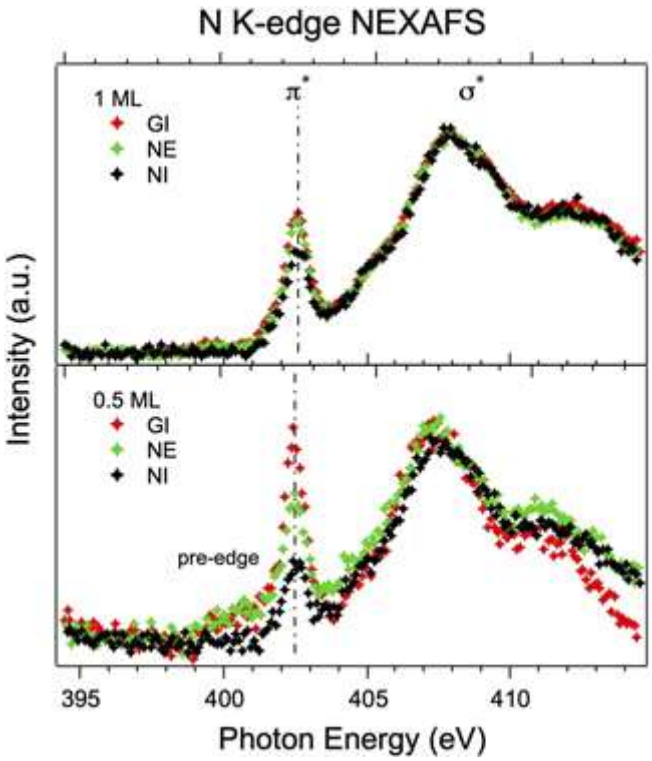

Figure 4. Polarization dependent N K-edge NEXAFS results of *m*-MTDATA/PPT with different coverages. The intensities are normalized to the σ^* to enhance the π^* polarization dependence.