

Angular dependent NEXAFS study of the molecular orientation of PTCDA multilayers on Au (111) surface

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The molecular orientation of perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) multilayers adsorbed on Au (111) surface has been investigated using angular dependent O *K*-edge near edge X-ray absorption fine structure (NEXAFS) spectroscopy. The significant angular dependence of important resonant structures (π^* and σ^*) reveals that PTCDA molecules adopt an ordered geometry on the substrate surface. The average tilt angle of the PTCDA molecular planes is $27^\circ \pm 10^\circ$ from the Au (111) surface.

NEXAFS, perylene-3,4,9,10-tetracarboxylic acid dianhydride, organic electronics, molecular orientation

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In recent years, organic semiconductors have been widely used as active components in many electronic and optoelectronic devices [1–3]. In most of these devices, molecule/metal interfaces are ubiquitous. It is well known that molecular morphology, organization and electronic structure at interfaces play important roles in determining device performance [4]. In particular, molecular orientation is likely to influence interfacial electronic properties [5,6]. Therefore, it is of importance to prepare organic thin films containing ordered molecules to better understand and enhance device performance.

PTCDA ($C_{24}O_6H_8$, chemical structure shown in Figure 1) is an n-type organic semiconductor with an optical transport band gap of 2.2 eV. This gap can be modified by substituting hydrogen or oxygen atoms for various functional groups. PTCDA and its derivatives [7] are widely applied in the fields of organic photovoltaic cells (OPVCs) and organic light emitting diodes (OLEDs) [8].

PTCDA molecules can grow in an ordered fashion on various substrates by organic molecular beam deposition (OMBD) [1,9]. The adsorption behavior of ultrathin layers of PTCDA (e.g. sub-monolayer, monolayer and bilayers) on Au (111) has been investigated by scanning tunneling microscopy (STM) [10–12]. However, less effort has been devoted to multilayers because of the limitations of STM. Previously, we reported a qualitative analysis of the angular dependent NEXAFS spectra at the C *K*-edge obtained for PTCDA molecules adsorbed on Au (111)/mica surface [13]. Angular dependent NEXAFS has been found to be a powerful tool for characterizing the adsorption geometry of planar aromatic molecules on a solid substrate [14]. In addition, NEXAFS is also useful for studying absorption sites [15,16] and bond lengths [12,17] between adsorbates and substrate atoms, although these were not investigated in this work. In this paper, quantitative analysis of the average molecular tilt angle for PTCDA multilayers adsorbed on Au (111) single crystal surface was performed by angular dependent NEXAFS at the O *K*-edge.

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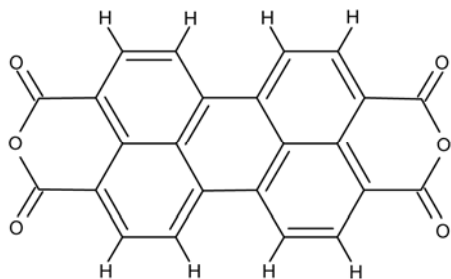


Figure 1 The molecular structure of PTCDA.

1 Experimental

NEXAFS measurements were carried out at the Photoemission Spectroscopy Endstation at the 4B9B beamline of the Beijing Synchrotron Radiation Facility of the Institute of High Energy Physics, Chinese Academy of Sciences. The O *K*-edge NEXAFS spectra were performed in total electron yield (TEY) mode with a photon energy resolution of 500 meV. To eliminate the effect of fluctuation of the incident beam intensity, all spectra were first normalized to the incident beam flux (monitored by refocusing mirror I_0) and later normalized to the same edge jump [18].

Au (111) single crystal was cleaned *in situ* by repeated cycles of sputtering and annealing. The cleanliness of the crystal surface was checked by Auger photoemission spectroscopy (AES) and photoemission spectroscopy (PES). PTCDA molecules, which were thoroughly degassed for several hours, were deposited onto the clean Au (111) substrate at room temperature in an ultrahigh vacuum (UHV) chamber with a base pressure better than 1×10^{-8} torr. A deposition rate of ~ 2 ML/min was precalibrated using a quartz crystal microbalance (QCM) at the Surface Physics Endstation of the National Synchrotron Radiation Laboratory.

2 Results and discussion

In molecular systems, NEXAFS monitors resonant electronic transitions from the inner shell of specific atomic species (C 1s, O 1s or N 1s) to unoccupied molecular orbitals or states (π^* and σ^* orbitals). It has been well established that the resonant intensity is enhanced if the electric field vector E of synchrotron light polarization is parallel to the direction of the molecular orbital, and the intensity of the resonance is suppressed if E is perpendicular to the orbital direction [14]. For planar π -conjugated molecules like PTCDA, σ^* and π^* orbitals are essentially oriented in-plane and out-of-plane, respectively. Therefore, the molecular orientation within a layer can easily be derived from the relationship between the resonant intensities and incident angle of light.

Angular dependent O *K*-edge NEXAFS spectra of PTCDA multilayers (nominal coverage of 10 ML) adsorbed

on Au (111) surface are shown in Figure 2. Sharp resonant peaks below 538 eV arise from O $1s \rightarrow \pi^*$ transitions, whereas resonances located at higher energy originate from O $1s \rightarrow \sigma^*$ transitions. The strongest π^* resonant peak is asymmetric with a dominant component (labeled 1) and a subtle shoulder (labeled 2) at slightly higher photon energy. Peaks 1 and 2 are assigned to the transitions of carbonyl oxygen atoms (C=O) to the lowest unoccupied molecular orbital (LUMO) and higher orbitals (LUMO+1 and LUMO+2), respectively [19]. Resonant peak 3 is attributed to the transition from the bridging O atoms (C—O—C) to the LUMO+1 (and perhaps LUMO+2 and LUMO+3) [19].

The spectra show that the intensity of the π^* resonances vary significantly with incident angle, and reach maximum and minimum values at $\theta=10^\circ$ and $\theta=90^\circ$, respectively. The σ^* resonances show the opposite behavior. This polarization dependence directly suggests the formation of ordered layers of PTCDA molecules on the Au (111) surface.

In terms of quantitative analysis, the intensity of π^* resonances (I_{π^*}) at various incident angles (θ) can be expressed as follows [14]:

$$I_{\pi^*} = CP(\sin^2 \alpha \sin^2 \theta + 2 \cos^2 \alpha \cos^2 \theta) + C(1-P)\sin^2 \alpha, \quad (1)$$

where C is a normalization constant, P is the linear polarization factor (0.75), and α is average tilt angle of π^* vector orbital versus the surface normal. In multilayers, the interaction between the molecules and substrate is too weak to affect the direction of π^* orbitals. Therefore, α is equal to the average tilt angle of the molecular planes of PTCDA with respect to the surface plane (see Figure 2 inset).

The integrated intensities of the first two and first three π^* resonances as a function of θ together with theoretical

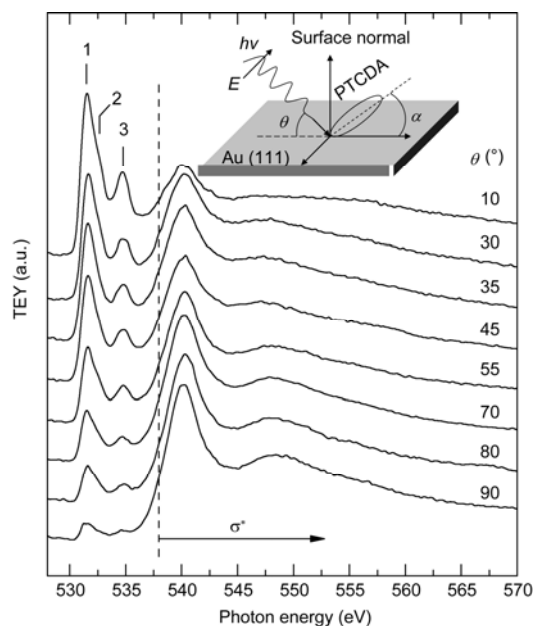


Figure 2 Angular dependent O *K*-edge NEXAFS spectra of PTCDA multilayers on Au (111) surface. Incident angles are designated with respect to the surface plane. The inset shows the geometry of the experiment.

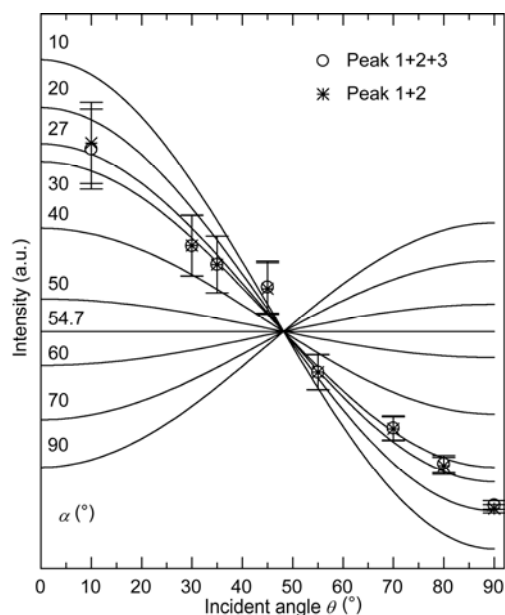


Figure 3 The integrated intensities of the first two (stars) and first three (open circles) resonances against θ for multilayer thin films of PTCDA. The solid lines represent the theoretical angular dependences for various tilt angles. Normalization constants are $C_{1+2}=16.07$ and $C_{1+2+3}=24.13$.

curves for different tilt angles (solid lines) obtained using eq. (1) are presented in Figure 3. The error bars correspond to uncertainties introduced by the normalization and integral, and are estimated to be 10% of the intensity [20]. The average tilt angle α for molecular planes of PTCDA on Au (111) surface was determined to be $27^\circ \pm 10^\circ$. The overall uncertainty of 10° takes into account fitting assumptions, fitting error, the degree of polarization of the X-ray beam, and the misalignment between the surface and reference manipulator orientation [21].

3 Conclusions

In conclusion, PTCDA multilayers were deposited on Au (111) surface by OMBD. Angular dependent O *K*-edge NEXAFS spectroscopy was applied *in situ* to investigate the molecular orientation at the PTCDA/Au (111) interface. It is concluded from quantitative analysis of the angular dependence that PTCDA molecules are ordered within the film with an average tilt angle of $27^\circ \pm 10^\circ$ from the substrate surface.

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