

Energy Band Dispersion in Well Ordered N, N'-3,4,9,10- Perylenetetracarboxylic diimide Films

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Abstract

The electronic properties of well ordered N,N'-dimethyl-3,4,9,10-perylenetetracarboxylic-diimide (DiMe-PTCDI) films prepared on sulfur passivated GaAs(001) substrates were studied by means of photoemission spectroscopy. From the photon energy dependence of normal emission spectra an intermolecular energy band dispersion of about 0.2 eV was determined for the highest molecular orbital (HOMO). Simulation of the density of states reveals that the HOMO band has a single π -character. The observed energy band dispersion thus originates from the intermolecular π - π interaction and is modeled using the tight binding model. The analysis provides a value of 0.04eV for the transfer integral. The inner potential was treated as a fit parameter such that the expected periodicity of the dispersion in the reciprocal space was obtained.

Introduction

Organic semiconductors have become a very active area of research in the last decade, mainly due to their potential applications in novel (opto-) electronic devices. A major branch of functional organic materials with interesting properties are the π -conjugated systems [1]. The electronic properties relevant for the device performance depend not only on the molecular structure but also on the molecular arrangement. In particular well ordered organic crystals or thin films are beneficial for achieving high carrier mobilities [2-4] The ability of these materials to transport charges (holes and electrons) due to the π -orbital overlap of neighboring molecules provides their semiconducting and conducting properties. The self-assembling or ordering of these organic materials enhances this π -orbital overlap and is the key to improvement in carrier mobilities.

Many organic crystals are formed by regularly repeating a small unit along one direction. In such systems the electronic energy levels of the units with the same energy may interact via the outermost orbitals leading to a splitting of the respective energy levels. The width of the resulting energy band then depends on the magnitude of interaction.

We can experimentally probe the energy dispersion using Angular Resolved Ultraviolet Photoemission Spectroscopy [5-7] or by measuring the energy dependence of the valence electrons emitted normal to the substrate surface [8-9] in order to determine the dispersion parallel and perpendicular to the sample surface, respectively. For organic semiconductors the intermolecular energy band dispersion is difficult to observe since the width of the bands is expected to be very small due to the weak van-der-Waals (vdW) interaction.

Experiments for π -conjugated polymers [8-10] and also for small molecule films like C₆₀ [11] revealed band widths of about 0.4eV. Recently the intermolecular energy dispersion was measured for the archetypal organic semiconductor 3,4,9,10 - perylene-tetracarboxylic dianhydride (PTCDA) deposited onto MoS₂ to be 0.2eV [12].

Here the photon energy dependence of normal emission spectra of N,N'-dimethyl-3,4,9,10-perylenetetracarboxylic diimide (DiMe-PTCDI) thin films is determined. The overall energy shift of the HOMO feature which originates from the HOMO-HOMO interaction in the well ordered DiMe-PTCDI films is found to be about 0.2 eV. This reveals a small energy band dispersion for wave vectors varied along the direction perpendicular to the sample surface. Moreover, the spectral features in the photoemission spectra are assigned by comparing them with a simulated density of states (DOS).

The perpendicular component of the initial state wave vector is usually determined assuming free electron-like final states and an inner potential V_0 which has to be determined. V_0 is treated as a fit parameter to obtain the expected periodicity of the dispersion in the reciprocal space. As reported in a previous paper [12], the tight binding model is a suitable approach to determine such energy-band dispersion. The same approach is applied here taking into account the complementary results providing information on the intermolecular spacing.

Experimental Details

Thin films of DiMe-PTCDI were prepared by organic molecular beam deposition (OMBD) onto sulphur passivated, tellurium doped n-GaAs(100) substrates (Freiberger Compound Materials GmbH, $N_D=2 \times 10^{17} \text{cm}^{-3}$) kept at room temperature. Before depositing the organic material, the substrates were first degreased in consecutive ultrasonic baths of acetone, ethanol and de-ionised water for 5 min each, then etched in a solution of $\text{S}_2\text{Cl}_2:\text{CCl}_4$ (1:3) for 10 seconds, followed by rinsing in CCl_4 , acetone, ethanol and de-ionised water for 5 seconds each and finally dried in a N_2 flow. After this procedure the substrate was transferred into an ultra-high vacuum (UHV) chamber and annealed for 30 min at 470°C and a pressure below $5 \cdot 10^{-9}$ mbar. The resulting sulphur passivated GaAs(100) surfaces, from now on being denoted as S-GaAs, exhibit 2×1 surface reconstructions as judged by low energy electron diffraction. Additional details about the passivation process and surface reconstruction are given elsewhere [13]. The DiMe-PTCDI material was purchased from Sensient GmbH, further being purified twice by sublimation at 575 K under high vacuum ($\sim 10^{-4}$ Pa).

The DiMe-PTCDI film was deposited at a rate of 0.2 nm/min to obtain a total thickness of 15 nm. The thickness was monitored by a quartz microbalance situated in the vicinity of the sample and calibrated using atomic force microscopy measurements.

The photoemission spectra were measured using a CLAM 4 analyzer at the Russian-German beamline at BESSY. Monochromatized synchrotron radiation in the range of $h\nu=35\div 90\text{eV}$ obtained using a plane grating monochromator served as a light source. The spectra were measured at normal emission with an incident angle of light of 65° . The total resolution of the UPS spectra over the whole energy range used in the present measurements was better than 0.1eV as estimated from the Fermi edge of silver.

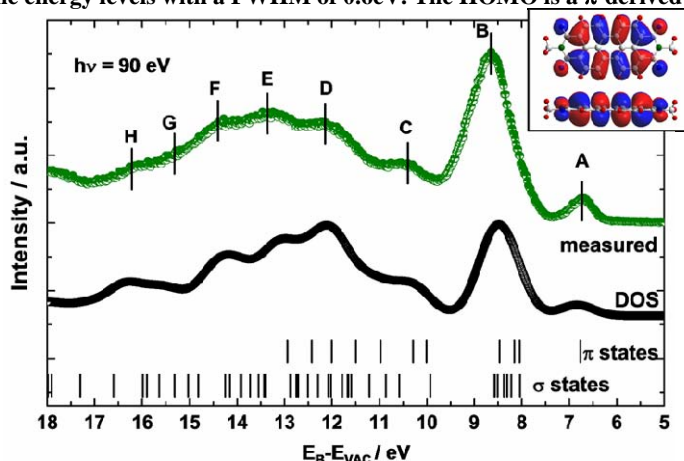
HOMO features were fitted using Gaussian functions in order to obtain their energy positions in the spectra accurately.

Molecular orbital calculations were performed using the Gaussian '98 package [14] with the B3LYP method and 6-311G(d) basis set to describe the core orbitals and the inner and outer part of the valence orbitals. The Levenberg-Marquardt method was used to fit the observed HOMO positions to a cosine function in the tight binding model.

Results and Discussion

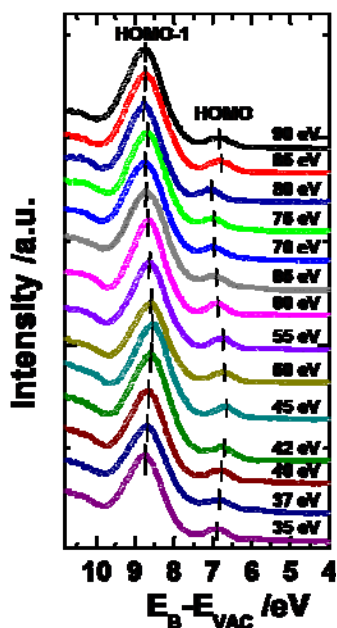
The upper spectrum in figure 1 shows the measured spectrum of the DiMe-PTCDI film at a photon energy $h\nu=90\text{eV}$ energy. Eight features (A-H) are observable in the photoemission spectrum at binding energies with respect to the vacuum level of 6.7eV, 8.6eV, 10.4eV, 12.3eV, 13.2eV, 14.4eV, 15.3eV and 16.1eV, respectively. The HOMO (feature A) and the HOMO-1 (feature B) appear as separate peaks while the remaining ones overlap. The vertical bars in figure 1 represent the calculated binding energies of each molecular orbital (MO) state for a single molecule, while the lower curve shows the calculated density of states (DOS). The DOS was obtained by Gaussian broadening of each orbital energy with a full width at half maximum (FWHM) of 0.6eV.

Figure 1. Valence band and DOS of DiMe-PTCDI thin films and calculated DOS. The MO energies are shown by vertical bars. The DOS curve was calculated by Gaussian broadening of the energy levels with a FWHM of 0.6eV. The HOMO is a π -derived state



The value of the Gaussian FWHM was taken equal to the FWHM of the experimentally observed HOMO state. In order to compare the simulated DOS and the measured valence band spectrum the energy scale of the calculated spectrum was shifted by 0.73 eV towards higher binding energies. The value of the Gaussian width represents the spectral broadening due to solid-state effects such as charge-induced intermolecular polarization [15], vibrational excitations or final-state lifetime [16] and structural disorder if present.

Figure 2. Measured valence band spectra of a DiMe-PTCDI thick film in the photon energy range of $35 \leq h\nu \leq 90\text{eV}$



The HOMO originates from a single molecular orbital with π character which is distributed predominantly over the perylene core. The strong peak at a binding energy of 8.6 eV is characteristic for DiMe-PTCDI and stems from both π and σ -bonds in the imide, carboxylic and methyl groups. For binding energies above 13.5 eV mostly molecular orbitals with σ -character contribute to the spectra.

Figure 2 shows the measured valence band spectra in the HOMO and HOMO-1 region and their dependence on energy. The HOMO feature reveals a weak, but clearly observable shift. We attribute the amount of observed peak shift of about 0.2eV to the intermolecular π - π interaction. While the dispersion of the HOMO position is obvious, it is much less pronounced for the HOMO-1 feature. This is explained by the higher binding energy and the predominant σ -character of the molecular orbitals contributing to HOMO-1.

The measured energy shift was converted into a dispersion relation assuming the three-step model [17] for the photoemission process as well as energy and momentum conservation before and after photo-excitation so that the following relations hold:

$$E_f = h\nu + E_i, \quad \vec{k}_f = \vec{k}_i + \vec{G}, \quad E_{Kin} = E_f \quad (1)$$

where E_i , E_f , \vec{k}_i and \vec{k}_f are the electron energies and the wave vectors before and after photoexcitation in the solid, and \vec{G} is a reciprocal lattice vector. E_i and E_f are defined relative to the vacuum level such that E_f corresponds to the kinetic energy of the emitted electrons E_{Kin} . Determination of the final momentum \vec{k}_f requires the knowledge of the final state band dispersion $E_f(\vec{k}_f)$ which is, however, generally unknown. Therefore, it is commonly assumed that the final state can be approximated by a free electron-like dispersion applying an appropriate inner potential V_0 :

$$E_f = \hbar^2 k^2 / 2m^* + V_0 \quad (2)$$

where m^* is the effective mass of the electron and V_0 is the constant inner potential in the solid for the final state free-electron like parabola. Then following relations are used:

$$E_i = E_{Kin} - h\nu \quad (3)$$

$$k_i^\perp = k_f^\perp = [2m^* \times (E_f - V_0)]^{1/2} / \hbar = [2m^* \times (E_{Kin} - V_0)]^{1/2} / \hbar \quad (4)$$

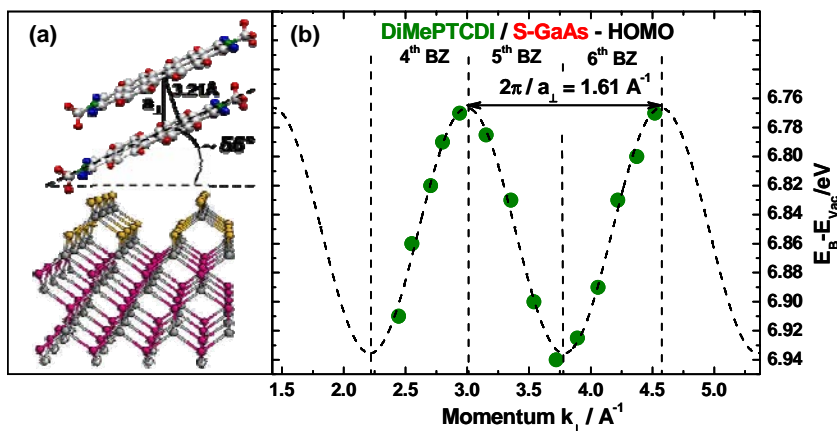
where k_i^\perp , k_f^\perp are the normal components of the wave vector before and after the photoexcitation in the solid, respectively. These equations indicate that the values of E_i and k_i^\perp can be determined from the measured E_{Kin} and $h\nu$. The effective mass of the excited electron m^* is approximated by the mass of free electron m_0 .

The energy band dispersion relation for DiMe-PTCDI is obtained by applying the one-dimensional tight-binding theory to the HOMO of the perylene core. For the formation of a 1D energy band it is assumed that a unit, i.e. a molecule, is repeating along an axis x with a period a . The interaction only takes place with the nearest neighbors its strength being defined by the value t , the transfer integral. By analogy to the Hückel theory [18], the energy E_B for the HOMO is expressed in terms of wave vector k_\perp as [8]:

$$k_\perp = [2m^* \times (h\nu - E_B - V_0)] \quad (5)$$

$$E_B(k_\perp) = E_B^0 + 2t \cos(a_\perp \times k_\perp) \quad (6)$$

Figure 3. (a) DiMePTCDI crystal plane and the relative orientation of molecules with respect to the S-GaAs(001) substrate; (b) the experimental dispersion for the HOMO band (filled circles) and the best fit curve (broken line) in the tight-binding model.



Using the normal emission spectra and equations (5) and (6) the energy of the highest valence band and its momentum can be calculated. However, for the experimental determination of the energy band dispersion we need to determine the values of t , a_{\perp} and V_0 .

Results of Raman, NEXAFS and Infrared Spectroscopy [19] revealed that the DiMe-PTCDI molecules deposited onto S-GaAs(001) are tilted with respect to the substrate surface by an angle of $(56^{\circ} \pm 4^{\circ})$ and are predominantly oriented with their long axis parallel to the [011] direction. With the distance between the intermolecular planes of 3.21 Å, as experimentally determined [20], we can calculate the length of repeating unit (lattice spacing normal to the surface) as $a_{\perp} = 3.9$ Å as depicted in the figure 3 (a).

The results of the best fit for the dispersion along with the experimental data are shown in figure 3(b). A cosine fit of the experimental data was performed where the inner potential V_0 and the transfer integral t are the two parameters. The best fit between calculated and experimental data is provided by the following set of parameters – inner potential $V_0 = -5.3$ eV and transfer integral $t = 0.04$ eV.

From the parameters determined from the HOMO band dispersion in the figure 3 (b) the effective mass of HOMO hole is obtained to be $m_h^* = 6.2 m_0$. We can use m_h^* to discuss the behaviour of a hole in a crystal lattice in terms of mobility. Thus, the hole mobility is approximately calculated as $\mu_h > 3.2 \text{ cm}^2/\text{V}\times\text{s}$, when τ , the relaxation time due to scattering, is considered to be larger than $\hbar/k_B \times T$. This value is to some extent high in comparison with the literature¹, but in a desirable range when discussing about the mobility of charges in the organic semiconductors used for practical applications (i.e FETs, LEDs).

As shown in the figure 3(b), we succeeded to observe the HOMO band dispersion for DiMe-PTCDI along surface normal. The energy-band dispersion is extended over three Brillouin zones (4th, 5th and 6th zone) with a bandwidth of about 0.2 eV.

These results clearly demonstrate the existence of energy band dispersion similar to that for PTCDA [12]. Here the calculated lattice spacing normal to the surface gives rise to the best fit of the energy dispersion to the experimental data using an inner potential V_0 of -5.3eV and a transfer integral of 0.04eV. The inner potential for PTCDA was found to be -5.1eV from the low energy transmission spectrum for an estimated lattice spacing of 3.8Å

As previously mentioned the observed HOMO band dispersion originates from π - π interaction along the molecular stacking direction. The HOMO for both perylene derivatives, DiMe-PTCDI and PTCDA [21], originates from a single molecular orbital with π character which is distributed predominantly over the perylene core. The results for the transfer integral and the inner potential of PTCDA are quite close for the ones of DiMe-PTCDI. This is supporting the reliability of the results since the interacting parts are the perylene cores of the molecules in both cases. The minor differences may be due to the difference of the intermolecular vdW interaction between the stacks of the two molecular films, considering that the lattice spacing is larger for DiMe-PTCDI than the one determined for PTCDA.

Summary

In this work we present valence band spectra from well ordered films of N,N'-dimethyl-3,4,9,10-perylenetetracarboxylic diimide. From the photon energy dependence of the highest occupied molecular orbital (HOMO), an energy dispersion of 0.2 eV was experimentally observed and attributed to the HOMO-HOMO interaction. The observed energy shift of the HOMO is explained in terms of k conservation rule in the photo-excitation process with a transfer integral t of 0.04eV and inner potential V_0 equal to -5.3eV. The lattice spacing normal to the surface was calculated taking into account the molecular orientations determined from NEXAFS, Raman and Infrared Spectroscopy.

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