

# ELECTRICAL CONDUCTIVITY IN 3,4,9,10-PERYLENETETRACARBOXYLIC DIANHIDRIDE (PTCDA)

## ELEKTRIČNA PREVODNOST V 3,4,9,10 PERILENDIANHIDRID TETRAKARBOKSILNI KISLINI (PTCDA)

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The transient photoresponse in 3,4,9,10-perylenetetracarboxylic dianhydride was examined in metal/organic semiconductor/metal heterostructures. Electron-hole pairs are generated within the structure for fields higher than  $5 \times 10^4$  V/cm as a consequence of the exciton dissociation. The mobility of the electrons perpendicular to the molecular layers increases with the applied electric field and saturates for fields higher than  $5 \times 10^4$  V/cm.

Key words: organic semiconductor, thin films, transient photoconductivity

Preučevali smo tranzientno fotoprevodnost v tankih plasteh organskega polprevodnika 3,4,9,10-perilendianhidrida tetra-karboksilne kisline. V plasti polprevodnika nastanejo pari elektron-vrzel z disociacijo eksitonov pri jakosti električnega polja nad  $5 \times 10^4$  V/cm. Gibljivost elektronov pravokotno na molekularne plasti narašča z jakostjo električnega polja in doseže nasičenje pri jakosti  $5 \times 10^4$  V/cm.

Ključne besede: organski polprevodnik, tanke plasti, prehodna fotoprevodnost

## 1 INTRODUCTION

Intramolecular bonding in ordered organic semiconducting thin films is characterized by a strong van der Waals character. Consequently, most of the materials that bear a significant technological relevance exhibit a markedly anisotropic structure. Anisotropic structural properties are, in turn, reflected in optical and electronic properties that are strongly dependent upon the crystallographic direction.

3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) is a typical representative of such materials, and has attracted considerable attention due to its potential role as hole-conducting material in coherent light emitters<sup>1-5</sup>. The mobility of charge carriers in PTCDA has been reported to be highly anisotropic, and that only holes were transported in the direction perpendicular to the molecular plane<sup>6</sup>. In Ref. 6 the carrier-type anisotropy was inferred by comparing the performance of PTCDA-based field-effect transistors (transport parallel to the molecular planes) and PTCDA-based light-emitting diodes (transport perpendicular to the planes).

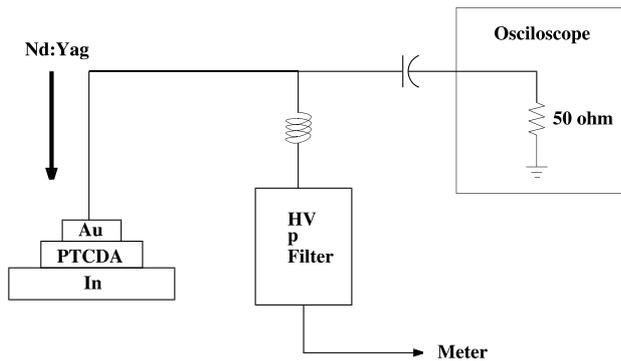
In this paper we present a bipolar nature of current in PTCDA by examining the transient behavior of the photoinduced charge carriers. We were able to distinguish the contributions of relatively fast holes and relative low-mobility electrons that are transported

perpendicular to the molecular planes in the high-applied-field regime.

## 2 EXPERIMENTAL DETAILS

The samples for transient photocurrent measurements consisted of PTCDA layers sandwiched between In and Au contacts. The samples were fabricated by vacuum evaporation in a chamber with a base pressure of  $< 5 \times 10^{-6}$  Torr. The structures were supported by undoped Si(100) substrates that were chemically cleaned by the RCA procedure<sup>7</sup> followed by oxide removal in diluted HF. Prior to the growth of PTCDA a 1000-nm-thick In layer was deposited from a resistively heated Ta boat. The growth of PTCDA layers was performed with the substrates at room temperature using a resistively heated tungsten basket. The source PTCDA material was previously purified by gradient sublimation. The topmost metallic contact consisted of a 80-nm-thick Au layer deposited from a Ta boat. During the evaporation the base pressure was always  $< 5 \times 10^{-6}$  Torr, and no intentional heating or cooling was applied to the substrates.

The experimental setup for the transient photoconductivity measurements is schematically presented in **Figure 1**. For the transient photoconductivity measurements we employed a frequency-tripled Nd:YAG laser with an effective wavelength of 355 nm. The laser was



**Figure 1:** Schematic representation of the measurement setup. The sample consisted of an 80-nm-thick Au layer on top of the 1000-nm-thick PCDTA layer, that was deposited onto the In support layer. The complete structure was fabricated by vacuum evaporation onto Si(001). The bias voltage is fed to the sample via a 100 mH coil from a voltage source. The photocurrent is detected as a voltage drop over the 50  $\Omega$  resistor by a 300 MHz oscilloscope. The light source employed in the experiments was a Nd:YAG laser operated at a wavelength of 355 nm

**Slika 1:** Shema eksperimentalne postavitve. Vzorec je bil sestavljen iz 80 nm debele plasti zlata, naporjene na 1000 nm debelo plast PTCDA. Spodnja plast vzorca je 1000 nm debela plast indija. Celotna struktura je bila naporjena na Si(001). Napetost je bila priključena na vzorec preko tuljave 100 mH. Električni tok je bil detektiran z osciloskopom 300 MHz kot padec napetosti na uporu 50  $\Omega$ . Uporabljena je bila svetloba Nd:YAG-laserja pri valovni dolžini 355 nm

operated at 10 Hz and a 2 ns pulse width. The pulse energy was 4 mJ, and the peak power was 1.4 MW. The pulse light intensity was reduced by passing the light through a parallel glass plate and exploiting only the reflected 4% of the light. This was repeated twice prior to illuminating the sample. Pulses were directed on the sample at normal incidence, illuminating an area of 2 mm<sup>2</sup>. The photocurrent was measured at the bias range of 10 V using the setup depicted in **Figure 1**. The bias voltage was fed to the sample from a Keithley 2400 SourceMeter via a 100 mH coil. The AC signal resulting from the photoinduced current from the sample was picked-up via a 100 pF capacitor and recorded using a 300 MHz storage oscilloscope. The measurement sequence was triggered by the laser pulse and consisted of points separated by 10 ps.

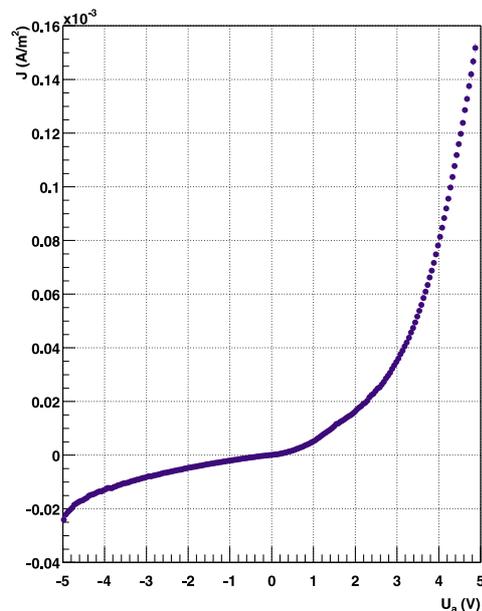
### 3 RESULTS AND DISCUSSIONS

For transient photoresponse measurements it is of benefit to employ an asymmetric metal/semiconductor junction. This ensures the polarization of photoinduced carriers at low applied bias voltages. The alignment of the energy levels at the metal-PTCDA interface was extensively studied by Soukiassian<sup>8,9</sup> and co-workers and Azuma et al.<sup>10</sup> using photoemission spectroscopy and by Forrest et al.<sup>11,12</sup> with transport measurements. Noble metals such as Au or Pt form chemically abrupt interfaces with PTCDA, resulting in an electrically blocking contact. The energy barrier height for a Au/PTCDA interface was found to be  $0.64 \pm 0.05$  eV<sup>11</sup>.

Indium, on the other hand, forms the In<sub>4</sub> PTCDA alloy at the interface<sup>8,9</sup>, yielding an ohmic contact. When a negative bias is applied to the In contact the current is dominated by the thermoionic emission of holes from the Au contact. Negative bias on a Au contact instead, favors electron transport from the Au contact.

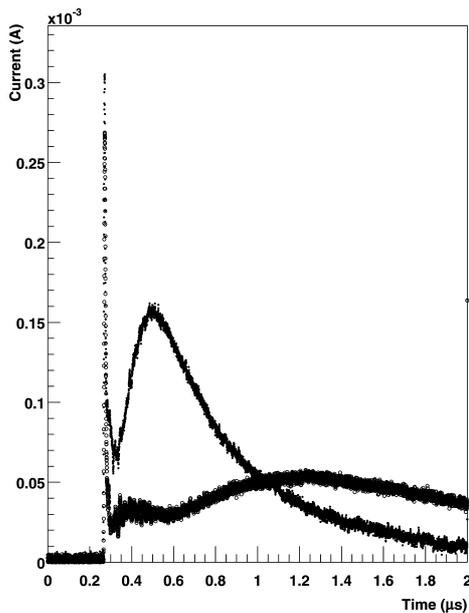
The Au/PTCDA/In structure is therefore expected to exhibit rectifying characteristics. That this is indeed the case we see in **Figure 2**, where we show the current-voltage characteristics for the same sample. From the asymmetry between the negative and positive bias we clearly see the difference in the electronic structure of the two metal/organic semiconductor interfaces. The structure is therefore expected to bear a nonzero built-in potential that will polarize photoinduced carriers. On such structures we have recorded the time dependence of the photoinduced currents.

In **Figure 3** we show the time dependence of the photocurrent for two different bias voltages. The filled circles represent data obtained using a bias voltage of 10 V, filled squares represent data obtained using a bias voltage of 5 V. The polarity of the bias was positive on the In contact and negative on the Au contact. The sample consisted of a 1000 nm PTCDA, 80-nm-thick topmost (facing the laser beam) Au contact and a 1000 nm bottommost contact. We see that biasing of the structure has a dramatic effect on the time evolution of the photoinduced current. However, the two curves do exhibit common features in the lineshape. Two discernible peaks can be identified in both curves. The rate of photocurrent increase in this initial time frame is



**Figure 2:** Current-voltage dependence of the structure comprising a 1000-nm-thick PTCDA layer sandwiched between an 80-nm-thick Au layer and 1000-nm-thick In layer

**Slika 2:** Tokovno-napetostna karakteristika 1000 nm debele plasti PTCDA, naporjene med 80 nm debelo plast zlata in 1000 nm debelo plast indija



**Figure 3:** Photocurrent as a function of time as measured on a structure comprising a 1000-nm-thick PTCDA layer sandwiched between an 80-nm-thick Au layer and 1000-nm-thick In layer. The polarity of the bias voltage was positive on In and negative on Au. Filled circles represent data obtained using a bias voltage of 10 V, open circles represent data obtained using a bias voltage of 5 V

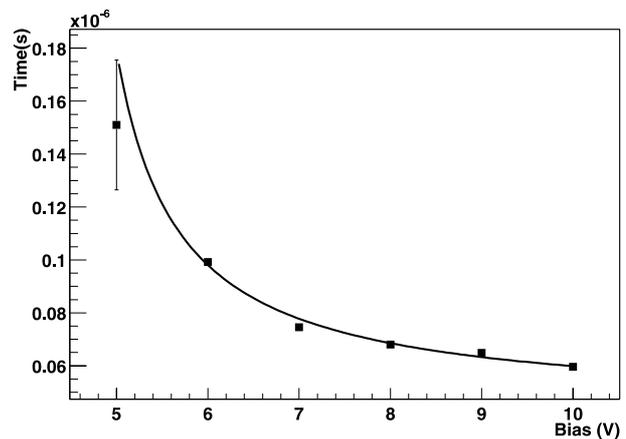
**Slika 3:** Časovna odvisnost električnega toka v 1000 nm debeli plasti PTCDA, naperjeni med 80 nm debelo plast zlata in 1000 nm debelo plast indija. Pozitivni kontakt priključene napetosti je bil na indiju, negativni pa na zlatu. Polni krogi so rezultati meritve pri napetosti 10 V, prazni krogi pa pri napetosti 5 V

the same for both curves, and in general it does not depend on the bias voltage. The first peak decreases relatively fast for both bias voltages (characteristic attenuation time being  $\tau_1 = 5 \times 10^{-9}$  s for the 10V bias voltage). The second peak is considerably broader and exhibits a typical attenuation time of  $\tau_2 = 4 \times 10^{-8}$  s. The rising edge of the second peak has a Gaussian shape that may reflect the Gaussian time dependence of the laser pulse. We observe an increase in the attenuation time of both peaks with decreasing bias voltage. As for the broader peak, we also observe a distinct shift of the peak centroid towards longer times with decreasing bias voltages.

To interpret such behavior we recall light absorption in PTCDA exhibits a broad energy distribution extending from 1.8 eV up to 3.6 eV<sup>4,13-15</sup> and may be accounted for by the exciton generation. The photogenerated excitons diffuse through the organic layer until they dissociate at a defect site or at a metal/organic-layer interface and contribute to the current. Scher and Rackovsky have investigated the effect of electric field on the exciton dissociation<sup>16</sup>. We have investigated the photocurrent response in the field range 0 -  $1 \times 10^5$  V/cm. Based on their model we may assume, that for an electric field higher than  $\approx 5 \times 10^4$  V/cm the vast majority of the excitons dissociate. We

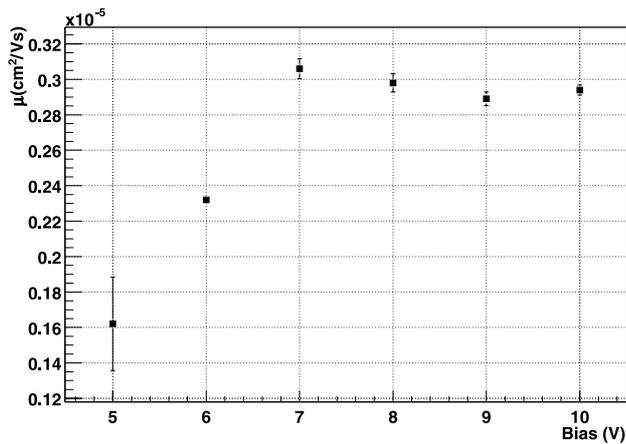
may therefore treat the photocurrent response as a bipolar carrier generation.

At the photon energy of 3.5 eV employed in our experiment the absorption coefficient is relatively low, ( $1 \times 10^5$  cm<sup>-1</sup>)<sup>13</sup> implying a penetration depth of 100 nm. The bulk of the photoinduced carriers is therefore created relatively close to the surface. Assuming that at bias values of 10 V all the excitons dissociate before they thermalize, we must consider the transport of holes and electrons separately. The bias conditions facilitate the transport of holes from the In contact to the Au. PTCDA is predominantly a hole-conducting material with a relatively high hole mobility in the direction perpendicular to the molecular planes<sup>6</sup> that are almost coincident with the growing plane<sup>4</sup>. Electrons, on the other hand, are mainly transported along the molecular planes with substantially lower mobility<sup>6</sup>. Considering this electronic transport anisotropy, and the biasing conditions (negative polarity on the Au contact), we submit that the first peak in **Figure 3** arises from relatively fast holes that are generated close to the sample surface and accumulated at the Au contact. With the progress of time the second peak starts to decrease. Assuming Gaussian non-dispersive transport we would expect a Gaussian shape of the decreasing slope of the peak. However, we were not able to fit the slope with a Gaussian function alone. A product of Gaussian and exponential functions yielded an excellent fit to the data for all curves obtained with bias voltages larger than 4 V. We interpret the observed behavior in terms of trap-limited current transport. After excitonic



**Figure 4:** The position of the lower peak in Figure 3 as a function of the applied bias. The polarity of the bias voltage ( $U$ ) was positive on In and negative on Au. The values for the data points presented by the solid squares were obtained by applying a least-squares fitting to the convolution of the Gaussian and exponential functions of the decreasing slope of the peak. The solid curve represents a least-squares fit to the function that is proportional to  $1/U$

**Slika 4:** Položaj nižjega vrha (slika 3) v odvisnosti od priključene napetosti  $U$ . Pozitivni kontakt je bil priključen na indij, negativni pa na zlatu. Položaj vrha je bil določen s prilagajanjem konvolucije Gaussove in eksponentne funkcije nižjemu vrhu. Položaju vrha v odvisnosti od priključene napetosti je prilagojena krivulja, ki je sorazmerna  $1/U$



**Figure 5:** Effective mobility ( $\mu_{eff}$ ) of the electrons as a function of the applied bias voltage ( $U$ ). The mobility increases with increasing voltage and saturates for voltages  $U < 7V$

**Slika 5:** Efektivna mobilnost  $\mu_{eff}$  elektronov v odvisnosti od priključene napetosti  $U$ . Mobilnost narašča z naraščajočo napetostjo in doseže nasičenje pri napetosti  $U < 7V$

dissociation into electrons and holes a fraction of the carriers become bound by traps<sup>16</sup>. These carriers are then re-emitted from the traps by thermionic emission, accounting for the exponential contribution to the decaying slope of the second peak.

By applying a least-squares fitting procedure using a convolution of Gaussian and exponential functions we were able to extract the position of the Gaussian peak as a function of applied bias. We selected the position of the Gaussian peak as a measure for the position of the charge-carrier front advancing towards the metallic contact. The results are illustrated in **Figure 4**. We see that the position of the Gaussian peak, as a function of bias  $U$ , exhibits a  $1/U$  dependence, as shown by the solid curve that represents a least-squares fit of the data points (solid squares) This dependence comes from the relation:

$$v = \mu_{eff} E \quad (1)$$

where  $v$  is the average carrier speed inside the PTCDA layer,  $\mu_{eff}$  is the effective mobility of the carriers, and  $E$  is the electric field intensity inside the PTCDA layer. In our treatment we will assume that the electric field inside the PTCDA is constant for bias values larger than 5 V<sup>17</sup>. We may, therefore, substitute  $E$  by  $U=d$  in equation (1, where  $d$  is the thickness of the PTCDA layer. We obtain the relation for the time needed for the charge carriers to travel across the PTCDA layer.

$$t = d^2/\mu_{eff} U \quad (2)$$

which is actually the time between the beginning of the leading edge of the first current pulse and the Gaussian peak of the second current pulse. The  $\mu_{eff}$  dependence on  $U$  was obtained from relation (2), and the results are presented in **Figure 5**. Mobility values are in the same range as those obtained by Forrest and co-workers<sup>11</sup>. The predominant mechanism for the charge-carrier mobility in PTCDA is assumed to be hopping<sup>4,6</sup>, so that

the mobility should follow the square-root dependence of the applied field ( $\mu_{eff} \propto \exp(\sqrt{E})$ ). This would imply a monotonic increase in carrier mobility with the applied field. What we observe instead is a saturation of the mobility values at approximately  $\mu_{eff} = 3 \times 10^{-2} \text{ cm}^2/\text{Vs}$ , for bias values greater than 7 V. With transient measurements alone it is difficult to explain why the saturation in mobility occurs. Possible mechanisms might include increased carrier injection into the layer, thereby enhancing the space-charge-limited transport that is common in materials with a long dielectric relaxation time compared to the carrier transit time, such as PTCDA.

## 4 SUMMARY

We have examined transient photoconductivity in PTCDA in the light of high-field transport through metal/PTCDA/metal heterostructures. The observed time dependence of the photocurrent may be related to the bipolar nature of charge carriers for field values higher than  $5 \times 10^4 \text{ V/cm}$ . Consequently, we may conclude that the excitons dissociate into electron hole pairs readily after their creation. By examining the evolution of the photoinduced carrier front as a function of the applied bias we were able to extract the mobility of the carriers. The observed values are in the range that agrees well with the values obtained in PTCDA synthesized by room-temperature vacuum evaporation. The field dependence of the carrier mobility, however, exhibits saturation for field values larger than  $7 \times 10^4 \text{ V/cm}$ , which might result from a space-charge build-up due to the photoexcited carriers.

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- <sup>17</sup>We observed a saturation of the accumulated electronic charge for bias voltages higher than 5 V. The results will be published in a forthcoming paper