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Organic Quantum Wells: Molecular Rectification and Single-Electron Tunnelling.

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PACS. 73.60H – Insulating thin films.
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Abstract. – We present the first direct observation of molecular rectification as a consequence of asymmetric tunnelling process through molecular quantum wells. In addition, single-electron tunnelling effects were observed which might be attributed to the charging of single molecules or molecular stacks. As molecular systems we used LB-film–based heterostructures consisting of an octasubstituted metallophthalocyanine and a perylene-3,4,9,10-tetracarboxyldiimide derivative sandwiched between two gold electrodes. By using a special thermal evaporation technique to deposit the top gold electrode, we have overcome the problem of short circuits and were able to fabricate highly reproducible devices.

In recent years researchers have seen very interesting charge transport effects in atomically abrupt semiconductor heterostructures, especially in the case of quantum-confined one- and zero-dimensional systems [1]. In addition, there have been efforts to build up tunnel junctions [2] and quantum wells [3] based on organic materials with the hope of observing useful electrical or optical properties. The basic idea behind such experiments is to employ the molecules as the functional units in which electrons are confined.

In previous studies, most organic heterostructures were fabricated by using organic molecular beam deposition (OMBD), [4, 5] or a layer-by-layer transfer using the Langmuir-Blodgett (LB) tecnique [6]. Once the organic films are fabricated, the main problem is the proper contacting with metal electrodes. Especially for sandwich structures that incorporate ultrathin films, the formation of short circuits is often discussed. Rectifying the behaviour of ordered LB film devices has been reported when different metals with different work functions are used as contacts [7]. In such cases, the molecular origin of the asymmetric conduction must be established by separating the electrodes from the active layer with passive organic barriers in order to prevent the formation of Schottky barriers [8]. Often, experiments are additionally complicated when metals which form oxide layers are used as contacts.

In contrast to the above-mentioned indirect evidence, the present paper describes the successful fabrication of organic tunnelling junctions which allow the direct observation of electrons tunnelling through molecular states, showing rectifying behaviour and single-electron effects.

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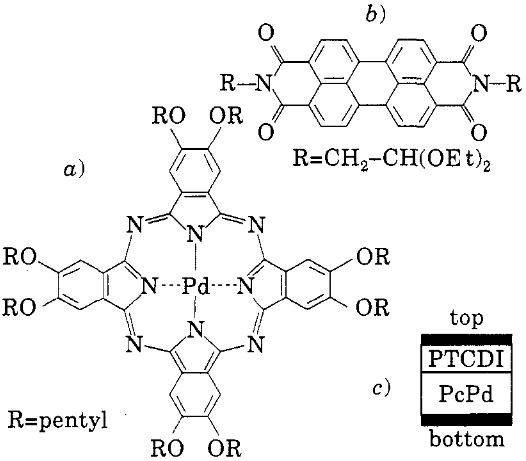

Fig. 1. – Chemical structure of the PcPd (*a*)) and PTCDI (*b*)). Inset *c*) shows the schematic structure of the PcPd/PTCDI heterojunction.

This success was reached by applying the following features: i) Special molecules were used that form highly ordered films [9]. ii) A smooth application of the top electrode allows the use of identical noble metals for both the bottom and the top electrode. iii) Microstructured electrodes reduce the influence of structural defects in the organic film. iv) By frabricating 52 equal junctions on one single substrate, we could check the reproducibility of the experimental curves. v) Finally, all measurements were performed at low temperatures (liquid helium) to suppress thermal-hopping processes.

As molecular systems we used LB-film–based heterostructures consisting of an octasubstituted metallophthalocyanine (PcPd) and a perylene-3,4,9,10-tetracarboxyldiimide derivative (PTCDI) (fig. 1). Sandwich structures were made of the sequence gold bottom electrode/LB film/gold top electrode, on highly polished BK 7 glass substrates. After a standard cleaning of substrates in an acetone ultrasonic bath, gold strips of a width of 30 μm and a thickness of 8 nm were deposited by employing photolithography and a lift-off process. Onto one end of each electrode we evaporate a 100 nm thick chromium/gold-pad as a bonding contact.

Both types of molecules were transferred from a pure water subphase. It should be mentioned that the LB transfer in both cases leads to films with upright standing molecules in contrast to the orientation of thermally evaporated phthalocyanine molecules which usually lie flat on the surface, at least for the first few monolayers. PcPd monolayers were transferred to the substrate by a vertical dipping process at a constant surface pressure of $\pi = 15\,\mathrm{mN/m}$. For down- and up-stroke we used a dipping speed of 10 and 16 mm/min, respectively. The PTCDI monolayers were transferred by dipping the substrate at an angle a few degrees off parallel to the surface, at a surface pressure of $\pi = 20\,\mathrm{mN/m}$. For both directions we used a dipping speed of 2 mm/min. Immediately after film preparation, the substrates were put into a high-vacuum chamber at a pressure of 10^{-6} mbar so that gold top electrodes with a thickness of 10 nm could be deposited. Very low evaporation rates were used so that a minimum of thermal stress is applied to the molecular films. To define the width of the top electrode, we used a metal mask with a slit of approximately 100 μm × 4 mm aligned perpendicular to the bottom electrode. This leads to an active junction area of $(100 \times 30)\,\mu\mathrm{m}^2$. To verify that both the bottom and the top electrodes were well conducting, we measured the resistances across the electrode strips from one end to the other. Values of about 200 Ω were measured. Many of the junctions were short circuits with unmeasurably

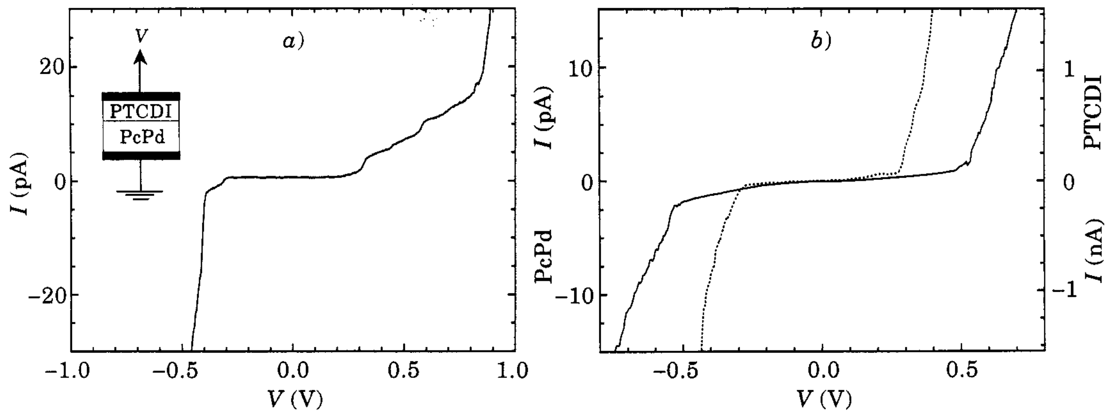

Fig. 2. – *I-V* characteristics of the 6 monolayer PcPd/6 monolayer PTCDI heterojunction (*a*)) and of the two symmetric sandwich structures consisting of 10 monolayers PcPd (·····) and 20 monolayers PTCDI (——) (*b*)). All measurements were taken at a temperature of 4.2 K.

small resistances. The working junctions exhibit resistances of at least 10 GΩ in the low-bias region, proving that the molecular films are well insulating.

We fabricated asymmetric sandwich structures of the form Au/6 monolayers PcPd/6 monolayers PTCDI/Au. Figure 2*a*) shows the corresponding *I-V* characteristic, measured at a temperature of 4.2 K. The device clearly exhibits rectifying behaviour. For both negative and positive bias an abrupt increase in current is observed, but the thresholds are very different at negative and positive bias, namely at − 0.4 V and + 0.9 V, respectively. In addition, a steplike behaviour in the current is observed between the two thresholds. In temperature-dependent measurements, the sharp bends and the steps vanish for temperatures above 50 K. This wash out might be caused by thermal-hopping processes. At room temperature the rectifying behaviour is still manifest as a global asymmetry of the curve. Figure 2*b*) shows control measurements with symmetric Au/PcPd/Au and Au/PTCDI/Au sandwiches. To point out the high reproducibility of the measurements, fig. 3*a*) shows the *I-V* characteristic of a different junction. In order to pinpoint the exact step positions, the corresponding derivative is shown in fig. 3*b*).

Molecular rectification. – To explain the rectifying behaviour, we consider the specific energy levels of the molecular states in the organic films. Figure 4 shows a diagram of the energy levels of the two molecules compared to the gold Fermi energy. The energy levels of the PcPd and the PTCDI are estimated from literature values for similar molecules [10, 11]. In addition, the HOMO/LUMO separations were calculated from the UV/VIS absorption spectra of the corresponding LB films. We assume that the thresholds in the *I-V* characteristic arise from the energetic shift of the highest occupied molecular orbitals (HOMO) relative to the gold Fermi levels, when a bias voltage is applied to the electrodes. If the HOMO levels energetically reach the gold Fermi level of the positive electrode, a tunnelling of electrons out of the HOMOs becomes possible. This means that holes are created in the molecular state which recombine with electrons from the negative-biased electrode. The external current arises from subsequent hole-tunnelling from one organic layer to the other. Following this model, the first increase in current should appear at a bias voltage similar to the initial potential difference between the gold Fermi level and the HOMO levels of the PcPd. But at this point, the HOMO levels of the PTCDI are still energetically lower than the gold Fermi level. Therefore, they are not available for holes to tunnel through and so the PTCDI layers act as a barrier. Only when the bias voltage is high enough to also

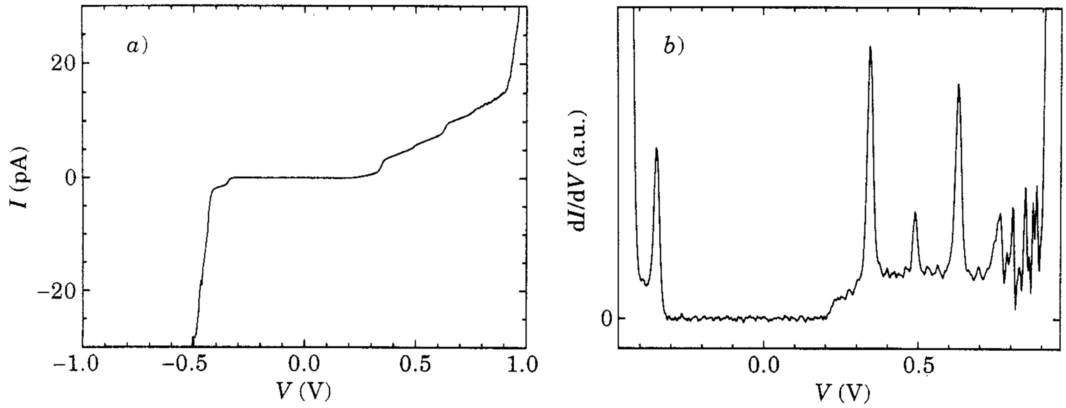

Fig. 3. – *I-V* characteristic of a sandwich structure identical to the one measured in fig. 2*a*) and the corresponding derivative that shows the position of the steps more clearly (*b*)).

open the HOMO levels of the PTCDI does the current increase. Since there is only a small barrier between one electrode and the furthermost organic layer (there is no additional barrier between the molecules and the electrodes), a bias voltage between the electrodes also shifts the HOMO levels of the molecules. The asymmetric arrangement of the organic layers between the electrodes leads to the asymmetric thresholds in current.

To verify that the asymmetry of the measured *I-V* characteristics is actually a consequence of the different molecular states, we fabricated symmetric sandwiches countaining homolayers of only one type of molecules. The homolayer samples were made by exactly the same process as the asymmetric heterolayer. In one case we transferred 10 monolayers of PcPd. For a second sample we transferred 20 monolayers of PTCDI. The corresponding *I-V* curves are shown in fig. 2*b*). In both cases we observed symmetric characteristics. This strongly suggests that the asymmetry of the *I-V* curves is an effect of the corresponding molecular states. In addition, the symmetry of the curves emphasizes the similar electrical behaviour of the two gold/organic film interfaces at the bottom and top electrodes.

The two symmetric sandwich structures exhibit thresholds at the voltages ± 0.27 V and ± 0.55 V for the PcPd and the PTCDI, respectively. Considering the estimated energy levels of the corresponding HOMOs (fig. 4), those thresholds are again consistent with the above-mentioned model of hole tunnelling. It turns out that this type of tunnelling experiment could be a powerful method for precise determinations of the energy levels of molecular states. To our knowledge, fig. 2 shows the first *direct* observation of molecular rectification as a consequence of asymmetric tunnelling processes.

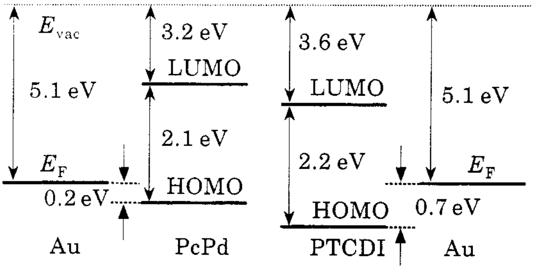

Fig. 4. – Schematic diagram of estimated energy levels of the PcPd and the PTCDI compared to the gold Fermi level.

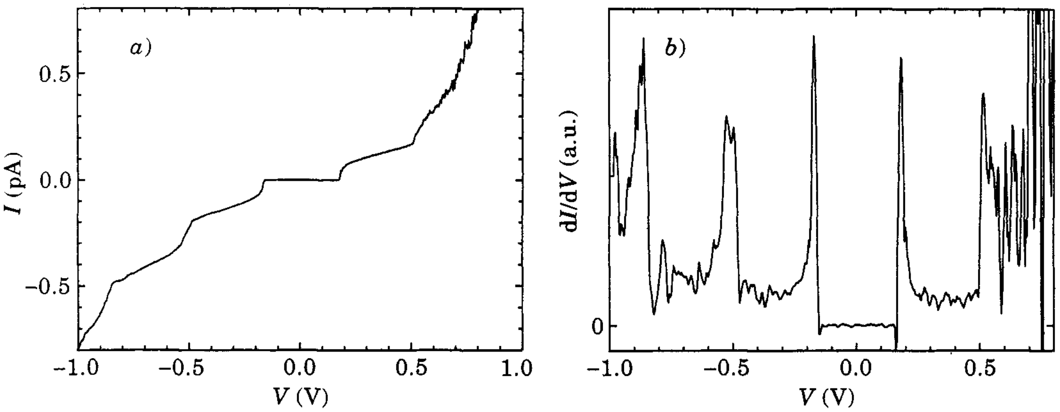

Fig. 5. – *I*-*V* characteristic of the symmetric Au/Polymer/PcPd/Polymer/Au heterojunction measured at 4.2 K (*a*)) and the corresponding derivative (*b*)).

Single-electron effects. – An additional feature of the *I*-*V* characteristics are steplike increases in current. These steps are reminiscent of Coulomb charging effects in quantum dots of inorganic semiconductors [12] and we tentatively interpret them as single-electron effects here as well. In the context of the semi-classical picture of Coulomb charging and single-electron tunnelling into small-capacitance particles [12], one expects an initial voltage gap of $e/2C$ followed by steps in the *I*-*V* curve with a voltage spacing of e/C, where C is the capacitance of the small particle. Taken together, these effects are described by current jumps at voltages $V_n = ne/2C$ for $n = 1, 3, 5, \ldots$.

The first steps in the *I*-*V* characteristic of fig. 3 occur symmetrically to zero volts at the values ± 0.35 V. In the positive-bias region four equidistant steps follow with a spacing of 0.14 V. When the HOMO levels of the PTCDI open (see above), the current increase is so high that no further peaks are visible.

Compared to the above-mentioned model of single-electron charging, the first observed steps are shifted by an offset in the bias voltage. This shift is supposed to be caused by the HOMO levels of the PcPd which first have to be opened, before a tunnelling process can occur. On the other hand, one might identify the first symmetric steps in the current as already belonging to $n = 5$, which means that three electrons can tunnel through the capacitance at the same time. Following this idea, the observed peak positions exactly fit into the single-electron model. In this case the first steps, which then are expected at ± 0.07 V and ± 0.21 V are just suppressed by the not yet opened HOMO levels of the PcPd without causing a global shift of the steps by an offset in voltage.

To check whether the observed single-electron phenomena are actually arising from a charging effect of the PcPd molecules, we fabricated a sandwich structure of the form Au/Insulator/PcPd/Insulator/Au. As insulator we used on both sides a 12 monolayer LB film of the polymer polyisobutylmethacrylate. Those films were transferred to be substrate by using standard parameters from [13]. In the middle of the two polymer buffer layers we incorporated a 1-monolayer PcPd film. The *I*-*V* characteristic of this symmetric sandwich is shown in fig. 5*a*). The curve clearly exhibits equidistant steps which are symmetric for positive and negative biases. In order to see the position of the steps more distinctly, fig. 5*b*) shows the derivative. Now the observed steps fit exactly to the picture of single-electron tunnelling mentioned above. Even the steps that belong to the first electron that charges the capacitance are visible, since the spacing between the steps is larger than for the rectifying heterolayer, namely 0.34 V.

To verify that the observed charging effect is actually connected to the charging of single molecules (or single molecular stacks), we apply a rough estimate for the particle radius. By assuming the charged particle to be a free sphere with radius r, the capacitance is given by $C = 4\pi\varepsilon\varepsilon_0 r$. The dielectric constant of the PcPd is assumed to be 2.5 [14]. With a voltage spacing of 0.34 V and a corresponding capacitance of $C = 4.7 \cdot 10^{-9}$ F one calculates a particle radius of 16 Å. This value indeed points to a molecular scale. Therefore, one can speak of the molecules themselves acting as separate quantum wells.

Our above assumption of current flowing through a single molecule (or a molecular stack) is justified by considering the absolute value of the conductance of our device. In fig. 3 and fig. 5 we observed current steps of the order of a few pA at voltages of some tenths of a volt. These are typical values observed in a STM when the dominating tunnelling process is assumed to occur between the furthermost atom of the tip and the substrate. Now the question remains as to how a single electron effect could occur in such macroscopic devices as our Au/organic film/Au sandwiches. One possible explanation would be a selection process arising fluctuations in the thickness of the sandwich. This explanation is indeed obvious if we consider the roughness of the electrode surfaces. Similar to the operation of a STM, the external current through the sandwich might be dominated by a tunnelling current through a single pathway which is defined by the smallest distance between the two electrodes. To clear up this question, further investigations are in progress.

In conclusion, we have for the first time directly observed molecular rectification and single-electron effects in organic quantum wells. These results are fully consistent with theory. Our observations were possible by overcoming the problem of the proper contacting of thin organic films with well-defined electrodes. We believe, that the present work opens a wide range of future molecular tunnelling experiments.

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