Modulated charge separation at tetraphenyl porphyrin/Au interfaces

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A frequency and temperature dependent change of the sign of modulated surface photovoltage signals from metal-free tetraphenyl porphyrin (H_2TPP)/Au junctions has been observed. The sign of the modulated photovoltage signal could be switched by using continuous (bias) illumination, while the sign depends on the wavelength of the bias light. The light induced modulation of the negative and positive charges in the H_2TTP layer can be interpreted in terms of internal photoemission of electrons from Au into H_2TTP and of hole escape after exciton dissociation at the H_2TPP/Au junction. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2719629]

Separation of light induced charge in junctions with organic semiconductors plays an important role for further development of organic solar cells.[1,2] In comparison with conventional semiconductors, charge separation is more intricate in junctions with thin organic films due to the complexity of involved elementary processes.[3,4] The separation of charge carriers in space can be measured by surface photovoltage (SPV) techniques.[5] The photovoltage (PV) signal is given by the amount of photoinduced charge carriers and their charge separation length.[6] For this reason, it depends on both the absorption and transport properties of the investigated system. Modulated PV signals may be additionally limited by relaxation or charge back-transfer processes.[5] In this work, we investigate charge separation processes at tetraphenyl porphyrin (H_2TPP)/Au junctions as a model system by using the modulated SPV technique in the capacitor arrangement.[7]

The dominating elementary processes involved in charge separation at H_2TPP/Au junctions under illumination are sketched in Fig. 1. Light can be absorbed by the H_2TPP layer as well as by the Au substrate. Excited electron-hole pairs rapidly form excitons, which may diffuse in the H_2TPP layer over distances of less than 10 nm.[8] Some of the excitons reach the H_2TPP/Au interface where they may dissociate. Holes may escape from the H_2TPP/Au interface since they have a reasonable mobility. The holes escaping from the H_2TPP/Au interface cause positive charging of the surface region of the sample and, therefore, a positive surface photovoltage. Absorption of light in the Au substrate may lead to internal photoemission of electrons from Au into unoccupied states of the H_2TPP layer.[9] This causes negative charging of the H_2TPP layer and consequently a sign change of the SPV in comparison with the PV induced by the holes escaping from the H_2TPOP/Au interface. We interpret our experimental findings on this process.

Organic H_2TPP layers were evaporated on glass substrates coated with a thin Ti adhesion layer and a 100-nm-thick Au layer. The substrates were cleaned ultrasonically in acetone and isopropanol and dried in N_2 before evaporation in high vacuum at room temperature. The depo-

sition rate of the H_2TPP layers (5,10,15,20-tetraphenyl-21*H*, 23*H*-porphine, by Sigma-Aldrich, Inc.) was controlled by using a quartz thickness monitor and set to about 1 Å/s. The thicknesses of H_2TPP layers were varied between 5 and 75 nm. The samples were stored in vacuum or nitrogen ambient after evaporation and between measurements.

SPV spectra were excited with a halogen lamp and a quartz prism monochromator. The modulation frequency was varied by a chopper between 2.3 and 330 Hz. The in-phase PV signal was detected by a lock-in amplifier. SPV measurements were carried out in vacuum, nitrogen and oxygen atmospheres. Temperature dependent SPV measurements were performed between −60 and 170 °C in vacuum (base pressure $<10^{-5}$ mbar).

Red and blue light emitting diodes (LEDs) were used for constant additional (bias) illumination (intensity ~30 mW). The used LEDs have their emission maximum at 1.98 eV (10% of the maximum at 1.93 and 2.08 eV) and at 2.7 eV (10% of the maximum at 2.53 and 2.85 eV), respectively. For comparison, the absorption maximum of the Soret band is at photon energies of about 2.9 eV, whereas the *Q* bands have maximum absorption at about 2.4, 2.2, 2.1, and 1.9 eV.[10]

Figure 2 shows SPV spectra of a 50-nm-thick H_2TPP layer deposited on Au. The PV signals are positive at higher modulation frequencies and negative at the lowest modulation frequency. Positive (negative) surface polarization is induced by positive (negative) charging of the H_2TPP layer near the surface. Transport processes of excess holes and electrons in the H_2TPP layer compete with each other, while the modulation of the much faster excess holes dominates at higher frequencies. The PV signals decrease strongly with increasing modulation frequency.

The transitions to the *Q* bands with their characteristic peaks are clearly distinguished in the SPV spectra at higher modulation frequencies, while PV signals, which are related to transitions into the Soret band, could not be detected for the given layer thickness (Fig. 2). The reason for the disappearance of the Soret band in the SPV spectra is that the competition between separation of electrons and holes may be quite close under certain conditions. At the lowest modulation frequency, the Soret band appears in the SPV spec-

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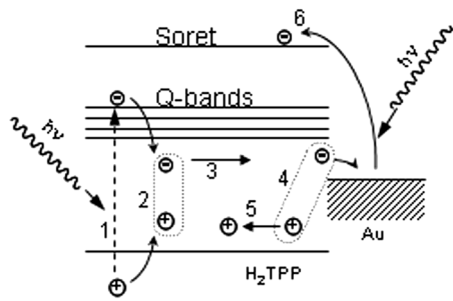b)Electronic mail: dittrich@hmi.de

FIG. 1. Sketch of dominating elementary processes being involved in charge separation at H2TPP/Au junctions under illumination [(1) absorption, (2) exciton formation, (3) exciton diffusion, (4) exciton dissociation, (5) escape of holes, and (6) internal photoemission].

FIG. 3. Dynamic photovoltage signal as function of temperature under excitation with a red LED [(a), full triangles] or blue LED [(b), triangles]. The figure also shows the measurements without and with continuous bias light, blue bias LED [(a), full stars] and red bias LED [(b), stars], respectively.

trum, but the spectral features below the Soret band cannot be clearly assigned to the transitions into the Q bands since they are blurred by the superposition of the two SPV mechanisms. The change sign of the SPV with modulation frequency may yield information about the characteristic time. This time is of the order of 0.1 s at room temperature and has to be assigned to the back transfer of photoemitted electrons.

The modulated PV signals also depend on the gas atmosphere. In oxygen-containing atmosphere, the modulated PV signal increases reversibly by up to four times in comparison with vacuum or nitrogen atmospheres. Adsorbed oxygen molecules are acceptor like[11] and polarize the H_2TPP surface more negatively. This causes a more efficient separation of holes escaping from the H_2TPP/Au interface towards the surface.

Figure 3 shows the 2.3 Hz modulated photovoltage signal as a function of temperature under excitation with bias red or blue LEDs of a 20 nm H_2TPP/Au sample. The qualitative behavior is not a function of the thickness of the H_2TPP layers or the bias wavelength. The PV signals are positive at lower temperatures and increase slightly with increasing temperature up to room temperature. At higher temperatures, the PV signals decrease and change their signs at about 130 °C (red LED) and 120 °C (blue LED). For comparison, the sign of the modulated PV signals changed (red LED) at 80 and 140 °C for 5- and 75-nm-thick H_2TPP layers, respectively. This is not surprising since the relative influence of internal photoemission of electrons from Au into
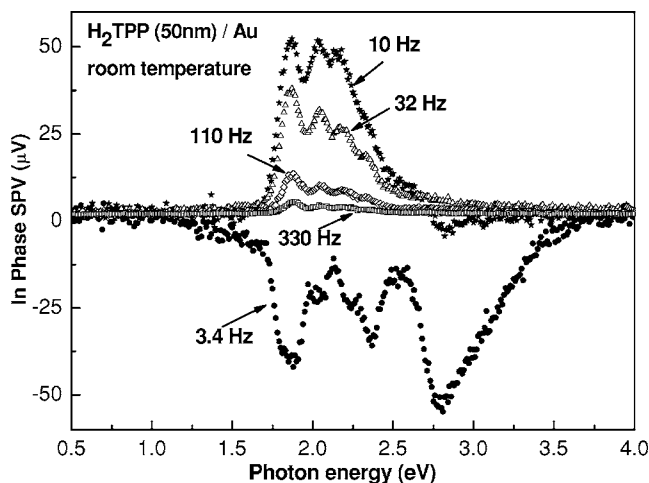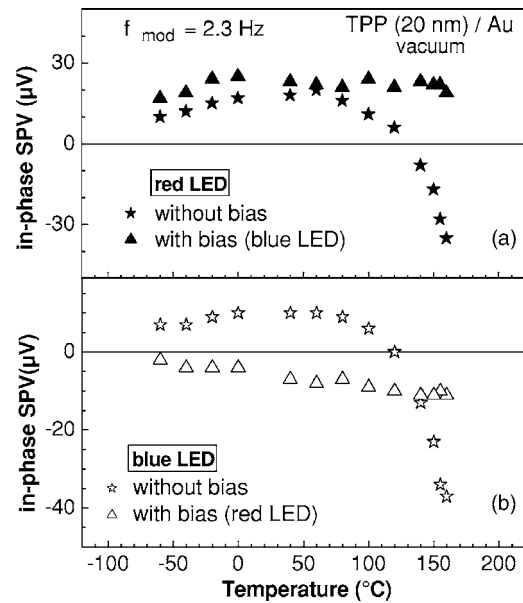

FIG. 2. Surface photovoltage spectra of a 50-nm-thick H2TPP layer deposited on Au for various modulation frequencies.

H_2TPP increases with decreasing thickness of the H_2TPP layer. At high temperatures, the negative PV signals increase strongly with temperature.

The temperature dependent sign change of the PV signals is evidence of at least two competing mechanisms of charge separation. As mentioned above, positive PV signals are induced by the escape of holes from the H_2TPP/Au interface, whereas internal photoemission of electrons from Au into H_2TPP is responsible for negative PV signals. With increasing temperature, the carrier mobility and recombination probabilities increase. Hole transport dominates the modulated photovoltage at moderate temperatures due to the relatively high hole mobility. With increasing temperature, the exciton diffusion length decreases and, therefore, the rate of hole escape from the H_2TPP/Au interface decreases. For this reason, electron transport becomes more important for the modulated PV.

Under continuous bias illumination, the temperature dependence of the modulated PV becomes weak and the sign change disappears (Fig. 3). The modulated PV signals are positive for modulated red and continuous blue and negative for modulated blue and continuous red light, respectively. Therefore, the continuous bias light illumination suppresses one of the competing mechanisms of charge separation. The negative modulated PV signal increases with increasing temperatures at lower temperatures and saturates at high temperatures.

Continuous illumination causes a permanent charging of the H_2TPP layer due to charge separation. The light of the red and blue LEDs is absorbed differently in the H_2TPP/Au system since the absorption coefficient of the Soret band (absorption in the blue) is larger by more than one order of magnitude than for the Q bands (absorption in the red).[8] We assume that blue and red bias illuminations cause predominantly positive or negative permanent charging near the H_2TPP/Au junction, respectively. In the case of increased permanent concentration of excess holes in the H_2TPP layer, electrons emitted from Au into the H_2TPP layers recombine

near the H_2TPP/Au junction and do not contribute significantly to the modulated charge separation. On the contrary, holes do not contribute predominantly to the modulated PV signal in case of increased permanent concentration of electrons near the H_2TPP/Au junction. In addition, the bias illumination creates space charge and consequently a built-in electrical field, which limits the charge distribution modulation.

The existence of various mechanisms of charge separation at H_2TP/Au junctions has been demonstrated. The mechanisms are linked to exciton dissociation, internal photoemission, and transport of positive or negative charge in the H_2TPP layer. The interplay of these mechanisms depends on modulation frequency, adsorbed gas molecules, temperature, and continuous bias illumination, and the sign of modulated PV signals can be easily switched. The conditions under which one process dominates the other are rather involved. Besides transport and recombination, the field distribution plays a role. The latter is also important for the modulated charge separation. More detailed experiments and simulations will be needed to model the positive and negative charge center modulation. The obtained results are of interest for applications in sensors, organic electronics, and photovoltaics.

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