Light-induced charge separation in thin tetraphenyl-porphyrin layers deposited on Au

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Charge separation processes in metal-free tetraphenyl-porphyrin (H_2TPP) layers deposited on Au substrate have been studied using surface photovoltage spectroscopy. The results show that dissociation of excitons at the H_2TPP/Au interface causes charge separation by holes escaping from the interface region. This interface features a potential barrier due to the ground state of the H_2TPP being 0.81 eV below the Fermi level of the Au substrate. Surface photovoltage is built up by internal photoemission at the H_2TPP/Au interface, which leads to electron injection into the H_2TPP layer with a slow electron backtransfer. The latter is thermally activated with an activation energy of 0.4 eV, which can be attributed to negative polarons in H_2TPP.

I. INTRODUCTION

Charge separation at interfaces between metals and layers of semiconducting organic molecules with a π-electron system is of both fundamental and practical interests. In particular, the formation of barriers and the dissociation of excitons at internal interfaces are important for charge-selective contacts. One of the most prominent such contacts is based on a heterojunction comprising C_{60} as a strong electron acceptor and a conjugated polymer as the electron donor.[1] Besides the contact charge selectivity, charge transport in the organic layer is crucial for subsequent charge separation due to the very low drift velocities, which are usually of the order of 10^{-3}–10^{-7} cm^2/V s.[2] Furthermore, many questions about elemental excitations in organic semiconductors and the formation of excitons or charged polarons remain unresolved. For example, the ultrafast photogeneration of charged polarons has been observed in conjugated polymers,[3] while the photogeneration of charge carriers is usually considered as a secondary process, induced by exciton dissociation in high electric fields.[4] A deeper understanding of charge separation and transport processes is important for applications in optoelectronics, such as organic light-emitting diodes or organic solar cells.

Interfaces between metals and organic semiconductors have been extensively studied and information about work functions and interface dipoles is available for many systems.[5,6] For example, the molecular alignment at metal/organic semiconductor interfaces depends sensitively on the kind of organic molecule and metal used.[7] Abrupt, nonreacted interfaces are formed with noble-metal contacts.[8] These studies are usually performed by photoelectron spectroscopy under ultrahigh-vacuum conditions.

Internal barrier heights can also be studied by using internal photoemission spectroscopy, in which the photocurrent is measured, for example, in organic light-emitting diodes.[9] Significant offsets of the barrier heights between the highest occupied molecular orbital (HOMO) of the organic semiconductor and the Fermi level of the metal are often observed at metal/organic semiconductor interfaces.

Surface photovoltage spectroscopy (SPS) using a Kelvin probe[10] is a sensitive tool for studies of charge separation in very thin organic layers. For example, photoinduced charge carriers have been investigated at MEH-PPV (poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene]) coated Au or GaAs surfaces.[11] However, none of the past SPS studies recognized internal photoemission as a source of detectable surface photovoltage (SPV) and could separate it from additional SPV processes, taking place in thin organic films deposited on Au.

In this work, we have applied SPS to investigate the temperature-dependent charge separation in thin layers of metal-free tetraphenyl-porphyrin (H_2TPP) deposited on Au. Porphyrin is a relatively small organic molecule with a π-electron system. It plays an important role in biology and in photosynthesis.[12] The absorption spectrum of H_2TPP shows several characteristic absorption bands (the Soret band around 2.9 eV and the Q bands at about 2.4, 2.2, 2.1, and 1.9 eV).[13] The transition at 1.9 eV is ascribed to the HOMO-LUMO (lowest unoccupied molecular-orbital) transition. The other transitions stem from $\pi \to \pi^*$ transitions at energies above the HOMO-LUMO energy. The thickness of the H_2TPP layers was varied between 5 and 75 nm and the ambient was high vacuum or oxygen atmosphere. The results are compared with charge separation due to sensitization of TiO_2 with a monolayer of H_2TPP molecules. Charge separation processes due to internal photoemission and exciton dissociation at the internal H_2TPP/Au interface are demonstrated.

II. EXPERIMENT

Organic H_2TPP layers were evaporated on glass substrates coated with a thin Ti adhesion layer and a 100-nm-thick Au layer. For optical control measurements,

H$_2$TPP layers were evaporated on bare glass substrates. The substrates were cleaned ultrasonically in acetone and isopropanol and dried in N$_2$ before evaporation in high vacuum at room temperature. The deposition rate of the H$_2$TPP layers (5,10,15,20-tetraphenyl-21*H*, 23*H*-porphine, by Sigma Aldrich Inc.) was controlled using a quartz thickness monitor and set to about 1 Å/s. The samples were stored in vacuum or nitrogen ambient after evaporation and between measurements.

In comparison, a compact 100-nm-thick TiO$_2$ layer (prepared by sol-gel processing) has been sensitized with a monolayer of 5-(4-carboxyphenyl)-10,15,20-tris(4-methylphenyl) porphyrin (TMPP). The molecules were synthesized by an already described method.[14] TiO$_2$ layers were modified with dyes by soaking the films in a saturated *n*-hexane/DCM 80/20 solution of porphyrin. The molecules form a stable link at the TiO$_2$ surface.[15]

The SPS setup comprised a Kelvin probe (Besocke Delta Phi, Germany) and a quartz prism monochromator (SPM2). A halogen (250 W) lamp was used for illumination. The SPS technique monitors light-induced changes of the work-function difference between the sample and a vibrating gold grid. The work function of the vibrating gold grid is assumed to be independent of illumination. Therefore, the measured light-induced work-function difference corresponds to the light-induced change in the contact potential difference (ΔCPD), which is equal to the negative surface photovoltage (-SPV). The resolution time of the measurement was about 1 s depending on the integration time constant of the lock-in amplifier in the Kelvin probe controller. A SPV spectrum was measured for about 30 min. The measurements were preformed at the illuminated organic layer surface. A high-intensity (33 mW) red light-emitting diode (LED) was used for time-dependent measurements of ΔCPD. The measurements were performed in high vacuum at temperatures up to 160 °C and in oxygen atmosphere.

III. RESULTS AND DISCUSSION

A. Surface photovoltage spectra of a monolayer vs a deposited layer

Figure 1(a) shows the measured absorption spectrum of a 50-nm-thick H$_2$TPP layer deposited on glass. The transitions into the *Q* and *S* bands have their maxima at 1.86, 2.04, 2.19, 2.35, and 2.86 eV (*Q*1–*Q*4 and *S* band, respectively). As is well known, the absorption of the *S* band is much stronger than the absorption of the *Q* bands.

The SPV spectrum of a monolayer of TMPP adsorbed on TiO$_2$ demonstrates the sensitization of TiO$_2$ with TMPP [Fig. 1(c)]. The sign of the light-induced change of the work function is negative, i.e., the work function decreases. This corresponds to an electron injection into the TiO$_2$ and to positive charging of the surface (a negative light-induced change of the work function means a positive SPV). The transitions into the *Q* and *S* bands can be clearly resolved in the SPV spectra of a TMPP monolayer deposited on TiO$_2$. If we take the transition second knee as a reference point,[16] then the *Q*1 and *S* band appear at 1.9 and 2.9 eV, respectively, which points to a slight blueshift of 40 meV. The blueshift can be
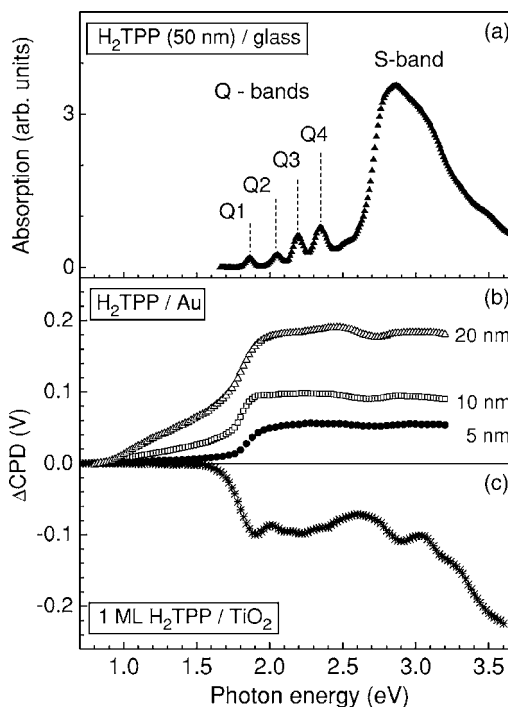

FIG. 1. (a) Absorption spectrum of a 50-nm-thick H$_2$TPP layer (b) SPV spectra of H$_2$TPP layers (thicknesses of 5, 10, and 20 nm) deposited on Au, and (c) SPV spectrum of a monolayer of TMPP deposited on TiO$_2$.

explained by a quantum size effect. Furthermore, the photovoltage sets on already at photon energies of about 1.6 eV, probably due to surface states.

The sensitization due to the *S* band into the TiO$_2$ is very weak in comparison with the sensitization due to the *Q* bands. A possible reason for this can be that electrons are also excited in the TiO$_2$ due to defect states and those electrons may be captured by positively charged TMPP molecules. The change of the SPV at photon energies above 3.1 eV is due to the onset of absorption in the TiO$_2$ substrate.

SPV spectra of H$_2$TPP layers with different thicknesses deposited on Au are shown in Fig. 1(b). The sign of the light-induced change of the work function (or CPD change) is positive for the H$_2$TPP layers deposited on Au, in contrast to the TMPP monolayer adsorbed on TiO$_2$. Therefore, H$_2$TPP layers, deposited on Au, negatively charge during illumination. There is also a strong SPV signal for H$_2$TPP layers deposited on Au at photon energies below 1.8 eV.

Positive light-induced CPD changes are typically observed for *p*-type inorganic semiconductor surfaces, even for nanometer-scale particles, since most of the light is absorbed within the first few nanometers of the surface charged region (SCR).[10] H$_2$TPP is a hole conductor and sometimes is denoted as a *p*-type-like material. Unlike in an inorganic semiconductor, the positive CPD change cannot straightforwardly be ascribed to surface charge separation processes. This is because surface gap states, and SCR, have been proven not to exist in organic molecular films[17] measured in UHV. Diffusion profiles, i.e., Dember effect and bulk absorption profiles, might create a detectable SPV (Ref. 10) but are not expected for such thin layers and certainly cannot explain the SPV changes observed deeper into the IR.
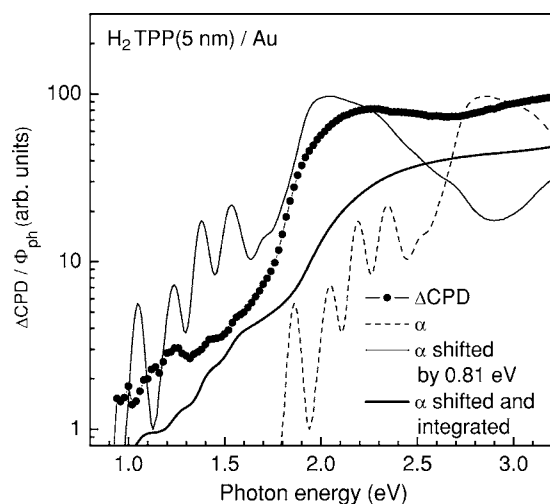
FIG. 2. Spectra in arbitrary units of the ΔCPD signal normalized to the photon flux (full circles), the absorption coefficient (dashed curve), the redshifted (by 0.81 eV) absorption coefficient (thin solid curve), and the redshifted and integrated absorption coefficient (thick solid curve).

The reasons for the positive polarity of the CPD change and for the IR SPV are not the only questions that arise. The SPV signal is determined by light absorption, separation of excess charge carriers, and their transport. One would expect a well pronounced correlation between SPV spectral features and peaks in the absorption spectrum. However, the SPV spectra of H_2TPP layers deposited on Au do not show pronounced features, which can be directly related to transitions into the Q bands. The SPV signal induced by transitions into the S band is surprisingly weak in comparison to the SPV signal at photon energies below 2 eV.

B. Internal photoemission

For a better comparison with absorption spectra, the SPV spectra were normalized to the photon flux. Figure 2 shows the SPV spectrum of the 5-nm-thick H_2TPP layer normalized to the photon flux on a logarithmic scale. The normalized SPV signal increases strongly at about 1.8 eV and pronounced shoulders or small peaks appeared at photon energies of about 1.53, 1.39, and 1.23 eV. At photon energies below 1.1 eV, the noise level dominates. These features and the strong increase of the photovoltage at about 1.8 eV correlate very well with transitions into the $Q2$, $Q3$, $Q4$, and S bands if the absorption spectrum is shifted by 0.81 eV toward lower photon energies. The redshifted absorption spectrum and the redshifted and integrated absorption spectrum are also plotted in Fig. 2. The normalized SPV spectrum can be well understood as a superposition of redshifted absorption and integrated absorption spectra slightly influenced by the absorption spectrum. The need of superposition with the integrated redshifted absorption spectrum is caused by the finite time of measurement in accordance with the very slow relaxation mechanisms of the SPV signal in this case.

Internal photoemission of excited electrons from the Au substrate into available states in the H_2TPP layer may be the only mechanism to explain the negative photoinduced charging of the H_2TPP layer. It also explains the correlation of features in the SPV spectra with characteristic features in the redshifted absorption spectrum [schematically shown in Fig. 3(a)]. Therefore, the energy difference between the HOMO level of H_2TPP and the Fermi level in the Au substrate is 0.81 eV. For comparison, the energy difference between the HOMO level of copper phthalocyanine, which also belongs to a similar class of organic molecules as H_2TPP, and the Fermi level in Au amounts to 0.9 eV.[18] For thin H_2TPP layers of up to about 20 nm, the maximal charge separation length is given by the layer thickness. This results in a linear scaling of the photovoltage signal with the layer thickness if the internal photoemission is assumed to be independent of the H_2TPP layer thickness, as has been observed.

The photovoltage signal at low photon energies depends on the ambient, especially on the oxygen pressure. This is demonstrated in Fig. 4 for the 10-nm-thick H_2TPP layer measured at two oxygen pressures. With increasing oxygen pressure, the photovoltage signal below 1.8 eV reversibly decreases. The photovoltage signal at photon energies above 2 eV tends to increase with increasing oxygen pressure. Oxygen is an electron acceptor.[19] It produces a net negative charging of the surface and therefore band bending in the H_2TPP layer. Previous studies have shown that a negatively charged depletion region is formed at the organic/metal or metal/organic interfaces due to increased charge-carrier concentrations and a reduction in the HOMO-Fermi level gap after oxygen adsorption.[20] The band bending reduces the effective separation length of electrons injected from the Au substrate into the H_2TPP layer and therefore the SPV signal [Fig. 3(b)]. After pumping the chamber back to high vacuum, the internal photoemission transitions are recovered.
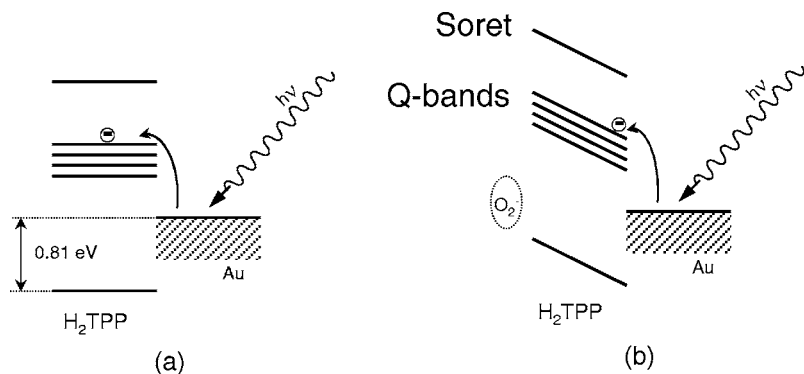

FIG. 3. Schematic of internal photoemission of electrons from the Au substrate into the H_2TPP layer in (a) oxygen-free and (b) oxygen containing atmosphere.
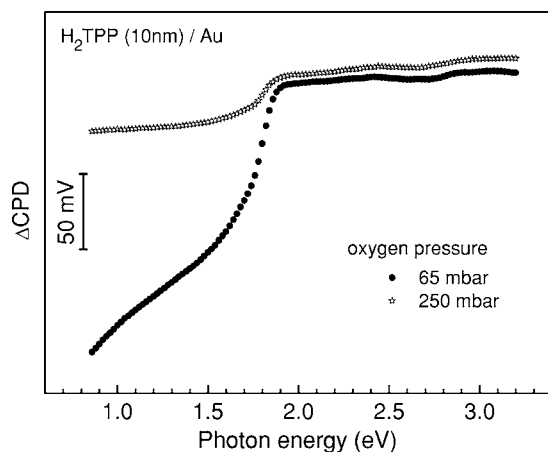
FIG. 4. SPV spectra of the 10-nm-thick H_2TPP layer for two oxygen pressures.

C. Illumination-induced internal potential redistribution

The reason why the organic transitions are observed as positive work-function changes in the 1.9–3.2 eV range of the CPD spectra shown in Fig. 1(b) is not yet fully addressed. SPS is a quasi-steady-state measurement; the illumination wavelength is continuously changed. The outcome is permanent interface negative charging of the organic layer due to internal photoemission. The illumination-induced potential redistribution created in the IR region is involved in exciton dissociation when light is absorbed in the organic layer. When such fields exist, then the positive (negative) polarons are swept toward the interface (surface), resulting in a positive work-function change.

D. Role of exciton dissociation

From the SPS data, it is difficult to make a clear conclusion about internal built-in fields in thermodynamic equilibrium for the H_2TPP/Au system. Backtransfer of electrons at the interface should take place in order to observe whether SPS screens additional charge-transfer processes. Therefore, illumination-induced CPD transient caused by blinking of high-intensity red LED at different H_2TPP thicknesses was measured. The red light of the used LED is mainly absorbed by the $Q2$ transition in the H_2TPP layer. This absorption induces formation of (electrically neutral) excitons that cannot be detected by photovoltage measurements. Electrons excited by red light in the Au layer can be injected into the S band of the H_2TPP layer inducing photovoltage as shown above. With increasing thickness of the H_2TPP layer, the amount of red light absorbed in the H_2TPP layer increases, whereas the amount of red light absorbed in the Au substrate decreases.

Figure 5 compares the time-dependent development of the SPV signal of 5-nm- and 75-nm-thick H_2TPP layers after switching on and off the red LED light at room temperature. For the 5-nm-thick H_2TPP layer, the SPV ($=-\Delta CPD$) decreases within several seconds after switching on the light and increases after switching off the light during darkness until the light is switched on again. This means that the SPV
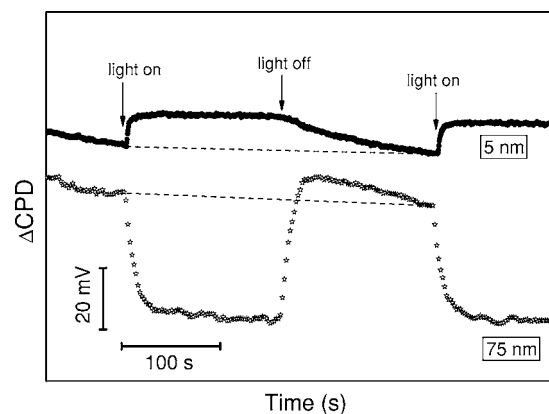

FIG. 5. Time dependencies of the onsets and offsets of the SPV signal for 5-nm- and 75-nm-thick H_2TPP layers. The excess charge carriers were excited with a red light-emitting diode.

signal of the 5-nm-thick H_2TPP layer is induced by only one mechanism of charge separation, namely, the internal photoemission of electrons from the Au substrate into the H_2TPP layer. The backtransfer of injected electrons from the H_2TPP layer toward the Au substrate is a very slow process, limiting the SPV.

Similar negative SPV was also measured for 10 and 20 nm H_2TPP deposited on Au. The work function of the H_2TPP layer was found to be 0.5 eV lower than the Au substrate.[21] If a thermodynamic equilibrium at the interface is reached and a Schottky contact is formed between the p-type-like H_2TPP and the Au, then electrons should be transferred into Au. The organic energy levels, denoted here as bands, should bend down away from the interface going into the organic layer. Such band bending should create a negative SPV,[10] if the SPV is measured at the surface. Interface band bending might exist and will have some contribution to the negative SPV observation.

For the 75-nm-thick H_2TPP layer, the SPV signal increases within several seconds after switching on the red light, i.e., positively charging the surface of the thick H_2TPP layer. However, there is an overshoot of the SPV signal of the 75-nm-thick H_2TPP layer after switching off the light. This overshoot is of the same order as the SPV signal of the 5-nm-thick H_2TPP layer and it relaxes slowly as for the 5-nm-thick H_2TPP layer. It can be concluded that the SPV signal of the 75-nm-thick H_2TPP layer is formed by at least two charge separation processes, each in an opposite direction. The slow process is the same as for the 5-nm-thick H_2TPP layer, i.e., internal photoemission from the Au substrate. The fast process is related to the generation of electron-hole pairs in the H_2TPP layer and to a transport process, much faster than the electron backtransfer.

The fast process has to be limited by hole transport since the hole mobility is higher by about an order of magnitude than the electron mobility in H_2TPP layers.[22] The sign of the fast component of the SPV signal means that holes move from the H_2TPP/Au interface toward the surface of the H_2TPP layer. We assume that excitons diffuse toward the H_2TPP/Au interface, where they can dissociate. The holes have a certain escape probability from the interface region

into the bulk and the H_2TPP surface. Only excitons generated below the exciton diffusion length from the H_2TPP/Au interface can reach the interface and dissociate. The hole transport dominated charge separation depends only weakly on the oxygen pressure since the electric field supports the hole escape from the H_2TPP/Au interface region.

Positive SPV is caused by holes, which are swept or diffuse toward the surface. It is not expected for p-type inorganic semiconductors, where electrons are swept in the surface built-in field to the surface. H_2TPP, although a hole conductor material, does not act as a p-type-like material when it comes to SPV. For p-type inorganic semiconductors, positively charged surface states create a surface built-in field. The positive SPV, if related to internal potential redistribution, is caused by negative charging of the surface. Indeed, the positive SPV increases in oxygen ambient. Therefore, oxygen, which is acceptorlike, is mainly adsorbed at the layer surface. The increased positive SPV may suggest that oxygen adsorption creates a negatively charged depletion region near the H_2TPP free surface. Since the positive SPV observation does not support this assumption, the SPV process is not necessarily induced by surface charge separation processes and the oxygen may negatively charge the layer surface. The role of oxygen is not yet fully understood. Positive SPV also supports previous observations that showed no evidence of surface states in UHV.

E. Electron backtransfer

The thermal activation of the electron backtransfer can be studied for the thin H_2TPP layer deposited on Au before the fast relaxation process becomes dominant. Figure 6 depicts the Arrhenius plots of the absolute photovoltage signals measured at a constant LED on-off frequency (0.05 Hz) from the H_2TPP layers with thicknesses of 5, 10, and 20 nm as a function of $1/T$. At higher temperatures, the signals tend to saturate. The activation energy of $\sim$0.4 eV may indicate polaron formation in the organic semiconductors.[23,24]

IV. CONCLUSIONS

SPV of H_2TPP thin layers and possibly other organic semiconductors is a summation of more than one process.
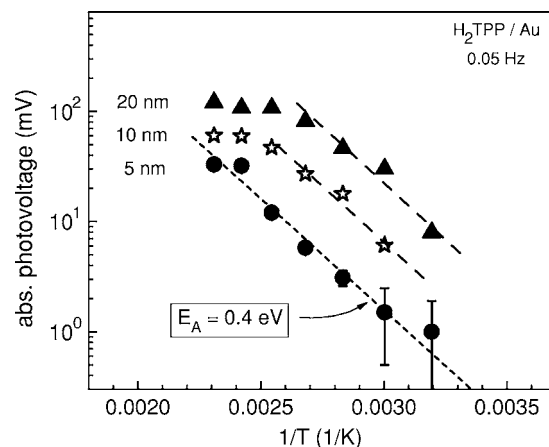

FIG. 6. Arrhenius plots of the SPV signals measured with a repetition rate of 0.05 Hz for the 5-nm-, 10-nm- and 20-nm-thick H_2TPP layers.

Analyzing the SPV mechanism should be taken carefully. Internal photoemission of electrons from a metal into very thin layers of organic semiconductors can play a dominant role in charge separation. Due to internal photoemission, the light is absorbed in a wide energy range, from deep IR to the UV. The electron backtransfer is a slow process and thus internal photoemission can create an illumination-induced potential distribution that would influence SPV response.

The barrier height between the HOMO level in H_2TPP and the Au substrate is 0.81 eV. In addition, no clear evidence for interface SCR was observed; yet, if SCR does exist, its width is few nanometers. Electrons injected into organic semiconductors by internal photoemission can be generally used as probes for transport studies. In addition, an activation energy of $\sim$0.4 eV was found and may indicate polaron formation in the organic semiconductors.

In thicker layers of H_2TPP, the diffusion of excitons, their dissociation, and transport of holes become more important. This process is screened by the internal photoemission in SPS measurement. Positive polarons are transferred or swept toward the layer surface. This process is not expected for p-type inorganic semiconductors but is observed for p-type-like organic semiconductor, probably because the surface is negatively charged, possibly due to surface oxygen absorption.

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