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Efficient bulk photogeneration of charge carriers and photoconductivity gain in arylamino-PPV polymer sandwich cells

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Stationary photoconductivity has been measured for sandwich cells of poly(phenylimino-1,4-phenylene-1,2-ethenylene-2,5-dioctyloxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene) between gold and aluminum electrodes. Films with thicknesses below and above 1 μm were examined in order to separate photocurrent contributions arising from processes at the polymer/electrode interfaces and the bulk. Spectra recorded under forward bias were almost identical in shape and size for irradiation through either the anode or the cathode indicating that the photocurrent is dominated by bulk photogeneration of charge carriers. Large charge carrier collection efficiencies exceeding those of typical PPV derivatives are derived from these experiments. The photogeneration is clearly enhanced within the tail of the polymer absorption and photoaction spectra recorded under forward bias resemble well the shape of solid-state photoexcitation spectra. We presume that both photoluminescence and photoconductivity in the studied arylamino-PPV compound are dominated by the excitation of states or sites rather deep in the density of states distribution. Under reverse bias the photoaction spectra depend strongly on illumination conditions. For illumination through the positively biased aluminum electrode the photocurrent spectra are almost symbatic with the polymer absorption while antibatic behavior is observed upon illumination through the gold electrode. The data can qualitatively be explained by the buildup of a negative space-charge region by immobile photogenerated electrons. Upon illumination through the positively biased aluminum electrode collection efficiencies of up to 2000% are observed. This is attributed to photocurrent multiplication arising from the accumulation of electrons near the interface, which promotes tunneling of holes into the film. [S0163-1829(99)02903-3]

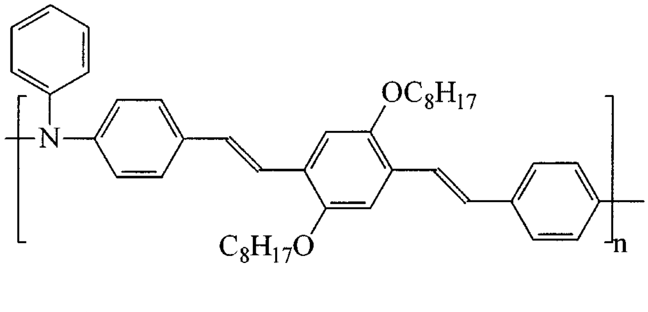
I. INTRODUCTION

There has been considerable research activity on the photogeneration of charge carriers in conjugated polymers, stimulated by the request for materials for efficient xerographic layers or solar cells.[1,2] Even though the xerographic discharge experiment is known to be the most accurate method to determine the quantum efficiency of photocharge generation, the analysis of the photocurrent of devices, in which a photoactive film is sandwiched between two electrodes is commonly used to gain information about the efficiency of charge carrier photogeneration in polymer layers.[3–10] Recent reports have analyzed the photocurrent action spectra of sandwich cells of poly(p-phenylene vinylene)s (PPV) and its soluble derivatives. Harrison and Grüner observed a clear influence of the direction of the applied electric field on the shape of the photocurrent spectra in ITO/PPV/Al and ITO/MEH-PPV/Al sandwich devices (film thicknesses between 100 and 800 nm).[11] The effect could in part be explained by a low mobility of the minority carrier (electrons) in the PPV layer. When charge carriers are photogenerated only in a region close to the cathode the electrons have to move across the whole layer. Low electron mobility will result in the buildup of a space-charge field, which compensates the external bias. Effective collection efficiencies are, therefore, only observed for excitons generated close to the anode. Thus, depending on polarity, photoaction spectra of sandwich devices show antibatic and symbatic response as also observed by others.[12,13] The further analysis of the spectra indicated that the photogeneration efficiency of this PPV derivative had to be enhanced at the edge of the polymer absorption.[14] Lee, Yu, and Heeger reported that the spectral response of PPV sandwich cells with a PPV layer thickness of approximately 0.3 μm exhibited an enhanced photocurrent at the onset of the polymer absorption.[15] The data could be rather well fitted by a model assuming enhanced recombination of carriers generated near the surface.

Photocurrents of sandwich devices of a soluble PPV ether (layer thickness approximately 100 nm) measured upon illumination through the transparent ITO hole injection contact were larger if the ITO bottom electrode was biased as the anode.[16] The experimental observations were explained by the enhanced dissociation of excitons near the interface via transfer of the excited electron to the positively biased electrode (also called photoinjection of holes). This contribution is dominated by excitons generated close, that is within the diffusion length of the excitons, to the charge injecting electrode. Only minor contributions to the photocurrent were assigned to bulk photogeneration. The photocurrent dropped by three orders of magnitude when a 8–10-nm-thick SiO barrier layer was inserted between ITO and the polymer. SiO is known to prevent charge carrier injection from the electrodes but to affect discharge of carriers only marginally. In this case the photocurrent was given by the bulk photogeneration of charge carriers. Quantum yields of the intrin sic photocurrent were up to 1×10^{-4} at a field of 2.1×10^{7} V/m. It was further concluded that the photocurrent at reverse polarity (Al positively biased) is also dominated by photoinjection of holes, but the contribution is smaller than under forward bias conditions. In contrast to this the photocurrent of PPV-amine [poly(methylimino-1,4- phenylene-1-phenyl- 1,2-ethenylene- 2,5-dimethoxy-1,4-phenylene-2-phenyl-1,2-ethenylene-1,4-phenylene] sandwich cells (film thickness approximately 100 nm) with illumination through the ITO electrode was nearly independent of polarity and the presence of an SiO blocking layer. The bulk photogeneration efficiency, calculated from the photocurrent under reverse bias, was up to 5×10^{-2} at a field of 8×10^{7} V/m.[17] Also recently, photoconductivity of MEH-PPV based sandwich devices with active layer thicknesses between 120 and 5700 nm have been compared in order to extract information on the charge generation mechanisms.[18] In this work, no detailed information is given on the shape of the photoaction spectra and the effect of illumination direction.

This paper presents the analysis of the photoaction spectra of sandwich devices based on poly(phenylimino-1,4-phenylene-1,2-ethenylene-2,5-dioctyloxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene) (arylamino-PPV) between a gold bottom contact and an aluminum top electrode. Cells have been prepared either with ''thin'' (typically 300 nm) or ''thick'' (film thicknesses in the micrometer range) active polymer layers. Photoaction spectra were recorded as a function of wavelength and bias for illumination either through the bottom or top electrode. Particular attention is paid to external contributions such as the photoinjection of charge carriers and photocurrent multiplication. The particular PPV-derivative differs from the more frequently used compounds such as PPV and MEH-PPV as it contains a triphenylamino-(TPA) group in the main chain. This group is known to facilitate hole transport. Recent experimental and theoretical work has emphasized that certain excited states enhance photogeneration of charge carriers.[19] These states involve transitions from delocalized occupied molecular orbitals to localized unoccupied levels, where the hole is confined on a particular site while the electron is delocalized or vice versa. In the arylamino-PPV transitions are likely to occur with the hole localized on the TPA unit and large photogeneration yields are expected for certain transitions.

II. EXPERIMENT



Poly(phenylimino-1, 4-phenylene-1, 2-ethenylene-2,5-dioctyloxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene) (arylamino-PPV) was synthesized by polycondensation using the principle of HORNER.[20,21] Samples were prepared by spin coating and dropcasting from toluene solution on top of glass supports covered with semitransparent gold (Au) forming the bottom electrodes. During evaporation of the solvent the dropcast samples were kept in toluene atmosphere for 12 h in order to assure homogeneous drying of the polymer film. The transmission of the Au electrode was determined to be about 30%. The polymer films had typical thicknesses of 300 nm and 6 μm, respectively. The samples were kept in vacuum at 330 K for 12 h to remove residual solvent prior to evaporating the semitransparent aluminum (Al) top electrode. The arrangement of the bottom and top electrode strips gave sandwich cells with an area of 0.056 cm^2. The transmission of the Al contact was 10% in the whole visible spectral range. It should be mentioned that a high surface roughness of the samples, especially of the dropcast films, could not be avoided even though the preparation was done very carefully. The roughness was observed with α-step measurement and with an optical microscope, but a closer analysis of the sample surface has not been performed.

Photoconductivity experiments were performed in dry nitrogen atmosphere in a temperature stabilized setup.[22] The spectral intensity variation of the xenon lamp that was used for illumination was corrected such that a constant photon flux of about 10^{13} ph/cm^2 sec was established at the film side facing the light source. Data were recorded pointwise and refer to photocurrents established after 80 sec illumination. The sample was then kept in the dark for 80 sec and the dark current was measured. For Au biased as the cathode dark currents were lower than 10 nA/cm^2, typically two orders of magnitude lower than the currents measured under illumination. In the case of positively biased Au dark currents were comparable to the photocurrents, but could still be clearly distinguished from the currents under illumination. For data analysis the dark current was subtracted from the current measured under illumination to give j_{photo}.

III. RESULTS

As a convention for the following discussion we use the subscripts + and − for Au being the anode and the cathode, respectively. Indices Al and Au indicate the electrode through which the film was illuminated.

Figure 1 shows the absorption spectrum and the action spectra of the photocurrents ($j_{\text{photo}}=j_{\text{light}}-j_{\text{dark}}$) of a 310-nm-thick arylamino-PPV film sandwiched between Al and Au upon irradiation through the Au electrode. It is noteworthy that a polymer film of only 310 nm thickness has an optical density of up to 2, meaning that in a broad range of the polymer absorption all incident photons are absorbed. Even though the bias dependence of the photocurrents shows neither antibatic nor symbatic features for Au being negatively ($j_{-\text{Au}}$) and positively ($j_{+\text{Au}}$) biased, comparison of the absolute values of the photocurrents at $\lambda=445$ nm ($j_{-\text{Au}}=1$ nA/cm^2 and $j_{+\text{Au}}=29$ nA/cm^2, respectively) shows that there is a pronounced polarity dependence. For both polarities j_{photo} rises for wavelengths below and above the absorption maximum ($\lambda=442$ nm).

The field dependence of the dark current was asymmetric for thin as well as for thick films. This indicates a diodelike

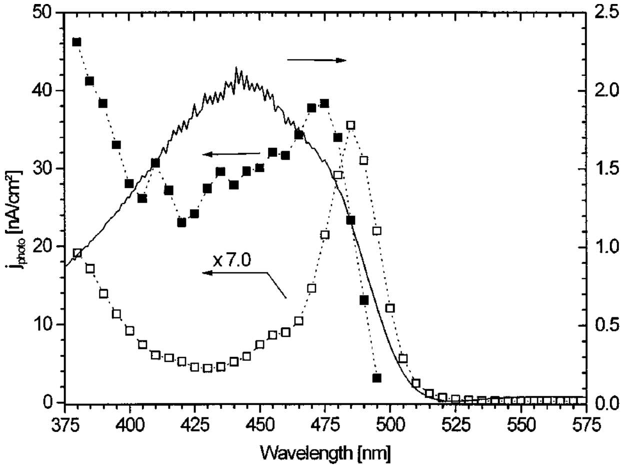


FIG. 1. Photocurrent spectra of a 310-nm-thick Au/arylamino-PPV/Al sandwich device. An external voltage of 2 V (E=6.45 V/μm) was applied, with the Au electrode biased as anode (■) and as cathode (□). j_{photo} is defined as the difference in current with and without illumination. The spectra were recorded in dry nitrogen atmosphere ($p=1$ bar) at room temperature. The sample was illuminated through the Au bottom electrode with a constant photon flux of 10^{13} ph/(cm^2 sec) at the film side facing the light source. The absorption spectrum of the sample is also shown (solid line).

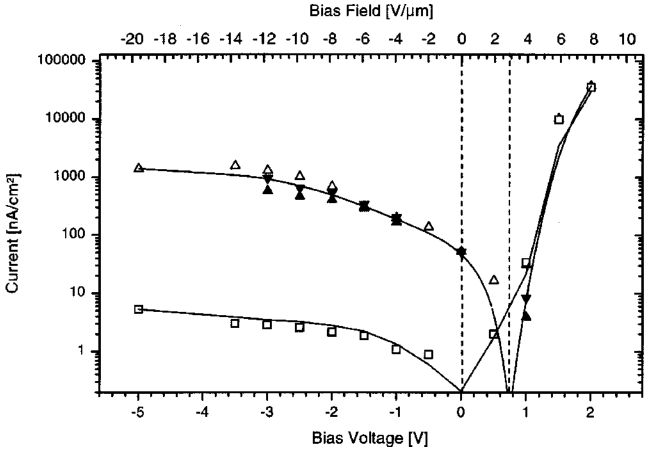


FIG. 2. Current voltage characteristics of a 255-nm-thick Au/arylamino-PPV/Al device. Squares represent currents without illumination, triangles are data recorded under different illumination conditions. Illumination through Al was at $\lambda=450$ nm (△) with a constant photon flux of 1.5×10^{12} ph/(cm^2 sec). For illumination through Au a photon flux of 10.5×10^{12} ph/(cm^2 sec) was used and excitation wavelengths were $\lambda=375$ (▲) and 485 nm (▼). Experimental conditions were the same as for Fig. 1. No dark current correction has been made to the currents recorded under illumination. The electric field applied to the Au contact is indicated at the upper x axis.

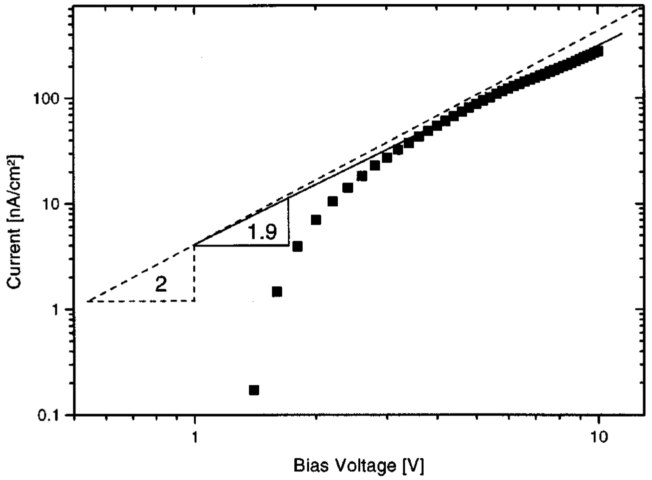


FIG. 3. I/V characteristic of the dark current in a 5.6-μm-thick Au/arylamino-PPV/Al device. The linear increase for high bias fields is shown by the solid line. For comparison theoretical expectations for space-charge limited currents are indicated by the dashed line. Experimental conditions were the same as for Fig. 1.

behavior of the devices (Fig. 2). Current densities under reverse bias (j_-) were very low, indicating that the barrier for hole injection from the Al top electrode must be large. When the bottom electrode was biased as the anode the current rose rapidly with increasing voltage. Close inspection of the I/V characteristics of thick samples at voltages larger than 2 V revealed space-charge limited current (SCLC) behavior $j\propto U^2$, indicating that at forward bias the current through the device is mostly determined by the transport of charge carriers through the film (Fig. 3). Using

$$j_{\text{SCLC}}=\frac{9}{8}\,\varepsilon_0\varepsilon\mu\,\frac{U^2}{d^3} \tag{1}$$

and $\varepsilon=3$ the mobility was estimated to be $\mu=2.06\times10^{-6}$ cm^2/V s. As electrons are rather immobile in PPV's, this mobility may be identified as the hole mobility in arylamino-PPV. Note that this value lies well between the low-field hole mobility for poly(dialkoxy-p-phenylene vinylene) as determined from SCLC experiments[23] and that in PPV measured with the time-off-flight technique.[24] Absolute values of j_{light} under reverse bias measured upon illumination from the Al electrode ($\lambda=450$ nm) and from the Au side ($\lambda=375$ and 485 nm) were larger than j_{dark}. An open circuit voltage of 0.75 ± 0.1 V could be inferred from the abscissa intercept of j_{photo} under forward bias. This reflects the difference in work function between Au (5.2 eV) and Al (4.3 eV).[25] As a result of this built-in voltage j_{light} was smaller than j_{dark} for forward bias voltages $\lesssim1$ V, whereas for higher voltages $j_{\text{light}}>j_{\text{dark}}$.

Figure 4 compiles data on the spectral dependence of j_{photo} of a 305-nm-thick Al/arylamino-PPV/Au device for reverse and forward bias and upon excitation through Al and Au, respectively. Again, the difference between j_+ and j_- over the whole wavelength range reflects the asymmetry of the device. The large range of the charge collection efficiencies for the different excitation and bias conditions indicates that processes other than intrinsic charge carrier generation might contribute to j_{photo}. The efficiencies have been calculated under the assumption that all photons are absorbed. A correction to the number of absorbed photons has not been performed, as due to the very small optical density in the tail of the polymer absorption this would lead to large errors in the calculation of the number of absorbed photons in the long-wavelength range. Therefore, the wavelength below

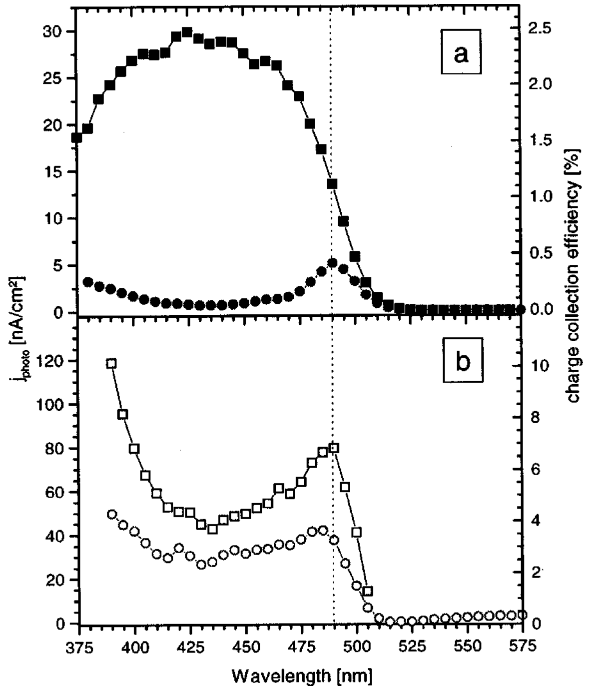


FIG. 4. Photocurrent spectra of a 310-nm-thick Au/arylamino-PPV/Al sandwich device. Illumination was through the Al electrode (squares) and through the Au electrode (circles) with a constant photon flux of 7.5×10^{12} ph/(cm^2 sec) at the film side facing the light source. An external voltage of 2 V ($E=6.45$ V/μm) was applied, with the Au electrode biased as cathode (a, solid symbols) and as anode (b, open symbols). The spectrum was recorded at room temperature in dry nitrogen atmosphere ($p=1$ bar) and j_{photo} was calculated as the difference in current with and without illumination. Charge collection efficiencies calculated under the assumption that all incident photons are absorbed in the film are indicated at the right ordinate. The dotted line indicates the wavelength above which the transmission of the film exceeds 10%.

which the absorption is higher than 90% and for which, thus, correction is not at all necessary, is indicated in the figures.

The same set of experiments has been performed on thick dropcast films. For a 7.5-μm-thick arylamino-PPV film sandwiched between Al and Au electrodes and Au being negatively biased, the spectral dependence of j_{photo} was the same as for thin films [Fig. 5(a)], except that the onset of j_{photo} is shifted to longer wavelengths. Photocurrents and charge collection efficiencies were, however, two orders of magnitude higher for thick devices. Under forward bias the photoaction spectra were clearly different from those of thin films [Fig. 5(b)]. Here, a relatively narrow peak located at the onset of the polymer absorption was found upon irradiation through Al and Au, respectively.

The spectral dependence of the photocurrent of a second device of 6.7 μm thickness under reverse bias is shown in Figs. 6(a) and 6(b) as a function of bias. For these experiments, ITO was used as the bottom electrode instead of Au, but it turned out that both electrode materials give similar photocurrents for illumination through the substrate within the main polymer absorption. This device which had a rather rough surface exhibited even higher collection efficiencies for illumination through the top electrode under reverse bias.

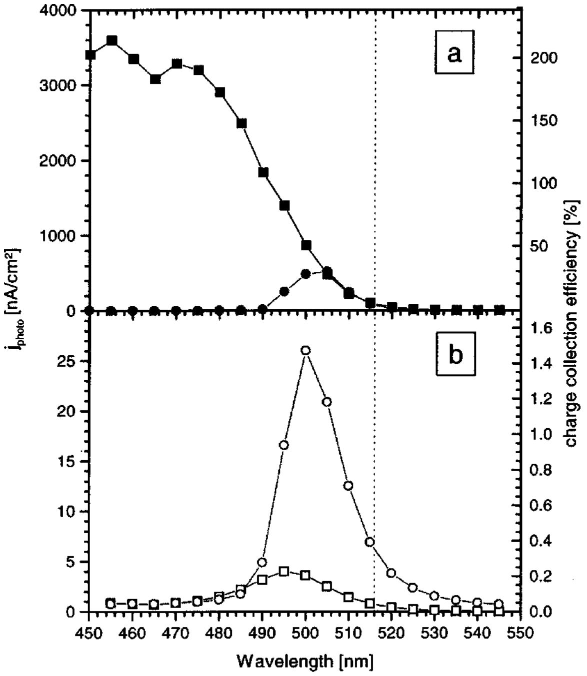


FIG. 5. Photocurrent of a 7.5-μm-thick arylamino-PPV film sandwiched between Au and Al electrodes. The device was illuminated through Al (squares) and through Au (circles) with a constant photon flux of 7.5×10^{12} ph/(cm^2 sec). If Au was biased as the anode (b, open symbols) an external voltage of 2 V (E=0.27 V/μm) was applied. In the case of Au being the cathode the external voltage was 100 V ($E=13.3$ V/μm) (a). Experimental conditions were the same as for Fig. 5. The right ordinate gives the charge collection efficiencies for all spectra. The dotted line indicates the threshold wavelength for 10% transmission.

IV. DISCUSSION

A. Photocurrent under forward bias

The j_{photo} of spincoated arylamino-PPV samples for illumination through the positively biased Au electrode [Fig. 4(b)] does not follow the absorption of the material. The shape of the photoaction spectra indicate an efficient photogeneration of charge carriers in the tail of the polymer absorption. In particular, photoaction spectra for thick Au/arylamino-PPV/Al samples under forward bias were dominated by a pronounced peak at the edge of the polymer absorption. Under these conditions the material was completely illuminated throughout the whole thickness and, due to the large film thickness, the total number of excitons generated per time unit was still high. Since similar shapes of the photoaction spectra are observed for both illumination directions, surface-near generation processes in conjunction with a filter effect by the polymer absorption can be safely excluded.

There is a striking similarity between the photoaction spectra and the photoluminescence-excitation (PLE) spectra measured on the same sample (Fig. 7). As the underlying mechanism for photoluminescence and for photoconductivity is the generation and the decay of excitons in the polymer, this finding was not completely surprising. However, the shape of the PLE spectra depends strongly on sample thickness and differs significantly from spectra measured in dioxane solution and in films of only ≈100 nm thickness,

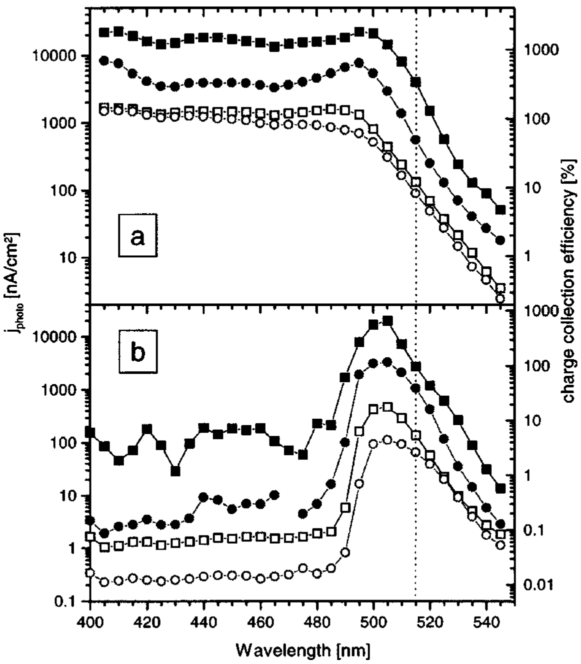


FIG. 6. Field dependence of the photocurrent of a 6.7-μm-thick arylamino-PPV film sandwiched between ITO and Al electrodes. The photon flux for illumination through Al (a) and through ITO (b) was 7.5×10^{12} ph/(cm^2 sec) and 1.5×10^{13} ph/(cm^2 sec), respectively, and was kept constant for all wavelengths. ITO was biased as cathode with external voltages of 100 V ($E=14.92$ V/μm) (■), 75 V ($E=11.19$ V/μm) (●), 50 V ($E=7.46$ V/μm) (□) and 30 V ($E=4.48$ V/μm) (○). Experimental conditions were the same as for Fig. 5. Charge collection efficiencies calculated under the assumption that all incident photons are absorbed in the film are shown at the right ordinate. The dotted line indicates the wavelength above which the transmission of the film exceeds 10%.

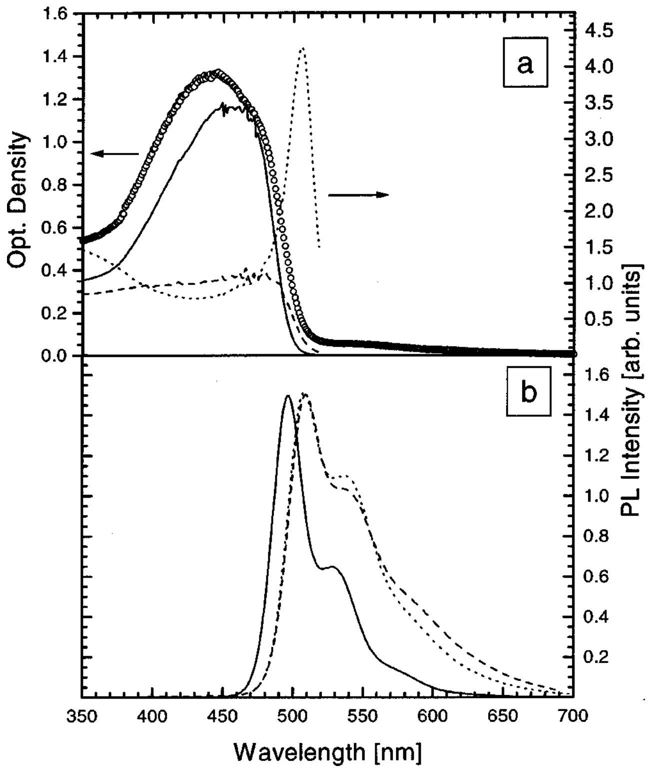


FIG. 7. Photoluminescence excitation spectra (a) and emission spectra (b) of arylamino-PPV. Solid lines represent data for a dilute solution, dashed lines were measured on a 255-nm spincoated sample and dotted lines on a 7.5-μm-thick film. The excitation spectra were recorded for an emission wavelength of 540 nm. For the fluorescence spectra the samples were excited at 350 nm. The absorption spectrum of the 255-nm-thick spincoated sample is shown by open circles. All spectra were recorded at ambient conditions.

whereas the PL emission spectra remain unchanged (Fig. 7). A detailed analysis of the possible extrinsic and intrinsic processes that can lead to this behavior is a subject discussed elsewhere,[26] and a brief discussion with respect to the photocurrent spectra can be found later in the text.

The observation that $j_{+\mathrm{Au}}$ is higher than $j_{-\mathrm{Au}}$ by almost one order of magnitude has often been attributed to photoinjection of holes from the positively biased Au (or ITO) electrode. This process can exceed intrinsic photogeneration by usually 1–2 orders of magnitude.[16,17] The unipolar photocurrent arises from excitons that can reach the electrode within their lifetimes where the electron is dragged into the anode, leaving a free hole in the polymer layer. Since the lifetime of excitons in disordered polymer layers barely exceeds 1 ns the photoaction spectrum caused by photoinjection generally matched the absorption. However, this process can be ruled out in case of arylamino-PPV for several reasons. First, $j_{+\mathrm{Al}}\approx j_{+\mathrm{Au}}$ within the polymer absorption, even though the penetration depth of light was smaller than the film thickness. This is particular true for the thick polymer layers. Second, as mentioned above, j_{photo} as a function of wavelength did not follow the absorption spectrum for either illumination direction but it almost matched the photoluminescence excitation spectra. This fact is most evident when comparing the photoaction and PLE spectra of thick samples [Figs. 5(b) and 7] and indicates that $j_{+\mathrm{Au}}$ and $j_{+\mathrm{Al}}$ originate mostly from bulk processes. Photoinjection of holes from the positively biased Au electrode must, therefore, be quite inefficient in our sandwich devices. Similar conclusions have been drawn from photocurrent experiments on a related amino-PPV compound.[17] One reason for a low efficiency of photoinduced hole injection might be a low barrier at the interface due to the low ionization energy of the amino-PPV compound. Considering the reversible oxidation potential (0.66 V versus Ag/AgCl) of the arylamino-PPV and assuming an absolute work function of the Ag/AgCl reference system of 4.7 eV (Refs. 27 and 28) the barrier for hole injection from Au (work function $\phi_{\mathrm{Au}}=5.1-5.4$ eV) should indeed be rather small.

For a homogeneous photoconductor without surface contributions the photocurrent is given by[29,30]

$$j_{\mathrm{photo}}=G\Phi_{\mathrm{cg}}\,\frac{\text{Absorbed photons}}{\text{Area}\times\text{Time}}. \tag{2}$$

Here, Φ_{cg} is the efficiency for charge carrier generation and G is the photoconductivity gain. The gain is strongly influenced by the type of photoconductor, depending on whether only one or both carriers are mobile or whether or not carriers can be replenished at the electrodes. The Al electrode is a blocking contact for both the injection of holes and electrons while the appearance of SCLC already at rather moderate bias indicates that holes can enter the polymer rather easy through the Au/polymer interface. In this case the gain is given by

$$G=\tau(\mu_n+\mu_p)\,\frac{U}{d^2}, \tag{3}$$

where μ_n and μ_p are the mobilities of electrons and holes, respectively, and τ is the lifetime of the nonreplenished carrier (electron), which is terminated when either the electron leaves the film into the cathode or recombines with a hole. For $\mu_n \ll \mu_p$ the gain in Eq. (3) can be expressed as the ratio between τ and the transit time for holes t_h. In the absence of recombination τ is given solely by the electron transit time and the upper limit for G is reached:

$$G_{\max}\cong\frac{\mu_p}{\mu_n}. \tag{4}$$

Thus, large gain factors leading to charge collection efficiencies much larger than unity can be expected. Under forward bias, even at moderate fields, a large number of holes is diffusing towards the negative Al electrode. It is thus expected that the electron lifetime is terminated by recombination with holes rather than by escape into the electrode. For bimolecular recombination

$$\frac{dn}{dt}=-\frac{n}{\tau}=-\gamma np. \tag{5}$$

Here, n and p are the electron and hole densities, respectively. The recombination coefficient for Langevin recombination is given by[31]

$$\gamma=\frac{e(\mu_n+\mu_p)}{\varepsilon_0\varepsilon}. \tag{6}$$

For a constant hole current (neglecting recombination or space-charge effects) p is equal to

$$p=\frac{j_h}{e\mu_h F} \tag{7}$$

with F the field across the sample. In this case the decay of the electron density is given by the recombination lifetime

$$\tau_r=\frac{\varepsilon_0\varepsilon F}{j_h}, \tag{8}$$

yielding

$$G=\frac{\tau_r}{t_h}=\frac{\varepsilon_0\varepsilon\mu_h U^2}{j_h d^3}\cong\frac{j_{h,\mathrm{SCLC}}}{j_h}. \tag{9}$$

Thus, for all cases a gain larger than unity is expected if the current is smaller than the limiting space-charge limited current $j_{h,\mathrm{SCLC}}$. We have estimated τ_r and t_h for the thin and thick device under a forward bias of 2 V. At this condition j_h is approximately 10.000 nA/cm^2 for a 310-nm-thin layer and 5 nA/cm^2 for the 7.5-μm-thick sample. Assuming a hole mobility of 2×10^{-6} cm^2/V s we obtain $\tau_r\approx2$ ms, $t_h\approx0.2$ ms for the thin layer and $\tau_r\approx t_h\approx0.15$ s for the thick film. Thus a gain larger than unity is predicted for the thin layer while $G\approx1$ for the thick layer. Note, that the Au/arylamino-PPV contact is not fully Ohmic. Close inspection of the current/voltage curves for the thin (Fig. 2) and thick device (Fig. 3) proves that the current under 2 V forward bias is not transport limited, indicating that a certain barrier for hole injection is still present. Thus, replenishing of holes might be restricted, which reduces the photoconductivity gain. Evidence for nonunity gain in the thin layer devices under forward bias stems from the difference between $j_{+\mathrm{Au}}$ and $j_{+\mathrm{Al}}$. While an argumentation based on mobilities would predict a higher photocurrent for illumination through the anode (when the electron does not need to travel through the whole film) the inverse effect is observed. If, however, the gain is larger than unity and proportional to the lifetime of the electrons in the film, this effect will be less prominent when electrons are generated very close to the anode, where they can be dragged into the electrode rather fast before recombining with an injected hole. In accordance with this photocurrents are similar in thick devices for both illumination directions when the wavelength is within the main absorption band of the polymer. Since $j_h\approx j_{h,\mathrm{SCLC}}$ for the thick device at 2 V, $G=1$ and the charge collection efficiency should be equal to the quantum efficiency of charge generation. Note, however, that with an electron mobility of 10^{-8} cm^2/V s and a field of 6.5 V/μm an electron still needs approximately 15 ms to drift over a distance of 100 nm, which is well above the recombination time in the thin layer. A more detailed discussion would require knowledge of the electron mobility in this material.

Comparing the two illumination directions under forward bias for thick samples, we consistently observed a higher photocurrent maximum for illumination through the hole injecting electrode, even though photocurrents are the same within the main polymer absorption range. This seems to be inconsistent with our interpretation that the photoconductivity under these conditions is given by bulk photogeneration of charges and $G=1$, only. We have performed some preliminary xerographic photogeneration experiments on approximately 6 μm samples. At the same field strength as for the experiments shown in Fig. 5(b) the photogeneration efficiency was approximately 0.05% at the main polymer absorption peak and increased to about 0.15% at 491 nm. This is quite similar to the values found for illumination through the negatively biased aluminum electrode. The reason for the high peak photocurrents upon illumination through gold is so far not understood. One might assume that the field profile is rather inhomogeneous for SCLC, leading to a spatial variation of the generation yield in the polymer layer. At a forward bias of 2 V the current has, however, not completely entered the space-charge limited current regime and the field is expected to be still rather homogeneous.

B. Photocurrent under reverse bias

In the case of Au being negatively biased dark currents and consequently hole densities were much lower than under forward bias and charge carriers could not easily be replenished by the electrodes. Therefore, the restricted electron mobility in arylamino-PPV is expected to influence the photoaction spectra significantly under reverse bias conditions. In particular, the buildup of a negative space-charge region in the bulk should reduce the photoconductivity gain, except for photons being absorbed close to the electron-collecting anode (Al). Therefore, j_{photo} should follow the absorption spectrum for illumination through the Al electrode while an antibatic behavior is expected for illumination through Au. In accordance with this $j_{-\mathrm{Al}}$ for the thin devices followed an almost symbatic behavior, but the photocurrent spectrum was broadened towards longer wavelengths. $j_{-\mathrm{Au}}$ was smaller than $j_{+\mathrm{Au}}$ and $j_{+\mathrm{Al}}$ within the polymer absorption range and peaked at the edge of the polymer absorption, where the absorption of photons near the electron-collecting Al contact was maximized. Similar features were observed for the photocurrent of thick films under reverse bias and upon illumination through Al, but in this case charge collection efficiencies were even above unity, with values of up to 2000%. These observations clearly indicate that extrinsic processes contribute to j_{photo} under reverse bias and that they most likely occur near the polymer/Al interface.

High charge collection efficiencies well exceeding 100% have been explained by photocurrent multiplication. The effect was well established in amorphous silicon carbide films, where photocurrent multiplication of 300 times could be observed.[32] In later studies on low molecular weight organic pigment films the multiplication increased to up to 130 000-fold.[33,34] This phenomenon was interpreted in terms of tunneling injection from a metal electrode under a high electric field that is caused by the accumulation of photogenerated charge carriers near a blocking contact. Bearing the high surface roughness of our samples (especially of thick films prepared by dropcasting), in mind, the following situation seems to be reasonable: The evaporated Al electrode on top of the polymer film can not follow the high surface roughness and thus yields areas where the contact between the metal and the polymer is poor or even nonexistent. Photogenerated electrons might become trapped in these regions of poor contact as they can not reach the electrode. Accumulation of those trapped electrons close to the interface would then give rise to high space-charge fields, resulting in enhanced Fowler-Nordheimer-type tunneling of holes from the positively biased Al electrode into the polymer film.

There are several indications that the corresponding photoactive zone for the generation of electrons extents quite deep into the layer. The spectra for illumination through Al are considerably broadened towards longer wavelengths when compared to the absorption spectra. For illumination through Au the photocurrent $j_{-\mathrm{Au}}$ increased already at wavelengths where the transmission of light through the film was still well below 10% and only a small number of photons reached the polymer/Al interface. These effects were more evident for thick films.

While the existence of photocurrent multiplication processes under reverse bias is clearly proven by the collection efficiencies well above unity for thick samples, this process might be less prominent for thin spincoated samples. Based on our data we can neither exclude nor prove the presence of this contribution in thin layers. Note, however, that the surface roughness of spincoated films is rather small in comparison to thick devices.

C. Photogeneration yields

Setting $G=1$ the quantum yield for photogeneration at 475 nm derived from $j_{+\mathrm{Al}}$ or $j_{+\mathrm{Au}}$ in Fig. 5(b) is 0.05% at a field of 0.27 V/μm. At the same wavelength, taking $G\approx 10$, $j_{+\mathrm{Al}}$ in Fig. 4(b) gives $\phi_{cg}\approx 0.6\%$ at a field of 6.5 V/μm. These values are large compared to the carrier generation yields at the same electric fields for polyphenylvinylene[16] or a PPV-ether,[17] and they even exceed yields determined for a related PPV-amine.[17] We propose that the presence of a strong hole-attracting moiety such as the diphenylamino group in the PPV-amine or the TPA segment in our arylamino-PPV drastically enhances the photogeneration yield. But, while the PPV-ether exhibited a constant rise in quantum yield with increasing photon energy, our experiments showed an enhanced response at the absorption edge. In those experiments on PPV-amine sandwich cells only thin samples with typically 100-nm-thick spin coated films were used and thus the total number of photons absorbed in the film at the absorption edge was low. Considering the shape of the photoaction spectra of the arylamino-PPV samples under forward bias we can conclude that even though there is a clear enhancement in photogeneration efficiency at the edge of the absorption, the photocurrent starts to decay gradually at wavelengths where both the thin and the thick samples still absorb more than 90% of the incident light. There are, however, no distinct features in the polymer absorption spectrum, which relate to this particular wavelength region of maximum photoresponse. The analysis of the wavelength and field dependence of the photogeneration efficiency in arylamino-PPV will be subject to further xerographic studies.

A closer inspection of the PL excitation spectra and the photoaction spectra under forward bias leads to the conclusion that the PL intensity and the photocurrent scales with the penetration depth of the exciting light. For example, the PL intensity measured on a thick film is lowest if the penetration depth of the light is short (the fluorescence quantum yields are as small as 5% in the solid state compared to a yield of ≈66% in solution[35]) The particular shape of the spectra can be interpreted as the excitation of localized active sites with extended absorption in the red, diluted in nonfluorescent surroundings attributed to the majority of polymer chains. Those sites might be assigned to isolated long chains in the high molecular weight fraction of the material or, less likely, stable aggregates of chains, and thus represent an intrinsic property of the bulk material. Alternatively a transition in the tail of the absorption with a weak oscillator strength in absorption but with a large fluorescence yield and charge generation efficiency can be proposed, presuming that energy relaxation from higher excited states is almost absent. Such a transition with high charge generation efficiency might also exhibit a pronounced charge transfer character as mentioned in the introductory chapter but a final assignment of the optical transitions in arylamino-PPV requires further investigation.

We like to point out that PLE spectra of PPV samples with enhanced response within the tail of the absorption have recently been reported[15,36] In this case electron accepting carbonyl groups were created near the surface of the film by photooxidation. At the same time the photogeneration was largest for wavelengths where the light penetrates only a small distance into the film. It has been concluded that the emissive species are not responsible for the extrinsic photoconductivity. Our investigations on arylamino-PPV show similar shapes of the photoaction (under forward bias) and PLE spectra measured on the same samples. We do, therefore, conclude that the particular shapes of the PLE and photoaction spectra are not due to photooxidation close to the surfaces and that photoconductivity and photoluminescence involve the same species.

IV. CONCLUSIONS

The dependence of the shape and size of photocurrent spectra of sandwich devices of arylamino-PPV between Au and Al on bias and illumination conditions seems to be strongly related to the presence of mobile holes in the film. Under forward bias a strong hole current flows through the device. Therefore, electrons which are photogenerated in the film will easily recombine with holes and there will be no buildup of a negative space-charge region due to trapped electrons. The photocurrent is then proportional to the charge carrier generation rate and the lifetime of the separated geminate charge carrier pair. Under these conditions the photoaction spectrum is dominated by bulk photogeneration and photoaction spectra are almost identical for illumination through either the bottom and top electrode. In thin films the transit time for holes is estimated to be smaller than the electron-hole recombination time and a photoconductivity gain larger than unity is predicted. Photogeneration efficiencies as deduced from the photoaction spectra under forward bias are rather large. Values of approximately 1% at a field of only 6.5 V/μm are among the highest efficiencies ever reported for pure PPV derivatives. No interface effects such as photoinduced charge injection could be identified. For both thin and thick layers the photoaction spectra resemble well the shape of the corresponding photoluminescence excitation spectra.

Under reverse bias dark currents are extremely low and presuming a low electron mobility, there will be a buildup of a negatively charged space-charge zone by photogenerated electrons. If light is penetrating through the cathode (Au) the buildup of this zone in the bulk of the film reduces the photocurrent well below values recorded under forward bias. If, however, light penetrates through the anode (Al) accumulation and trapping of electrons close to the electrode will create an additional space-charge field, which promotes the tunneling injection of holes into the film. This mechanism explains in particular the high collection efficiency of up to 2000% under this illumination and bias condition. Again, additional extrinsic processes such as photoinduced electron injection might be possible, but they could not be identified based on our experiments.

We like to point out that the studied PPV derivative has a rather low ionization potential (0.66 V versus Ag/AgCl), which closely matches the work functions of ITO (4.8 eV) or Au (5.1–5.4 eV). This gives rise to a very pronounced rectifying current-voltage diode behavior with rectifying ratios of up to 10^4 at 2 V. Consequently hole densities will be large even at low forward bias fields. Also, the close match between the polymer highest occupied molecular orbital and the work function of the hole injecting contacts might reduce extrinsic contributions such as the photoinjection of holes at the contact.

As a concluding remark we like to stress that the analysis of photoaction spectra recorded under different conditions such as both illumination directions, various film thicknesses, and bias is essential for the identification of the dominant charge generation processes such as bulk photogeneration and photocurrent multiplication phenomena. For example, the pronounced peak in the photoaction spectra of thick samples under forward bias and for illumination through the anode could be easily misinterpreted as an antibatic peak, with a predominant charge generation close to the cathode. Only taking into account the experimental results under the same bias but with illumination through the cathode could exclude this interpretation.

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