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Space Charge Distribution in Luminescent Conjugated Polymers

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Summary: We have used for the first time the laser intensity modulation method (LIMM) to resolve the depth profile of space charges in films of poly[(2-(2-ethylhexyl)-5-methoxy-1,4-phenylene)vinylene] (MEH-PPV), poly(pyridine-2,5-diyl) (PPY) and poly(fluorene) (PFO). The results demonstrate that in conjugated polymers space charges can not only be created but also stored permanently.

Keywords: conjugated polymers; light-emitting diodes

Introduction

Impressive scientific and technological progress has recently been achieved in the area of organic light-emitting diodes. An equal fundamental research motivation has been the desire to better understand and control charge injection into, charge migration through, and radiative recombination in macromolecular solids. Charge injection is influenced by space charge distribution1) and therefore it is of fundamental interest to know whether the current in the device is injection-limited or transport-limited2). If the barrier height ϕ between the electrode work function and the HOMO or LUMO levels of the polymer is lower than about 0.3 eV in most conjugated polymers, the injection rate becomes higher than the transport rate in the bulk of the polymer, thus charge is injected faster than it can be transported in low-mobility materials. The result is an accumulation of space charge near the injecting contact, which shields the external electric field and hinders further charge injection. On the other hand, if the injection barrier is high (about 1 eV), the injection rate becomes so low that every injected charge can be led away fast enough. Thus a very small and homogeneously distributed space charge is expected in such systems.

We used for the first time a well established thermal wave method (laser intensity modulation method, LIMM)3,4) to resolve the depth profile of space charge and the distribution of the internal electric field in 3-4 μm films of poly[(2-(2-ethylhexyl)-5-

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methoxy-1,4-phenylene)vinylene] (MEH-PPV), poly(pyridine-2,5-diyl) (PPY) and poly(fluorene) (PFO).

Experimental

MEH-PPV, PPY, and PFO were synthesised as described previously$^{5)}$. 4-5 µm films were prepared by spin coating from a polymer solution onto glass substrates that carry a 100-nm gold electrode (rear electrode). A second 100-nm gold electrode (front electrode) was evaporated on top of the film and covered with a 20-nm bismuth layer to enhance the heat absorption of the laser beam.

The LIMM experiment is explained in more detail elsewhere$^{6)}$ and only briefly described here. The set-up (Fig. 1) consists of a HeNe laser, its beam being intensity-modulated by an acoustic-optical modulator with a frequency f supplied by a frequency generator. The laser beam hits the front electrode. Heat is absorbed and transformed into a heat wave that penetrates into the sample. The pyroelectric response of the sample is detected as a small AC current between the gold electrodes, which is amplified by a current-to-voltage converter (CVC) using a gain of 10^5 V/A and measured with a lock-in amplifier.

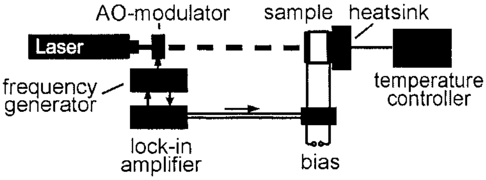

Fig. 1: Experimental set-up for the laser intensity modulation method (LIMM).

In addition, a galvanic decoupler has been used to allow the application of a DC bias to the very sensitive AC current measurements across the sample electrodes.

Depending on the modulation frequency f of the incident laser beam and on certain thermal parameters of the material, the heat wave establishes a dynamic temperature profile $T(z)$ with respect to the coordinate z along the film normal. The resulting inhomogeneous thermal expansion modifies the space charge distribution $r(z)$ and gives rise to a small pyroelectric current (with A irradiated area, L film thickness)

$$I_{\mathrm{p}}(f) = 2\pi \mathrm{i} \cdot f \cdot \frac{A}{L} \int_0^L r(z) \; T(f,z) \; \mathrm{d}z . \qquad (1)$$

After measuring $I_p(z)$, the distribution function $r(z)$ has to be inferred via inversion of the integral Equation 1 using the temperature profile $T(f,z)$, that can be calculated for the specific thermal parameters. This is, however, known to be an ill-posed inverse problem. In order to solve such ill-posed inverse problems, special mathematical methods, i.e. regularisation methods, are necessary.

Results

Figure 2 shows a typical LIMM spectrum of a 4-μm thick PPY sample between Au electrodes. The sample was poled using a DC electric field of 25 MV/m for several minutes and measured under electric field.

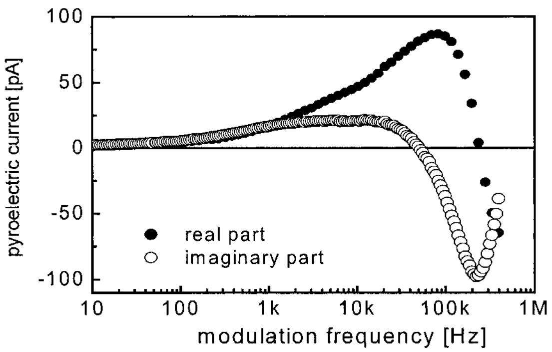

Fig. 2: LIMM spectrum of a Au/PPY/Au sample with laser incident on the front electrode. Measurements were performed at room temperature using an applied electric field of 25 MV/m.

The lower panel of Fig. 3 shows the space charge profile in the PPY film. Directly behind the front electrode, a pronounced space charge layer is detected, which has the same polarity as the nearby electrode and is therefore denoted as a homo-charge layer. Deeper in the bulk of the film, at about 500 nm, a second weaker space charge layer is found that is of opposite polarity (denoted as hetero-charge layer). The upper panel shows the electric field profile in the film, demonstrating how the accumulated space charge distorts the internal field. We assign the positive layer to be due to the injection of positive charge carriers from the anode into near-surface traps and the second hetero-charge layer to intrinsic charge carriers that have been separated within the external electric field and accumulated in the trapping zone.

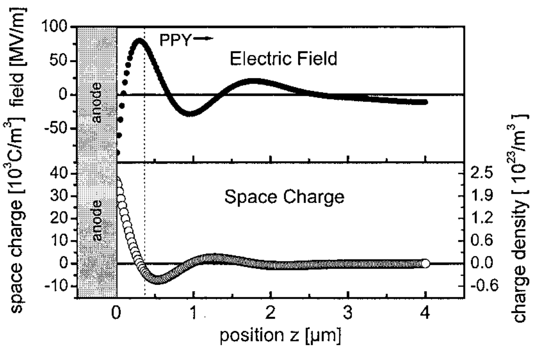

Fig. 3: Distribution of electric field (upper panel) and space charge (lower panel) obtained from the LIMM spectrum in Fig. 2 via regularisation.

The stability of the accumulated space charge was investigated by measuring the pyroelectric signal for different values of the applied electric field. Figure 4 shows such pyroelectric current - voltage curves.

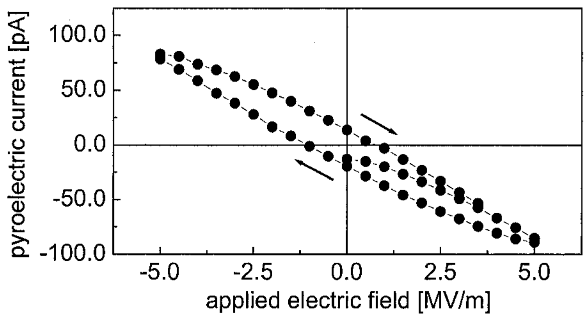

Fig. 4: Pyroelectric current-voltage characteristics of a 4-μm thick Au/PPY/Au sample. To account for the slow response of the pyroelectric signal to changes of the external bias, the sample was allowed to settle for 10 min before each bias reading. Measurements were performed at room temperature using a modulation frequency of 33 kHz.

Obviously the pyroelectric current shows clear hysteresis behaviour. Thus, the polymer can be charged by application of an electric field. A significant amount of the accumulated charge remains stored in the material and can only be removed by an electric field. An assessment of the magnitude of the charge density profile allows to estimate the density of permanently stored charge to be as high as 2×10^{21} m^{-3}. In PPY space charges can not only be created but also stored.

We have compared the pyroelectric response of PPY with that of other conjugated polymers, i.e. with MEH-PPV and PFO. The LIMM spectra for the three polymers using equal external electric field and electrode configuration are depicted in Fig. 5.

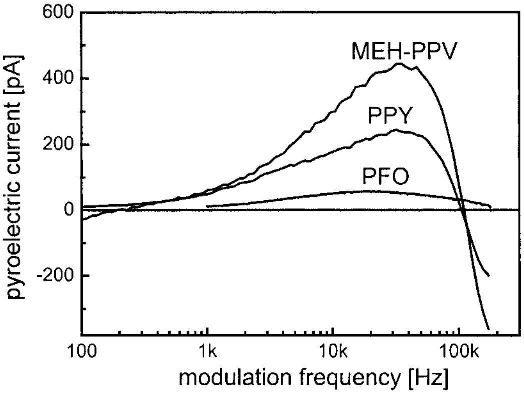

Fig. 5: LIMM spectra of the three conjugated polymers under investigation represented by their real part. All three polymers where subjected to an electric field of 25 kV/m and measured at room temperature.

As expected, enhancement of the space charge accumulation is found in MEH-PPV corresponding to the lower injection barriers for holes ($\phi\approx0.3$ eV). On the other hand, it is noticeable that the pyroelectric current in PFO is much weaker than in PPY, although hole injection should also be improved due to a lower barrier height (ϕ(Au-PFO) ≈0.6 eV and ϕ(Au-PPY) ≈0.9 eV). Furthermore, neither in MEH-PPV nor in PFO, a considerable poling effect could be measured. After removing the external bias, the pyrocurrent returned to zero or to a constant, very small value.

The three polymers were subjected to an instantaneous switching of the external bias and the temporal pyroelectric response was observed. This reveals another difference in the charge accumulation and transport behaviour between the polymers. While, in PPY accumulation and annihilation of space charge occurs in the time scale of several minutes, PFO and MEH-PPV films seem to instantaneously react to an external bias. A more detailed analysis of the temporal pyroelectric current may provide information about the nature and depth of the relevant traps and will be subject of a future work.

Discussion

The results show significant accumulation of space charge in the three conjugated polymers under study with no definite correlation to the injection barrier heights. Especially in PPY, where the difference between the Au electrode work function and the valence/conduction band (HOMO/LUMO) of the polymer is in the range of 1 eV, only small space charge should be expected in the material because of the very low injection rate. We therefore suggest the following model that is illustrated in Fig. 6 to explain the emergence of space charges in these devices.

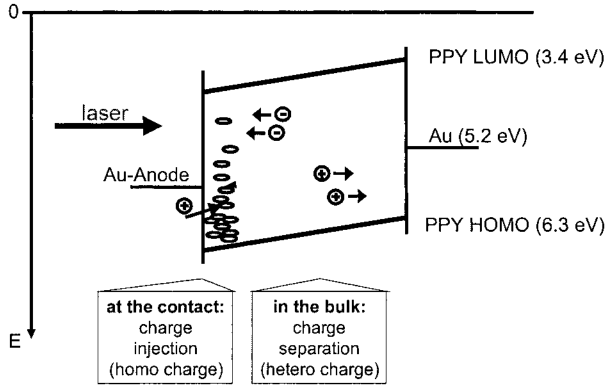

Fig. 6: Proposed model to explain the pyroelectric results in PPY. Charge carriers are injected directly into deep traps at the surface of the polymer layer. Simultaneously, mobile charged states in the bulk are separated by the influence of the external electric field.

We presume an increased concentration of deep traps near the front surface of the sample. These traps can have various origins (intrinsic lattice defects introduced during the casting of the film, extrinsic impurities introduced by the ambient atmosphere before the evaporation of the top electrode, etc.). An injection of carriers is then conceivable by direct transfer from the electrode into the deep traps at the surface rather than over the barrier into the transport level. As a result, deeply trapped charge is accumulated as space charge near the front electrode. Any spatial redistribution of the space charges requires detrapping of the charge carriers and, depending on the depth of the traps, the response to an external bias can be instant or very slow. Detrapping of charge from deep traps in the time scale of minutes has also been reported by Campbell and Bradley7). A more detailed analysis of the pyroelectric current transients will be covered in a later publication.

More difficult to understand is the smaller hetero-charge layer deeper in the bulk of the sample. A possible explanation could be that intrinsic charge arising from charged defects form mobile states (polarons) which subsequently separate in the external electric field. There are, however, also some questions left by this explanation.

Conclusions

In PPY and MEH-PPV, charge storage has a significant influence on the internal electric field in the sample and films can be charged permanently depending on their bias history. The space charge in the polymer cannot follow changes of the external bias instantaneously - the samples are still redistributing internal charges after minutes. This behaviour should be kept in mind when making measurements of electronic properties of these polymers. PFO differs more significantly from the other polymers, showing a very low concentration of deep traps. In addition, the charges in PFO can be redistributed in less than one second since only shallow traps are addressed in this material.

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