Negative capacitance in organic semiconductor devices: Bipolar injection and charge recombination mechanism

E. Ehrenfreund[a)]
Linz Institute for Organic Solar Cells (LIOS), Johannes Kepler University, Altenbergerstrasse 69, 4040 Linz, Austria and Department of Physics Technion, Israel Institute of Technology, Haifa 32000, Israel

C. Lungenschmied, G. Dennler,[b)] H. Neugebauer, and N. S. Sariciftci
Linz Institute for Organic Solar Cells (LIOS), Johannes Kepler University, Altenbergerstrasse 69, 4040 Linz, Austria

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The authors report negative capacitance at low frequencies in organic semiconductor based diodes and show that it appears only under bipolar injection conditions. They account quantitatively for this phenomenon by the recombination current due to electron-hole annihilation. Simple addition of the recombination current to the well established model of space charge limited current in the presence of traps yields excellent fits to the experimentally measured admittance data. The dependence of the extracted characteristic recombination time on the bias voltage is indicative of a recombination process which is mediated by localized traps. © *2007 American Institute of Physics*.
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The study and understanding of the optical and electronic properties of organic light-emitting diodes (LEDs) are of general importance and interest due to their potential as alternatives for classic inorganic LEDs. The light emitted by LEDs is generated by electroluminescence (EL), thus detailed knowledge on bipolar injection and electron hole (e-h) recombination is needed in order to optimize their device performance. Admittance spectroscopy allows us to differentiate between transport and relaxation processes that manifest themselves on various time scales. The emphasis in this work is on the low frequency (ω) regime, where a negative contribution to the capacitance C has been observed in some devices. Under strong bias conditions, the negative contribution dominates at low frequencies and $C(\omega)$ becomes even negative.[1–8] In our devices based on an active layer of a poly(phenylene vinylene) (PPV) derivative, this negative capacitance (NC) phenomenon occurs only when charges of both polarity are injected. We show that the recombination current leads to NC and derive a simple expression for its frequency dependence. The NC dependence on the bias voltage V_b is inconsistent with Langevin-type bimolecular recombination, indicating that the e-h recombination is mediated by localized traps.

The diode devices used in this study were prepared in sandwich geometry based on structured and cleaned indium tin oxide (ITO) covered glass substrates (Merck, Inc.). A 70 nm thick layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (Baytron-PH, used as purchased from H. C. Starck) was applied on the ITO by spin coating. After drying a poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1-4-phenylene vinylene] (MDMO-PPV, from Covion) film was cast from chlorobenzene yielding a 130 nm thick active layer. Al ("device A") or LiF/Al ("device B") top electrodes were deposited via thermal evaporation. The LiF layer has a nominal thickness of 0.7 nm. While a considerable barrier for electron injection exists between Al and MDMO-PPV, an almost Ohmic contact is expected for LiF/Al.[9] The complex admittance $Y(\omega)$ is measured using the HP 4192A impedance analyzer operated in the autobalance mode, with fixed ac amplitude $v_{ac}(\omega)=0.2$ V.

Figure 1 shows a series of measurements of the capacitance $C \equiv \mathrm{Im}(Y/\omega)$ vs $f(=\omega/2\pi)$ from $f=1$ kHz to 1 MHz at various bias voltages ($V_b=+3$ to $+7$ V) for device A (top electrode: Al). For $V_b<7$ V, the main characteristics are (a) a kneelike feature due to the effect of transit time τ_t is observed at $f \simeq 1/\tau_t$;[10,11] (b) at lower frequencies, C is strongly

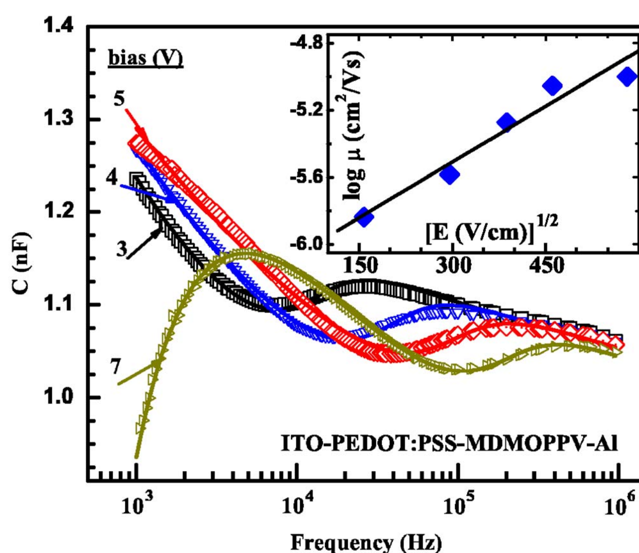

FIG. 1. (Color online) C vs f for device A (Al electron injecting electrode) for $V_b=+3$, +4, +5, +7 V. Empty symbols: measured data; solid lines: fit to the data using Eq. (1); for $V_b=+7$ V Eq. (3) was used as well. Inset: μ_{dc} versus the square root of the net electric field ($E^{1/2}$), extracted using the transit time obtained from the fits. The solid line is a linear fit of $\log(\mu_{dc})$ vs $E^{1/2}$.

a)Electronic mail: eitane@tx.technion.ac.il
b)Presently at Konarka Austria GmbH, Altenbergerstrasse 69, 4040 Linz, Austria.

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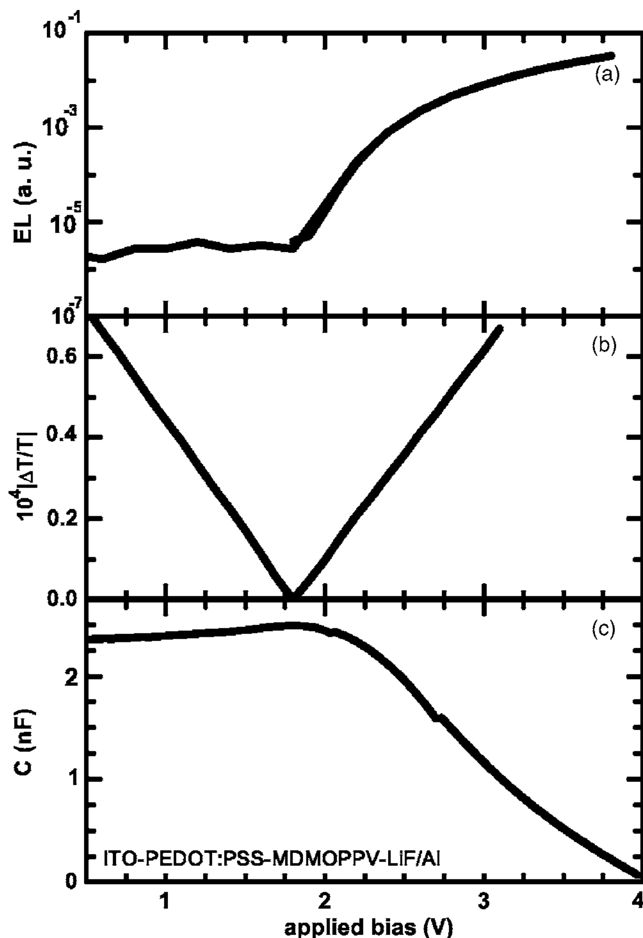

FIG. 2. EL (a), EA (b) and C (c) vs V_b for device B (LiF/Al electron injecting electrode). In (b) the magnitude of EA is plotted. There is a sign change in EA at $\simeq$1.8 V, above which bipolar injection sets on and both EL and negative contribution to C are apparent.

increasing with decreasing f due to trapping.[10,11] The average charge carrier mobility is derived from the extracted transit time using[12] $\mu_{dc}=4L^3/3\tau_t E$, where E is the electric field. The linear dependence of $\log(\mu_{dc})$ on $\sqrt{E}$ (Fig. 1, inset) is characteristic to polymer devices.[11,13] Also seen in Fig. 1 is a negative contribution to $C(f)$ at $f \leqslant 5$ kHz for $V_b=7$ V (and higher bias).

In order to study the negative contribution to $C(f)$ on a broader frequency range we utilized device B in which the LiF/Al electrode allows easier injection of electrons into the active layer. In Fig. 2(b) we show the electroabsorption (EA) magnitude ($|\Delta T/T|$) vs V_b. The zero crossing at $V_b \simeq +1.8$ V yields the internal field V_{int}/L. The actual field across the active layer is therefore $E=(V_b-V_{int})/L$. Figure 2(a) shows that the EL due to e-h radiative recombination sets on just at $V_b \simeq V_{int}$, proving the occurrence of bipolar injection already at this bias. The measurements of $C(f=40$ Hz) in the same voltage range [Fig. 2(c)] show that the negative contribution to C starts concurrently with the bipolar injection. At higher V_b the negative contribution overwhelms and C becomes negative. The results for $C(f)$ vs f in device B (LiF/Al top electrode) for various applied bias voltages are displayed in Fig. 3. In the bipolar injection regime ($V_b>+1.8$ V), the negative contribution to $C(f)$ becomes increasingly important as the frequency decreases. At $V_b \simeq +10$ V the negative contribution dominates and $C(f)$ becomes negative below $f \simeq 4$ kHz. Based on Figs. 2 and 3 we conclude that NC is due to the presence of charges of both polarities within the active layer of the device.

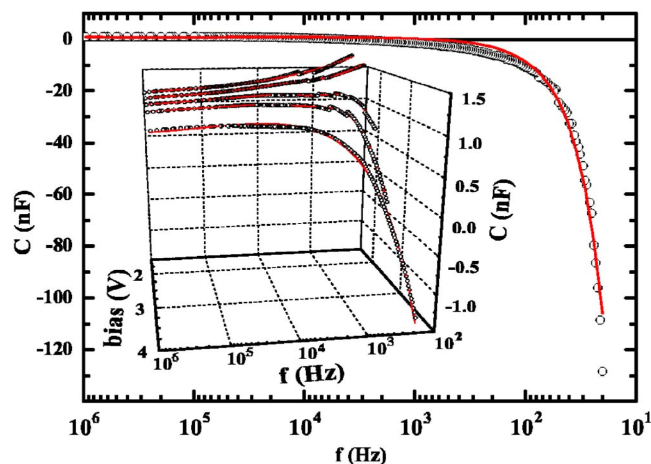

FIG. 3. (Color online) Frequency dependence of the capacitance for device B (LiF/Al electron injecting electrode) at $V_b=+10$ V (two-dimensional plot) and various other bias voltages (three-dimensional inset). Empty symbols: measured data; solid lines: fit to the data using Eqs. (1) and (3).

We first summarize previous models that describe the frequency dependent single carrier transport in low mobility organic diodes. Assuming a space charge limited current (SCLC) device with traps, the admittance is written as,[11]

$$Y_{SC}(\omega) = \frac{C_g}{\tau_t}\left\{\frac{(\omega\tau_t)^3}{2i\tilde{\mu}^2[1-\exp(-i\omega\tau_t/\tilde{\mu})]+2\tilde{\mu}\omega\tau_t - i(\omega\tau_t)^2}\right\}, \tag{1}$$

where C_g is the geometrical capacitance and $\tilde{\mu}$ is a normalized dimensionless mobility defined as $\tilde{\mu}=\mu(\omega)/\mu_{dc}$, where $\mu(\omega)$ is the frequency dependent mobility. In media governed by dispersive transport, we use the expression:[11] $\tilde{\mu}(\omega)=1+M(i\omega\tau_t)^{1-\alpha}$, where α is the dispersive exponent and M is a proportionality constant. The capacitance, $C_{SC}(\omega)=\mathrm{Im}(Y_{SC}(\omega)/\omega)$, calculated using Eq. (1), is then used to fit the measured dynamic capacitance in Fig. 1 for $V_b<7$ V. The resulting fits, shown as solid lines through the data points, appear to be very good, yielding reasonable values for the device parameters: μ_{dc}, α, and M. The parameter values agree very well with previously published data.[11,13] The observed exponential dependence of the mobility on the electric field, $\mu_{dc}=\mu_0\exp(\beta\sqrt{E})$ (see the inset of Fig. 1), is also in agreement with previous measurements. Thus, the description of our device in terms of SCLC including traps is reasonably justified.

Under the conditions of bipolar injection, the active layer contains both electrons and holes. When the e-h recombination rate is finite, there exists a finite volume in which electrons and holes overlap, resulting in a "recombination current." In response to a small voltage step ΔV applied at time $t=0$, and superimposed on a large dc bias, there appears an additional, time dependent, current [denoted hereafter as $j_r(t)$] due to the recombination. $j_r(t)$ should be proportional to the probability of recombination. We expect, then, $j_r(t)$ to monotonically grow from zero at $t=0$ and to reach slowly the steady state value at $t=\infty$. The related capacitance is given by the Fourier decomposition,[14]

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$$\Delta C_r(\omega) = \frac{1}{\Delta V}\int_0^\infty j_r(t)\cos \omega t dt. \quad (2)$$

In general, Eq. (2) yields a negative $\Delta C_r(\omega)$ for $j_r(t)$ as described above (with $dj_r/dt > 0$ and $d^2 j_r/dt^2 < 0$).[15] For example, in a trap mediated monomolecular recombination process, the rate equation for the charge density n is $dn/dt = G - n/\tau_r$, where G is the bias dependent generation rate and τ_r is the recombination time. Applying a small step ΔG at $t=0$ superimposed on a large fixed G, the recombination current is given by $j_r(t) = \Delta n/\tau_r$, where Δn is the additional response due to ΔG. Solving the rate equation we obtain $j_r(t) \propto [1 - \exp(-t/\tau_r)]$. Equation (2) then yields

$$\Delta C_r(\omega) = -\chi C_g/(1+\omega^2\tau_r^2), \quad (3)$$

where χ is a dimensionless parameter that depends on the volume where both electrons and holes overlap and on τ_r. We obtained identical frequency dependence for the negative capacitance in the case of bimolecular recombination. The total capacitance is now given by the simple addition: $C(\omega) = C_{SC}(\omega) + \Delta C_r(\omega)$. In Fig. 3 we show (solid lines) the fits obtained using Eqs. (1) and (3) for the measured capacitance in the bipolar injection regime for various bias voltages. In all cases the fits account very well for the frequency dependence of the measured total capacitance, including the negative contribution.

We envision two possible recombination mechanisms: direct Langevin-type bimolecular recombination and recombination mediated by localized traps. For the bimolecular case, τ_r should decrease with increasing carrier density and mobility. Since the carrier density and mobility increase with bias (Fig. 1), τ_r should decrease with increasing bias voltage. This is not observed: the values of τ_r that we obtained from the fits increase from about 0.5 ms at $V_b = +2$ V to 1–2 ms at $V_b = +10$ V. For the case of trap mediated recombination, on the other hand, τ_r should be interpreted as the characteristic capture time for positive (negative) charge into an already negatively (positively) charged trap. The capture rate is not expected to increase with the bias, hence no decrease in τ_r is expected with increasing bias. Furthermore, the dimensionless parameter χ increases with the bias voltage. This is expected since at higher bias voltage the carrier concentration is higher, thus more traps are involved in the recombination process.

In summary, we have shown that NC at low frequencies occurs in organic semiconducting diodes under bipolar injection and explained it by the e-h recombination. The time dependent recombination current leads to a negative contribution to the low frequency capacitance. By suggesting a simple and straightforward recombination current model, we have accounted for $C(f)$ on a wide frequency range, including the NC region and deduced the characteristic time constant for the capture/recombination process. The bias dependence of τ_r is inconsistent with a bimolecular recombination process. We thus conjecture that in organic bipolar devices, the e-h recombination is governed by trap mediated processes.

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