

Origin of Negative Capacitance in Bipolar Organic Diodes

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 (Received 4 December 2017; published 14 March 2018)

Negative differential capacitance (NC) occurring at low frequencies in organic light-emitting diodes (OLEDs) is a poorly understood phenomenon. We study the origin of the NC effect by systematically varying the number of electron traps in OLEDs based on the polymeric semiconductor poly(*p*-phenylene vinylene). Increasing the electron trap density enhances the NC effect. The magnitude and observed decrease of the relaxation time is consistent with the (inverse) rate of trap-assisted recombination. The absence of NC in a nearly trap-free light-emitting diode unambiguously shows that trap-assisted recombination is the responsible mechanism for the negative contribution to the capacitance in bipolar organic diodes. Our results reveal that the NC effect can be exploited to quantitatively determine the number of traps in organic semiconductors in a nondestructive fashion.

DOI: [10.1103/PhysRevLett.120.116602](https://doi.org/10.1103/PhysRevLett.120.116602)

Impedance spectroscopy is a powerful technique to study charge transport and recombination in semiconductors, since it enables us to differentiate between processes that are relevant on different time scales [1]. In organic light-emitting diodes (LEDs), where electrons and holes are simultaneously injected, a negative contribution to the differential capacitance C has been observed at low frequencies [2–6]. For an applied voltage just above the built-in voltage V_{BI} , the differential capacitance can even become negative. Several explanations have been proposed, including bimolecular recombination [2], electron injection through interfacial states [3], accumulation of charges at an organic-organic interface [4], trap-assisted monomolecular recombination [5,6], self-heating [7], and energetic disorder [8]. The concept of a negative capacitance in semiconducting devices was first discussed by Ershov *et al.* [9]. Recombination of electrons and holes results in a recombination current j_r . The negative contribution to the capacitance (NC) can be related to a time domain response on a voltage step ΔV . A positive derivative of the transient recombination current dj_r/dt will result in a negative contribution to the capacitance [9]. For a single exponential transient given by $j_r(t) = -j_0 \exp(-t/\tau_r)$, with j_0 the prefactor of the recombination current j_r , the capacitance is given by

$$C(\omega) = C_0 - \frac{\alpha\tau_r}{1 + \omega^2\tau_r^2}, \quad (1)$$

with C_0 the geometrical capacitance $\epsilon_0\epsilon_r A/d$, ω the angular frequency, α a proportionality factor that scales with j_0 , and τ_r the relaxation time [9]. In an early study by Ehrenfreund *et al.* on a poly(*p*-phenylene vinylene)- (PPV) derivative-based polymer-based light-emitting diode (PLED) [5], Eq. (1) was used to fit the frequency dependence of the

capacitance $C(\omega)$ at various voltages. A relaxation time τ_r of 0.5 ms was fitted, whereas the proportionality factor α was not addressed. The fact that at low frequencies $C(\omega)$ could be described by a voltage-independent τ_r was then considered as an indication for trap-assisted recombination. It was argued that for bimolecular recombination, τ_r should decrease with voltage due the increasing carrier density. However, the magnitude of τ_r was not further discussed. In a later study by Djidjou *et al.* [6], a similar approach was followed; to describe $C(\omega)$, they found $\alpha(V)$ to be exponentially dependent on voltage, combined with a voltage-independent τ_r . However, the functional dependence of $\alpha(V)$ and the magnitude of τ_r were not quantitatively addressed.

In the last two decades, effort has been dedicated to understanding the physical processes that govern PLED device operation. These processes include injection, transport, and recombination (radiative and nonradiative) of charge carriers. The hole transport in many conjugated polymers exhibits trap-free behavior, whereas the electron transport is strongly limited by traps [10]. For a range of conjugated polymers, these electron traps were observed to be situated at an energy of ~ 3.6 eV below the vacuum level with a typical density of $\sim 10^{23}$ m⁻³. The electron traps not only limit the electron transport, but the trapped electrons also recombine with free holes via a nonradiative trap-assisted recombination process, which competes with the emissive bimolecular Langevin recombination [10]. The rate for trap-assisted recombination R_{SRH} is given by [11,12]

$$R_{SRH} = C_n C_p N_t (np - n_1 p_1) / [C_n (n + n_1) + C_p (p + p_1)], \quad (2)$$

with N_t the electron trap concentration, $C_{n,p}$ the electron-hole capture coefficient given by $(q/\epsilon_0\epsilon_r)\mu_{n,p}$, with $\mu_{n,p}$ the electron-hole mobility, n and p the electron and hole density, and $n_1p_1 = N_{cv} \exp[-E_{\text{gap}}/kT] = n_i^2$ their product under equilibrium conditions [10]. For trap-assisted recombination of free holes with trapped electrons in a PLED, this expression can be simplified using $C_n = C_p$, $np \gg n_1p_1$, and $n \approx p$ to

$$R_{\text{SRH}} \approx C_p N_t p / 2. \quad (3)$$

As a result, the relaxation time τ_r for trap-assisted recombination in a PLED is then approximated by

$$\tau_r = \frac{2}{N_t C_p}. \quad (4)$$

Thus, for a quantitative analysis of a relaxation time τ_r resulting from trap-assisted recombination, knowledge of the number of traps and capture coefficient (charge carrier mobility) is required.

A more direct proof of whether charge traps are involved in the negative contribution to the capacitance as compared to the voltage independence of τ_r would be a direct variation of the relaxation time τ_r by changing the number of traps N_t . In the present study, we systematically vary the number of electron traps in PLEDs based on PPV derivatives. An increase of the negative contribution to the capacitance is observed by increasing the number of electron traps by addition of a fullerene-based electron acceptor. The observed changes in relaxation time are quantitatively in correspondence with trap-assisted recombination. In contrast, trapping effects can be strongly suppressed by blending the semiconductor with a large band gap host [13]. We demonstrate that this trap dilution nearly eliminates the negative contribution to the capacitance, unambiguously proving that recombination via traps is responsible for the negative capacitance observed in PLEDs.

In the present study, organic bipolar diodes were prepared using a PPV-based copolymer known as ‘‘Super Yellow’’ (SY PPV, Merck AG) [14]. The SY PPV was dissolved in toluene and subsequently spin coated onto a glass/ITO/PEDOT:PSS substrate. Cathode materials were then thermally evaporated on top of the polymer (chamber pressure 10^{-7} mbar). The corresponding device architecture of the PLED is ITO/PEDOT:PSS/polymer/Ba(5 nm)/Al(100 nm). The impedance data were taken using an Agilent 4284a LCR meter, with the dc bias swept from -2 to 5 V, superposed by an ac bias of 100 mV at various frequencies f . All devices were fabricated and measured under inert N_2 atmosphere. For PLEDs based on a polymer blend, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) was mixed with poly(vinylcarbazole) (PVK) in various ratios and dissolved in chlorobenzene.

As the first step, we carried out impedance measurements on a pristine SY-PPV-based PLED. We note that in earlier studies, the electron and hole transport of SY PPV has been well characterized. Using the electron and hole transport data also, the current and light output of the SY-PPV bipolar PLED were consistently modeled [15]. In Fig. 1, the capacitance C of a pristine SY-PPV PLED as a function of frequency [Fig. 1(a)] and bias voltage [Fig. 1(b)] is shown. At negative bias, the PLED is fully depleted, and the capacitance equals C_0 , the geometric capacitance of the device. At a low frequency of 20 Hz, the capacitance first slightly increases with voltage, reaching a maximum value close to the built-in voltage (V_{BI}) of the PLED. This maximum in the capacitance originates from hole accumulation at the polymer-anode interface as a result of hole diffusion to establish Fermi-level alignment [16]. At higher frequencies, the peak capacitance decreases. After the peak value, the negative contribution to the capacitance sets in, and the capacitance decreases with voltage until it reaches a minimum of only 0.2 nF at 2.5 V. As the frequency increases, the decrease of capacitance becomes weaker. By applying Eq. (1) to the experimental data with τ_r and α as fitting parameters, the frequency dependence of the capacitance at various voltages [Fig. 1(a)] and its decrease as a function of voltage at various frequencies [Fig. 1(b)] is fitted. We obtain a voltage-independent relaxation time τ_r of 2.5 ± 0.5 ms for the SY-PPV-based PLED. We note that the negative effect on the capacitance only occurs in a limited voltage range. At higher voltages, the amount of injected charges strongly increases, and charge accumulation regions close to the electrodes are formed, leading again to an increase of the capacitance (the electrodes ‘‘grow’’ into the active polymer layer). The obtained τ_r of 2.5 ms is close to the relaxation time of 0.5 ms as reported earlier for poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene) (MDMO-PPV) [5]. Furthermore, we also obtain the voltage dependence of α , as shown in Fig. 1(c). Similar to Djidjou *et al.* [6], a steep increase of α with voltage is found. From modeling of SY-PPV-based hole- and electron-only devices, the hole mobility $\mu_p = 3 \times 10^{-12}$ m²/V s and electron trap density $N_t = 1 \times 10^{23}$ m⁻³ have been determined [15]. Using a relative dielectric constant $\epsilon_r = 3$, the capture coefficient for a trapped electron to capture a free hole given by $C_p = q\mu_p/\epsilon_r\epsilon_0$ amounts to 1.8×10^{-20} m³s. The estimated relaxation time $\tau_r = 2(N_t C_p)^{-1}$ then equals 1.2 ms. The experimentally obtained relaxation time τ_r of 2.5 ms is very similar to the estimated value of 1.2 ms for trap-assisted recombination. The proportionality factor $\alpha(V)$ is linearly dependent on the recombination current prefactor j_0 . In a PLED at low voltages, the total recombination is per definition proportional to the current I . As a result, the voltage dependence of j_0 and, therefore, α , should be identical to the voltage dependence of I . In Fig. 1(c), the normalized PLED current

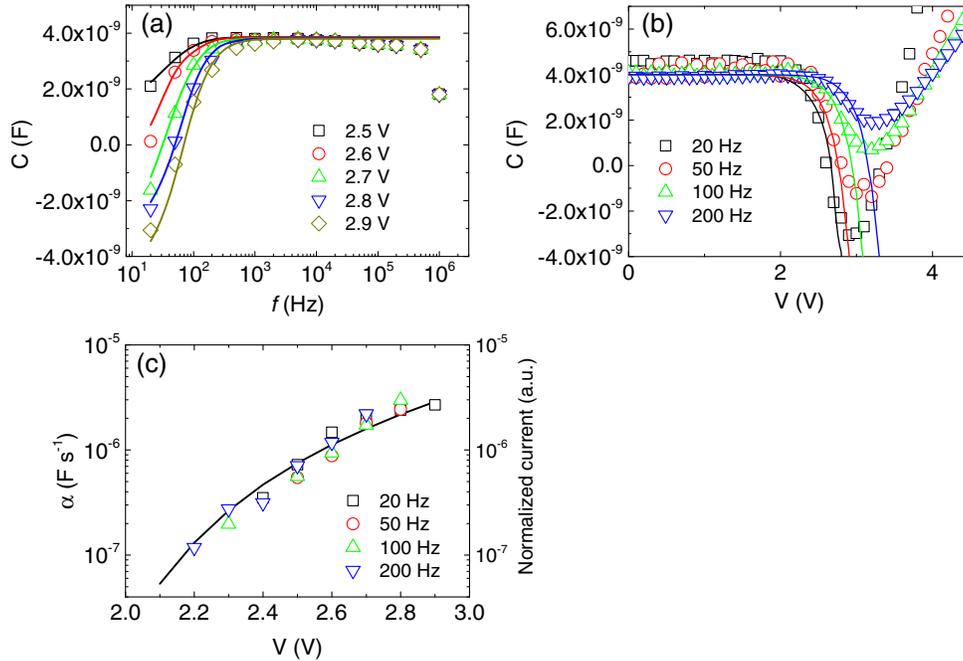


FIG. 1. (a) Differential capacitance C versus frequency at various bias voltages and (b) C - V characteristics of a SY-PPV PLED at different frequencies. The empty symbols represent the experimental data for an active layer thickness of 120 nm, while the solid lines are a fit to Eq. (1) using $\tau_r = 2.5$ ms. (c) $\alpha(V)$ values obtained from Eq. (1) at various frequencies (empty symbols). For comparison, also the normalized J - V characteristic (line) of a SY-PPV PLED in the voltage range where the NC effect is dominant is shown.

I is compared with $\alpha(V)$. It is shown that indeed their voltage dependence is identical. Furthermore, $\alpha(V)$ is frequency independent. The near-exponential dependence of $\alpha(V)$ is, therefore, the result of the density- and field-dependent charge carrier mobility in the space-charge-limited PLED. The absolute value of the proportionality factor amounts to $\alpha = 0.08I$. It should be noted that the proportionality factor α scales with the recombination volume represented by the region where the holes and (trapped) electrons overlap [5]. Confinement of the recombination zone close to the cathode will strongly reduce the contribution of trap-assisted recombination to the negative capacitance [6]. The calculated recombination profile for a SY-PPV PLED biased at 2.4 V shows that the trap-assisted recombination, which is dominant over bimolecular Langevin recombination, is confined in a region with a full width at half maximum of only ~ 10 nm as compared to the total PLED thickness of 120 nm, resulting in a small recombination volume with respect to the polymer-layer volume [17]. A reduction of the proportionality factor of 1 order of magnitude can, therefore, be expected. Thus, we find that the NC behavior of a pristine SY-PPV PLED can be described by a voltage-independent relaxation time that is close to the expected value for trap-assisted recombination. The voltage dependence of the proportionality factor α is governed by the PLED current that originates from the density and field dependence of the charge carrier mobility. Using the obtained $\alpha(V)$ relation [Fig. 1(c), solid line] and voltage-independent relaxation time τ_r of 2.5 ms, the decay

of the capacitance at various frequencies can be reproduced [Fig. 1(b), solid lines]. To further investigate whether the NC is indeed a trap-assisted recombination-induced phenomenon, we vary the number of electron traps in SY PPV and determine the dependence of τ_r and $\alpha(V)$ on trap density.

Electron traps are added by blending SY-PPV with fullerene-based phenyl-C61-butyric acid methyl ester (PCBM) molecules of which the lowest unoccupied molecular orbital (LUMO) at ~ -3.8 eV is far below the LUMO of SY PPV (~ -3.0 eV). PCBM was dissolved in chlorobenzene and added to the SY-PPV polymer solution with concentrations of 0.022%, 0.054%, and 0.130% (wt). These PCBM concentrations correspond to additional electron trap densities of 1.9×10^{23} , 4.6×10^{23} , and $1.1 \times 10^{24} \text{ m}^{-3}$, respectively. The C - V characteristics ($f = 20$ Hz) of the pristine SY-PPV PLED and the devices with various PCBM concentrations are shown in Fig. 2. By increasing the number of electron traps, the negative contribution to the capacitance becomes more pronounced and shifts to higher voltages. For the pristine SY-PPV PLED, with an electron trap concentration N_{t0} of $1 \times 10^{23} \text{ m}^{-3}$, first $\alpha(V)$ and relaxation time τ_0 are determined from the frequency response, similar to our discussion above. For the analysis of the PLEDs with additional PCBM electron traps, we can make use of the fact that the PLED current J is nearly independent of the number of electron traps, since the PLED current is hole dominated [15]. As a result, also the proportionality factor

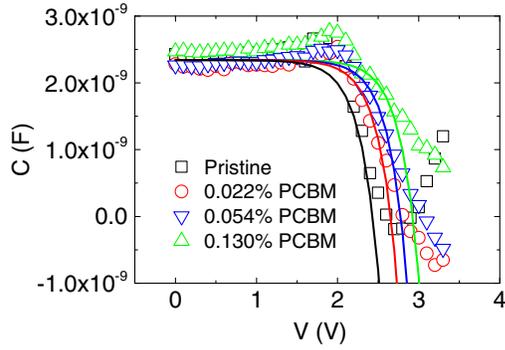


FIG. 2. Experimental C - V characteristics (symbols) at $f = 20$ Hz of a pristine SY-PPV-based PLED and SY-PPV PLEDs with additional PCBM electron traps, with concentrations of 0.022%, 0.054%, and 0.130% (wt), respectively. The active layer thickness of the PLEDs amounts to 150 nm. The solid lines are calculated using Eqs. (1) and (4).

$\alpha(V)$ is expected to be independent of the electron trap concentration. This strongly simplifies the analysis of the experimental data; by using $\alpha(V)$ of the pristine PLED [Fig. 1(c)], the only parameter to describe the NC effect of the PLEDs with additional PCBM traps is the relaxation time τ_r . In Fig. 3, the resulting rate τ_r^{-1} is shown as a function of the total trap concentration $N_{\text{tot}} = N_{i0} + N_{i\text{PCBM}}$. As expected for trap-assisted recombination, τ_r^{-1} vs N_{tot} shows a linear dependence given by $\tau_r^{-1} = N_{\text{tot}}/(\tau_0 N_{i0})$. Using the relation $\tau_r = \tau_0(N_{i0}/N_{\text{tot}})$ from Eq. (1), the negative contribution NC of the capacitance for the PLEDs with additional traps can then be predicted from the pristine device (τ_0, N_{i0}). As shown in Fig. 2, the measured C - V characteristics (symbols) match

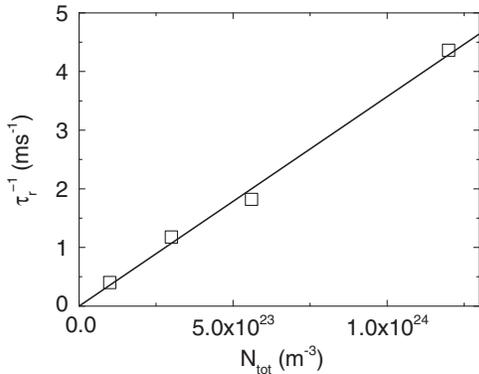


FIG. 3. Inverse relaxation time τ_r^{-1} as a function of total electron trap concentration $N_{\text{tot}} = N_{i0} + N_{i\text{PCBM}}$ for a pristine SY-PPV PLED (N_{i0}) and SY-PPV PLEDs with additional PCBM electron traps ($N_{i\text{PCBM}}$). The total number of electron traps N_{tot} ranges from $1 \times 10^{23} \text{ m}^{-3}$ for the pristine device to 2.9×10^{23} , 5.6×10^{23} , and $1.2 \times 10^{24} \text{ m}^{-3}$ for the PLEDs with PCBM concentrations of 0.022%, 0.054%, and 0.130% (wt), respectively. The solid line is the predicted dependence $\tau_r^{-1} = N_{\text{tot}}/(\tau_0 N_{i0})$ for trap-assisted recombination, with $N_{i0} = 1 \times 10^{23} \text{ m}^{-3}$ and $\tau_0 = 2.8$ ms.

well with the predicted values (lines) for every electron trap concentration. Thus, the NC effect changes with electron trap concentration, as expected for trap-assisted recombination being the dominant relaxation mechanism.

A final and unambiguous proof of the role of trap-assisted recombination to the negative contribution in the capacitance would be the absence of the NC effect in a PLED without traps. It has recently been shown that the effect of trapping in semiconducting polymers can be strongly suppressed by blending the active polymer with a large band gap host [13]. The effect of a simultaneous dilution of transport and trapping sites on charge transport can be easily explained by the Mark-Helfrich formalism for trap-limited currents governed by exponentially distributed trap states inside the forbidden band gap. For organic semiconductors, a simultaneous lowering of transport and trapping sites by 1 order of magnitude leads to an enhancement of the trap-limited current by 3 orders of magnitude [13]. Next to the enhancement of the trap-limited electron current, the trap dilution effect leads to a strong reduction of the trap-assisted recombination. It is, therefore, expected that in case trap-assisted recombination is responsible for the NC effect, dilution of traps will suppress this negative contribution to the capacitance. To study the effect of trap dilution on the capacitance at low frequencies, we blend MEH-PPV (semiconductor) with PVK (host) using MEH-PPV:PVK blend ratios of 1:0 (pristine MEH-PPV), 1:1 and 1:3 (wt), respectively. The C - V characteristics of the corresponding blend PLEDs at $f = 20$ Hz are shown in Fig. 4. Already for the 1:1 blend, the NC effect is small and also the peak in the capacitance at V_{BI} is more pronounced, since due to the reduced trap concentration also accumulation of free electrons at the cathode lead to a capacitance enhancement. The weakened NC effect is the result of Langevin recombination starting to dominate over trap-assisted recombination. The combination of both effects prohibits a further reliable quantitative analysis of the NC effect as a function of trap dilution. In the 1:3 blend PLED, where electron trapping is strongly suppressed [13], the

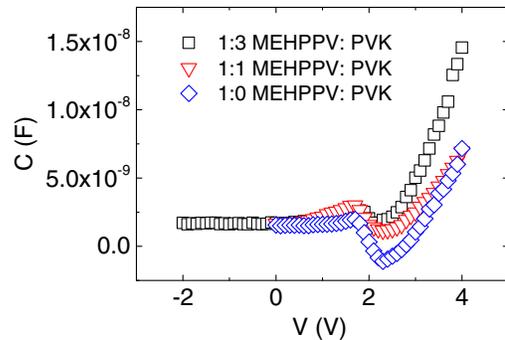


FIG. 4. C - V characteristics at $f = 20$ Hz of a pristine MEH-PPV PLED (1:0) and PLEDs consisting of MEH-PPV:PVK blends in ratios of 1:1 and 1:3, respectively. The thickness of the pristine and blend layer is 200 nm.

negative contribution to the capacitance is even completely eliminated. After the shallow maximum in the capacitance due to hole accumulation at the anode, the capacitance does not drop below its geometrical value C_0 . This once more confirms that trap-assisted recombination is the true and only origin of the negative capacitance as observed in bipolar organic devices.

In conclusion, the negative contribution to the capacitance observed in the low frequency C - V characteristics of bipolar PLEDs is characterized by a voltage-independent relaxation time that is nearly equal to the expected inverse rate for trap-assisted recombination. An enhancement of the number of electron traps by the addition of fullerene molecules leads to a more pronounced NC effect, which can be quantitatively explained by trap-assisted recombination. The absence of NC in a nearly trap-free PLED unambiguously shows that trap-assisted recombination is the only mechanism responsible for the negative contribution to the capacitance in bipolar organic diodes. Our results demonstrate that in future studies, impedance spectroscopy can be used as a tool to quantitatively determine trap densities in organic bipolar devices.

The authors would like to thank Davood Abbaszadeh for stimulating discussion, and Christian Bauer, Frank Keller, and Hanspeter Raich for technical support. We acknowledge the financial support by BASF Corporation.

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