# Trap-Assisted Recombination in Disordered Organic Semiconductors

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The trap-assisted recombination of electrons and holes in organic semiconductors is investigated. The extracted capture coefficients of the trap-assisted recombination process are thermally activated with an identical activation energy as measured for the hole mobility $\mu_p$. We demonstrate that the rate limiting step for this mechanism is the diffusion of free holes towards trapped electrons in their mutual Coulomb field, with the capture coefficient given by $(q/\varepsilon)\mu_p$. As a result, both the bimolecular and trap-assisted recombination processes in organic semiconductors are governed by the charge carrier mobilities, allowing predictive modeling of organic light-emitting diodes.

Over the last decades, organic electronics has become a field of material science advancing rapidly into the commercial domain. Knowledge of the physical processes governing the operation of organic devices is essential for optimizing their performance [1,2]. Recombination of electrons and holes in organic semiconductors is an important process; it determines the efficiency of organic light-emitting diodes (OLEDs), and is an unwanted loss process in organic solar cells. Bimolecular recombination [Fig. 1(a)] in organic semiconductors is of the Langevin type; i.e., the rate limiting step is the diffusion of electrons and holes toward each other in their mutual Coulomb field [3]. Such a behavior is characteristic for materials in which the mean free path of the charge carriers is smaller than a critical distance $r_c = q^2/4\pi\varepsilon_0\varepsilon_r kT$, with $q$ the elementary charge, $\varepsilon$ the dielectric constant, and $T$ the temperature, at which the Coulomb binding energy between an electron and hole equals $kT$. The charge transport in organic semiconductors is of a hopping nature, with a typical hopping distance of 1–2 nm, whereas $r_c$ amounts to 18.5 nm at $T = 300$ K ($\varepsilon_r = 3$). Therefore, the manifestation of Langevin recombination in organic semiconductors is expected [4] and experimentally verified [5]. This implies for the bimolecular recombination rate that $R_L = B_L(np - n_1p_1)$, with $n$ and $p$ the electron and hole density and $n_1p_1 = N_{cv}\exp[-E_{gap}/kT] = n_i^2$ their product under equilibrium conditions, where $n_i$ denotes the intrinsic carrier concentration in the material, and $B_L$ given by [3]

$$B_L = \frac{q}{\varepsilon}(\mu_n + \mu_p), \qquad (1)$$

with $\mu_n$ and $\mu_p$ the electron and hole mobilities, respectively. Even though the presence of Langevin recombination is widely recognized, some studies suggest modifications to the Langevin expression [6] due to bipolar mobilities [7] or inclusion of lateral hops [8].

Another important recombination process that dominates the recombination in indirect semiconductors as silicon and germanium is trap-assisted recombination [9,10]. This is a two-step process where a trap state, originating from imperfections or impurities in the crystal structure, creating energy levels inside the forbidden energy band gap, captures a charge carrier that subsequently recombines with a mobile carrier of the opposite sign because of their Coulombic interaction. Because of conservation of momentum this process cannot occur without the release of a phonon slowing the recombination process down. Therefore, in most cases the trap sites act as recombination centers for nonradiative recombination. Trap-assisted recombination was first described by Shockley, Read, and Hall (SRH) in 1952 [9,10]. The four basic steps involved in the recombination by trapping are depicted in Fig. 1 for recombination centers that are neutral when empty, and negatively charged when filled with a trapped electron. First [Fig. 1(b)] an electron is captured by a neutral center with a rate governed by a capture coefficient $C_n$. This trapped electron can subsequently be excited back to the conduction band [Fig. 1(c)] or is being captured by a hole [Fig. 1(d)] governed by a capture coefficient $C_p$. Another option is that an electron is captured from the valence band by a neutral center [Fig. 1(e)], which is a
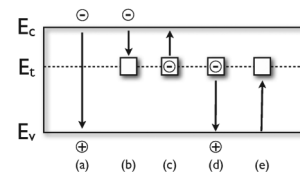


FIG. 1. Schematic representation of bimolecular recombination and the four processes involved in recombination by trapping: (a) bimolecular, Langevin recombination, (b) electron capture, (c) electron emission, (d) hole capture, and (e) hole emission.

generation process. In their work, SRH calculated the total trap-assisted recombination rate by assuming thermal equilibrium between the four processes, which requires the rate of capture and the rate of emission to be equal. As a result, the well-known SRH recombination rate is $R_{SRH} = B_{SRH}(np - n_1 p_1)$ with

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

where $C_n$ denotes the probability per unit time that an electron in the conduction band will be captured for the case that the trap is empty and able to capture an electron. Correspondingly, $C_p$ indicates the probability per unit time that a hole will be captured when a trap is filled with an electron and able to capture the hole. $N_t$ is the density of electron traps.

In many organic semiconductors the electron currents are strongly trap limited [11]. For poly(p-phenylene vinylene) (PPV) derivatives the trap-limited currents are well described using a model in which the electrons traps, with a typical density of $2 \times 10^{17}$ cm$^{-3}$, are Gaussianly distributed in energy, with the center of their distribution located 0.7–0.8 eV below the LUMO [12]. Remarkably, until recently the role of these traps in the recombination process in organic semiconductors had not been addressed. In organic solar cells with trap-limited electron currents, it was demonstrated that the SRH recombination mechanism is responsible for an increased response of the open circuit voltage ($V_{OC}$) on the incident light intensity [13]. At $V_{OC}$ there is no current extraction and all generated charge carriers recombine. As a consequence, the $V_{OC}$ behavior is strongly dependent on the presence of specific recombination mechanisms. From the measured response, a capture coefficient of $1.4 \times 10^{-18}$ m$^3$/s was reported at room temperature. In polymer light-emitting diodes (PLED), it was observed by Wetzelaer *et al.* [14] that the ideality factor of their current-voltage characteristic is exactly equal to 2, which is a fingerprint of SRH recombination, as derived by Sah *et al.* [15]. By measuring $V_{OC}$ as a function of light intensity of PLEDs made from various PPV derivatives, a SRH capture coefficient of $9 \times 10^{-19}$ m$^3$/s was derived, in close agreement with the value reported earlier for solar cells [16]. In this Letter, we report on the origin of the trap-assisted recombination mechanism. By studying its temperature dependence, it is demonstrated that the SRH capture coefficient in organic semiconductors is determined by the mobility of the free carrier. The limiting process is the diffusion of the holes towards the trapped electron in their mutual Coulomb field. As a result, both the bimolecular Langevin and trap-assisted Shockley-Read-Hall recombination strengths can be predicted from the mobility of the charge carriers.

As stated above, a way to extract the SRH capture coefficients is to measure the light-intensity dependence of the $V_{OC}$ of light-emitting diodes. In the absence of traps, where Langevin recombination is the dominant

recombination process, the response of $V_{OC}$ on light intensity is given by [17]

$$V_{OC} = \frac{E_{gap}}{q} - \frac{kT}{q} \ln\left(\frac{(1 - P)B_L N_{CV}^2}{PG}\right), \quad (3)$$

where $P$ is the dissociation probability of excitons, $E_{gap}$ is the energy gap, $N_{cv}$ is the effective density of states, $B_L$ is the bimolecular recombination strength, and $G$ is the generation rate of excitons. The generation rate $G$ is proportional to the light intensity in this equation, directly connecting the $V_{OC}$ to the light intensity. In the presence of trap-assisted recombination, the slope of the $V_{OC}$ vs the logarithm of the light-intensity relation exceeds that of the expected $kT/q$ from Eq. (3), and can be well described by adding the SRH recombination strength [Eq. (2)] to the Langevin recombination strength [Eq. (1)], $B = B_L + B_{SRH}$ in the model [13].

Up to this point, in literature, analysis of trap-assisted recombination has only been performed at room temperature [13,18–22]. The temperature dependence of the SRH recombination will provide information about the physical origin of this process in organic semiconductors. Figure 2 depicts the temperature dependence of the $V_{OC}$—light-intensity measurements for a polymer LED consisting of the sandwich structure ITO/poly (3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT: PSS)/poly(2-methoxy-5-(2′-ethylhexyloxy)-p-phenylenevinylene) (MEH − PPV)/Ba(5 nm)/Al(100 nm). The transport and trapping parameters for MEH-PPV are well established since this material has served as a workhorse for the organic electronics community for the past decades [23,24] and is therefore a thoroughly benchmarked and electrically parametrized material (Supplemental Material; Sec. 1 [25]). The slope is observed to lower slightly from $1.8kT/q$ at 295 K to $1.7kT/q$ at 215 K. To analyze the data, we use a numerical device model [26] in which drift and diffusion of charge
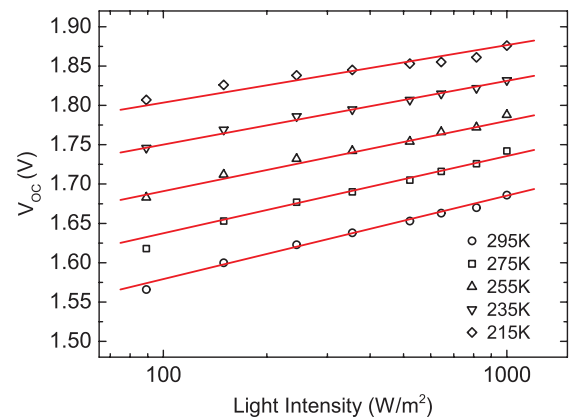


FIG. 2 (color online). Measured (symbols) and calculated (solid lines) $V_{OC}$ as a function of the incident light intensity for an MEH-PPV PLED (138 nm) at various temperatures.

carriers, the effect of space charge on the electric field, density-, and field dependent mobility [27], a distribution of traps for the electrons [12], and a field and temperature-dependent generation rate of free charge carriers is included. For MEH-PPV, the field-, density-, and temperature-dependent mobilities of electron and holes, as well as the trapping behavior of electrons all have been determined independently in previous studies using single-carrier devices [12]. As a result, the only unknown parameter to describe the measured light dependence of the $V_{OC}$ is the SRH capture coefficient. The calculated dependence of $V_{OC}$ on light intensity is shown in Fig. 2 by the solid lines. Subsequently, the capture coefficients acquired are depicted in an Arrhenius plot in Fig. 3. The SRH capture coefficient decreases with decreasing temperature, and is thermally activated with an activation energy of 0.42 eV. Remarkably, the temperature activation of the capture coefficient is exactly equal to the activation energy of the hole mobility as deduced from space-charge-limited currents in MEH-PPV based hole-only devices, structured as ITO/PEDOT:PSS/MEH-PPV/Au(100 nm). This indicates that the SRH capture coefficient is related to the hole mobility.

In order to rationalize this result, we consider two limiting cases for SRH recombination. In the first case $C_p \ll C_n$, meaning that the time for a hole to capture a trapped electron is significantly larger than the time for an electron to be captured by an empty trap. In LEDs typically $np \gg n_1 p_1$ and $n \approx p$, so that the SRH recombination rate reduces to

$$R_{SRH} = C_p N_t p. \qquad (4)$$

The second case to consider is the opposite of the first, $C_p \gg C_n$. For that case, the SRH equation reduces to
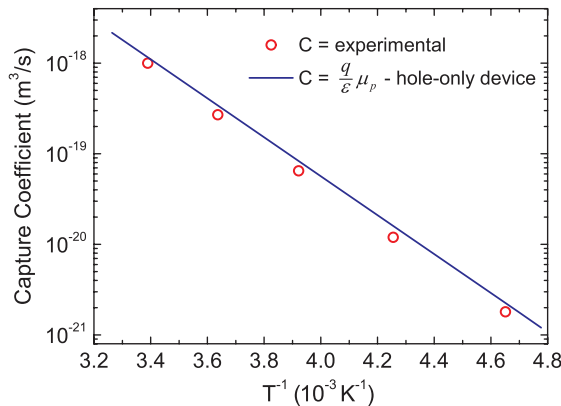
$$R_{SRH} = C_n N_t n. \qquad (5)$$

Both these equations resemble the equation for bimolecular Langevin recombination $R_L = B_L np (np \gg n_1 p_1)$, with $B_L$ replaced by $C_n$ or $C_p$. In the first case, $C_p \ll C_n$, the rate limiting step is the capture of a trapped electron by a free hole, which involves the process of two opposing charges being attracted to each other in their mutual Coulomb field, Figs. 1(d) and 1(e). This process is similar to bimolecular Langevin recombination, with the only difference that the trapped electron cannot move, meaning that $\mu_e = 0$. In that case, the SRH recombination coefficient $C_p$ for hole capture by a trapped electron would be

$$C_p = \frac{q}{\varepsilon} \mu_p. \qquad (6)$$

In Fig. 3 the calculated capture coefficient $C_p$ is plotted as a solid line, using the experimentally determined hole mobilities of MEH-PPV. As can be observed in Fig. 3, the value of the experimental capture coefficients determined from the intensity dependence of the $V_{OC}$ is in very good agreement with the predicted value from Eq. (6). This confirms that the SRH recombination in organic semiconductors is determined by diffusion of the free carrier towards the trapped carrier, similar to Langevin recombination where both free carriers diffuse towards each other.

In most organic semiconductors, trap-assisted recombination is of a nonradiative nature which denotes SRH recombination as a loss mechanism in LEDs [16]. However, for a white-emitting copolymer, where green- and red-emitting chromophores are incorporated in the blue-emitting polyfluorene backbone [28,29], it has been demonstrated that the blue part of the emission spectrum arises from Langevin recombination, whereas the red emission originates from SRH recombination of holes with electrons that are trapped on the red chromophore [14]. As a result, both Langevin and SRH can be simultaneously studied by measuring the light output-voltage ($L$-$V$) characteristics through selective optical filters (Supplemental Material; Sec. 2 [25]). Figure 4 depicts



FIG. 3 (color online).   Arrhenius behavior of the capture coefficient obtained from the $V_{OC}$-light-intensity fit for the 138 nm MEH-PPV device (red open circles). Also illustrated are the calculated capture coefficients using Eq. (6) with the effective hole mobility of a 140 nm hole-only device (blue line).
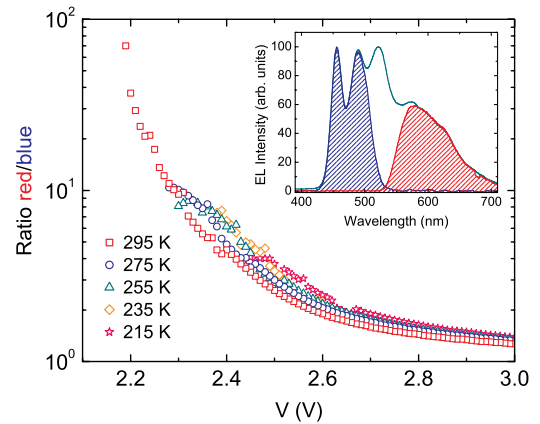


FIG. 4 (color online).   Ratio of the red (550 nm longpass filter) and the blue light (blue dichroic filter) of a white light-emitting copolymer as a function of voltage for various temperatures.

the ratio of the red (SRH) and blue (Langevin) emission as a function of voltage for various temperatures. Since Langevin is quadratic in carrier density, whereas SRH is linear, this ratio drops for increasing voltage. More importantly, the ratio is temperature independent: Since the blue-emission rate arises from Langevin recombination, the blue light curve follows the temperature dependence of the highest (hole) mobility in the Langevin expression [Eq. (1)]. The trap-assisted red emission on the other hand scales with the capture coefficient $C_p$ [Eq. (4)]. The temperature independence of their ratio unambiguously demonstrates that the SRH capture coefficient of the red emission is also dominated by the hole mobility, possessing the same temperature-, field-, and density dependence.

The understanding of trap-assisted recombination paves the way for a fully predictive description of current transport and recombination of organic LEDs. From single-carrier devices, the electron- and hole mobilities $\mu_e(n, E, T)$ and $\mu_p(p, E, T)$ can be derived, including their dependence on density, electric field, and temperature. Furthermore, from electron-only diodes, the number of electron traps $N_t$ can be derived. In a recent study, we demonstrated that at room temperature the inclusion of the measured SRH coefficient in an OLED device model gives a consistent description of the bipolar PLED characteristics without the need for adjusting the Langevin expression [16]. Moreover, now knowing the origin of SRH in organic semiconductors the modeling of bipolar organic LEDs does not require any additional parameter. The SRH capture coefficient is given by $C_p = q/\varepsilon \mu_p$, so that SRH recombination can be simply approximated by $R_{\mathrm{SRH}} = q/\varepsilon \mu_p(p, E, T) N_t p$, while Langevin recombination is given by $R_L = q/\varepsilon[\mu_e(n, E, T) + \mu_p(p, E, T)]np$. Together with an earlier reported universal Arrhenius relation of the mobility [30], the result described in this Letter for the first time enables full predictive modeling of organic LEDs. Furthermore, SRH-based loss processes in organic solar cells can from now on be quantitatively predicted.

In conclusion, we have investigated the mechanism of recombination via trapping, as an addition to bimolecular recombination. The temperature behavior of trap-assisted recombination revealed that the capture coefficient is thermally activated, equal to the activation of the experimental hole mobility. We have demonstrated that the trap-assisted recombination in disordered organic semiconductors is governed by the diffusion of the free carrier (hole) towards the trapped carrier (electron), similar to the Langevin recombination for free carriers where both carriers are mobile. As a result, with the charge carrier mobilities and amount of trapping centers known, the complete recombination process in disordered organic semiconductors can be predicted.

[1] C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987).
[2] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burn, and A. B. Holmes, Nature (London) **347**, 539 (1990).
[3] P. Langevin, Ann. Chim. Phys. **28**, 433 (1903).
[4] U. Albrecht and H. Bässler, Chem. Phys. **199**, 207 (1995).
[5] P. W. M. Blom, M. J. M. de Jong, and S. Breedijk, Appl. Phys. Lett. **71**, 930 (1997).
[6] C. Groves and N. C. Greenham, Phys. Rev. B **78**, 155205 (2008).
[7] J. J. M. van der Holst, F. W. A. van Oost, R. Coehoorn, and P. A. Bobbert, Phys. Rev. B **80**, 235202 (2009).
[8] S. L. M. van Mensfoort, J. Billen, M. Carvelli, S. I. E. Vulto, R. A. J. Janssen, and R. Coehoorn, J. Appl. Phys. **109**, 064502 (2011).
[9] W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).
[10] R. N. Hall, Phys. Rev. **87**, 387 (1952).
[11] P. W. M. Blom, M. J. M. de Jong, and J. J. M. Vleggaar, Appl. Phys. Lett. **68**, 3308 (1996).
[12] H. T. Nicolai, M. M. Mandoc, and P. W. M. Blom, Phys. Rev. B **83**, 195204 (2011).
[13] M. M. Mandoc, W. Veurman, L. J. A. Koster, B. De Boer, and P. W. M. Blom, Adv. Funct. Mater. **17**, 2167 (2007).
[14] G. A. H. Wetzelaer, M. Kuik, H. T. Nicolai, and P. W. M. Blom, Phys. Rev. B **83**, 165204 (2011).
[15] C. T. Sah, R. N. Noyce, and W. Shockley, Proc. IRE **45**, 1228 (1957).
[16] M. Kuik, H. T. Nicolai, M. Lenes, G. A. H. Wetzelaer, M. Lu, and P. W. M. Blom, Appl. Phys. Lett. **98**, 093301 (2011).
[17] L. J. A. Koster, V. D. Mihailetchi, R. Ramaker, and P. W. M. Blom, Appl. Phys. Lett. **86**, 123509 (2005).
[18] M. M. Mandoc, F. B. Kooistra, J. C. Hummelen, B. de Boer, and P. W. M. Blom, Appl. Phys. Lett. **91**, 263505 (2007).
[19] R. A. Street, M. Schoendorf, A. Roy, and J. H. Lee, Phys. Rev. B **81**, 205307 (2010).
[20] T. Kirchartz, B. E. Pieters, J. Kirkpatrick, U. Rau, and J. Nelson, Phys. Rev. B **83**, 115209 (2011).
[21] L. Tzabari and N. Tessler, J. Appl. Phys. **109**, 064501 (2011).
[22] S. R. Cowan, W. L. Leong, N. Banerji, G. Dennler, and A. J. Heeger, Adv. Funct. Mater. **21**, 3083 (2011).
[23] D. Braun and A. J. Heeger, Appl. Phys. Lett. **58**, 1982 (1991).
[24] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Science **270**, 1789 (1995).
[25] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.107.256805　　for

parameters used for the modeling and red and blue emission from a white copolymer.

[26] L. J. A Koster, E. C. P. Smits, V. D. Mihailetchi, and P. W. M. Blom, Phys. Rev. B **72,** 085205 (2005).

[27] W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, and M. A. J. Michels, Phys. Rev. Lett. **94,** 206601 (2005).

[28] M. de Kok, W. Sarfert, and R. Paetzold, Thin Solid Films **518,** 5265 (2010).

[29] M. A. Parshin, J. Ollevier, M. Van der Auweraer, M. M. de Kok, H. T. Nicolai, A. J. Hof, and P. W. M. Blom, J. Appl. Phys. **103,** 113711 (2008).

[30] N. I. Craciun, J. Wildeman, and P. W. M. Blom, Phys. Rev. Lett. **100,** 056601 (2008).