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Transition from trap-controlled to trap-to-trap hopping transport in disordered organic semiconductors

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We advance further the effective-medium theory to describe adequately nondispersive charge transport at arbitrary trap concentrations in a disordered organic material, with special emphasis on trapping phenomena at large trap concentrations when the transport through the trap-state manifold becomes possible. A key point of this model compared to the previous treatment [Phys. Rev. B **66**, 205208 (2002)] is that it accounts also for the dependence of the overlap integral upon the trap concentration due to dilution of transport sites by traps. While the previous and present treatments provide similar results for small and moderate trap concentrations, the present theory is superior regarding a quantitative understanding of charge transport at large trap concentrations, notably the transition from trap-controlled to trap-to-trap hopping transport that has been observed experimentally. The theory also provides a more accurate estimate for the effective energetic disorder parameter, σ_{eff}, introduced to account the effect of traps on charge transport in disordered organic solids for arbitrary trap concentrations. The theoretical results have been supported by experiments in the conjugated polymer polyfluorene doped with different concentration of tri-*p*-tolylamine that act as a trap by employing the technique of thermally stimulated luminescence.

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I. INTRODUCTION

Traditionally, the classical Hoesterey-Letson formalism[1] is used to describe charge-carrier transport in trap-containing organic materials. It originally was developed for organic crystals, where the charge transport near room temperature occurs via temperature-independent hopping among isoenergetic adjacent molecules,[1,2] and it is based on a discrete trap depth argument. The Hoesterey-Letson formula describes how a relative concentration c of traps, whose energy levels are offset of the mean transport energy, i.e., the valence or conduction band states, by the trap energy ε_t, affects the carrier mobility,

$$\mu(c) = \mu(c=0)h^{-1} = \mu(c=0)\frac{1}{1 + c\exp\left(\dfrac{\varepsilon_t}{k_B T}\right)}, \qquad (1)$$

where h is a trapping factor reflecting the increase of the transit time by the time spent by a carrier in traps, c is the relative trap concentration, $\mu(c)$ is the trap-controlled mobility, $\mu(c=0)$ is the trap-free mobility, and k_B is the Boltzmann constant. The trap depth $\varepsilon_t(\varepsilon_t > 0)$ is set by the difference between the HOMO (highest occupied molecular orbital) or LUMO (lowest unoccupied molecular orbital) levels of host and guest for holes (electrons).[3] This is a characteristic feature of organic solids in which the identity of the molecular constituent is preserved because intermolecular interactions are weak. It should be also mentioned that, with the exception of the class of (electro)chemically doped materials, the traps in organic semiconductors are assumed to be neutral when empty.

However, in a disordered organic solid, a description of charge transport in the presence of traps is more complex because both the intrinsic hopping states and the traps feature inhomogeneously broadened density of state (DOS) distributions that overlap. Since the temperature dependence of transport is set by the energy difference between occupied and transport states, each being dependent on the DOS itself, it can no longer be simply determined by a Boltzmann factor with the activation energy being the difference of the HOMO/LUMO levels of host and guest. Although it was demonstrated[4,5] that the Hoesterey-Letson formalism provides a reasonable zero-order approximation to describe trapping also in disordered materials, its predictions are not always in agreement with experimental data.[6–9] This is not unexpected, as the formalism was originally developed for systems devoid of disorder. It is based on the notion that the trap depth is a discrete quantity, which is no large valid for disordered organic solids.

Another peculiarity of trap-containing organic solids is the concentration dependence of the mobility at higher concentrations of traps. It turns out that, beyond a relative molar concentration of 0.05,…,0.1, $\mu(c)$ features a minimum and rises again at higher concentrations. The reason is again the commencement of direct trap-to-trap transport that overcompensates thermally activated release of carriers to the intrinsic transport states. This effect becomes more important as the trap energy ε_t increases. The effect resembles percolation above the critical percolation threshold although the critical concentration at which $\mu(c)$ increases is somewhat lower than the classic percolation theory would predict. The reason is that percolation theory is based upon a hard-core interaction potential among the transport sites while in organic systems the transfer matrix elements among the molecules vary exponentially in distance. Therefore, the critical percolation limit is eroded.[10] Experimentally, the effect is well documented in the literature. Examples are the works by Pai *et al.*[11] on polyvinylcarbazole doped with TPD and by Borsenberger *et al.*[12] on di-*p*-tolylphenylamine (DPT)-doped polystyrene containing different concentrations of *p*-diethylaminobenzaldelyde diphenylhydrozone (DEH) that forms a hole trap with a nominal trap depth of 0.32 eV.

Recently the charge-carrier transport in a disordered organic material containing traps was considered by the effective medium approximation (EMA) theory.[13] It has been demonstrated that this theory describes more adequately charge transport in presence of traps, as compared to predictions of the classical Hoesterey-Letson formalism, since it accounts for the effects of disorder. The EMA treatment was based on appropriate averaging of the Miller-Abrahams jump rates in the presence of an electric field, using suitably normalized bimodal Gaussian approximations for the cumulative DOS distributions.[13] The model properly accounts for the temperature and trap-concentration dependence of the mobility of the charge-carriers at small and moderate trap concentrations, while taking disorder into account. Besides, it contains no adjustable parameters except parameters that can directly be determined from experiment and agree reasonably well with experimental data.

However, the drawback of the above theory is that it fails to describe the dependence of charge-carrier mobility over the whole range of trap concentrations. The problem was that the theory predicted the onset of trap-to-trap hopping at anomalously low trap concentration already. In the present work we developed further the previous EMA formalism to describe charge transport in disordered organic semiconductors in the presence of traps that takes into account also the dependence of the overlap integral upon the trap concentration. We demonstrate that the present theory is able to describe properly the charge transport within the entire range of trap concentration. Thermally stimulated luminescence (TSL) studies of charge trapping in a polyfluorene (PF) conjugated polymer containing different concentrations of deliberately introduced traps support the present theory, as do previous experiments on charge-transport measurements in disordered organic materials containing traps.

II. THEORETICAL FORMULATION

We consider a disordered trap-containing medium with total number of sites N, which could be either intrinsic transport (hopping) sites or traps, and with the average intersite distance of $a=N^{-1/3}$. Let there be N_t the number of traps, then a relative concentration of traps is $c=N_t/N$. The difference $N_p=N-N_t$ determines the number of remaining transport sites in the medium and $N_p/N=1-c$. The transport sites and traps are introduced in a symmetrical manner, i.e., the average distance between traps is $a_t=N_t^{-1/3}=a/c^{1/3}$ and that between transport sites is

$$a_p=N_p^{-1/3}=(N-N_t)^{-1/3}=(N-cN)^{-1/3}=N^{-1/3}(1-c)^{-1/3}$$
$$=a/(1-c)^{1/3}.$$

The applied electric field $\boldsymbol{E}$ is chosen to be directed along $0x$ axis, i.e., $\boldsymbol{E}=\{E,0,0\}$. Let W_e^+ and W_e^- be effective jump rates along and opposite to the electric field direction, respectively, then the effective drift mobility μ_e by definition is

$$\mu_e=a\frac{W_e^+-W_e^-}{E}. \tag{2}$$

Here we consider only energetic disorder in the site manifold and the positional disorder is neglected. The intersite charge-carrier hopping can be described by the Miller-Abrahams jump rate expression[14] and in this case the parameters W_e^+ and W_e^- in the EMA theory can be determined as[13]

$$W_e^+=\langle W_{12}^+\rangle,\quad W_e^-=\langle W_{21}^-\rangle, \tag{3}$$

where

$$W_{12}^+=W_0\exp\left(-\frac{|\varepsilon_2-\varepsilon_1-eaE|+(\varepsilon_2-\varepsilon_1-eaE)}{2k_BT}\right), \tag{4}$$

$$W_{21}^-=W_0\exp\left(-\frac{|\varepsilon_1-\varepsilon_2+eaE|+(\varepsilon_1-\varepsilon_2+eaE)}{2k_BT}\right). \tag{5}$$

Here ε_k is the energy of site k.

A key point of the present treatment is that we take into account also the dependence of the overlap integral of the transport sites W_0 upon the trap concentration c, which was neglected in the previous treatment.[13] It should be noted that in reality the change of trap concentration c results in change of both the average distance between transport sites due to the dilution of medium and the average distance between traps, while the localized wave function decay length b of a carrier on both transport sites and traps remains unaffected. However, our EMA formalism based on a two-site cluster approximation considers the intersite distance a in the medium to be constant; therefore, in order to treat the effect, we introduce the trap-concentration dependent localization radius for a trapping site as $bc^{1/3}$ and for a transport site as $b(1-c)^{1/3}$, where b is the localization radius in real medium.

Here for simplicity we assume that the localization radius is equal for transport sites and traps and that the localization radius does not depend on trap concentration. The latter assumption might be justified if the dielectric permittivity of the medium is not notably changed by the guest molecules, which can be the case when polarities of host and guest molecules are similar. Although experimentally it was documented that the localization radius in molecularly doped polymers could be somewhat different when the same charge-transporting molecules are doped into different polarity neutral polymer binder,[15] there have been no systematical studies available of this problem. However, the comparison of the EMA calculations with experimental results presented below suggests that such a simplification is reasonable and does not alter considerably the final results on trap-concentration dependence of the charge mobility in considered materials.

In the framework of this model, the concentration dependence of the overlap integral could be expressed as follows:

(a) for transitions between transport sites

$$W_0 = \nu_0 \exp\left(-2\frac{a}{b}\frac{1}{(1-c)^{1/3}}\right), \tag{6}$$

(b) for trap-to-trap transitions

$$W_0 = \nu_0 \exp\left(-2\frac{a}{b}\frac{1}{c^{1/3}}\right), \tag{7}$$

(c) for transitions from transport site to trap or from trap to transport site

$$W_0 = \nu_0 \exp\left(-\frac{a}{b}\left[\frac{1}{(1-c)^{1/3}} + \frac{1}{c^{1/3}}\right]\right). \tag{8}$$

It is important to note that, for the sake of completeness, all possible overlap integrals expressed above are considered; however, they play a different role in the calculation of charge mobility depending on trap-concentration range. The overlap integral given by the Eq. (6) dominates the trap-controlled hopping transport at small and moderate trap concentrations since it determines the $\mu(c=0)$ term in the Eq. (1) and coefficient in the Eq. (21) (see below) describing this transport regime. The trap-to-trap hopping transport at large trap concentrations is determined mostly by the overlap integral given by Eq. (7). As will follow from further consideration, the contribution of this overlap integral given by Eq. (8) into the effective charge mobility turns out to be proportional to the product $(1-c)c$ [cf. the middle term in Eq. (13) below]. In other words, in the two-site model, one should account for the product of the transfer integral [Eq. (8)] between trap and transport site and the probability that one site is occupied by a trap and the other one by an intrinsic transport site. Therefore, this transfer integral can be important only at intermediate trap concentrations. Further, the above expressions for overlap integrals have been formulated upon certain assumptions. Equations (6) and (7) assume a homogenous trap distribution in the matrix, which might not be the case in real samples on a microscopic scale. Nonetheless, it seems to be realistic approximation as Pai *et al.*[11] showed that at large trap concentrations in experiment $\log_{10}(\mu)$ indeed scales linearly versus $c^{-1/3}$.

It worth noting that the model suggested above does not alter significantly the results of previous EMA calculations[13] of the charge mobility at relatively small trap concentrations $c \ll 1$ when the dilution of transport sites by traps is disregarded, but it has a considerable impact on the results of calculation of charge-carrier mobility at large trap concentrations when trap-to-trap transitions start to dominate. Moreover, as will be demonstrated below, accounting for the concentration dependence of the overlap integral W_0 affects considerably the critical concentration c_{cr} and, consequently, the critical temperature T_{cr} at which transition from the trap-controlled to the trap-to-trap hopping transport occurs comparing to those obtained in Ref. 13.

Further we should perform configuration averaging in Eq. (3). In order to calculate W_e^+ one has to choose distribution functions for the starting states described by occupational density of states distribution $P(\varepsilon_1)$ and for the target states described by the density of states (DOS) distribution $P(\varepsilon_2)$ for the case of a strong energetic disorder in the form suggested earlier,[13]

$$\begin{aligned} P(\varepsilon_1) = {} & \frac{A(1-c)}{\sigma_0\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\varepsilon_1}{\sigma_0} + \frac{\sigma_0}{k_BT}\right)^2 + \frac{1}{2}\left(\frac{\sigma_0}{k_BT}\right)^2\right] \\ & + \frac{Ac}{\sigma_1\sqrt{2\pi}} \exp\left[\frac{\varepsilon_t}{k_BT} - \frac{1}{2}\left(\frac{\varepsilon_1}{\sigma_1} + \frac{\sigma_1}{k_BT} + \frac{\varepsilon_t}{\sigma_1}\right)^2 \right. \\ & \left. + \frac{1}{2}\left(\frac{\sigma_1}{k_BT}\right)^2\right], \end{aligned} \tag{9}$$

$$P(\varepsilon_2) = (1-c)\,\delta(\varepsilon_2) + c\,\delta(\varepsilon_2 + \varepsilon_t), \tag{10}$$

where

$$A = \frac{1}{(1-c)\exp\left[\frac{1}{2}\left(\frac{\sigma_0}{k_BT}\right)^2\right] + c\exp\left[\frac{\varepsilon_t}{k_BT} + \frac{1}{2}\left(\frac{\sigma_1}{k_BT}\right)^2\right]}. \tag{11}$$

Here, it is assumed that the energy distributions of the density of transport and trap states are described by Gaussian functions of width σ_0 and σ_1, respectively.

For calculation of W_e^- one should substitute $\varepsilon_1 \leftrightarrow \varepsilon_2$ in Eqs. (9) and (10). The result for the effective drift mobility μ_e after performing of configuration averaging reads

$$\mu_e = \mu_2 \frac{Y_e^+ - Y_e^-}{f}, \tag{12}$$

where

$$\begin{aligned} Y_e^{\pm} = {} & A(1-c)^2 i_1^{\pm} \exp\left[-2\frac{a}{b}\left(\frac{1}{(1-c)^{1/3}} - 1\right)\right] + A(1-c) \\ & \times c[i_2^{\pm} + i_3^{\pm}\exp(xy)]\exp\left[-\frac{a}{b}\left(\frac{1}{(1-c)^{1/3}} + \frac{1}{c^{1/3}} - 2\right)\right] \\ & + Ac^2 i_4^{\pm}\exp(xy)\exp\left[-2\frac{a}{b}\left(\frac{1}{c^{1/3}} - 1\right)\right], \end{aligned} \tag{13}$$

$$\begin{aligned} i_1^{\pm} = {} & \frac{1}{2}\exp\left(\frac{x^2}{2}\right)\left\{\left[1 - erf\left(\frac{\pm f}{\sqrt{2}}\right)\right]\exp\left(-\frac{x^2}{2} \pm xf\right) \right. \\ & \left. + \left[1 - erf\left(\frac{x \mp f}{\sqrt{2}}\right)\right]\right\}, \end{aligned} \tag{14}$$

$$\begin{aligned} i_2^{\pm} = {} & \frac{1}{2}\exp\left(\frac{x^2}{2}\right)\left\{\left[1 - erf\left(\frac{\pm f + y}{\sqrt{2}}\right)\right]\exp\left(-\frac{x^2}{2} + x(\pm f + y)\right) \right. \\ & \left. + \left[1 - erf\left(\frac{x \mp f - y}{\sqrt{2}}\right)\right]\right\}, \end{aligned} \tag{15}$$

$$i_3^{\pm}=\frac{1}{2}\exp\left(\frac{x^2\eta^2}{2}\right)\left\{\left[1-erf\left(\frac{\pm f-y}{\eta\sqrt{2}}\right)\right]\times\exp\left(-\frac{x^2\eta^2}{2}+x(\pm f-y)\right)+\left[1-\mathrm{erf}\left(\frac{\eta^2 x\mp f+y}{\eta\sqrt{2}}\right)\right]\right\}, \tag{16}$$

$$i_4^{\pm}=\frac{1}{2}\exp\left(\frac{x^2\eta^2}{2}\right)\left\{\left[1-\mathrm{erf}\left(\frac{\pm f}{\eta\sqrt{2}}\right)\right]\exp\left(-\frac{x^2\eta^2}{2}\pm xf\right)+\left[1-\mathrm{erf}\left(\frac{\eta^2 x\mp f}{\eta\sqrt{2}}\right)\right]\right\}, \tag{17}$$

$$x=\frac{\sigma_0}{k_BT},\quad \eta=\frac{\sigma_1}{\sigma_0},\quad y=\frac{\varepsilon_t}{\sigma_0},\quad f=\frac{eaE}{\sigma_0},$$

$$\mu_2=\frac{ea^2\nu_0}{\sigma_0}\exp\left(-2\frac{a}{b}\right), \tag{18}$$

where $\mathrm{erf}(z)=(2/\sqrt{\pi})\int_0^z dt\exp(-t^2)$ is the error function.

In the present treatment we restrict our consideration to the case of weak electric fields, when $f\to 0$ $(E\to 0)$ and of relatively deep traps, when $y\gg 1$. Then, for the whole range of trap concentration $(0\leqslant c\leqslant 1)$ one obtains from Eqs. (12)–(18)

$$\frac{\mu_e}{\mu_2}=\frac{\sigma_0}{k_BT}\frac{1+c^2\exp\left[-2\frac{a}{b}\left(\frac{1}{c^{1/3}}-1\right)+\frac{\varepsilon_t}{k_BT}\right]}{1+c\exp\left[\frac{1}{2}\left(\frac{\sigma_0}{k_BT}\right)^2(\eta^2-1)+\frac{\varepsilon_t}{k_BT}\right]}\times\exp\left[-\frac{1}{2}\left(\frac{\sigma_0}{k_BT}\right)^2\right]. \tag{19}$$

In the derivation of Eq. (19) we neglected terms proportional to the product $(1-c)c$ which, as analysis showed, have a negligibly small contribution to the result. The obtained Eq. (19) in the range of small trap concentrations when $c_{1/2}<c<c_{cr}$ can be well approximated by

$$\frac{\mu_e}{\mu_2}=\frac{1}{c}\frac{\sigma_0}{k_BT}\exp\left[-\frac{1}{2}\left(\frac{\sigma_0}{k_BT}\eta\right)^2-\frac{\varepsilon_t}{k_BT}\right], \tag{20}$$

or

$$\mu_e=\frac{1}{c}\frac{ea^2\nu_0}{k_BT}\exp\left(-2\frac{a}{b}\right)\exp\left[-\frac{1}{2}\left(\frac{\sigma}{k_BT}\eta\right)^2-\frac{\varepsilon_t}{k_BT}\right]. \tag{21}$$

In the range of large trap concentration when $c_{cr}<c\leqslant 1$ the following approximation of Eq. (19) is appropriate:

$$\frac{\mu_e}{\mu_2}=c\frac{\sigma_0}{k_BT}\exp\left[-2\frac{a}{b}\left(\frac{1}{c^{1/3}}-1\right)\right]\exp\left[-\frac{1}{2}\left(\frac{\sigma_0}{k_BT}\eta\right)^2\right], \tag{22}$$

or

$$\mu_e=c\frac{ea^2\nu_0}{k_BT}\exp\left(-2\frac{a}{b}\frac{1}{c^{1/3}}\right)\exp\left[-\frac{1}{2}\left(\frac{\sigma_0}{k_BT}\eta\right)^2\right]. \tag{23}$$

Here $c_{1/2}$ is a trap concentration at which the charge mobility drops by a factor of 2 with respect to trap-free mobility and it can be obtained by

$$c_{1/2}=\exp\left[-\frac{\varepsilon_t}{k_BT}-\frac{1}{2}\left(\frac{\sigma_0}{k_BT}\right)^2(\eta^2-1)\right]. \tag{24}$$

The effective charge-carrier mobility reaches the minimum value at a critical trap concentration c_{cr}. The critical trap concentration c_{cr} is determined by the intersection point of the lines described by Eqs. (20) and (22) and it can be obtained from the following transcendental equation:

$$c_{cr}=\exp\left[-\frac{1}{2}\frac{\varepsilon_t}{k_BT}+\frac{a}{b}\left(\frac{1}{c_{cr}^{1/3}}-1\right)\right]. \tag{25}$$

The exponent $-2a/(bc^{1/3})$ in Eq. (23) reflects the well-known mean distance between traps. Therefore, at trap concentration within the range $0<c<c_{1/2}$, one expects the trap-perturbation transport, for the range $c_{1/2}<c<c_{cr}$ the transport is trap-controlled, and the trap-to-trap transport regime dominates at the trap concentration $c_{cr}<c\leqslant 1$. It is worth noting that in the latter case, Eq. (23) describing the charge mobility at dominated trap-to-trap transitions differs from that of Ref. 13 by the presence of the term $bc^{1/3}$ instead of b in the exponent, which seems to be a quite natural result, and it has been proved by experimental observation of a linear dependence of $\log_{10}(\mu)$ versus $c^{-1/3}$.[11] Thus, the critical trap concentration c_{cr} denotes the concentration of traps at with transition from trap-controlled to the trap-to-trap hopping transport occurs at a given temperature T and trap depth ε_t. In a similar manner one can define a critical trap depth ε_{cr} for a given trap concentration c and temperature T

$$\varepsilon_{cr}=-2k_BT\left[\ln(c)+\frac{a}{b}\left(1-\frac{1}{c^{1/3}}\right)\right]. \tag{26}$$

By the same way, a critical temperature T_{cr} can be introduced for a given trap concentration c and trap depth ε_t and it is obtained as

$$T_{cr}=-\frac{1}{2k_B}\frac{\varepsilon_t}{\ln(c)+\frac{a}{b}\left(1-\frac{1}{c^{1/3}}\right)}. \tag{27}$$

This implies that at $T>T_{cr}$ the trap-controlled transport regime occurs, which can be described by Eq. (20), while at $T<T_{cr}$ the trap-to-trap hopping transport dominates described by Eq. (22). As this takes place, an apparent Arrhenius activation energy defined as $\varepsilon_a=-k_B[d\ln\mu_e/d(1/T)]$ can be expressed either as $\varepsilon_a=\varepsilon_t+\eta^2\sigma_0^2/k_BT$ at $T>T_{cr}$ (i.e., to be the sum of two components) or as $\varepsilon_a=\eta^2\sigma_0^2/k_BT$ at $T<T_{cr}$.

Let us compare the parameters of c_{cr} and T_{cr} calculated by the present theory with that which follows from the previous treatment from Ref. 13. Assuming ε_t=0.4 eV, T=300 K, and a/b=5, one obtains from Eq. (25) c_{cr}=0.108. Employment of the equation $c_{cr}=\exp(-\varepsilon_t/2k_BT)$ from Ref. 13 yields c_{cr}=0.000436, i.e., a considerably smaller critical concentra-

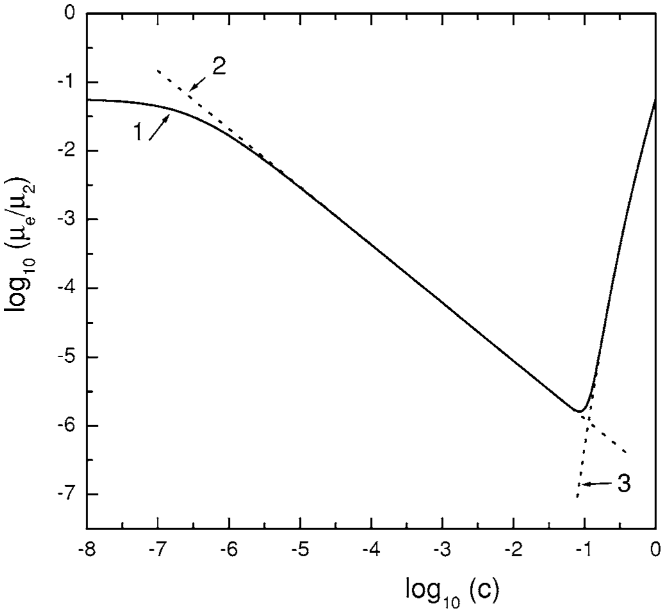


FIG. 1. The trap concentration dependence of the charge-carrier mobility, $\log_{10}(\mu_e/\mu_2)$ vs $\log_{10}(c)$, calculated by the present EMA theory for a hypothetical organic disordered system using the Eqs. (19), (20), and (22) (curves 1, 2, and 3, respectively). The following parameters were used for calculation: $\sigma_0/k_BT=3$, $\varepsilon_t/\sigma_0=5$, $\sigma_1/\sigma_0=1$, and $a/b=5$.

tion of traps. In similar manner, at $\varepsilon_t=0.4$ eV, $c=0.108$, and $a/b=5$, one obtains from Eq. (27) $T_{cr}=300$ K, while the equation $T_{cr}=-\varepsilon_t/2k_B\ln(c)$ from the previous treatment[13] predicts a considerably higher critical temperature $T_{cr}=1043$ K. The latter implies that the trap-controlled transport regime occurs in a considerably broader temperature range than that predicted in Ref. 13. It should be noted that the critical temperature T_{cr} matches a temperature range commonly used in experiments. Thus, accounting for the dependence of the overlap integral W_0 on trap concentration c results in considerable change of both critical trap concentration c_{cr} and the critical temperature T_{cr} at which the transition trap-controlled transport to trap-to-trap hopping transport occurs comparing to that predicted by previous treatment.[13]

Calculations of charge-carrier mobility versus trap concentration for a hypothetical organic disordered system using Eqs. (19), (20), and (22) are illustrated in Fig. 1 by curves 1, 2, and 3, respectively. The trap-concentration dependence of charge mobility calculated by Eq. (12) at $E\rightarrow 0$ practically overlaps with curve 1. The intersection point of lines 2 and 3 in Fig. 1 determines, as mentioned above, the critical trap concentration c_{cr}. It should be noted that the present theory predicts that (i) the c_{cr} is shifted towards higher trap concentrations and (ii) the charge mobility in vicinity of c_{cr} is much lower as compared with results of the previous treatment[13] ignored the dependence of the overlap integral W_0 upon the trap concentration c.

Figure 2 compares the results of EMA calculation of the trap concentration of charge-carrier mobility in an organic disordered system using Eq. (12) (solid curve) with available computer simulation data[6] (symbols). It should be noted that all material parameters used for the calculation (such as $\varepsilon_t=0.195$ eV, $\sigma_0=0.065$ eV, $T=400$ K, $E=2\times 10^5$ V/cm) were exactly the same as employed earlier in the computer simulation[6] of charge transport in this system. Hence, as one can see, the prediction of the EMA theory is in good quantitative agreement with results of computer simulation (symbols in Fig. 2) obtained for the whole range of the trap concentrations.

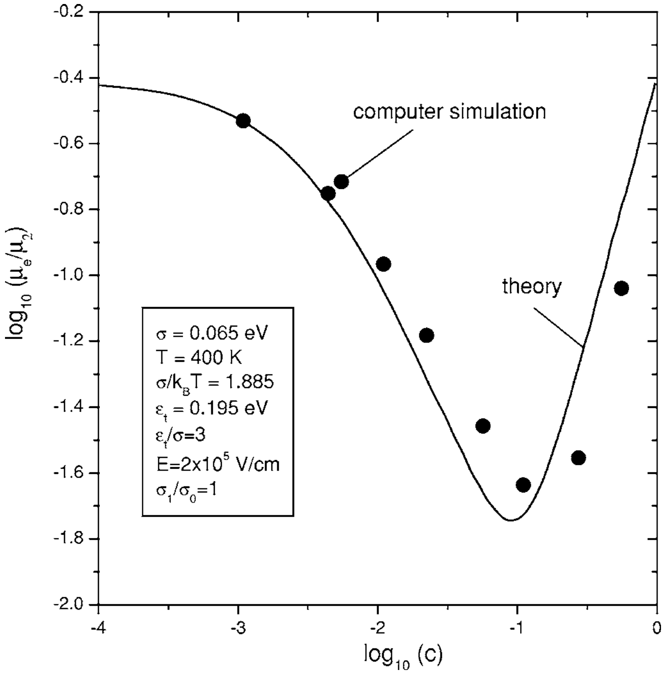


FIG. 2. The trap concentration dependence of the charge-carrier mobility $\log_{10}(\mu/\mu_2)$ vs $\log_{10}(c)$ for an organic disordered system calculated by the EMA theory (solid curve) and obtained by the computer simulation (Ref. 5) (symbols).

As one can see from Figs. 1 and 2, the present EMA theory reproduces a nonmonotonous dependence of charge mobility with trap concentration qualitatively similar to what has been observed experimentally. Figure 3 shows theoretical fitting by Eq. (19) (solid line) of the concentration dependence of the hole-drift mobility measured in di-*p*-tolylphenylamine (DPT)-doped polystyrene containing different concentrations of the trap DEH ($\varepsilon_t=0.32$ eV) (symbols).[12] It should be mentioned that the measurements have been done at relatively large electric field of 3.6×10^5 V/cm, which is much higher than the fields at which one could expect considerable contribution from the diffusion transport[16] at the given temperature and film thickness. Therefore the transport is drift dominated. The latter conclusion is also supported by observation of nondispersive photocurrent transients at all trap concentrations.[12] All material parameters used in the calculation were taken from experiment and they are presented in the inset of Fig. 3, so one can compare quantitatively the calculation results with experimental data for the same system. The only adjustable parameter was $a/b=5$, the ratio between the average intersite distance and the localization radius. As one can see from Fig. 3, there is an excellent agreement between the present theory and experiment over the whole trap concentration range, in-

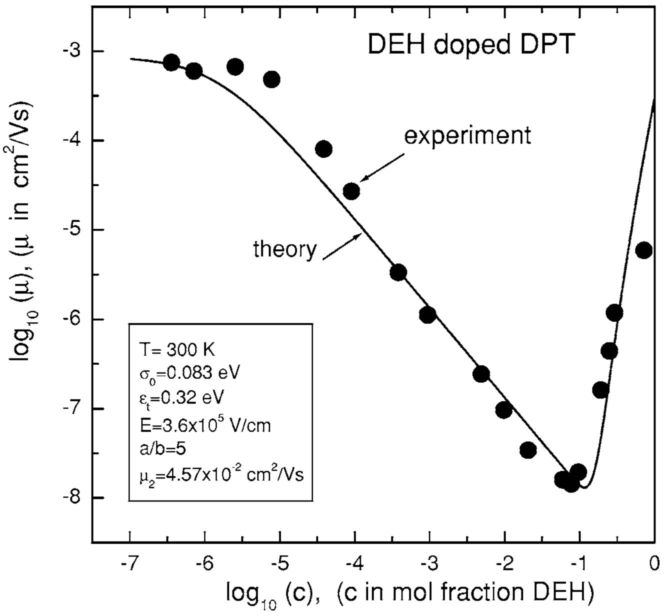


FIG. 3. The experimental concentration dependence of the hole-drift mobility measured in DPT doped polystyrene containing different concentration of traps due to DEH (symbols) (Ref. 12) and that are calculated by the present theory (solid line). Material parameters are the following: $\sigma_0/k_BT=3.2$, $\varepsilon_t/\sigma_0=3.85$, and $a/b=5$.

cluding the critical trap concentration value c_{cr}, and also the magnitude of the relative decrease of charge mobility at c_{cr} compared to trap-free mobility is well reproduced. Note that the previous EMA treatment,[13] which ignored the dependence of the overlap integral upon the trap concentration, has failed to properly describe charge mobility at trap concentrations larger than c_{cr}.

Further, let us consider so-called effective disorder parameter σ_{eff} for trap-containing disordered materials. This parameter for the whole trap-concentration range $0 \leqslant c \leqslant 1$ can be obtained as

$$\left(\frac{\sigma_{eff}}{\sigma_0}\right)^2 = 1 + 2\left(\frac{k_BT}{\sigma_0}\right)^2 \ln \times \left\{ \frac{1 + c \exp\left[\frac{\varepsilon_t}{k_BT} + \frac{1}{2}\left(\frac{\sigma_0}{k_BT}\right)^2 (\eta^2 - 1)\right]}{1 + c^2 \exp\left[\frac{\varepsilon_t}{k_BT} + 2\frac{a}{b}\left(1 - \frac{1}{c^{1/3}}\right)\right]} \right\}. \tag{28}$$

For the trap concentration range $c_{1/2} < c < c_{cr}$, it reduces to

$$\left(\frac{\sigma_{eff}}{\sigma_0}\right)^2 = 1 + 2\left(\frac{k_BT}{\sigma_0}\right)^2 \left[\ln(c) + \frac{\varepsilon_t}{k_BT} + \frac{1}{2}\left(\frac{\sigma_0}{k_BT}\right)^2 (\eta^2 - 1)\right]. \tag{29}$$

When $\eta=1$, Eq. (29) transforms to the known expression previously obtained by the EMA theory,[13]

$$\left(\frac{\sigma_{eff}}{\sigma_0}\right)^2 = 1 + 2\left(\frac{k_BT}{\sigma_0}\right)^2 \left[\ln(c) + \frac{\varepsilon_t}{k_BT}\right]. \tag{30}$$

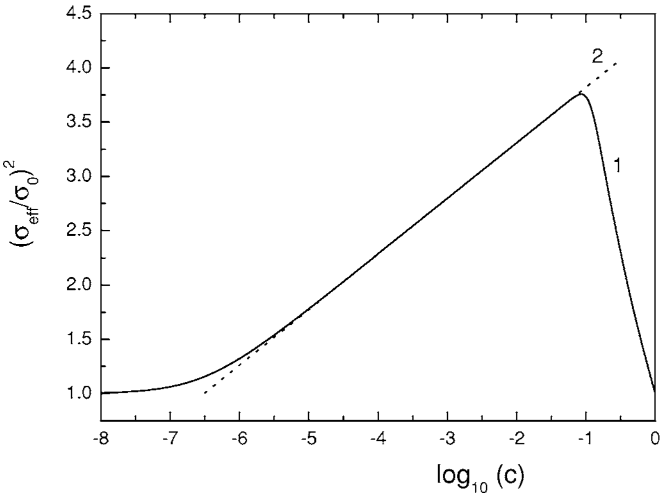
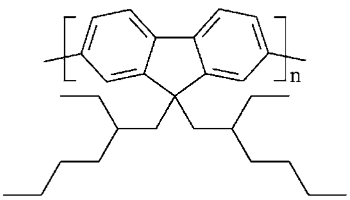


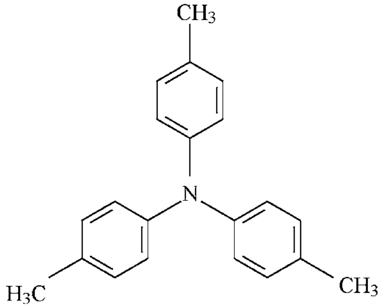
FIG. 4. The trap concentration dependence of the effective disorder parameter, $(\sigma_{eff}/\sigma_0)^2$ vs $\log_{10}(c)$, calculated by the present theory for a disordered organic material using the Eqs. (28) and (29) (curves 1 and 2, respectively) and the following parameters: $\sigma_0/k_BT=3$, $\varepsilon_t/\sigma_0=5$, $\sigma_1/\sigma_0=1$, and $a/b=5$.

The trap-concentration dependence of $(\sigma_{eff}/\sigma_0)^2$ calculated by Eqs. (28) and (29) for a disordered organic material is illustrated in Fig. 4 (curves 1 and 2, respectively). Material parameters used in the calculation are given in the figure caption. As one can see from Fig. 4, as expected, the effective disorder parameter σ_{eff} increases with increasing trap concentration within the range of relatively small trap concentrations, but it tends to decrease at large trap concentration level when the trap concentration exceeds the c_{cr}. It worth noting that a qualitatively similar behavior was observed in charge-transport measurements as performed in poly(*N*-epoxypropylcarbazole) (PEPCz) doped with triphenylamine,[17] which is known to act as a moderately deep hole trap in the polymer. It was indeed found that the apparent activation energy of the drift-hole mobility first increases with increasing the additive (trap) concentration, reaches the largest value of 0.43 eV at an intermediate trap concentration of several percents, and then decreases as trap concentration increases. At a triphenylamine concentration of 28% the apparent activation energy of the hole mobility measured in polymer film at $E=6\times10^5$ V/cm drops to the value of 0.23 eV that is even smaller of that for undoped PEPCz (0.35 eV).[17] This implies that hopping charge transport occurs via the trap sites at sufficiently large triphenylamine concentration and the DOS distribution of trap states is narrower than that of PEPCz matrix and is associated with a smaller apparent activation energy of the mobility. The results presented in Fig. 4 also suggest that Eq. (29) or (30) can be used only in a limited range of trap concentrations when $c_{1/2} < c < c_{cr}$ and imposes a certain limitation for application of the above equations. Therefore, the more general Eq. (28) is more appropriate for practical usage since it is valid for arbitrary trap concentrations $0 \leqslant c \leqslant 1$.

To compare the EMA theory prediction on the effective disorder parameter given by Eq. (28) with experimental results for conjugated polymers, we have employed TSL techniques to study the energetic disorder in a conjugated poly-



PF2/6



TTA

FIG. 5. The molecular structures of poly[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl] (PF2/6) and tri-p-tolylamine (TTA).

mer with controllable trap concentration. TSL is especially suitable technique allowing the estimation of the width of the DOS distribution in disordered organic solids, and it has been recently applied to study intrinsic energetic disorder in molecularly doped polymers, π- and σ-conjugated polymers, pendant-group polymers, and in some vapor-deposited molecular glasses.[18–21] In the subsequent sections we describe the experimental TSL studies of the effective energetic disorder in a polyfluorene derivative containing different concentration of deliberately introduced traps and compare the experimental data with the EMA calculation results.

III. EXPERIMENTAL

Poly[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl] (PF2/6) polymer (molecular weight of Mn=83500) have been synthesized via the Yamamoto route[22] in Bergische Universität Wuppertal. Details of the synthesis were reported elsewhere.[23] Charge-transporting molecules of tri-p-tolylamine (TTA) were supplied by the Eastman Kodak Company. All materials were used as received. The structural formulas of PF2/6 and TTA are displayed in Fig. 5. Films of doped polymer were prepared by dissolving the appropriate ratios of TTA and PF2/6 in toluene (3% solids), and then casting the resulting solutions on a metal substrate. After deposition, the films were dried at 10^{-3} Pa at room temperature.

TSL is the phenomenon of luminescent emission after removal of excitation under conditions of increasing temperature. Generally, in the TSL method, the trapping states are first populated by photogeneration of charge carriers, usually at low temperatures in order to prevent a fast escape. Then, the trapped charge carriers are released by heating up the sample with a linear temperature ramp, while the luminescence due to radiative recombination is recorded as a function of temperature. If an energy distribution of the trap states exists, TSL spectra are complicated convolution of contributions from different traps at different energies and the fractional heating techniques have to be applied, which are based on cycling the sample with a large number of small temperature oscillations superimposed on a constant heating run. Thus, the TSL is a useful tool for determining the trap depths even when traps are not well separated in energy or are continuously distributed, and it also allows analysis of the trap spectra even when they are complex. Unfortunately, the interpretation of TSL phenomena in disordered organic materials with hopping charge transport is not so straightforward as in inorganic crystalline materials due to the presence of strongly localized energetically disordered states forming a Gaussian DOS distribution and the lack of the band edge, therefore it is not obvious which sites play a role of traps and which are regular transport state. Therefore, a hopping model of TSL in disordered organic materials has been recently suggested,[18–21] which describes most of the basic features of the TSL in disordered organic materials and permits the calculation of the DOS distribution from the TSL data.

TSL measurements were carried out using a home-built setup operable from 4.2 to 350 K using a temperature-controlled helium cryostat. After cooling down to 4.2 K, the samples were photoexcited, usually for 30 s, by a high-pressure 500 W mercury lamp with an appropriate set of glass optical filters for light selection. After the photoexcitation, the TSL was detected in a photon-counting mode with a cooled photomultiplier, positioned next to the cryostat window. The TSL measurements were performed either at a constant heating rate of $\beta=0.15$ K/s or in the fractional heating regime. The latter procedure allows the determination of trap depth when different groups of traps are not well separated in energy or are continuously distributed. The details of our TSL method were described previously.[18,19]

IV. RESULTS AND DISCUSSION

Figure 6 shows the TSL glow curves of PF2/6 doped with TTA with relative concentration of 0, 3×10^{-4}, 5×10^{-3}, 2×10^{-2}, 1.8×10^{-1} (curves 1–5, respectively). The TSL glow peak of undoped PF2/6 (Fig. 6, curve 1) is a rather narrow single peak located at low temperatures with maximum at $T\cong45$ K and is similar to that observed recently in another polyfluorene derivative poly[9,9-bis(5-methylheptyl)fluorene-2,7-diyl].[20] The observed low-temperature TSL peak in PF2/6 films can be explained in terms of the hopping model of TSL recently developed analytically by Arkhipov *et al.*,[18,21] which is based on the concept of thermally stimulated carrier random walk within a positionally and energetically random system of hopping sites. A specific feature of disordered solids is that *intrinsic hopping states*, localized within the tail of the DOS, can act as traps at very low temperatures. TSL of polyfluorenes has been recently described[20,24] and the peak was as-

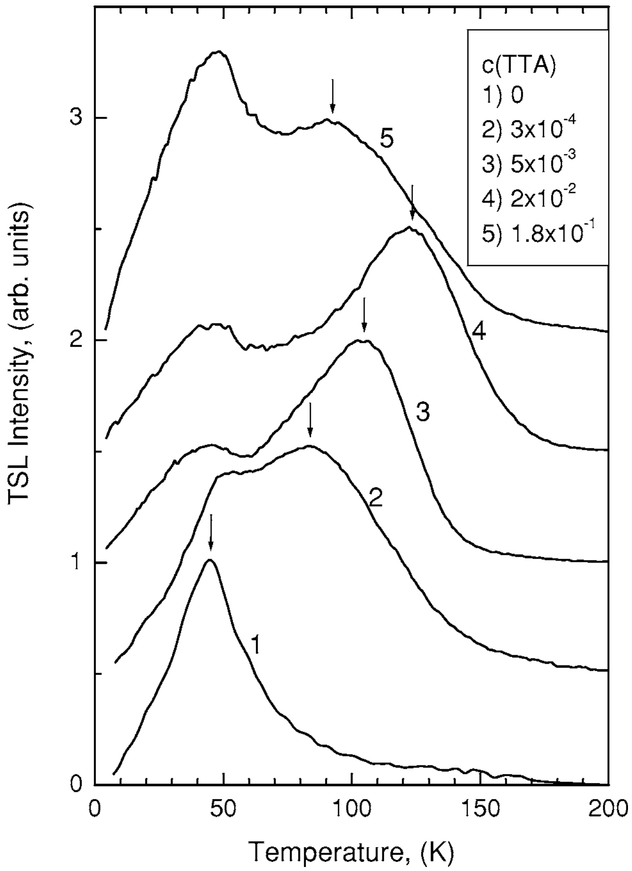


FIG. 6. TSL glow curves of PF2/6 polymer doped with TTA with relative concentration of 0, 3×10^{-4}, 5×10^{-3}, 2×10^{-2}, 1.8×10^{-1} (curves 1-5, respectively).

cribed to detrapping of holes from shallow localized states most probably related to the tail states of the intrinsic DOS distribution. Such low-temperature hole trapping is evidence for a weak energy disorder in the PF2/6 films most probably due to a well-ordered "semi-crystalline" morphological structure of the films. Analysis of the TSL data within the hopping model of TSL yields the width of the intrinsic DOS distribution σ of about 0.04 eV.[20] This conclusion agrees with charge-transport data indicating that hole mobilities in PFs are much higher that electron mobility.[25] It should be noted that recently it was demonstrated[24] that PF2/6 is characterized by a quasicontinuous trap distribution with the mean activation energy linearly increasing with temperature as revealed by fractional TSL measurements (not shown here). The latter dependence was also found to be practically the same in doped PF2/6 films at all TTA concentrations. Similar behavior was found before for many conjugated polymers.[18–21]

As expected, doping of PF2/6 films with TTA molecules results in appearance of additional TSL peak located at somewhat higher temperature because the HOMO level of TTA is known to be above that of the polymer matrix. Remarkably, the temperature position of the above high-temperature TSL peak is not constant but rather sensitive to the trap concentration; namely, it gradually shifts to higher temperatures with increasing trap concentration at small relative TTA concentrations (Fig. 6, curves 2–4), but it shifts back towards low temperatures with further increase of c when trap concentrations are large (cf. curves 4 and 5 in Fig. 6). Thus, there is an intermediate TTA concentration of about $c \leqslant 0.02-0.04$ at which the high-temperature shift of the TSL peak is maximal. It should be mentioned that the change of the temperature position of the high-temperature peak corresponds to the change of the mean activation at the peak maximum. The above behavior of the TSL in TTA doped PF2/6 films can be well analyzed in terms of the effective energetic disorder described in Sec. II. Indeed, the above-mentioned concentration of $c \leqslant 0.02-0.04$ resembles the critical trap concentration and the low-temperature shift of the TSL peak at larger concentrations can be explained in terms of percolative-type motion of carriers within the manifold of trapping states, since the distance between TTA molecules becomes sufficiently close for transport.

Such interpretation is based on the reasoning that the activation energy of the TSL peak maximum is proportional to the effective energetic disorder parameter σ_{eff}, as was observed experimentally for different disordered materials[26] and supported by the hopping model of TSL.[18,21] Actually, since TSL measurements are performed after some dwell time on samples, which have been photoexcited at helium temperature, the population of localized (trapping) sites occurs in the process of low-temperature energetic relaxation of photogenerated carriers that could be well described by both the effective medium approach developed by Movaghar[27,28] and the variable-range hopping theory by Arkhipov *et al.*[21] for energetic relaxation of carriers. According to these theories, the energetic relaxation of randomly generated particles in the *zero-temperature* limit occurs through a nonactivated downward hopping with the decay of the mean energy following the expression[27,28]

$$\varepsilon_R = \sigma[3 \ln \ln(t/t_0)^{1/2}], \qquad (31)$$

where ε_R is the mean energy of the charge-carrier packet relative to the center of the DOS distribution, t is the time, and t_0 is the dwell time of a carrier at a lattice site without disorder [for a charge carrier, t_0 is accepted as 10^{-13} s (Ref. 28)]. The low-temperature relaxation prosess described by Eq. (31) practically saturates on experimental time scale of minutes and therefore the parameter σ can, at least roughly, be evaluated from the activation energy at the TSL peak maximum, assuming that the latter corresponds to the mean energy of the relaxed charge-carrier packet, ε_R. It should be noted that in such consideration one should account also for the fact that the thermal release of carriers occurs to the effective transport energy level[18,20,26] that normally is located below the center of the DOS. Nonetheless, the parameter σ is roughly proportional to the activation energy measured in the TSL maximum and, correspondingly, to the temperature of the TSL peak maxim as the mean activation energy measured by the fractional TSL generally scales linearly with temperature.[20,26] This conclusion was proved by TSL studies of disordered organic solids for which σ parameters have been determined from charge-transport measurements, i.e., the larger energetic disorder parameter σ the higher temperature of the TSL peak maximum.[26] Therefore, σ can be

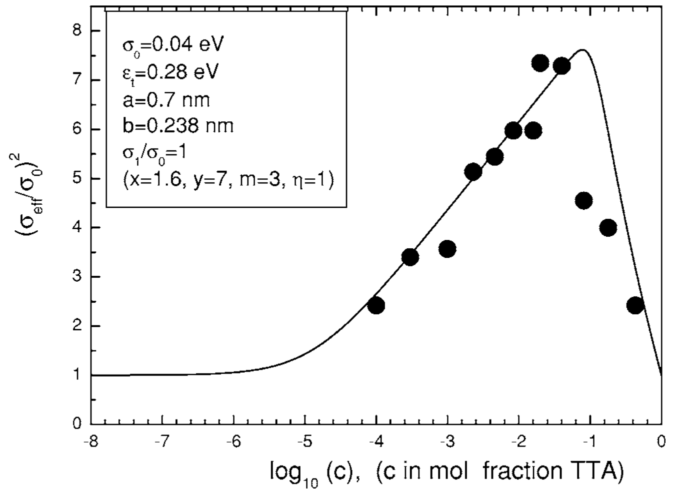


FIG. 7. The effective disorder parameter $(\sigma_{eff}/\sigma_0)^2$ versus $\log_{10}(c)$ derived from TSL measurements (symbols) and theoretical fitting by the Eq. (28) (solid curve). The material parameters used for calculation are shown in the inset.

roughly estimated from the temperature of TSL peak maximum by comparing it with that measured in a reference material for which the disorder parameter is known.

The nonmonotonous dependence of the high-temperature TSL peak temperature position with TTA concentration should reflect the nonmonotonous dependence of the effective energetic disorder parameter σ_{eff}. Results of a simple analysis of the TSL data presented in Fig. 7 supports such a conclusion. As was discussed above, we assumed here that ratio (σ_{eff}/σ_0) is proportional to $(T_{(c)}/T_0)$, where $T_{(c)}$ is the temperature of the high-temperature TSL peak maximum at the TTA concentration c and T_0 is the temperature of the TSL peak maximum of undoped PF2/6, and that σ_0 for undoped PF2/6 was estimated to be 0.04 eV.[20] Symbols in Fig. 7 are experimental data $(\sigma_{eff}/\sigma_0)^2$ versus $\log_{10}(c)$ derived from TSL measurements and the solid curve is the fitting by the Eq. (28). We used the following material parameters for the fitting, namely the width of the intrinsic DOS $\sigma_0=0.04$ eV (taken from Ref. 20), localization radius $b=0.238$ nm (determined for TTA in Ref. 29), and assuming that the trap depth due to TTA $\varepsilon_t=0.28$ eV that is equal to the activation energy measured at the TSL peak maximum at $c(TTA)=0.02$. It was also assumed that the average intermolecular distance is $a=0.7$ nm, which is quite typical for conjugated polymers, and $\sigma_1/\sigma_0=1$. Despite of the simplified analysis of the TSL data, Fig. 7 demonstrates a good coincidence between experimental and the theoretical calculation of the effective disorder parameter for the doped polyfluorene systems.

It should be noted that comparison of TSL and transport data assumes that the energetic disorder, which governs the temperature dependence of charge mobility, does not change notably upon freezing down the samples to low temperatures. This conclusion is supported by charge-transport studies in some conjugated polymers over a very broad temperature range[30] and by successfully predictable transition from nondispersive to dispersive transport regimes at low temperature in disordered organic materials.[31] Therefore the low-temperature TSL method probes virtually the same distribution of localized states and its analysis can yield an effective density of states width in good agreement with the values estimated from transport.[18] It should be mentioned that the decrease of the σ_{eff} at large trap concentrations might be also understood in terms of the effective transport energy level, which could be affected by large concentration of traps; namely, it gradually shifts to deeper states at high trap densities as recently suggested by Arkhipov *et al.*[32] and this could result in weakening temperature dependence of the mobility. TSL peak demonstrates a considerable shift to lower temperatures at high trap concentration that can also be interpreted by lowering the effective transport level. Indeed, in the TSL of hopping transport materials, the thermal release of charge carriers from tail states of the DOS to the effective transport energy level is a rate-limiting step,[18,21] and therefore it is natural that TSL is also sensitive to the trap affected effective transport energy level at large trap concentrations.

Finally, it should be mentioned that the nonmonotonous trap concentration dependence of the mobility and the effective energetic disorder discussed here resembles a recently found dependence of the charge mobility upon dopant concentration in so-called chemically doped organic semiconductors.[33,34] The origin for the phenomena is, however, different. As was stated above, in the present paper we consider the traps that are neutral when empty, while the chemical doping implies doping by ionized moieties. The latter can occur, for instance, when an organic semiconductor is doped by a strong acceptor or donor molecule whose electron affinity is large enough (or its ionization potential is low enough) to allow charge transfer in the ground state from matrix to dopant.[35] Experimental studies of some chemically doped materials[33] have shown a decrease of the charge mobility with increasing dopant concentration at low-to-moderate doping levels while the mobility increases pronouncedly at large doping concentration. Moreover, a doping-induced broadening of the DOS distribution has been straightforwardly demonstrated in recent studies.[36–39] This effect was attributed to strong Coulomb interaction of charge carriers localized in intrinsic hopping sites of the matrix with randomly distributed dopant ions.[34,40] Theoretical calculations by Arkhipov *et al.*[40] have proved that at moderate chemical doping the Coulomb traps associated with ionized dopants enhance the energetic disorder and remarkably that the low-energy tail of the intrinsically Gaussian-shaped DOS changes to a weaker-decaying power-law dependence $(\sim\varepsilon^{-4})$. At high chemical dopant concentrations, the mobility increases due to increasing density of charge carriers that lifts up the Fermi level as shown by Pasweer *et al.*[41] and due to strong overlap of the Coulomb traps which effectively lowers the energy barrier between them and eventually smoothens the random potential landscape.[34] The latter is quite feasible for the Coulomb traps in organic materials where the dielectric permittivity is typically low (~2–3), resulting in a very large Coulomb trap cross section of 10–20 nm, which should include several hundreds of intrinsic hopping sites.

The situation considered in the present paper is very different from that in chemically doped materials due to the cross section of "neutral" traps is much smaller (usually equal to the size of a charge-transporting molecule-hopping site) and that we consider a very low density of charge carriers, which is typically realized in time-of-flight experiments being performed in a weak signal mode. Besides, a characteristic property of the chemically doped semiconductors is that the Coulomb interaction between ionized dopants and charge carriers causes a significant change of the functional dependence of the DOS distribution[40] from a Gaussian to an exponential or power-law dependence, while such an interaction is irrelevant to materials containing neutral traps and the low-energy tail of the cumulative DOS could still be reasonably well approximated by a Gaussian profile.[4,18,32]

V. CONCLUSION

In the present paper we considered the charge transport in disordered organic materials at different trap concentration with a special emphasis on trapping phenomena at large trap concentrations when the transport through the trap-state manifold becomes possible. The effect of charge-carrier traps over the entire range of trap concentrations was thoroughly studied theoretically and the results were compared with charge-trapping experiments. We advanced further the effective medium theory to describe more adequately nondispersive charge transport for arbitrary trap concentration. A key point of this treatment compared to the previous one (Ref. 13) is that the present model accounts also for the dependence of the overlap integral upon the trap concentration due to the dilution of transport sites by traps, which turns out to be of key importance at large trap concentrations. While both treatments provide similar results for small and moderate trap concentrations, the present theory was found to describe more adequately the charge transport at large trap concentrations and predicts successfully the transition from trap-controlled to trap-to-trap hopping transport. The latter was evidenced by good quantitative agreement between the calculation results and relevant experimental data. Our theory supports the notion that the so-called effective energetic disorder parameter σ_{eff} (reflecting an interplay of disorder effects and traps) can be used as a new material parameter within the disorder formalism to describe charge-transport phenomena in trap-containing disordered organic materials and we also provide a more accurate estimation for the σ_{eff} to account the effect of traps for arbitrary trap concentrations.

The trap concentration dependence of σ_{eff} was also measured in a polyfluorene conjugated polymer deliberately doped with different concentration of traps due to the tri-*p*-tolylamine additives by TSL method which is known to be very sensitive to the energetic disorder in organic solids. It is remarkable that σ_{eff} parameter shows a nonmonotonous dependence on trap concentrations; i.e., it first increases with increasing trap concentration at low and moderate trap concentrations, but then tends to decrease at large concentrations. The obtained experimental results on the conjugated polymer agree well with the prediction of the theory. An important implication of the presented study is that charge-trapping experiments, like thermally stimulated current and thermally stimulated luminescence methods, widely used for study of disordered organic materials containing traps, do not provide a value for the *exact* difference between HOMO/LUMO levels of host and guest materials (true trap depth) as commonly assumed, but rather provide only an effective value which is a function of trap depth, energetic disorder, and trap concentration. We also demonstrate that the TSL method is a useful method to extract information on charge transport in disordered organic materials.

Finally it should be mentioned that the EMA is a useful method for study of different aspects of the charge-carrier transport in disordered organic semiconductors. Although initially it was accepted that the EMA is well suited for description of mainly weakly disordered systems, the later works of Movaghar *et al.* (see, for instance, Ref. 42) have convincingly demonstrated that this method can be also applied to strongly energetically disordered systems. Adopting the concept of the effective transport energy level allowed us to formulate the EMA for materials with large degree of disorder as well (see, for review, Ref. 43), which allowed correct reproducing of major transport properties in organic solids including materials in which polaron effects are important, trap-containing materials and the peculiarities of charge transport at low electric fields. Good agreement with experiment and computer simulation results verifies the validity of the EMA approach.[43]

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