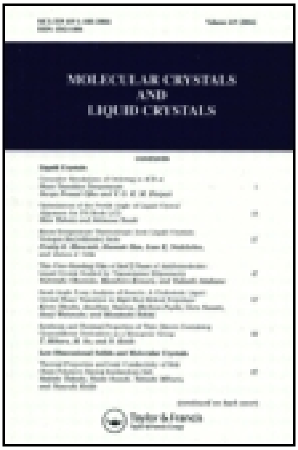

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Localized Trions as Metastable Charged States in Conjugated Polymers

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We have shown that a charged trion consisting of two on-chain polarons of the same sign and a trapped polaron of the opposite sign can be metastable with respect to both dissociation and recombination. A trion can be created upon fusion of a free polaron with a neutral pair, which eliminates a high Coulomb potential barrier for fusion of two charge carriers into a bipolaron. We argue that trions can be created by photoexcitation of a conjugated polymer, in which illumination creates a high density of geminate pairs. Since the metastable trion is anchored by a deep-trapped charge, it is immobile and can be considered as a coulombically

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trapped bipolaron, although the last may not exist as a free particle. We employ the concept of localized trions in order to explain the reversible photoinduced fatigue of thermally stimulated luminescence in films of poly[methyl(phenyl)silylene].

Keywords: bias-stress effect in organic FET; charge trapping; metastability; thermally stimulated luminescence

1. INTRODUCTION

Metastable charged states are known to have several negative effects in electronic devices based on organic materials in general and conjugated polymers in particular. Charge carriers (polarons) and coulombically bound polaron pairs, stabilized by trapping, can efficiently quench excitons [1–3], which imposes a serious limitation on the electroluminescence quantum yield in organic light-emitting diodes (OLED). Localization of charges in the channel of an organic thin-film transistor (TFT) permanently screens the gate potential and thereby causes instability and/or degradation of the device characteristics [4,5]. Time-of-flight (TOF) measurements have shown that deep traps do not limit the TOF hole mobility in most of technologically important conjugated polymers [6], while it has been normally impossible to measure the electron mobility in these materials presumably because of a high density of deep electron traps.

Recent studies of the bias-stress effect in the channel of polymer TFTs [4] have revealed (i) an unusually small cross-section of hole localization, which results in a low rate of charge accumulation, and (ii) increasing localization rate per unit carrier at higher hole densities in the channel resembling a bimolecular process. It has been shown that conventional trapping is generally too fast to account for the stress effect because the equilibrium density of trapped carriers has to be established in the time, at which the conductive channel is formed. In TFTs, the bias-stress effect develops slowly when the transistor is turned on for an extended time; this effect is usually reversible, although annealing is sometimes required to fully recover the unstressed state. Hole bipolarons (BPs), i.e., bound pairs of polarons of the same (positive) sign, were suggested as a possible explanation for these observations [6]. The concept of bipolaron formation was also used to explain the effect of a magnetic field on the electrical and optical properties of chemically doped conjugated polymers and oligomers [7–14]. Formation of BPs in pristine photoexcited polymers is still a subject of controversy [15]. Recently, resonance quenching was observed in electrically and electroluminescence-detected magnetic resonance (EDMR and ELDMR, respectively) in tris (8-hydroxyquinolinato)aluminum-based OLEDs [13,14]. This effect was attributed to the magnetic-field-enhanced formation of BPs [13,14].

Early models of BPs [11] accounted only for the electron-phonon coupling and disregarded electron-electron interactions. According to these models, BP is energetically more stable than two separate polarons. In the meantime, it has been recognized that the electron-electron interactions play an important role in electronic processes running in conjugated polymers. It has been found that if both the electron-phonon and electron-electron interactions are taken into consideration, two polarons are more stable than a bipolaron at low carrier concentrations, while BPs can be formed only at a high carrier density when the BP lattice is formed [12]. This is realistic in doped materials but virtually impossible in photoexcited pristine polymers. In general, it is not clear whether the electron-phonon coupling is strong enough to stabilize BPs in semiconducting conjugated polymers, in which (i) site-selective PL measurements show a very small Stokes shift [16], and (ii) the results of charge transport measurements are in good agreement with the disorder model [6,17] even though the occurrence of the polaronic effect has never been really proven. Even though a bound state of two polarons of the same sign is possible, the Coulomb repulsion must lead to a very small cross-section of the BP formation, which casts serious doubts upon the possible presence of BPs at low carrier densities in photoexcited polymers.

It was shown that the Coulomb interactions between charge carriers, molecular dipoles, and ionized dopants often control both photoelectrical and transport properties in conjugated polymers [18–23]. Particularly, it was suggested [24–27] that a bipolaron can be stabilized by either the image force potential at a metal/organic interface or by counterions. The latter option requires the chemical doping of a material with very strong donors or acceptors (when a dopant is ionized in the ground state). However, the accidental doping with strong donors/acceptors seems to be unlikely in wide-gap semiconducting materials, which is evidenced by low dark conductivity [6,28] and the virtual absence of charged chemical traps in these materials [29,30]. In addition, the stability of BPs to the recombination with counter-charges was not considered, and the issue of the small cross-section of BP formation was not addressed.

In the present paper, we show that metastable charged species can be formed by two on-chain carriers of the same sign coulombically bound to an oppositely charged defect or impurity. Below, we will call these species as (localized) trions. In contrast to previous treatments [24–27], this model does not necessarily require the presence of ionized dopants in the ground state, but it assumes the occurrence of deep traps for the counter-charge, which is physically feasible in disordered organics. Since conjugated polymers are typically hole-transporting materials, trions should, most probably, be formed by pairs of on-chain holes stabilized by trapped off-chain electrons. The density of electron traps in most conjugated polymers is high, as it follows from the non-existence of electron transport in these materials. It will be shown that metastable trions can be formed even if electron-phonon interactions are not strong enough for the formation of metastable on-chain BPs. Since a trion is composed of a neutral geminate pair (GP) and a charge carrier, the Coulomb barrier to its formation is much lower and, concomitantly, the cross-section is much larger than that to the fusion into a BP of two charge carriers of the same sign. The trion model will be used in order to explain the reversible photoquenching of thermally stimulated luminescence (TSL) found in a σ-conjugated polymer poly[methyl(phenyl)silylene] (PMPSi).

2. EXPERIMENTAL

The chemical structure of PMPSi is shown in the inset in Figure 1. PMPSi was synthesized by sodium-mediated Wurtz coupling polymerization from the corresponding dichlorosilane which was freshly

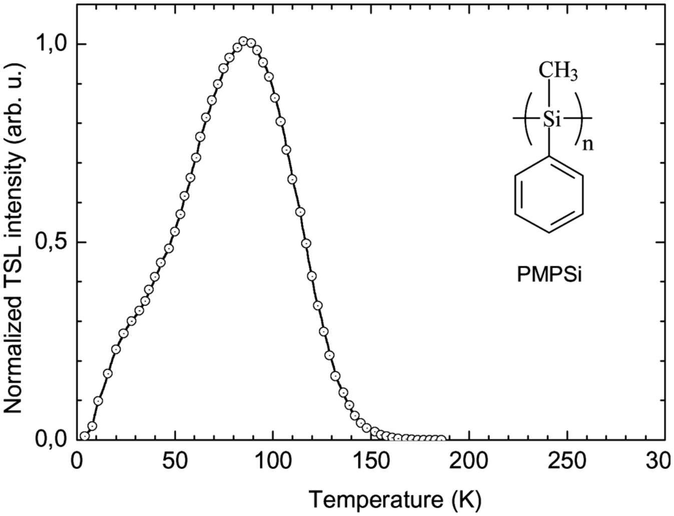

FIGURE 1 TSL glow curve of PMPSi film measured upon the 30-s photoexcitation. Inset: the molecular structure of poly[methyl(phenyl)silylene] (PMPSi).

distilled prior to use [31]. After polymerization, PMPSi was reprecipitated twice from tetrahydrofuran with isopropyl alcohol. The material was used as received. Polymer films of PMPSi were prepared from toluene solutions by spin coating on quartz substrates. After deposition, the films were dried for at least 4 h at 330 K at a pressure of 10^{-4} mbar.

The TSL measurements were carried out using a homebuilt system operating at $4.2-350$ K. After cooling down to 4.2 K, the samples were photoexcited by a high-pressure 500-W mercury lamp with an appropriate set of glass optical filters for light selection. The excitation density of the UV emission from the lamp was around 20 mW/cm^2. After the photoexcitation was terminated, the TSL intensity was measured as a function of temperature in the photon-counting mode with a cooled photomultiplier positioned immediately next to the cryostat window. The measurements were performed in helium atmosphere at a constant heating rate of 0.15 K/s. Further experimental details can be found elsewhere [32–34]. The afterglow decay kinetics [33] was measured at very long delay times, from 1 s to $\sim 10^3$ s after switching off the excitation (the integration time of 1 s) with the same equipment as was used for the TSL measurements, but at a constant temperature, normally at $T = 4.2$ K.

3. RESULTS

Typical TSL glow curves of PMPSi films measured on the 30-s photoexcitation are plotted in Figure 1. It should be noted that the TSL signals observed in this polymer are relatively strong compared with those for other conjugated polymers. The TSL glow curve of PMPSi reveals a broad peak located at relatively low temperatures. No TSL was found at higher temperatures, at $T > 200$ K, indicating the absence of deep hole traps in the material. The observed characteristic features of TSL in this polymer can be explained in terms of the recently developed model of thermally assisted hopping relaxation of charge carriers [33,35]. This model is based on the assumption that TSL originates from the radiative recombination of sufficiently long-distance geminate pairs of charge carriers (i.e., geminate pairs with sufficiently large separation between constituting charges) created during the photoexcitation of a sample at a low (helium) temperature. According to this model, the TSL kinetics is controlled by the thermal release of charge-carriers from tail states of the intrinsic density-of-states (DOS) distribution and, possibly, from traps.

Films of PMPSi also show a strong isothermal afterglow at helium temperature, which was observed in the studied samples after

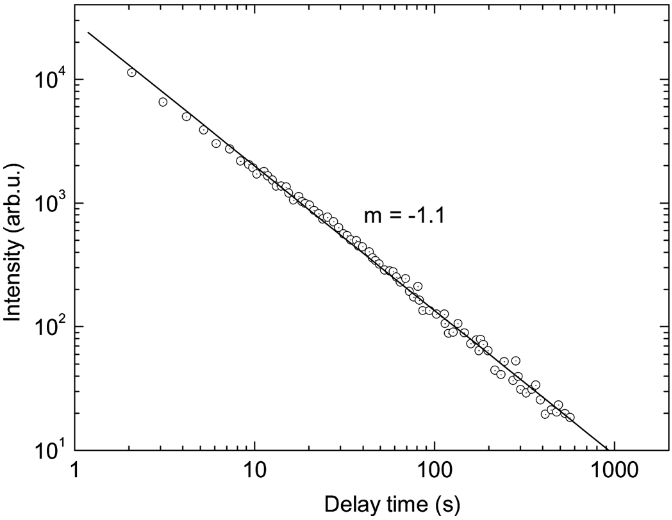

FIGURE 2 Decay kinetics of the spectrally integrated isothermal afterglow emission in a PMPSi film measured at large delay time (>1 s) after 313 nm light excitation at 4.2 K.

switching off the excitation (Fig. 2). In order to avoid the artifacts caused by this emission, the samples were usually kept at 5 K for at least 10 min before the TSL heating run began. The afterglow, measured with the delay time of ≥1 s after terminating the excitation, decays in a power-law fashion and is still detectable at times up to several hundreds of seconds.

A major result of this study is the observation of a pronounced reversible light-induced fatigue of the TSL intensity in PMPSi films. Figure 3 shows the dependence of the normalized total time-integrated TSL intensity of PMPSi (curve 1) on the time of UV illumination at 4.2 K. As one can see, the TSL intensity of a PMPSi film increases with exposure time up to ~30 s (curve 1) and then tends to decrease. It is important to note that the TSL curve shape was virtually the same at all exposures indicating no notable photodestruction of the studied samples.

Such a non-monotonic dependence of the TSL intensity upon the exposure has never been observed in other organic materials. At a fixed excitation intensity, the TSL signal normally increases with the exposure time and then reaches the saturation provided that no irreversible photodegradation occurs in the studied sample [36]. For comparison, the typical monotonic dependence of the TSL intensity on the excitation time,

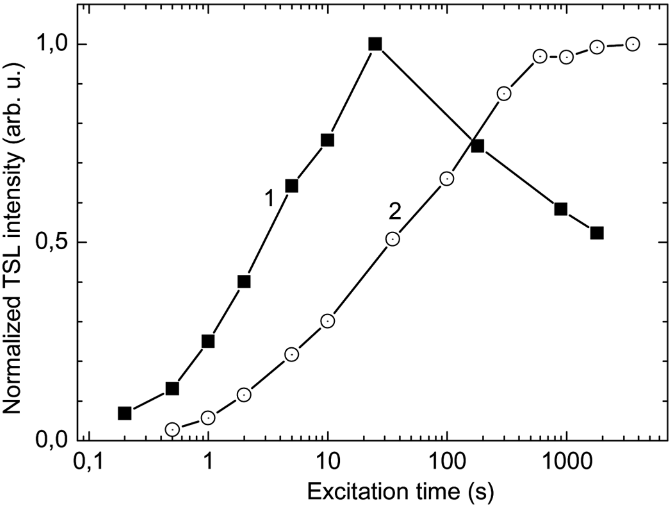

FIGURE 3 Time-integrated TSL intensity of PMPSi and MDMO-PPV films upon the time of UV photoexcitation at 4.2 K (curves 1 and 2, respectively).

observed in the well-known π-conjugated polymer poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV), is also shown in Figure 3 (curve 2). A similar behavior was observed in other conjugated polymers such as various PPV derivatives, polyfluorenes, poly-*p*-phenylenes, etc. The saturation of the TSL intensity can be explained by the fact that the incident light generates not only new charge carriers during the optical excitation, but it releases also already trapped charge carriers due to the effects of both direct light absorption by charged traps and exciton quenching at charged traps. This will result in a specific equilibrium concentration of occupied traps which can be significantly lower than the total trap density. Thus, the charge-exciton annihilation should lead to the saturation of the TSL signal with increase in the excitation exposure, but cannot explain the decrease of the TSL at large exposures as observed in PMPSi in the present article.

The observed fatigue effect was fully reversible without any indication of material photodegradation. Repeated measurements of the TSL upon a short-time (∼30 s) exposure immediately after the TSL measuring cycle at a large exposure already showed a partial restoration of the TSL intensity, while the prolonged (hours) annealing of samples in the same cryostat at room temperature led to the full recovery of the TSL intensity. The recovery of the TSL intensity upon annealing the sample at higher temperatures suggests that the relaxation of photoinduced metastable species is of activated character. It should be noted that the illumination of a sample with UV light at 4.2 K did not cause any optically detectable photodegradation, although photodestruction products could be detected in this material upon UV illumination at room temperature [37].

4. DISCUSSION

Since the light-induced fatigue of the TSL intensity in PMPSi films shows the complete reversibility after many measurement cycles, it cannot be caused by the photodegradation of the polymer. No change in the absorbance of the studied polymer films was observed and, therefore, the effect of photobleaching can also be excluded. Charge carrier accumulation in an illuminated organic film is controlled by several processes, notably by (i) exciton dissociation into metastable GPs at charge-transfer centers, (ii) exciton quenching by impurities and photogenerated charges, (iii) energy relaxation of photogenerated carriers towards the deep tail of the DOS distribution, (iv) photorelease of trapped charge carriers, and (v) recombination of GPs. At large illumination times, the interplay between these processes should yield a steady-state density of photogenerated charges occupying states within the deep tail of the DOS distribution. Since the sample remains neutral upon photoexcitation and the GP lifetime is determined by the release of localized holes, deep-trapped electrons cannot be responsible for the observed fatigue. A drop in the TSL intensity after prolonged irradiation, therefore, indicates the formation of some sort of quenching species which are more stable than trapped carriers but are not related to any photoinduced structural and/or chemical changes. Trions are perfect candidates for this role.

An on-chain pair of positively charged polarons (holes), located nearby a negatively charged localized state, can be stabilized by both the electron-phonon interaction and the Coulomb interaction with the trapped electron. The total electrostatic energy of this trion includes then the positive on-chain, $E_c^{(on)}$, and negative off-chain, $E_c^{(off)}$, contributions,

$$E_c^{(on)} = \frac{e^2}{4\pi\varepsilon_0\varepsilon_{on}a}, \qquad E_c^{(off)} = -\frac{2e^2}{4\pi\varepsilon_0\varepsilon_{off}\sqrt{(a/2)^2 + b^2}}, \tag{1}$$

where a is the distance between the on-chain holes, b the distance from the chain to the trapped electron, ε_{on} and ε_{off} are the on- and off-chain permittivities, respectively, and e is the polaron charge. Note that, together with the polaronic contribution E_p, the energy

$E_c^{(on)}$ determines the BP binding energy $E_b^{(BP)} = E_p - E_c^{(on)}$, while $E_c^{(off)}$, which reflects the measure of the stabilizing effect on BP given by the trapped electron and the size a of the BP, corresponds to the minimum of this energy. The difference between ε_{on} and ε_{off} is mostly due to a strong anisotropy of the electronic polarization typical of conjugated polymers [38]. For $\varepsilon_{on} = 5, \varepsilon_{off} = 3$, and $a = b = 0.5\,\text{nm}$, Eq. (1) yields $E_c^{(on)} \approx 0.6\,\text{eV}$ and $E_c^{(off)} \approx -1.7\,\text{eV}$.

The trion metastability requires that its state must be separated by potential barriers from all other states which can be products of its decay. In principle, a trion can decay in two ways. First, it can dissociate into a free hole polaron and a coulombically bound pair of hole and electron polarons. This process is endothermic. The trion will be metastable with respect to this reaction if the following relation is fulfilled:

$$E_c^{(off)} + E_c^{(on)} - E_p < E_c^{(GP)}. \tag{2}$$

Here, $E_c^{(GP)}$ is the Coulomb energy of the polaron pair,

$$E_c^{(GP)} = -\frac{e^2}{4\pi\varepsilon_0\varepsilon_{off}b}, \tag{3}$$

i.e., $E_c^{(GP)} \approx -1.0\,\text{eV}$ for $b = 0.5\,\text{nm}$ and $\varepsilon_{off} = 3$. This estimate indicates that the trion is metastable with respect to the reaction trion $\rightarrow h + GP$ even if the polaronic contribution to its binding energy is zero.

A trion can also recombine into a free hole polaron: trion $\longrightarrow h + \delta E$, where δE is the energy released upon recombination. Despite the fact that three particles are involved, trions can recombine rapidly if this process is exothermic, i.e., if $\delta E \geq 0$. Otherwise, one should expect the slow thermally activated recombination. In order to calculate δE, one has to account for (i) the polaron binding energy, (ii) the energy of the on- and off-chain Coulomb interactions, (iii) the LUMO-HOMO gap E_g, and (iv) the activation energy of the electron trap E_t. The energy δE is negative and, concomitantly, the trion is metastable with respect to the recombination into a free hole if

$$E_g - E_t - E_p + E_c^{(on)} + E_c^{(off)} < 0, \tag{4}$$

i.e., if $E_p > E_g - E_t + E_c^{(on)} + E_c^{(off)}$. For $E_g = 2\,\text{eV}$, $E_t = 1\,\text{eV}$, a = b = 0.5 nm, $\varepsilon_{off} = 3$, and $\varepsilon_{on} = 5$, Eq. (4) predicts metastable trions with binding energies of not smaller than 0.7 eV even if the polaron binding energy is not larger than the on-chain Coulomb energy and the formation of metastable BPs is absolutely impossible. Therefore, trions seem to be more likely candidates for the role of metastable charged centers in photoexcited conjugated polymers and oligomers. It is worth noting that although Eq. (4) includes both E_g and E_t, the stability of a trion is actually controlled by the difference between these energies, $E_g - E_t$, i.e. by the energy of the electron trap counted from the HOMO of the host material.

Another important issue is the mechanism and cross-section of the trion formation. Accumulation of trions is possible at relatively low polaron densities typical of photoexcited samples only if the respective cross-section is not too small. We recall that the formation of BPs, be it possible, is notoriously difficult, because this process requires crossing a relatively high Coulomb potential barrier. Its height can be estimated as $e^2/4\pi\varepsilon_0\varepsilon_{on}a \approx 0.6\,\text{eV}$ for $a = 0.5\,\text{nm}$ and $\varepsilon_{on} = 5$. Various scenarios of the trion formation can be envisaged. One obvious possibility is a Langevin-type capture of a hole BP by a deep-trapped negative polaron, which is the exothermic and, therefore, relatively fast process. However, this mechanism implies the fusion of positive polarons into BPs as a preliminary step. Therefore, it requires the existence of metastable BPs. If so, its overall cross-section would still be controlled by the BP formation rate.

Another possibility is the fusion into a trion of a free hole polaron and a coulombically bound pair of an on-chain hole and a deep-trapped electron. Note that the occurrence of such pairs in photoexcited conjugated polymers has been proven by numerous techniques including TSL measurements [32–34], field- and dopant-assisted exciton quenching [2,39–41], optically detected electron spin resonance [3,13,14,42], delayed fluorescence [43,44], etc. The large density and lifetimes of short geminate pairs are evidenced by the high intensity and large decay time of the low-temperature afterglow as depicted in Figure 2. The time-integrated intensity of the isothermal afterglow emission (Fig. 2) caused by the recombination of short geminate pairs considerably exceeds the integrated TSL signal, which suggests a much larger concentration of short-distance geminate pairs than that of the long-distance ones which contribute to the TSL signal. The Coulomb barrier for the fusion into a trion of a free hole polaron and a geminate pair is much lower than that for the BP formation because an on-chain hole has to approach a dipole rather than a single carrier. Moreover, if the on- and off-chain permittivities are considerably different, e.g., $\varepsilon_{off} = 3$ and $\varepsilon_{on} = 5$, this barrier almost completely vanishes. This mechanism implies a larger probability of the trion formation from a more stable geminate pair of charge carriers. One should expect that a geminate pair is more stable and its lifetime is longer if the hole is also localized either at a defect or in a state which belongs to the upper tail of the HOMO DOS distribution. Note that the hole localization should further stabilize the trion with respect to both the dissociation into free carriers and the recombination into a single on-chain hole.

As has been shown above, deep-trapped electrons stabilize trions and play a role of ‘anchors’ which immobilize these particles at variance with on-chain BPs, which can still move despite their large polarization energy. Photoexcitation is not a unique origin of deep-trapped electrons in conjugated polymers. Intentional and/or accidental doping with electron scavengers is notorious in these materials [6]. In the presence of deep traps, short-distance electron-hole pairs can be stable even without optical excitation, especially in strongly energetically disordered materials, in which the localization of holes in the deep tail of the DOS can further stabilize these pairs. Therefore, metastable trions can also be formed in both diodes and thin-film transistors based on either intentionally or accidentally doped polymers. It should be mentioned that the importance of polaron effects for the charge transport in PMPSi has been shown [45–47] and the polaron binding energies of 0.16 eV [45] and 0.29 eV [47] have been reported for this polymer. Finally, we should mention the further experiments on trion metastable charged states in conjugated polymers are in progress.

5. CONCLUSIONS

Charged trions, consisting of two on-chain polarons of the same sign (e.g., positive polarons) and either a trapped polaron or a charged defect/impurity of the opposite sign (e.g., deep-trapped electron), can be metastable with respect to both dissociation and recombination. Although a trion can be considered as a bipolaron trapped in the potential well of an oppositely charged Coulomb center, a possible scenario of the trion formation does not require the fusion of two carriers into a bipolaron as an intermediate step. Instead, a trion can be formed upon the capture of a free polaron by a neutral pair of charges of opposite signs, which eliminates the necessity of overcoming a high Coulomb potential barrier for the fusion of two charge carriers into a bipolaron. Therefore, trions can be formed even at a relatively low carrier density, e.g., in a pristine photoexcited conjugated polymer. Since a metastable trion has to be anchored by either a deep-trapped charge or a charged defect, it is immobile and can be considered as a localized state of either polarons or bipolarons, although the latter may not exist as free particles. Interestingly, the formation of trions, in fact, inverts the sign of a charged localized state: a negatively charged deep trap is effectively replaced by a positively charged localized trion.

The concept of localized trions has been used in order to explain the reversible photoinduced fatigue of the thermally stimulated luminescence in PMPSi films. It turns out that the total TSL intensity in this material decreases after the prolonged optical excitation suggesting a slow accumulation of some type of charged states that are more stable than the trapped carriers or long metastable geminate electron-hole pairs. Localized trions can be such metastable states. They can be photogenerated via the fusion of a photogenerated quasi-free hole and a coulombically bound pair of an on-chain hole and a deep-trapped electron. Trions can also be responsible for the reversible photoquenching of steady-state luminescence observed at room temperature in some conjugated polymers [48] and the reversible photoluminescence switching in single polymer chains [49].

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