

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/264395923>

# Temperature Effects on the Scattering of Polarons and Bipolarons in Organic Conductors

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · JULY 2014

Impact Factor: 2.69 · DOI: 10.1021/jp505590g · Source: PubMed

---

CITATIONS

3

---

READS

24

3 AUTHORS, INCLUDING:



Wiliam Ferreira da Cunha

University of Brasília

44 PUBLICATIONS 174 CITATIONS

SEE PROFILE



Geraldo Magela e Silva

University of Brasília

90 PUBLICATIONS 509 CITATIONS

SEE PROFILE

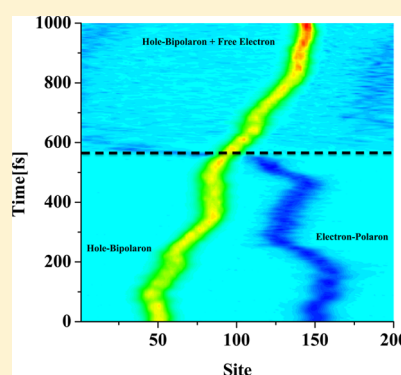
# Temperature Effects on the Scattering of Polarons and Bipolarons in Organic Conductors

Luiz Antonio Ribeiro Junior,<sup>\*,†</sup> Wiliam Ferreira da Cunha,<sup>\*,‡</sup> and Geraldo Magela e Silva<sup>‡</sup>

<sup>†</sup>Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

<sup>‡</sup>Institute of Physics, University of Brasilia, 70919-970, Brasilia, Brazil

**ABSTRACT:** The scattering process between an electron-polaron and a hole-bipolaron has been simulated using a version of the Su–Schrieffer–Heeger (SSH) model modified to include an external electric field, Coulomb interactions, and temperature effects in the scope of nonadiabatic molecular dynamics. The simulations reveal remarkable details concerning the polaron–bipolaron recombination reaction. It is found that there exists a critical temperature regime below which a hole-bipolaron and a mixed state composed by an electron-polaron and an exciton are formed and a hole-bipolaron and a free electron are the resulting products of the collisional process, if the temperature is higher than the critical value. In addition, it is obtained that both channels depend sensitively on the strength of the applied electric field. These significant results may provide guidance to understand processes regarding electroluminescence in polymer diodes.



## INTRODUCTION

Conjugated polymers have attracted considerable interest as potential candidates for the development of optoelectronic devices since the discovery of poly(paraphenylene vinylene) (PPV) and its electroluminescence properties in the past few decades. Their optoelectronic features combined with potential advantages in terms of easy synthesis, flexibility, low cost, and large-area capability make them more attractive materials for the electronics industry to provide new display technology than their inorganic counterparts. They have been successfully implemented as the active component in various applications such as organic photovoltaics devices (OPVs)<sup>1</sup> and polymer light emitting diodes (PLEDs).<sup>2</sup> In these devices, the generation of excited states is of fundamental physical importance. Particularly, the charge carrier recombination is the key step behind the mechanism of electroluminescence in PLEDs.

Experiments have shown, through optical and magnetic data, that some doped polymers showed signals involving polarons and bipolarons, which proves the coexistence of these charge carriers in conjugated polymers.<sup>3,4</sup> Thus, there exists a great possibility of collision and recombination between them. A considerable amount of theoretical work focused on understanding the processes underlying the excited states formation in conjugated polymers. The collision mechanism of oppositely charged carriers has also been extensively reported.<sup>5–13</sup> Nevertheless, theoretical studies that take into account the temperature influence on such mechanisms remain unavailable. It is worthy to mention that, from the experimental point of view, the PPV is one of the best choices for the fabrication of PLEDs, especially for the characteristic of forming thermally stable thin films with high photoluminescence yields. It was also experimentally obtained that the photoexcitation dynamics in

PPV is similar to that of polyacetylene,<sup>14</sup> which allows the use of polyacetylene in theoretical studies in order to obtain a good physical insight about processes involving charge transport and recombination in real systems. Furthermore, it should be emphasized that the collision between an electron-polaron and a hole-bipolaron was experimentally obtained as a possible channel to produce a new polaronic state in PPV-based light emitting diodes.<sup>15</sup>

Recently, it was experimentally reported that the capture of a positive bipolaron by a deeply trapped negative polaron is one of the mechanism of trion formation in a PPV derivative.<sup>16</sup> Sun and collaborators investigated theoretically the recombination process between an oppositely charged polaron–bipolaron pair in conjugated polymers using a modified version of the SSH model.<sup>17</sup> They pointed out that below a critical electric field, the polaron and bipolaron can scatter into an excited polaron with high yield. Above the critical electric field, the polaron and bipolaron will pass through each other and continue moving as isolated structures. By use of a similar approach, the results obtained by Onodera showed that polarons and bipolarons can freely pass through each other without attractive or repulsive interactions.<sup>18</sup> Theoretical studies carried out by e Silva have shown that the presence of a bipolaron limits the polaron movement in a such way that the polaron cannot cross the bipolaron keeping its integrity after the nonreactive collisional process, resulting in a physical picture where the polaron mobility is compromised.<sup>19</sup> It is possible that all the results regarding the polaron–bipolaron reaction are not fully comprehensive so that further investigations are needed.

Received: June 5, 2014

Revised: July 21, 2014

Recently, a previous work of ours has also shown that for several electric fields regimes, the presence of impurities in a conjugated polymer lattice favors the excited states formation improving the excitation yields when the scattering between a oppositely charged polaron–bipolaron pair is considered.<sup>20</sup> In another theoretical work,<sup>6</sup> it was reported that when a polaron pair enters the coupling area, considering an intrachain scattering process, its velocity slightly increases but the collisional process of two oppositely charged polarons is the same as that in the isolated single polymer chain case, as if the second chain does not exist at all. This means that interchain coupling effect on such mechanism is not important in the cases of intrachain scattering. The same behavior can be expected when the collision process between a polaron–bipolaron pair is taken into account. There are, however, still many controversial aspects regarding the influence of some physical process such as temperature, electric field strength, Coulomb interactions, and impurity effects on the formation of excited states via recombination process between oppositely charged carriers, which requires a detailed phenomenological descriptions.

In this paper, a systematic numerical investigation considering the influence of temperature effects, electron–electron interactions, and an external electric field on the collisional process of an oppositely charged polaron–bipolaron pair is performed using a cis-polyacetylene chain. An extended version of the SSH model that includes the Brazovskii–Kirova type symmetry-breaking term is used considering also the extended Hubbard model (EHM). Temperature effects are included by means of a canonical Langevin equation. The results show that the products formed from the polaron–bipolaron reaction, mainly when temperature effects are considered, open a new channel to understanding the polymer luminescence processes and can provide guidance for improving the electroluminescence yields in PLDEs.

## MODEL AND METHOD

The overall SSH-type Hamiltonian<sup>21,22</sup> modified to include the Brazovskii–Kirova type symmetry-breaking term,<sup>23</sup> Coulomb interactions, and an external electric field is given by

$$\begin{aligned}
 H_{\text{SSH}} = & - \sum_{n,s} (t_{n,n+1} C_{n+1,s}^\dagger C_{n,s} + hc) \\
 & + U \sum_i \left( C_{i,\uparrow}^\dagger C_{i,\uparrow} - \frac{1}{2} \right) \left( C_{i,\downarrow}^\dagger C_{i,\downarrow} - \frac{1}{2} \right) \\
 & + V \sum_i (n_i - 1)(n_{i+1} - 1) + \sum_n \frac{K}{2} y_n^2 \\
 & + \sum_n \frac{p_n^2}{2M}
 \end{aligned} \quad (1)$$

where  $t_{n,n+1} = e^{-i\gamma A} [(1 + (-1)^n \delta_0) t_0 - \alpha y_n]$ , in which  $t_0$  is the transfer integral of  $\pi$ -electrons between nearest neighboring sites in a regular lattice,  $\alpha$  is the electron–phonon coupling,  $\delta_0$  is the Brazovskii–Kirova symmetry-breaking term, and  $n$  the site index.  $\gamma \equiv ea/(\hbar c)$ , where  $a$  is the lattice constant,  $c$  is the speed of light, and  $e$  the absolute value of the electronic charge.  $y_n$  is defined as  $y_n \equiv u_{n+1} - u_n$  in which  $u_n$  is the lattice displacement of an atom at the  $n$ th site. The electric field is included in the Hamiltonian as a scalar potential  $A$  having the time dependence in the form of a half Gaussian.<sup>24,25</sup> The operator  $C_{n,s}^\dagger$  ( $C_{n,s}$ ) creates (annihilates) a  $\pi$ -electron state at the

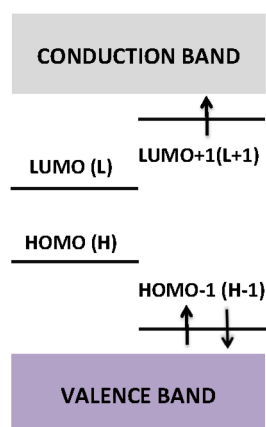
$n$ th site with spin  $s$  and  $n_i = C_{i,\uparrow}^\dagger C_{i,\uparrow} + C_{i,\downarrow}^\dagger C_{i,\downarrow}$ .  $U$  gives the strength of the on-site and  $V$  the nearest-neighbor electron–electron interactions.<sup>26</sup>  $p_n$  is the conjugated momentum to  $u_n$ .  $K$  is the harmonic constant that describes a  $\sigma$  bond, and  $M$  is the mass of a CH group. The parameters used here are those well accepted for a polyacetylene chain:<sup>27–33</sup>  $t_0 = 2.5$  eV,  $M = 1349.14$  eV·fs<sup>2</sup>/Å<sup>2</sup>,  $K = 21$  eV Å<sup>−2</sup>,  $\delta_0 = 0.05$ ,  $\alpha = 4.1$  eV Å<sup>−1</sup>,  $a = 1.22$  Å, and a bare optical phonon energy  $\hbar\omega_Q = \hbar(4K/M)^{1/2} = 0.16$  eV.

The initial configuration for the system, i.e., the bond and electronic structures, is obtained by solving the self-consistent equations for the lattice configuration  $y_n$  and the electronic wave functions.<sup>13</sup> Once the initial structure was determined, the temporal evolution of the system is carried out by means of the Ehrenfest molecular dynamics, in which the lattice backbone dynamics is performed classically through the Euler–Lagrange equations<sup>20</sup> and the wave functions are obtained by solving the time-dependent Schrödinger according to Ono's method.<sup>34</sup> The occupation number of the instantaneous eigenstates, as discussed in the next section, is calculated according to ref 35. Since the approach adopted here treats the lattice backbone classically, it is possible to use the Langevin equation to take into account temperature effects. In this way, a white stochastic signal  $\zeta(t)$  is considered as the fluctuation term having the following properties:  $\langle \zeta(t) \rangle \equiv 0$  and  $\langle \zeta(t)\zeta(t') \rangle = \Lambda \delta(t - t')$ . A dissipation term is also included in this formalism in order to keep the temperature constant after a transient period. The relationship between  $\zeta$ ,  $\gamma$ , and the temperature  $T$  is given by the fluctuation–dissipation theorem,  $\Lambda = 2k_B T \gamma M$ . It should be emphasized that this methodology to consider temperature effects in one-dimensional conjugated polymer lattice has been used successfully in the literature.<sup>25,35–41</sup>

## RESULTS AND DISCUSSION

Systematic numerical investigations are carried out considering the temperature influence over the collision dynamics of a bipolaron–polaron pair in systems composed of 200-site cis-polyacetylene chains. A long polymer chain is necessary to avoid the overlap between the two deformations created after the charge remotion (hole–bipolaron) and injection (electron–polaron). For the electric field, turned on quasi-adiabatically,<sup>37</sup> the values used in the simulations varied from 0.5 to 2.0 mV/Å with an increment of 0.5 mV/Å, whereas the temperature regimes considered range from 50 to 250 K with a step of 25 K.

For the on-site electron–electron interactions the value considered is  $U = 0.2t_0$ . The nearest-neighbor Coulomb repulsion strength was defined using the relation  $V = U/2$ . In this context, Figure 1 presents the schematic diagram of energy levels for a lattice containing a hole–bipolaron and an electron–polaron. These charge carriers are formed by removing or adding electrons to the polymer chain, causing lattice distortions and the rising of energy levels inside the band gap. A single polymer chain containing a hole–bipolaron is represented by the absence of electrons in the (H) and (L) levels, which yields a  $+2e$  charge. On the other hand, an electron–polaron is represented by occupied levels (H − 1) and (L + 1), in which the upper one is occupied by one electron and the lower one occupied by two electrons, yielding a  $-e$  charge. One can see the characteristic larger narrowing of the bipolarons energy levels when compared to those of the polaron, which indicates that the bipolarons are quasi-particles more stable than polarons in conjugated polymers.



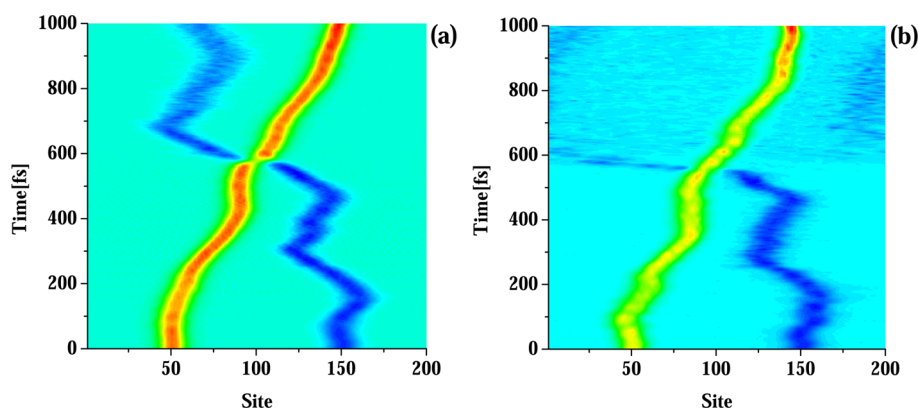
**Figure 1.** Schematic diagram of energy levels for a polymer chain containing an electron-polaron and a hole-bipolaron.

First, we have investigated the contribution of low temperature regimes in the mechanisms involved in polaron–bipolaron scattering. Figure 2 presents the evolution of the mean charge density  $\bar{\rho}(t) = 1 - [\rho_{n-1}(t) + 2\rho_n(t) + \rho_{n+1}(t)]/4$  at temperatures of 75 K (Figure 2a) and 150 K (Figure 2b). The positive bipolaron (red structure) is initially located at the 50th site, while the negative polaron (blue structure) is at 150th site. The two charge carriers are separated far enough from one another so that they behave as independent structures. Considering an electric field strength of 1.0 mV/Å, after a small transient time for the field response, the charge carriers begin to move toward one another because of the opposite charges. One can readily note the difference between the polaron and the bipolaron dynamics regarding the response of the applied electric field. This is natural if one considers the difference between the masses and charges of these quasi-particles. In this way, the polaron and the bipolaron are accelerated and rapidly reach their saturation velocities. Before the collision, the motion for both charge carriers is the same as that reported in the literature.<sup>25</sup> Initially, the polaron and the bipolaron move linearly with time. However, after about 100 fs the adding up of thermal energy begins to become considerable and the polaron starts to perform a random walk along the chain influenced by the thermal random forces. Because of its larger effective mass, the bipolaron starts to perform a random walk dynamics only after 300 fs. Furthermore, it is easy to verify in Figure 2a that the random walk displacement of the polaron

is higher than the displacement imposed by the random forces to the bipolaron. As aforementioned, this fact can be understood by considering the charge and mass differences between these charge carriers.

At around 600 fs, when the collision takes place, one can see in Figure 2a that the polaron can easily pass through the bipolaron because of its high kinetic energy, a process that yields the formation of a mixed state composed of a polaron and an exciton, while the bipolaron remains intact. The polaron–exciton structure formed is manifested by the charge delocalization pattern presented by the electron-polaron after 700 fs. A small fraction of the electron that occupies the (L + 1) level is excited to the conduction band, forming a bond state structure between the electron-polaron and the excited fraction of the electron. The channel reported in Figure 2a (channel 1) is observed in our simulations to occur for temperatures regimes smaller than 75 K and electric field strengths higher than 1.0 mV/Å. Otherwise, for temperatures higher than this critical value (considering field strengths smaller than 1.0 mV/Å) the motion of the charge carriers is damped, as reported in ref 25, the collision between the charge carriers driven by the external electric field is not observed, and the random walk dynamics dominates.

The role played by the temperature in the collisional process between the charge carriers can be verified considering a temperature regime twice as high as the previous and an electric field strength of 1.5 mV/Å, as shown in Figure 2b (channel 2). The polaron is annihilated after the collision with the bipolaron, a channel that gives rise to a final state composed of a hole-bipolaron and a completely free electron. The effects caused by the temperature increase can be noted by first observing the diffusive pattern presented by the charge concentration of the quasi-particles, if compared with the case shown in Figure 2a. Also, the lattice oscillations imposed by the random forces are of such amplitudes that the polaron and the bipolaron can, as a matter of fact, be said to be of reduced stability, although it is still possible to identify such carriers immediately before the collision. After the collision, one can see that the once localized electron-polaron begins to spread over the lattice until it is completely delocalized at around 600 fs. This delocalization is the typical signature of the absence of the polaron structure in the system and the generation of a free electron. Another observed fact, due to temperature increasing, is that the collision process occurs 50 fs earlier than the channel reported in Figure 2a. These results suggest a different value for the

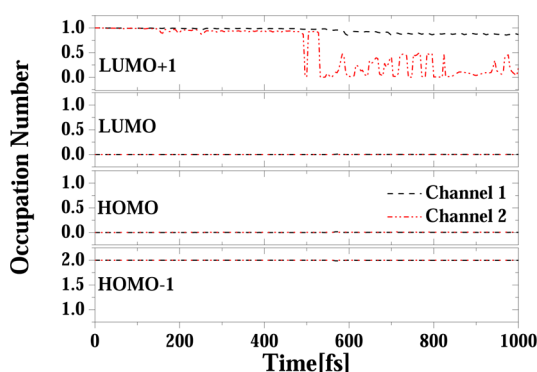


**Figure 2.** Mean charge density time evolution: (a) channel 1, electric field strength of 1.0 mV/Å and temperature of 75 K; (b) channel 2, electric field strength of 1.5 mV/Å and 150 K.



critical electric field strength than that reported recently by Sun and collaborators.<sup>17</sup> They have indicated that the critical electric field for the polaron–bipolaron scattering without a reaction that leads to a new state is of 0.8 mV/Å. Our results present the formation of a polaron–exciton structure as a new state, for a critical field strength of 1.0 mV/Å. Indeed, the markedly different behavior is caused by the temperature influence over the system, a kind of effect absent in the work of Sun.<sup>17</sup> As discussed, the lattice vibrations dampened the charge carrier motion for electric field strengths to smaller than 1.0 mV/Å. This results in a transition for the quasi-particle from a drift driven dynamics by the electric field to a random walk dynamics imposed by the random thermal forces. In this way, we believe that an approach that takes into account the thermal effects over the charge carrier collision may provide a more realistic physical picture.

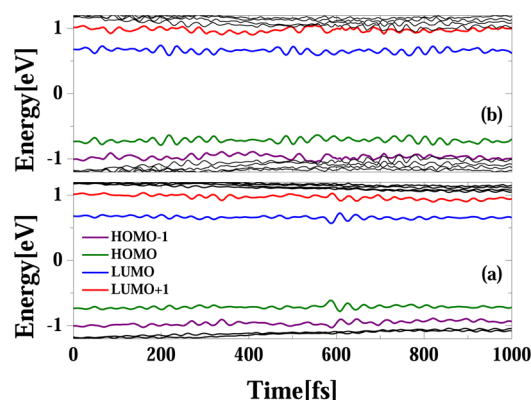
An important feature to recognize the new states formed after the polaron–bipolaron collision is the time evolution of the electronic occupation number of the intragap energy levels presented in Figure 3. Note that this figure shows the time



**Figure 3.** Time evolution of the occupation number for the intragap energy levels, where the black lines represents channel 1 (75 K) and the red lines channel 2 (150 K).

evolution of the occupation numbers for the intragap levels related to Figure 1. Considering the channel 1 (black lines in Figure 3), before the transient period in which the occupation number oscillates because of the collision, it is possible that the final state in LUMO + 1 level is not occupied by an integer number, which is evidence of partial electron excitation. Indeed, that fraction of the electron is excited to a higher level inside the conduction band, forming a bond state between the electron–polaron and the excitation characterizing the generation of a polaron–exciton structure, while the occupation of the other three levels remains the same. For channel 2 (red lines in Figure 3), after 500 fs the occupation number drops dramatically to zero, which indicates the complete annihilation of the polaron, leading to a free electron that is excited to the conduction band and the charge delocalization through the lattice. One can see that for the polaron annihilation process in channel 2, the occupation number for the other levels also remains the same as before the collision, showing mainly that the bipolaron keeps its integrity. In this way, these results indicate in general that an electron transfer from the polaron level LUMO + 1 to levels inside the conduction band will allow excited polarons only for very low temperature regimes (below 75 K) and free carriers for temperatures higher than this critical value.

Whereas the occupation number analysis is the most suitable tool in studying the process that leads to the formation of excited polarons and free charges, the stability of the quasi-particles is better described by means of the energy levels time evolution. We finish our discussion by presenting in Figure 4



**Figure 4.** Time evolution of the energy levels for (a) channel 1, 75 K and (b) channel 2, 150 K.

the time evolution profile for the intragap energy levels of the simulations shown in Figure 2. As can be seen from Figure 4, at the beginning there are four intragap levels, which are localized electron states caused by the presence of a polaron and a bipolaron in the lattice. According to their wave functions, we know that the bipolarons energy levels present a larger narrowing when compared to those of the polaron. For clarity, we have used different colors where the polaron levels are represented by the purple (HOMO – 1) and red (LUMO + 1) lines and those of the bipolarons by the green (HOMO) and blue (LUMO) lines. Figure 4a depicts the process discussed in channel 1, where a polaron–exciton structure is formed. The collisional process between the polaron–bipolaron pair is noted to take place at about 600 fs, when the resulting phonons are represented by the little deeper oscillations of the energy levels inside the band gap. As both structures remain intact after the scattering process, one can see that there are four intragap levels until the end of the simulation. On the other hand, for processes discussed in channel 2, the signature of the loss of stability for the polaron is related to the red (LUMO + 1) and purple (HOMO – 1) states returning to the conducting and valence bands, respectively, as shown in Figure 4b. As in Figure 4a, it is possible to note that the bipolaron remains stable through the rest of the simulation, since the green (HOMO) and blue (LUMO) bipolaron levels remain consistently inside the band gap. Furthermore, the oscillations presented by the energy levels result from the motion of the sites of the lattice influenced by the thermal random forces, as can be seen in Figure 4a and Figure 4b.

## SUMMARY AND CONCLUSIONS

On the basis of a tight-binding electron–phonon interaction model modified to include an external electric field, electron–electron interactions, and temperature effects, the scattering processes between an electron–polaron and a hole–bipolaron have been simulated in a conjugated polymer lattice, using a nonadiabatic molecular dynamic method. The results show that there are two channels resulting from the scattering process between the polaron–bipolaron pair: channel 1, below the

critical temperature regime, where the positive bipolaron and a mixed state composed of the negative polaron and an exciton are formed, and channel 2, where a positive bipolaron and a free electron are the resulting products of the collisional process, when the temperature is higher than the critical value. Furthermore, it is found that both channels depend sensitively on the strength of the applied electric field. These significant results reveal remarkable details concerning the polaron–bipolaron recombination reaction and may enlighten the understanding of electroluminescence processes in polymer light emitting diodes.

## AUTHOR INFORMATION

### Corresponding Authors

\*L.A.R.J.: e-mail, luiju@ifm.liu.se.

\*W.F.d.C.: e-mail, wiliam@unb.br.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the Swedish Research Council (VR) for financial support, the Swedish National Infrastructure for Computing (SNIC), and the financial support from the Brazilian Research Councils CNPq, CAPES, and FINATEC.

## REFERENCES

- (1) Jailaubekov, A. E.; Willard, A. P.; Tritsch, J. R.; Chan, W.-L.; Sai, N.; Gearba, R.; Kaake, L. G.; Williams, K. J.; Leung, K.; Rossk, P. J.; Zhu, X.-Y. Hot Charge-Transfer Excitons Set the Time Limit for Charge Separation at Donor/Acceptor Interfaces in Organic Photovoltaics. *Nat. Mater.* **2013**, *12*, 66–73.
- (2) White, M. S.; et al. Ultrathin, Highly Flexible and Stretchable PLEDs. *Nat. Photonics* **2013**, *7*, 811–816.
- (3) Lanea, P. A.; Wei, X.; Vardeny, Z. V. Studies of Charged Excitations in  $\pi$ -Conjugated Oligomers and Polymers by Optical Modulation. *Phys. Rev. Lett.* **1996**, *77*, 1544–1547.
- (4) Bobbert, P. A.; Nguyen, T. D.; van Oost, F. W. A.; Koopmans, B.; Wohlgenannt, M. Bipolaron Mechanism for Organic Magnetoresistance. *Phys. Rev. Lett.* **2007**, *99*, 216801–4.
- (5) Lei, J.; Sun, Z.; Zhang, Y.; Xie, S. Effect of Spin Polarization on Exciton Formation in Conjugated Polymers. *Org. Electron.* **2011**, *10*, 1489–1494.
- (6) An, Z.; Di, B.; Wu, C. Q. Inelastic Scattering of Oppositely Charged Polarons in Conjugated Polymers. *Eur. Phys. J. B* **2008**, *63*, 71–77.
- (7) Sun, Z.; Stafström, S. Bipolaron Recombination in Conjugated Polymers. *J. Chem. Phys.* **2011**, *135*, 074902–7.
- (8) Sun, Z.; Stafström, S. Spin-Dependent Polaron Recombination in Conjugated Polymers. *J. Chem. Phys.* **2012**, *136*, 244901–5.
- (9) Di, B.; Meng, Y.; Wang, Y. D.; Liu, X. J.; An, Z. Formation and Evolution Dynamics of Bipolarons in Conjugated Polymers. *J. Chem. Phys. B* **2011**, *115*, 964–971.
- (10) Di, B.; Meng, Y.; Wang, Y. D.; Liu, X. J.; An, Z. Electroluminescence Enhancement in Polymer Light-Emitting Diodes through Inelastic Scattering of Oppositely Charged Bipolarons. *J. Chem. Phys. B* **2011**, *115*, 9339–9344.
- (11) Ribeiro, L. A.; da Cunha, W. F.; Neto, P. H. O.; Gargano, R.; e Silva, G. M. Impurity Effects on Polaron-Exciton Formation in Conjugated Polymers. *J. Chem. Phys.* **2013**, *139*, 174903–6.
- (12) Li, Y.; Gao, K.; Sun, Z.; Yin, S.; sheng Liu, D.; jie Xie, S. Intrachain Polaron Motion and Geminate Combination in Donor–Acceptor Copolymers: Effects of Level Offset and Interfacial Coupling. *Phys. Rev. B* **2008**, *78*, 014304–13.
- (13) da Cunha, W. F.; Junior, L. A. R.; Gargano, R.; e Silva, G. M. Critical Temperature and Products of Intrachain Polaron Recombination in Conjugated Polymers. *Phys. Chem. Chem. Phys.* **2014**, *16*, 17072–17080.
- (14) Wei, X.; Hess, B. C.; Vardeny, Z. V.; Wudl, F. Studies of Photoexcited States in Polyacetylene and Poly(para-phenylenevinylene) by Absorption Detected Magnetic Resonance: The Case of Neutral Photoexcitations. *Phys. Rev. Lett.* **1992**, *68*, 666–669.
- (15) Swanson, L. S.; Shinar, J.; Brown, A. R.; Bradley, D. D. C.; Friend, R. H.; Burn, P. L.; Kraft, A.; Holmes, A. B. Electroluminescence-Detected Magnetic-Resonance Study of Polyparaphenylenevinylene (PPV)-Based Light-Emitting Diodes. *Phys. Rev. B* **1992**, *46*, 15072–15077.
- (16) Kadashchuk, A.; Arkhipov, V. I.; Kim, C. H.; Shinar, J.; Lee, D. W.; Hong, Y. R.; Jin, J.-I.; Heremans, P.; Bäessler, H. Localized Trions in Conjugated Polymers. *Phys. Rev. B* **2007**, *76*, 235205–10.
- (17) Sun, Z.; Li, Y.; Gao, K.; Liu, D.; An, Z.; Xie, S. Dynamical Study of Polaron–Bipolaron Scattering in Conjugated Polymers. *Org. Electron.* **2010**, *11*, 279–284.
- (18) Onodera, Y. Polarons, Bipolarons, and Their Interactions in cis-Polyacetylene. *Phys. Rev. B* **1984**, *30*, 775–785.
- (19) Lima, M. P.; e Silva, G. M. Polaron Stability Under Collision with Different Defects in Conjugated Polymers. *Int. J. Quantum Chem.* **2006**, *106*, 2603–2608.
- (20) Ribeiro, L. A.; da Cunha, W. F.; de Oliveira Neto, P. H.; Gargano, R.; e Silva, G. M. Dynamical Study of Impurity Effects on Bipolaron–Bipolaron and Bipolaron–Polaron Scattering in Conjugated Polymers. *J. Phys. Chem. B* **2013**, *117*, 11801–11811.
- (21) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. Solitons in Polyacetylene. *Phys. Rev. Lett.* **1979**, *42*, 1698–1701.
- (22) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. Solitons Excitations in Polyacetylene. *Phys. Rev. B* **1980**, *22*, 2099–2111.
- (23) Brazovskii, S.; Kirova, N. Physical Theory of Excitons in Conducting Polymers. *Chem. Soc. Rev.* **2010**, *39*, 2453–2465.
- (24) Stafström, S. Electron Localization and the Transition from Adiabatic to Nonadiabatic Charge Transport in Organic Conductors. *Chem. Soc. Rev.* **2010**, *39*, 2484–2499.
- (25) Ribeiro, L. A.; da Cunha, W. F.; Neto, P. H. O.; Gargano, R.; e Silva, G. M. Effects of Temperature and Electric Field Induced Phase Transitions on the Dynamics of Polarons and Bipolarons. *New J. Chem.* **2013**, *37*, 2829–2836.
- (26) Yu, Z. G.; Wu, M. W.; Rao, X. S.; Bishop, A. R. Excitons in Two Coupled Conjugated Polymer Chains. *J. Phys.: Condens. Matter* **1996**, *8*, 8847–8857.
- (27) Neto, P. H. O.; da Cunha, W. F.; Teixeira, J. F.; Gargano, R.; e Silva, G. M. Electron–Lattice Coupling in Armchair Graphene Nanoribbons. *J. Phys. Chem. Lett.* **2012**, *3*, 3039–3042.
- (28) Ribeiro, L. A.; da Cunha, W. F.; Neto, P. H. O.; Gargano, R.; e Silva, G. M. Predicting the Equilibrium Structure of Organic Semiconductors with Genetic Algorithms. *Chem. Phys. Lett.* **2013**, *555*, 168–172.
- (29) Ribeiro, L. A.; da Cunha, W. F.; Neto, P. H. O.; e Silva, G. M. Dynamics of Photogenerated Polaron–Excitons in Organic Semiconductors. *Phys. Proc.* **2012**, *28*, 112–116.
- (30) Johansson, A.; Stafström, S. Polaron Dynamics in a System of Coupled Conjugated Polymer Chains. *Phys. Rev. Lett.* **2001**, *86*, 3602–3605.
- (31) Johansson, A.; Stafström, S. Nonadiabatic Simulations of Polaron Dynamics. *Phys. Rev. B* **2004**, *69*, 235205–7.
- (32) An, Z.; Wu, C. Q.; Sun, X. Dynamics of Photogenerated Polarons in Conjugated Polymers. *Phys. Rev. Lett.* **2004**, *93*, 216407–4.
- (33) e Silva, G. M.; Terai, A. Dynamics of Solitons in Polyacetylene with Interchain Coupling. *Phys. Rev. B* **1993**, *47*, 12568–12577.
- (34) e Silva, G. M. Electric-Field Effects on the Competition between Polarons and Bipolarons in Conjugated Polymers. *Phys. Rev. B* **2000**, *61*, 10777–10781.
- (35) Ribeiro Junior, L. A.; da Cunha, W. F.; e Silva, G. M. Singlet–Singlet Exciton Recombination: Theoretical Insight into the Influence of High Density Regime of Excitons in Conjugated Polymers. *J. Phys. Chem. B* **2014**, *118*, S250–S257.

(36) Ribeiro, L. A.; Neto, P. H. O.; da Cunha, W. F.; Roncaratti, L. F.; Gargano, R.; da Silva Filho, D. A.; e Silva, G. M. Exciton Dissociation and Charge Carrier Recombination Processes in Organic Semiconductors. *J. Chem. Phys.* **2011**, *135*, 224901–224906.

(37) Ribeiro, L. A.; da Cunha, W. F.; Neto, P. H. O.; Gargano, R.; e Silva, G. M. Impurity Effects and Temperature Influence on the Exciton Dissociation Dynamics in Conjugated Polymers. *Chem. Phys. Lett.* **2013**, *580*, 108–114.

(38) Sun, Z.; Stafstöm, S. Dynamics of Exciton Dissociation in Donor–Acceptor Polymer Heterojunctions. *J. Chem. Phys.* **2013**, *138*, 164905–8.

(39) Neto, P. H. O.; da Cunha, W. F.; Roncaratti, L. F.; Gargano, R.; e Silva, G. M. Thermal Effects on Photogeneration of Free Carriers in Organic Conductors. *Chem. Phys. Lett.* **2010**, *493*, 283–287.

(40) Roncaratti, L. F.; Gargano, R.; de Oliveira Neto, P. H.; da Cunha, W. F.; da Silva Filho, D. A.; e Silva, G. M. Temperature-Induced Oscillating Electric Dipole in Conjugated Systems. *Chem. Phys. Lett.* **2012**, *593*, 214–217.

(41) Roncaratti, L. F.; Gargano, R.; e Silva, G. M. Theoretical Temperature Dependence of the Charge-Carrier Mobility in Semi-conducting Polymers. *J. Phys. Chem. A* **2009**, *113*, 14591–14594.