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Interchain interaction effects on polaron–bipolaron transition on conducting polymers

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Abstract We investigate the effects of interchain interaction on the polaron–bipolaron transition on conjugated polymer. We use a Su-Schrieffer-Heeger model modified to include interchain interaction, an external electric field and electron–electron interaction via extended Hubbard terms. We study the dynamics within the time-dependent unrestricted Hartree-Fock approximation. We find that adding a hole in interacting conducting polymer chains bearing a single positively charged polaron leads to the direct transition of polaron to bipolaron state. The transition which is produced is single-polaron to bipolaron transition whose excitation spectrum explains the experimental data. The competing mechanism of two polarons merging to form a bipolaron is also observed under special circumstances. We also find that depending on how fast the hole is inserted, a structure that contains a bipolaron coupled to a breather is created. The bipolaron-breather pair can be decoupled under the action of an external electric field.

Introduction

Organic light-emitting diodes, transistors and lasers are fabricated thanks to the properties of conjugated polymers [1, 2]. Their semiconductor properties are related to the nonlinear electronic response of the coupled electron–lattice system [3, 4]. These non-degenerate ground state π-electron materials are able to form, by the electron–lattice interaction, self localized electron states called polaron and bipolaron. The non-linear electronic excitations of the the π-electron system distinguish the semiconductor physics of these materials from that of three-dimensional inorganic semiconductors. Bipolarons and polarons are though to play the leading role in determining the charge injection, optical and transport properties of conducting polymers [5, 6]. Bipolarons were introduced by Brazowskii and Kirova [7], and along side with polarons are self-localized particle-like defects associated with characteristic distortions of the polymer backbone and with quantum states deep in the energy gap due to strong electron–lattice coupling. Polaron have spin ±1/2 and electric charge $\pm e$, whereas bipolarons are spinless with charge $\pm 2e$. It should be pointed out that there exist some controversy on the existence of bipolarons [8]. Nevertheless, as far as the present model is concerned in the description of conducting polymers, bipolarons are a natural outcome.

A critical problem in the understanding of these materials is the consistent description of the dynamics of mechanism of creation, stability and transition of polarons to bipolarons.

UV–Vis-NIR spectroscopy studies on poly(p-phenylene vinylene) combined to the follow-up of the kinetics of doping with iodine vapor were reported and interpreted as direct observations of the formation of polaronic charge carriers [1, 9]. However, by following different doping levels with I_2 doping, bipolaron formation is identified as well showing that polarons and bipolarons coexist in the oxidized polymer. These results corroborate the findings of Steinmüller et al. [10] where the evolution of the gap states of bithiophene as a model system for polythiophene for different n-doping levels was followed by ultraviolet photo-emission spectroscopy

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(UPS) and electron-energy-loss spectroscopy (EELS). In both spectroscopies the behavior of the states formed in the gap indicated two doping regimes. The EELS results suggested a polaron to bipolaron transformation. The UPS results were consistent with this interpretation, showing first in the low-doping regime the appearance of two states in the band gap which move close together in the higher-doping regime. This constituted direct observation of the a transition from a polaron to bipolaron states. Optical spectroscopy experiments [3] of field-induced charge (charge injection in semiconductor device structures as the means for introducing charged excitations into conjugated polymers other that doping or photo-excitation) in poly(3-hexyl thienylene) also indicated optical-absorption bands assigned to polarons with additional bands assigned to bipolarons.

The polaron–bipolaron transition problem was explicitly addressed by Cik et al., in poly(3-dodecyl thiophene) in connection with temperature changes [11]. They found that when the sample was heated and subsequently cooled, there was an amplification of the diamagnetic inter- and intra-chain bipolarons. Kaufman and Colaneri study of polypirrole [12] by optical-absorption spectroscopy and ESR also pointed that the metastable states possess spin, while the stable states do not. Their data revealed a slow transition, consistent with the diffusion rate limited by the mobility of the dopant.

Many efforts have been devoted to describe the polaron–bipolaron conundrum theoretically. Electronic structure calculations [13], extensions of the Su-Schrieffer-Heeger model [14, 15], the Pariser-Parr-Pople model [16], as well as combinations of them [17] have been used to determine the relative prevalence of each excited state in various regimes. The dependence of the transition between polarons and bipolarons on the electron–electron Coulomb interactions (on-site Hubbard *U* and inter-sites *V*) has provided contradictory results. While strong Coulomb interactions destabilize the bipolaron in Refs. [14] and [15], it favors bipolaron in comparison to polaron in Ref. [16]. On the other hand, there exist a remarkable agreement concerning the role of impurities in the stabilization of bipolarons. Several different approaches [14, 17–19] point to bipolaron system been more stable than the polaron system when dopants are taken into account.

Two mechanisms have been put forward to explain the transition from polaron to bipolaron states. Polarons recombination into bipolaron [11, 12, 20], where the bipolaron is generated when polarons with the same electric charge meet each other; and single-polaron to bipolaron transition [1, 18, 21], where the polaron structure is transformed by the addition of one extra charge. The realm of each one of these two mechanisms is still subject of controversive discussion in the literature.

Here, we report the results of dynamical calculations on polaron–bipolaron transition mechanism with interacting chains. We use the Su-Schrieffer-Heeger model [22] modified to include the Coulomb interaction via extended Hubbard model, Brazovskii-Kirova (BK) symmetry breaking terms, the action of an external electric field, and interchain interactions [17]. The time-dependent equations of motion for the lattice sites and the π-electrons are numerically integrated within the time-dependent Hartree-Fock approximation.

In agreement with UV–Vis-NIR spectroscopy [1], UPS and EELS measurements [10], our theoretical studies of the transition indicate that the single-polaron to bipolaron transition is the preferred mechanism of polaron–bipolaron transition in conjugated polymers. Besides that, once the transition is achieved the bipolaron shows no signs of dissociation into two polarons in our simulations, where no additional counterion nor photo-excitation were considered (It has been reported that bipolarons can be dissociated int two polarons after a photoexcitation [23]). Nevertheless, it should be noted that two polarons combination leading to one bipolaron is also obtained here in the special case where one of the interacting chains bears a high density of polarons.

We find that a breather mode of oscillation is created at the lattice in connection with the transition around the bipolaron. The breather amplitude is associated with how fast the extra charge is added to the system. The presence of this breather coupled to the single-polaron–bipolaron transition could possibly be detected in the IR spectrum giving additional evidence of the underlying transition mechanism. Moreover, the created bipolaron is trapped by the breather.

Model

We consider a SSH-Extended Hubbard type Hamiltonian modified to include an external electric field and interchain interaction. The Hamiltonian is given by:

$$H = H_1 + H_2 + H_{int} \tag{1}$$

where,

$$\begin{aligned} H_j = & -\sum_{i,s}(t_{j_{i,i+1}} C^{\dagger}_{j_{i+1,s}} C_{j_{i,s}} + H.c) \\ & + U\sum_i (n_{j_{i\uparrow}} - \frac{1}{2})(n_{j_{i\downarrow}} - \frac{1}{2}) \\ & + V\sum_i (n_{j_i} - 1)(n_{j_{i+1}} - 1) \\ & + \sum_i \frac{K}{2} y^2_{j_i} + \sum_i \frac{M}{2} \dot{u}^2_{j_i}, \quad j = 1,2 \end{aligned} \tag{2}$$

and

$$H_{int} = -\sum_{i=p,s}^{q} t_{\perp}(C^{\dagger}_{1_{i,s}} C_{2_{i,s}} + C^{\dagger}_{2_{i,s}} C_{1_{i,s}}) + \sum_{s} V_p (C^{\dagger}_{1_{m,s}} C_{1_{m,s}} + C^{\dagger}_{1_{m+1,s}} C_{1_{m+1,s}}) \tag{3}$$

$C^{\dagger}_{i,s}$ ($C_{i,s}$) is the creation (annihilation) operator of a π electron with spin s at the ith lattice site, $n_{i,s} \equiv C^{\dagger}{}_{i,s} C_{i,s}$ is the number operator, and $n_i = \sum_s n_{i,s}$. $y_n \equiv u_{n+1} - u_n$, where u_n is the displacement of nth CH-group from equilibrium position in the undimerized phase. $t_{j\_n,n+1} = exp(-i\gamma\ A)[(1 + (-1)^n \delta_0) t_0 - \alpha\, y_{j\_n}]$, t_0 is the transfer integral between the nearest neighbor sites in the undimerized chains, $t_{\perp}$ is the hopping integral between sites with the same index on different chains from p site to q site, α is the electron–phonon coupling, δ_0 is the BK symmetry-breaking parameter. M is the mass of a CH group, K is the spring constant of a σ-bond, U and V the on-site and nearest-neighbor Coulomb repulsion strengths, respectively. $\gamma \equiv ea/(\hbar c)$, e is the absolute value of the electronic charge, a the lattice constant, and c the light velocity. The relation between the time-dependent vector potential A and the uniform electric field E is given by $E = -\frac{1}{c}\dot{A}$. We use as parameters the commonly accepted values for conjugated polymers: $t_0 = 2.5$ eV, $t_{\perp} = 0.075$ eV, $K = 21$ eV Å^{-2}, $\alpha = 4.1$ eV Å^{-1}, $U = 0$ to $1.8 t_0$, $V = U/2$, $a = 1.22$ Å, $\delta_0 = 0.05\ t_0$, $V_p = 0.2$ eV, and a bare optical phonon energy $\hbar\omega_Q = \hbar\sqrt{4K/M} = 0.16\,\text{eV}$.

The dynamics of the lattice part is made with the Euler-Lagrange equations

$$\frac{d}{dt}\left(\frac{\partial\langle L\rangle}{\partial \dot{u}_{j_n}}\right) - \frac{\partial\langle L\rangle}{\partial u_{j_n}} = 0 \tag{4}$$

where

$$\langle L\rangle = \langle T\rangle - \langle V\rangle. \tag{5}$$

The Eq. 4 leads to

$$M\ddot{u}_n = F_n(t) \tag{6}$$

where we omitted the j index and $F_n(t)$ is obtained as

$$F_n(t) = -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + \alpha[e^{i\gamma A(t)}(B_{n,n+1} - B_{n-1,n}) + e^{-i\gamma A(t)}(B_{n+1,n} - B_{n,n-1})]. \tag{7}$$

Here $B_{n,n'} \equiv \sum_{k,s}{}' \psi^{*}_{k,s}(n,t)\psi_{k,s}(n',t)$. The prime on the summation means that the sum is taken over the occupied single-particle states in the initial stationary state.

The Schrödinger π-electrons equation of motion is solved within the unrestricted time-dependent Hartree-Fock approximation [17].

In order to perform the dynamics, an initial self-consistent state is prepared solving the equations of motion for the lattice and π-electrons simultaneously [24]. Periodic boundary conditions are considered. The initial state is taken in equilibrium ($E = 0$). Therefore, we have $\dot{u}_n = 0$ for all n in the initial state.

The equations of motion are solved by discretizing the time variable with a step Δt. The time step Δt is chosen so that the change of $u_i(t)$ and $A(t)$ during this interval is always very small in the electronic scale.

The solutions of the time dependent Hartree-Fock equations can then be put in the form,

$$\psi_{k,s}(n,t_{j+1}) = \sum_{l}\left[\sum_{m}\phi^{*}_{l,s}(m,t_j)\psi_{k,s}(m,t_j)\right] \times e^{-i\frac{\varepsilon_l \Delta t}{\hbar}}\phi_{l,s}(n,t_j), \tag{8}$$

where $\{\varphi_l\}$ and $\{\varepsilon_l\}$ are the eigenfunctions and the eigenvalues of the single-electron equations at a given time t_j.

The lattice equations are written as

$$u_i(t_{j+1}) = u_i(t_j) + \dot{u}_i(t_j)\Delta t \tag{9}$$

$$\dot{u}_i(t_{j+1}) = \dot{u}_i(t_j) + \frac{F_i(t_j)}{M}\Delta t. \tag{10}$$

Hence, the electronic wave functions and the displacement coordinates at the $j + 1$-th time step are obtained from the j-th time-step.

Simulation results

We injected one more hole in polymer chains bearing already positively charged polarons. Since charged excitations defects can be created by quite different means: photoexcitations, chemical doping or direct charge injection via electronic device, we performed simulations where the extra electron is taken from the system during different time intervals (ΔT). We varied ΔT from 0 to 100 fs. The shorter time intervals simulate photoexcitations and the direct charge injection. The longer time intervals account for the different impurity addition procedures associate with chemical doping. The electron is taken from the highest occupied level using the following expression

$$O_F(t) = \frac{1}{2}\left[1 + \cos\left(\frac{\pi(t - t_i)}{\Delta T}\right)\right] \tag{11}$$

for t between t_i and $t_i + \Delta T$. Here, t_i is the time when the hole injection begins and $O_F(t)$ is the occupation number of the Fermi level.

We have considered two polymeric interacting chains with $N = 60$ sites each, containing initially two positively charged polaron in all simulations. We use a mean charge density $\bar{\rho}_i(t)$, derived from the charge density $\rho_i(t)$, and the order parameter $\bar{y}_i(t)$ to analyze the simulations

$$\rho_i(t) = \sum_s \rho_s(i,t) \tag{12}$$

$$\bar{\rho}_i(t) = 1 - \frac{\rho_{i-1}(t) + 2\rho_i(t) + \rho_{i+1}(t)}{4}, \tag{13}$$

$$\bar{y}_i(t) = (-1)^i \frac{y_{i-1}(t) - 2y_i(t) + y_{i+1}(t)}{4}, \tag{14}$$

where $\rho_s(i,t)$ is given by

$$\rho_s(i,t) = \sum_k{}' \psi^*_{k,s}(i,t)\psi_{k,s}(i,t). \tag{15}$$

The calculated energies in each simulation are the electronic energy, the lattice potential energy, and the lattice kinetic energy. The lattice total energy is the sum of these energies. The dynamics of the system is followed during 100,000 time steps spanning 400 fs.

A smooth transition of one of the polarons to a bipolaron, in its respective chain, is obtained after the adiabatic removal ($\Delta T > 80$ fs) of the third electron. Figure 1 shows the time evolution of the energy levels neighboring and inside the energy gap. It can be seen that the energy levels associated with the polaron move in the middle-gap direction assuming a bipolaron conformation. The small oscillation of the levels are due to lattice oscillations induced by the hole injection perturbation.

Figure 2 presents bond length order parameter of chains 1 and 2. It should be noted that we use periodic boundary conditions, therefore, the order parameter of chain 1 (upper plot of Fig. 2) represents a polaron around site 1. The positively charged polarons repel each other and they stay as far as possible. The polaron–bipolaron transition occurs in chain 2. This clear transition happens in chain 2 as a spontaneous symmetry breaking. Nevertheless, the presence of an impurity on one chain leads to a symmetry breaking and the association of one polaron to it. It is obtained that the impurity associated polaron make the transition to bipolaron.

The effect of interchain interaction was addressed by varying the extent of the interacting region (p and q in he Hamiltonian). Figure 3 presents the result of transitions where two chains interact only on half of their length ($p = 31$ and $q = 60$). A polaron stays in the interacting region and the other stays in the non-interacting region due again to Coulomb repulsion. It is obtained that the polaron–bipolaron transition happens with the polaron in the interacting region. Therefore, the interchain interaction is also effective in promoting the transition.

Figure 4 presents a very special case where two polarons merge to create a bipolaron. This case is quite the originally suggested process for the polaron–bipolaron transition [25]. Here, after the hole injection, there appears an exciton lasting for about 200 fs and then the bipolaron takes place in the lattice. Nevertheless, it should be noted

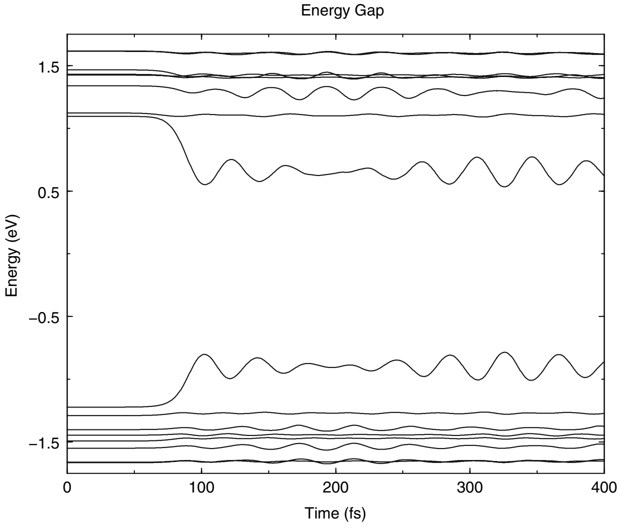

Fig. 1 Time evolution of energy levels inside and around the gap in an adiabatic transition. The spin up levels are shown. The system changes from polaron levels ($t < 80$ fs) to bipolaron levels configuration ($t > 100$ fs)

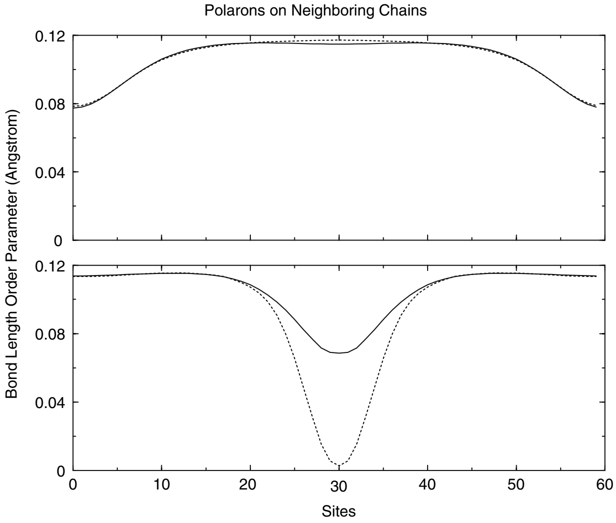

Fig. 2 Evolution of the bond length order parameter of two neighboring chains. Solid line: initial configuration; dotted line: final configuration. The polaron on chain 1 (upper plot) remains stable after the extra electron is adiabatically taken from the system, but the polaron on chain 2 makes a transition and it becomes a bipolaron

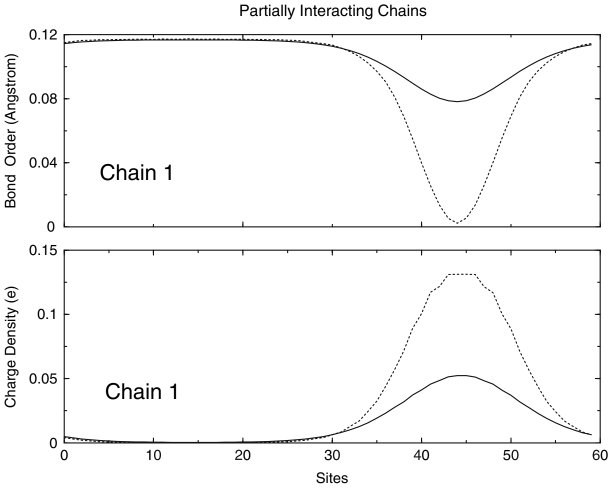

Fig. 3 Charge density and bond length order parameter of chain 1 for the simulation where two chains interact from site $p = 31$ to site $q = 60$. The polaron–bipolaron transition is clearly seen. Solid line: simulation time $t = 0$ fs; dotted line: simulation time $t = 400$ fs

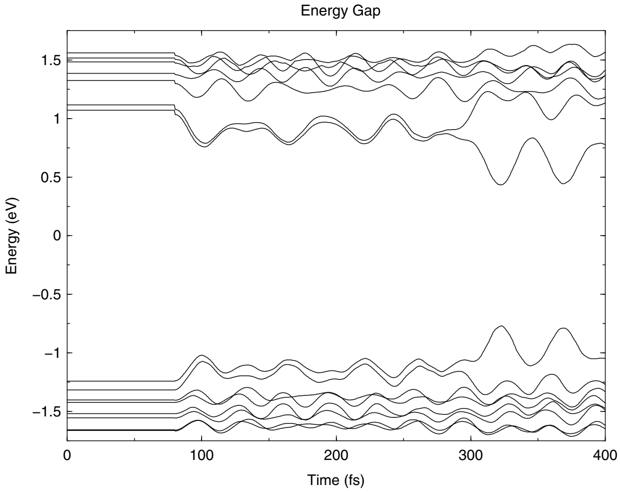

Fig. 4 Time evolution of energy levels associated with the gap when chain 1 has a high density of polarons and chain 2 has none. The presence of an exciton is observed, after the hole injection, from $t \simeq 80$ fs to $t \simeq 320$ fs. Then, the transition to a bipolaron is accomplished

that this happens when one chain has a high density of polarons and the other one has initially none of them. Since it seems a rather improbable configuration, the dominant process should be the direct polaron–bipolaron transition. In Fig. 5 we show the charge density behavior for this very case. It can be clearly seen that two polarons in chain 1 merges to a single bipolaron and another polaron appears in chain 2.

The fast removal of the third electron ($\Delta T < 80$ fs) leads to the appearance of a breather oscillation mode in the lattice. This breather appears at the bipolaron position. There exists an effective interaction between the bipolaron and the breather. As a matter of fact, the bipolaron is trapped by the breather [27].

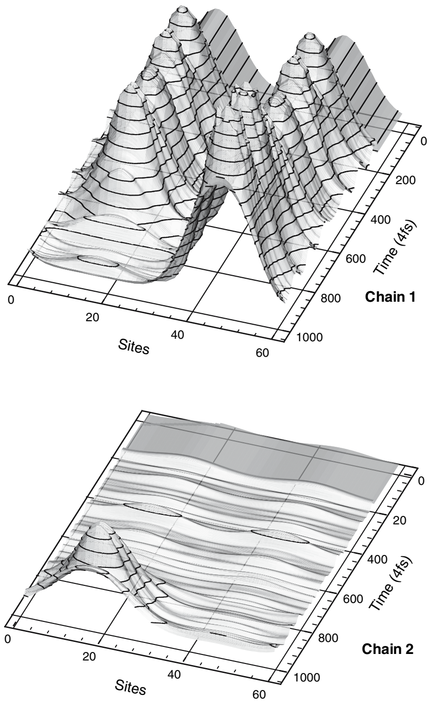

Fig. 5 Charge density of chains corresponding to simulation of Fig. 4. The initial polarons on chain 1 coalesce on a bipolaron (upper plot). There is also the creation of a polaron on chain 2 (lower plot)

Conclusions

The effect of interchain interaction on the transition of polarons to bipolarons on two interacting conjugated polymeric chains was investigated. This study was carried out through numerical calculations. A modified SSH type Hamiltonian considering an external electric field, Coulomb interactions, symmetry breaking terms and interchain interaction was used. The initial configuration is fully self-consistent and the time evolution of the system is carried out using the Schrödinger equation within the Unrestricted Hartree-Fock approximation and the Euler-Lagrange equations. This model results are considered to describe the polaron–bipolaron transition behavior in conjugated polymers in general capturing the essential physics of the process.

We present theoretical results pointing to direct single-polaron to bipolaron transition as the favored mechanism of bipolaron formation. This result is in accordance with previous results on polaron and bipolaron dynamics calculations [17] where a pair of polarons do not spontaneously merged to produce a bipolaron. The other transition mechanism, namely the merging of polarons, was indisputably observed in experiments only under exceptional conditions [11], where the sample was heated above 450 K and subsequently cooled, what is not the usual condition of bipolaron formation. Nevertheless, it should be pointed out that some simulations, with very special initial conditions, presented this kind of transition.

In the simulations, bipolarons once formed showed no sign of dissociation into two polarons, remaining the non-linear excitation that transport the excess of charge in the chain. It should be mentioned that our calculation are done for zero temperature. Thus, even if bipolarons are energetically favored, polarons could dominate at finite temperature [26].

Since we considered different characteristic time intervals for the hole insertion in the chain, in order to simulate different ways of bipolaron generation (photoproduction, chemical doping or direct charge injection), we obtained different responses from the lattice. It is found that the non-adiabatic electron removal led to the formation of an associated breather oscillation mode in the chain. Moreover, the breather interacts with the newly formed bipolaron trapping it around its position. The trapping and depinning of bipolarons from breathers have direct influence on the mobility of that charge carrier in the chain.

It should be noted that within our calculations, bipolarons are more stable than polarons and the changing of the Coulomb interaction parameters, from small values up to the commonly accepted values for conjugated polymers ($U = 1.8t_0$ and $V = U/2$), did not lead to any alteration in the relative prevalence of bipolarons and polarons.

Based on our numerical simulations, we suggested two experimental approaches to better understand the polaron–bipolaron transition mechanism. First, the verification of the presence and quantity of breathers associated with different transition regimes. Second, the change in bipolarons mobility due to the trapping effect of breathers.

Although several results point to an essentially one-dimensional character to the polaron–bipolaron transition [27], we showed that the interchain interaction is fundamental in a more accurate description of the phenomena. The effects of interacting regions in enhancing the transition as well as the sporadic recombination of polarons and the polaron jumping between chains are dependent on this interaction.

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