

Theoretical Temperature Dependence of the Charge-Carrier Mobility in Semiconducting Polymers[†]

Luiz F. Roncaratti,[‡] Ricardo Gargano,[§] and Geraldo Magela e Silva^{*§}

Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy, and Instituto de Física, Universidade de Brasília, 70919-970, Brasília, Brazil

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We present a theory of the temperature and electric field dependence on the mobility of polarons in conjugated polymers in terms of a tight-binding and stochastic approach. The polaron mobility is shown to have a strong dependence on the electric field, with two distinct regimes of temperature dependence. Lattice thermal oscillations enhance polaron mean velocity for electric fields of 1.0 mV/Å or higher. In contrast, its mobility is damped by thermal oscillations under weaker electric fields. This semiconductor/metallic analogous behavior comes from the difference between the inertial content acquired by polarons under stronger/weaker electric fields. These new results and their analysis shed new light on several experimental controversies.

Introduction

The discovery of electroluminescence in conjugated polymers has had a great impact in optoelectronic devices such as organic light emitting diodes (OLED's)^{1,2} and organic field-effect transistors (OFET's).^{3,4} The microscopic description of the temperature dependence of the charge carrier mobility in these materials is most needed and of fundamental importance. Alternative approaches considering master equations and isotropic hopping models on regular lattices have produced interesting results.⁵ Nevertheless, to gain insight on the temperature behavior of polarons on a single chain of conjugated polymer, a more detailed picture is necessary. We present a new model based on well-known theories that is in agreement with experimental data and able to predict new electric field effects on the charge mobility.

Polarons are self-localized, charged quasi-particles associated with characteristic distortions of the polymer backbone and with quantum states in the energy gap due to strong electron–lattice coupling. The experimental evidence shows that these distortions persist into the metallic regime. Specifically, the doping-induced infrared modes last even at high dopant concentrations.^{6–9} These modes are the signature of structural distortions that form around injected charges. Therefore, the infrared data imply that the metallic state is not a uniform bond-length polyene. Rather, it is basically a dimerized structure with a high density of localized structural defects, typically polarons.

Usually, the field and temperature dependent polaron mobility in polymeric light-emitting diode (LED) materials is described by hopping in a Gaussian density of states (DOS), whereas for field-effect transistor (FET) materials the gate bias and temperature dependencies are described by hopping in an exponential DOS. Monte Carlo calculations of hopping transport were done by Bäessler¹⁰ for the case of a Gaussian disorder model, exhibiting a non-Arrhenius temperature dependence $\mu \propto \exp(-c\bar{\sigma}^2)$, where $c \approx 0.44$ and $\bar{\sigma} \equiv \sigma/k_{\text{B}}T$. For the dependence on the electric field, a Poole–Frenkel $\mu \propto \exp$

$(\gamma E^{1/2})$ behavior was, in a given field range, found.¹¹ Nevertheless, as pointed out by Gartstein and Conwell,¹² a spatially correlated potential for the charge carriers is needed to explain the Poole–Frenkel behavior in a wide range of field values. Several suggestions were considered as a cause for this correlation, such as charge–dipole interactions^{13,14} or thermal fluctuations in molecular geometries.¹⁵

At low electric fields, and at room temperature, the polaron mobility amounts to $5 \times 10^{-7} \text{ cm}^2/(\text{V s})$, in poly(*p*-phenylene) derivatives.^{14,16} Typical field-effect mobilities, for spin-coated amorphous poly(3-hexylthiophene) P3HT films are in the region of 10^{-5} – $10^{-4} \text{ cm}^2/(\text{V s})$, whereas by ordering the polymer in the film the field-effect mobility increased to about $10^{-1} \text{ cm}^2/(\text{V s})$.¹⁷ That leads to reported hole mobilities differing typically by more than 6 orders of magnitude.^{16,18}

Theoretical studies carried out by Rakhmanova and Conwell,¹⁹ by e Silva,²⁰ and by Ma and Schollwöck²¹ deal with polaron motion on single chains under the influence of an external electric field. From these calculations it is possible to conclude that polarons are not stable for electric field strengths above 1.3 mV/Å. Typical electric field values for polymer LED's are about 1 mV/Å. In this case the excess energy in the system creates too much disturbance, e.g., in the form of lattice vibrations, to allow the polaron formation. In an actual physical system, e.g., an organic light-emitting diode (OLED), the energy excess may, to some extent, be transported away in the form of heat. That might lead to a stabilization of the polaron at higher field strengths than 3 mV/Å. The main reason for this deviation is probably due to excitations, i.e., allowed transitions between instantaneous eigenstates.²² This seems important for the stability of the system.

The purpose of this paper is to present a microscopic theoretical description of the temperature (*T*) and electric field (*E*) dependence of the mobility μ , and to analytically compare the results with experiments.

Methodologies

We consider that the essential physics of the mobility is contained in the Su, Schrieffer, and Heeger (SSH) Hamiltonian,²³ written below, and the Langevin approach^{24,25} introduced in the following:

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* Corresponding author. E-mail: magela@fis.unb.br.

[‡] Università di Perugia.

[§] Universidade de Brasília.

$$H = - \sum_{n,s} (t_{n+1,n} c_{n+1,s}^\dagger c_{n,s} + t_{n,n+1}^* c_{n,s}^\dagger c_{n+1,s}) + \frac{1}{2} \sum_n K(u_{n+1} - u_n)^2 + \frac{1}{2} \sum_n M \dot{u}_n^2 \quad (1)$$

where u_n is the displacement coordinate of the n th CH group with respect to the fully dimerized chain configuration, $c_{n,s}$ is the annihilation operator of a π -electron with s spin in the n th site and K is the harmonic constant and M is the mass of a CH group. The original SSH model is modified to include the electric field E in terms of a time dependent vector potential A , with $E = -(1/c)\dot{A}$. Defining $y_n \equiv u_{n+1} - u_n$ the hopping term can be written as

$$t_{n,n+1} = [t_0 - \alpha y_n] \exp(-i\gamma A) \quad (2)$$

where t_0 is the transfer integral between the nearest neighbor sites in the undimerized chain configuration and α is the electron–phonon coupling constant. $\gamma \equiv ea/(\hbar c)$, e being the absolute value of the electronic charge, a the lattice constant, and c the light velocity. The parameters used in this work are $t_0 = 2.5$ eV, $K = 21$ eV/Å², $\alpha = 4.1$ eV/Å, $a = 1.22$ Å, and a bare optical phonon energy $\hbar\omega_Q = (4K/M)^{1/2} = 0.16$ eV.²⁰

To time evolve the system, we prepare a stationary state fully self-consistent with the degrees of freedom of electrons and phonons.^{26–28} To perform the dynamics of the system, we solve the Schrödinger one-particle equations coupled with the Euler–Lagrange equations to treat the lattice.²⁷ The equation of motion at each site becomes $M\dot{v}_n = F_n(t)$, where

$$F_n(t) = -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + \alpha[e^{i\gamma A(t)}(B_{n,n+1} - B_{n-1,n}) + e^{-i\gamma A(t)}(B_{n+1,n} - B_{n,n-1})] \quad (3)$$

and $B_{n,n'} \equiv \sum_{k,s} \psi_{k,s}^*(n,t) \psi_{k,s}(n',t)$. The primed summation means a sum over the lowest lying occupied states. So, the lattice problem is coupled to the electronic problem due to the $B_{n,n'}$ terms.

Since our main objective is to characterize the dynamics under a temperature regime, we make use of the canonical Langevin dynamics^{24,25} adding a stochastic and a damping force and rewriting the site equation as

$$M\dot{v}_n = F_n(t) - M\Gamma v_n + \sqrt{6M\Gamma k_B T/\Delta t} \xi_n(t) \quad (4)$$

where $\xi_n(t)$ is as a white noise defined by $\langle \xi_n(t) \rangle = 0$ and $\langle \xi_n(t) \xi_{n'}(t') \rangle = \delta_{nn'} \delta(t - t')$. The random force acts on each site simulating a thermally excited lattice.

To solve the equations of motion, we use a discrete time variable with fixed time intervals Δt . The discrete time dependent Schrödinger equation is written as

$$\psi_k(t_{j+1}) = \exp\left(-i\Delta t \frac{H_{\text{ele}}(t_j)}{\hbar}\right) \psi_k(t_j) \quad (5)$$

where $H_{\text{ele}}(t_j)$ is the electronic part of the Hamiltonian (1) at time t_j . We use the expansion $\psi_k(t_j) = \sum_l C_{lk} \phi_l(t_j)$, with $C_{lk} = \langle \phi_l | \psi_k \rangle$. The eigenvalues and eigenvectors of $H_{\text{ele}}(t_j)$ are given by $\{\epsilon_l\}$ and $\{\phi_l\}$, respectively. The equation is then rewritten as

$$\psi_{k,s}(n, t_{j+1}) = \sum_l \left[\sum_m \phi_{l,s}^*(m, t_j) \psi_{k,s}(m, t_j) \right] \times \exp\left(-i \frac{\epsilon_l \Delta t}{\hbar}\right) \phi_{l,s}(n, t_j) \quad (6)$$

Finally, we obtain the wave functions, site positions, and velocities at time t_{j+1} , from the previous values at time t_j , by numerical integration of the Schrödinger eq 6 and the lattice equation of motion (4).

Results and Discussion

To see the effect of the external electric field and the thermal bath on the polaron mobility, we varied systematically E and T . For the electric field we take the following values: 0, 0.01, 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 E_0 , with $E_0 = 1.3$ mV/Å. The temperature values considered are 0, 7.5, 25, 50, 100, 150, 200, 250, and 300 K. In all cases the dynamics of the system is followed during 10^5 time steps spanning 400 fs ($\Delta t = 0.004$ fs). We have considered polymeric chains with $N = 200$ sites with periodic bound conditions and containing initially one single positively charged polaron at the 25th site in all simulations.

The damping constant can be determined by low temperature lattice thermal conductivity measurements. We estimate Γ with the same order of magnitude as expected from experimental data of Raman spectral line width in polydiacetylene ($\Gamma = 0.01\omega_Q$).²⁹

To analyze the simulations, we used the mean charge density $\bar{\rho}_n(t)$, derived from the charge density $\rho_n(t) = \sum_{k,s} \psi_{k,s}^*(n,t) \psi_{k,s}(n,t)$, and the order parameter $\bar{y}_n(t)$ given by²⁷

$$\begin{aligned} \bar{\rho}_n(t) &= 1 - [\rho_{n-1}(t) + 2\rho_n(t) + \rho_{n+1}(t)]/4 \\ \bar{y}_n(t) &= (-1)^n [\bar{y}_{n-1}(t) - 2\bar{y}_n(t) + \bar{y}_{n+1}(t)]/4 \end{aligned} \quad (7)$$

Figure 1 shows three examples of time evolution for $\bar{\rho}_n(t)$ and $\bar{y}_n(t)$. In (a) and (d) $E = 2.0 E_0$ and $T = 0$ K; in (b) and (e) $E = 0$ mV/Å and $T = 100$ K; and in (c) and (f) $E = 2 E_0$ and $T = 100$ K. In (d) one can see phonons (waves) produced by the polaron motion; (e) shows the phonons produced by the thermal bath, and (f) shows a situation where both are present.

Figure 2a shows how the electric field is turned on in a quasi-adiabatic way to avoid undesirable shakes in the chain caused by a fast transfer of momentum to the polaron. In this way, only after 100 fs does the electric field become constant in time. This time scale is chosen because it is the usual time resolution of ultrafast detection experiments of charged carriers in conjugated polymers.³⁰ We considered the polaron trajectory $x_p(t)$ as the trajectory of the polaron mean charge center and, from that, we measure the polaron velocity $v_p(t)$. When $T = 0$ K, and after 100 fs, these trajectories are smooth and linear, so that the velocity is constant. In Figure 2b we show the behavior of these trajectories for the values of electric field considered. When $E = 0$ mV/Å and $T \neq 0$, the polaron executes a Brownian motion around the initial position and its average velocity is zero. For these cases, Figure 2c shows the squared velocity, averaged over time, as a function of the lattice temperature. The lattice temperature is defined by the fluctuation–dissipation relation used to define the random force on (4). We can see that the average kinetic energy of the polaron K_p is a linear function of temperature, as we should expect if $K_p = m_p \bar{v}_p^2/2 = k_B T/2$ and $k_B/m_p \approx 1.5 \times 10^{-3}$ Å²/(fs² K) where m_p is the effective polaron mass. We consider polaron squared velocity

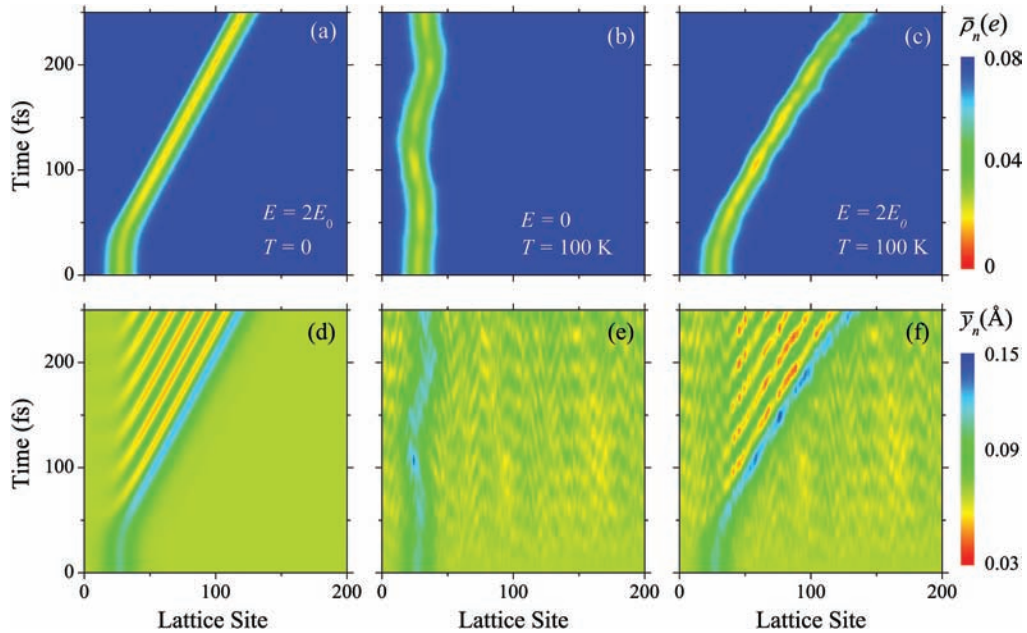


Figure 1. (a)–(c) Time evolution of the charge density $\bar{\rho}_n(t)$, in units of the electron charge e , for three different combinations of electric field ($E_0 = 1.3 \text{ mV/\AA}$) and temperature. (d)–(f) Corresponding bond length parameter, in angstroms. (a) shows a polaron with constant velocity, (b) a Brownian polaron, and (c) a polaron with a velocity enhanced by the thermal bath. In (d) and (f) we can see the phonons (waves) produced by polaron motion (behind it). In (e) and (f) we can see the phonons (waves) produced by the thermal bath.

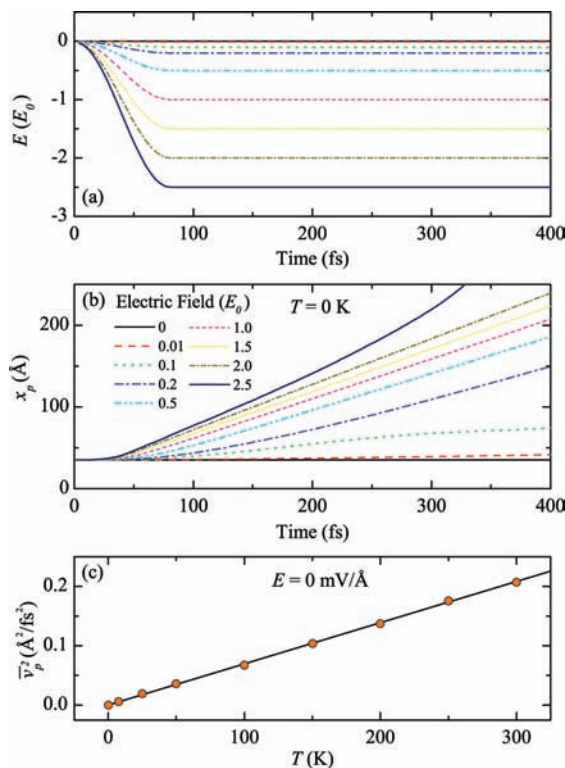


Figure 2. (a) Electric field turning on in a quasi adiabatic way. (b) Polaron trajectory $x_p(t)$. (c) Polaron squared velocity averaged over time as function of lattice temperature.

\bar{v}_p^2 averaged on the time interval $[t_a - t_b]$, where t_a is always 100 fs, the time necessary to reach a constant electric field, and t_b is chosen such that $x_p(t_b) = 244 = 200 \times 1.22 \text{ \AA}$ (length of the chain) to avoid polaron interaction with phonons accumulated behind it (periodic boundary conditions are assumed, see the waves in Figure 1d,f).

Two specific cases where the polaron mobility changes considerably with E and T are shown in Figure 3. In (a) we

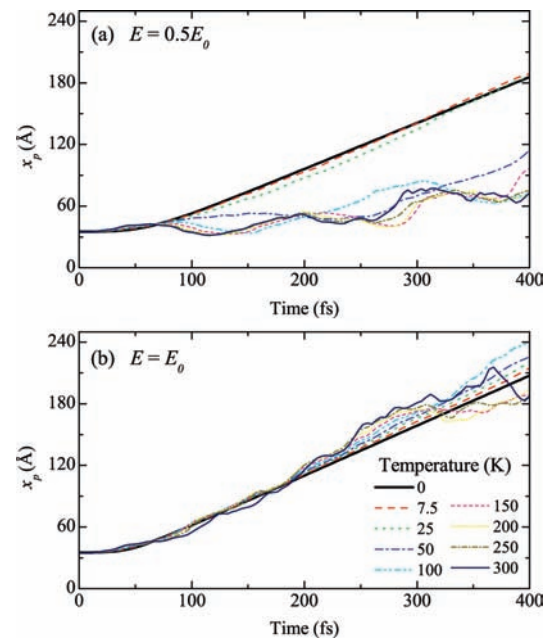


Figure 3. Polaron trajectories for different temperatures. In (a) $E = 0.5E_0$ and the polaron velocity is damped by thermal oscillations when $T > 25 \text{ K}$. In (b) $E = E_0 = 1.3 \text{ mV/\AA}$ and in this case the thermal bath enhances the polaron velocity.

show polaron trajectories for $E = 0.5E_0$. For this value of the electric field the polaron velocity is damped by thermal oscillations when $T > 25 \text{ K}$. In (b) $E = 1.0E_0$ and in this case the thermal bath enhances the polaron velocity.

Figure 4 summarizes our main result: the average velocity of the polaron as function of the electric field and temperature, i.e., $\bar{v}_p(E, T)$. In (a) we show a different curve for each electric field value and in (b) a different curve for each temperature value. These two plots put in evidence the two regimes for the polaron mobility with associated electric fields and temperatures. There is a clear phase transition when the electric field changes from $0.5E_0$ to $1.0E_0$ for temperatures greater than 100 K. This

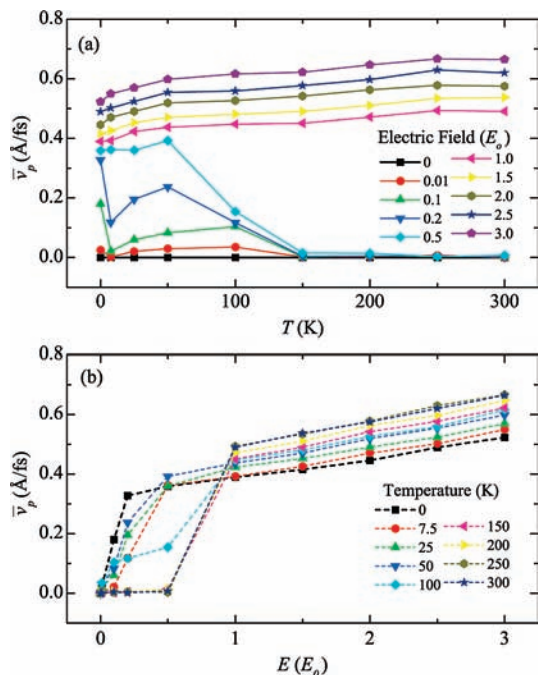


Figure 4. Average velocity of the polaron as function of the electric field and temperature $\bar{v}_p(E, T)$. (a) Different curves for each electric field value. (b) Different curves for each temperature value.

is a simulation result worth a careful experimental investigation with single polymer molecules or well oriented samples.

Conclusions

We have solved the time-dependent Schrödinger equation for the π electrons and the equations of motion for the lattice displacements with temperature effects. The polaron motion is described under a large range of electric fields (0–4.0 mV/Å) and temperature values (0–300 K). We unified the SSH model with Langevin dynamics for 1-D chains to describe the polaron mobility in a single charge transport model. This electric field-temperature-dependent model clearly presents two regimes for the polaron mobility near field values used in physical devices like OLED's and OFET's.³¹ Moreover, this model can be useful to describe thermoelectric properties of materials based on conjugated polymers, one-dimensional conductors or quantum wires.³²

It is found that the introduction of the damping factor Γ into the dynamics of the polaron enhances its stability under external electric fields. We have obtained stable polarons until $E_c = 2.6$ mV/Å. This value is twice the critical field found for single polarons without damping.^{20,33} The stabilizing effect comes from the damping down of the kinetic energy excess brought in by the external electric field.

The presence of two different regimes for the temperature dependence of the mobility is shown to be consistent with the large mobility differences reported for conjugated polymers.^{4,5,31} It is shown that the temperature could enhance or damp the polaron mobility depending on the external electric field strength. For electric fields of about 1 mV/Å or higher, the

temperature produces an increase of the mobility of the charge carriers in a way, which has been here presented, distinct from the conventional semiconductor mechanism.

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References and Notes

- (1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
- (2) Heeger, A. J. *J. Phys. Chem. B* **2001**, *105*, 8475.
- (3) Brown, A. R.; Jarrett, C. P.; de Leeuw, D. M.; Matters, M. *Synth. Met.* **1997**, *88*, 37.
- (4) Matsui, H.; Hasegawa, T.; Tokura, Y.; Hiraoka, M.; Yamada, T. *Phys. Rev. Lett.* **2008**, *100*, 126601.
- (5) Pasveer, W. F.; Cottaar, J.; Tanase, C.; Coehoorn, R.; Bobbert, P. A.; Blom, P. W. M.; de Leeuw, D. M.; Michels, M. A. J. *Phys. Rev. Lett.* **2005**, *94*, 206601.
- (6) Kuzmany, H.; Bartonek, M. *Europhys. Lett.* **1990**, *12*, 167.
- (7) Rabolt, J. F.; Clarke, T. C.; Street, G. B. *J. Chem. Phys.* **1979**, *71*, 4614.
- (8) Harada, I.; Furukawa, Y.; Tasami, M.; Shirakawa, H.; Ikeda, S. *J. Chem. Phys.* **1980**, *73*, 4746.
- (9) Benoit, C.; Bernard, O.; Palpecuer, M.; Tolland, M.; Abadie, M. J. M. *J. Phys. (Paris)* **1983**, *44*, 1307.
- (10) Bäessler, H. *Phys. Status Solidi B* **1993**, *175*, 15.
- (11) Blom, P. W. M.; de Jong, J. M.; van Munster, M. G. *Phys. Rev. B* **1997**, *55*, R656.
- (12) Gartstein, E. M.; Y. N. *Chem. Phys. Lett.* **1995**, *245*, 351. and Conwell.
- (13) Dunlap, D. H.; Parris, P. E.; Kenkre, V. M. *Phys. Rev. Lett.* **1996**, *77*, 542.
- (14) Novikov, S. V.; Dunlap, D. H.; Kenkre, V. M.; Parris, P. E.; Vannikov, A. V. *Phys. Rev. Lett.* **1998**, *81*, 4472.
- (15) Yu, D. L.; Z. G.; Smith; Saxena, A.; Martin, R. L.; Bishop, A. R. *Phys. Rev. Lett.* **2000**, *84*, 721.
- (16) Blom, P. W. M.; de Jong, M. J. M. *IEEE J. Sel. Top. Quantum Electron.* **1998**, *4*, 105.
- (17) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; Leeuw, D. M. *Nature* **1999**, *401*, 685.
- (18) Meijer, E. J.; Tanase, C.; Blom, P. W. M.; van Veenendaal, E.; Huisman, B. H.; De Leeuw, D. M.; Klapwijk, T. M. *Appl. Phys. Lett.* **2002**, *80*, 3838.
- (19) Rakhmanova, S. V.; Conwell, E. M. *Appl. Phys. Lett.* **1999**, *75*, 1518.
- (20) e Silva, G. M. *Phys. Rev. B* **2000**, *61*, 10777.
- (21) Ma, H.; Schollwöck, U. *J. Phys. Chem. A* **2009**, *113*, 1360.
- (22) Streitwolf, H. W. *Phys. Rev. B* **1998**, *58*, 14356.
- (23) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. B* **1980**, *22*, 2099.
- (24) van Kampen, N. G. *Stochastic Processes in Physics and Chemistry*; North-Holland: Amsterdam, 1981.
- (25) Zwanzig, R. *Adv. Chem. Phys.* **1969**, *15*, 325.
- (26) e Silva, G. M.; Acioli, P. H.; Ono, Y. *J. Phys. Soc. Jpn.* **1998**, *67*, 3881.
- (27) Lima, M. P.; e Silva, G. M. *Phys. Rev. B* **2006**, *74*, 224304.
- (28) Terai, A.; Ono, Y. *J. Phys. Soc. Jpn.* **1986**, *55*, 213.
- (29) Cerullo, G.; Lanzani, G.; Zavelani-Rossi, M.; de Silvestri, S.; Comoretto, D.; Moggio, I.; Dellepiane, G. *Synth. Met.* **2001**, *116*, 57.
- (30) Moses, D.; Dogariu, A.; Heeger, A. J. *Phys. Rev. B* **2000**, *61*, 9373.
- (31) Tanase, C.; Meijer, E. J.; Blom, P. W. M.; de Leeuw, D. M. *Phys. Rev. Lett.* **2003**, *91*, 216601.
- (32) Hicks, L. D.; Dresselhaus, M. S. *Phys. Rev. B* **1993**, *47*, 16631.
- (33) Di, B.; An, Z.; Li, Y. C.; Wu, C. Q. *Europhys. Lett.* **2007**, *79*, 17002.