Organic Electronics 23 (2015) 39–43

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Theoretical investigation on thermal effect in organic semiconductors

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ARTICLE INFO

Article history:
Received 5 March 2015
Received in revised form 10 April 2015
Accepted 15 April 2015
Available online 16 April 2015

Keywords:
Organic semiconductors
Fermi–Dirac distribution
Square-random distribution
Hot polaron

ABSTRACT

Thermal effect on a neutral and a doped polymer chain is studied in the frame work of Su–Schrieffer–Heeger tight-binding model considering electronic Fermi–Dirac distribution as well as atomic square-random distribution. It is found that in a neutral polymer chain, the band gap is decreasing as the temperature increases. For a doped polymer chain, extra electrons will occupy high energy levels. The localization and stability of the electronic self-trapped state will decrease with temperature. We also show that at temperature high enough ($\geqslant 340$ K in present parameters), a hot electron will get rid of the trap of the lattice and become extended over the whole polymer molecule. In addition, the effects of the quantity of charge carriers and the electron–phonon coupling at room temperature are also investigated.

1. Introduction

Organic semiconductors, including small molecules and conjugated polymers, have been widely investigated due to their attractive performance in optoelectronic and spintronic devices such as organic light emitting diodes (OLEDs) [1], organic photovoltaic (OPV) cells [2] and organic field effect transistors (OFETs) [3]. It has been well known that, under low temperature, a polymer chain (such as polyacetylene) is dimerized in structure. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are apparently separated with a gap of about 1–3 eV. So a pristine polymer is insulated or semiconducted. When an extra electron (a hole) is injected or doped, the original HOMO and LUMO will become localized due to the strong electron–phonon (e–ph) coupling, which means that the electron (hole) will form a self-trapped state, which is well known as a polaron [4]. If two extra electrons (holes) is injected into one non-degenerate polymer molecule, they will get together to form one self-trapped state called a bipolaron [5]. These charged excitations act as carriers for performance of organic devices.

Thermal effect is a fatal factor affecting the performance of an organic device. It may cause burning down when an organic device is operated under a not high bias or not long sustained duration as the Joule heat could not be released immediately. Temperature dependent photoluminescence (PL) is a primary consideration in organic devices. A number of temperature-dependent PL studies have provided valuable information about the absorption and emission characteristics of conjugated polymers [6–10]. These studies can provide deeper understanding of physical processes in conjugated polymers. Recently, spin and charge dependent thermoelectric transport has gained great attention for thermal energy conversion [11,12]. Organic polymers indubitably make a main opportunity for developing spintronic and thermoelectric nanodevices [13–15] because of their dominant properties such as adjustable HOMO–LUMO gap, strong electron–phonon coupling and weak spin–orbit interaction. Although the great technological interest toward organic materials for electronics and spintronics, the charge-transport mechanism in polymers as well as molecular semiconductors around room temperature is not well understood. For example, it is usually accepted that electronic charges are localized polarons or bipolarons in organic semiconductors. However, in molecular crystals majority of the experimental observations in the 100–300 K range indicate a decrease of the mobility with temperature, which suggests that the transport is described as bandlike or delocalized charge carriers [16–18]. The spectroscopic studies also seem to indicate that charge localization is unlikely due to the formation of a small polaron with the charge localized on a single molecule. These contrasting results show that organic semiconductors are much more sensitive to temperature than their inorganic counterparts.

Thermal effect not only influences the molecular site (carbon–hydrogen unit in most of organic polymers) position but also the electronic distribution [19]. The lattice fluctuations can be described related to temperature. Even at absolute zero temperature, the quantum effect will also result in a distribution of nuclei around its classical equilibrium position. With an all-quantum description, it has been indicated that the spatial delocalization

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http://dx.doi.org/10.1016/j.orgel.2015.04.008
1566-1199/

of the nuclei is accompanied by sizeable redistribution between the electronic potential and kinetic energy. The fluctuation of the site position due to quantum effect may be larger than the classical approach [20,21]. In addition to the lattice sites, thermal effect will also affect the distribution of π-electrons. At absolute zero temperature, for a neutral polymer chain with half-filled occupation, each level of the valence band is doubly occupied. For a charged chain, the extra electrons will occupy the lowest energy level of the conduction band. At a finite temperature, electrons may occupy the higher levels with Fermi–Dirac statistics due to the thermal effect. In an early work, we have found that an extra hot electron occupies LUMO or LUMO+*n* (unoccupied energy levels higher than LUMO), the resulting bond and electronic structures will be much different [22]. It was found that the formation of a polaron depends upon the energy of the hot electron. It is trapped by the lattice to form a localized polaron only when its energy is lower than a critical value.

In this paper, we will study the structure and property of an organic polymer by considering the thermal effect both on the lattice site position and the electronic distribution. For simplicity we treat the lattice site classically. The quantum effect is discussed in the results and discussion. The model and methods are introduced in Section 2. The main results and discussion are presented in Section 3. Finally, a conclusion is given.

2. Model and methods

A conjugated polymer chain is described with an extended Su–Schrieffer–Heeger (SSH) model [23,24]. The Hamiltonian is written as,

$$H = -\sum_n t_{n,n+1}(c_n^+ c_{n+1} + c_{n+1}^+ c_n) + \sum_n \frac{1}{2} K (u_{n+1} - u_n)^2. \tag{1}$$

The first term of the Hamiltonian is to describe the electron energy, where $t_{n,n+1} = t_0 - \alpha(u_{n+1} - u_n) - (-1)^n t_e$ is the transfer integral of the π electrons between sites n and $n+1$. t_0 is the electron transfer integral in a uniform lattice. α is the electron–lattice coupling between neighboring sites due to the lattice bond stretch or compression. u_n is the deviation of site n from the uniform configuration. t_e is the Brazovskii–Kirova symmetry breaking term [25], which indicates the non-degeneracy of a polymer. $c_n^+(c_n)$ denotes the electron creation (annihilation) operator at site n. The second term of the Hamiltonian describes lattice elastic potential energy, where K denotes the lattice elastic constant. The spin index is omitted.

For a given lattice configuration $\{u_n\}$, we obtain the electronic eigenstate $\psi_\nu = \sum_n Z_{\nu,n} |n\rangle$ and eigenenergy ε_ν by solving the eigenvalue equation,

$$-t_{n-1,n} Z_{\nu,n-1} - t_{n,n+1} Z_{\nu,n+1} = \varepsilon_\nu Z_{\nu,n}. \tag{2}$$

Under a given temperature, configuration $\{u_n\}$ is determined from the minimum of the free energy [26] $F = E - TS$ of the system. The internal energy E is given by,

$$E = \sum_\nu f_\nu \varepsilon_\nu + \sum_n \frac{1}{2} K (u_{n+1} - u_n)^2. \tag{3}$$

The electron occupation is given by the Fermi–Dirac distribution at temperature T,

$$f_\nu = \frac{g_\nu}{e^{(\varepsilon_\nu - \mu)/k_B T} + 1}, \tag{4}$$

where $g_\nu = 2$ is the degeneracy of the ν th energy level (with spin up and spin down). k_B is Boltzmann constant. T is the absolute temperature. μ is the chemical potential determined by the total number of π-electrons.

Entropy S is defined as follow [27],

$$S = -k_B T \sum_\nu [f_\nu \ln f_\nu + (1 - f_\nu) \ln(1 - f_\nu)]. \tag{5}$$

By minimizing the free energy, the lattice configuration is decided in a periodic boundary condition by

$$\begin{aligned} u_{n+1} - u_n = {} & \sum_{\nu,n} \left(\frac{2\alpha}{NK} Z_{\nu,n} Z_{\nu,n+1} \right) \{ f_\nu - \beta_\nu \varepsilon_\nu - \beta_\nu k_B T [\ln f_\nu - \ln(1 - f_\nu)] \} \\ & - \sum_\nu \left(\frac{2\alpha}{K} Z_{\nu,n} Z_{\nu,n+1} \right) \{ f_\nu - \beta_\nu \varepsilon_\nu - \beta_\nu k_B T [\ln f_\nu - \ln(1 - f_\nu)] \} \\ & + \frac{k_B T}{NK} \sum_{\nu,n} \beta_\nu s_n [\ln f_\nu - \ln(1 - f_\nu)] - \frac{k_B T}{K} \sum_\nu \beta_\nu s_n [\ln f_\nu - \ln(1 - f_\nu)] \\ & + \frac{1}{NK} \sum_{\nu,n} \beta_\nu \varepsilon_\nu s_n - \frac{1}{K} \sum_\nu \beta_\nu \varepsilon_\nu s_n, \end{aligned} \tag{6}$$

where $\beta_\nu = \beta e^{\beta(\varepsilon_\nu - \mu)} / [e^{\beta(\varepsilon_\nu - \mu)} + 1]^2$, $s_n = \left(\sum_\nu 2\alpha \beta_\nu Z_{\nu,n} Z_{\nu,n+1} \right) / \sum_\nu \beta_\nu$ and $\beta = 1/k_B T$.

Thermal effect on electron is introduced by Fermi–Dirac distribution as shown above. Thermal influence on the lattice configuration is described using a square-random distribution related to temperature. Thus, the related lattice displacement can be written as

$$u_n' = u_n + \delta u_n = u_n + (2R_n - 1)(k_B T / K)^{1/2}, \tag{7}$$

where R_n is a group of random number, which falls evenly in the range of [0,1].

Now by combining Eqs. (2) and (6), electronic states and lattice configurations can be calculated numerically. Then introducing the thermal derivation δu_n by Eq. (7), the related electronic state and charge density distribution due to thermal effect are calculated. Due to the randomness of R_n, the results are averaged 200 samples to reduce statistical errors.

To check the localization of the doped extra electrons, we define localized factor $\eta_n = \sum_\nu f_\nu Z_{\nu,n}^* Z_{\nu,n} - 1$, and localized width is described by $n_0^2 / \sum_n \eta_n^2$, where n_0 is the number of injected charges. In addition, we introduce the formation energy of an excitation (polaron) to describe its stability. Firstly the neutral state without any doping is obtained from Eqs. (2) and (6). Then extra electronic charges are injected and the occupation among the levels is determined by the Fermi–Dirac distribution. The total energy of the system is the sum of lattice elastic energy and electronic energy. The formation energy of an excitation is defined by the difference between the total energy of the charged system before and after lattice relaxation.

Without loss of generality, the model parameters we use in this work are $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $t_e = 0.05$ eV, and $K = 21$ eV/Å^2. These parameters are usually chosen for polyacetylene [24], but we expect that the results can be qualitatively valid for other conjugated polymers.

3. Results and discussion

Firstly, we consider the thermal effect on an isolated neutral polymer chain with (CH) unites $N = 200$. At absolute zero temperature, the system is obtained to be perfect dimerized because of the Peierls distortion. The band gap between LUMO and HOMO is about 1.75 eV. Fig. 1 shows the band gap at different temperature. We can find that the system maintains dimerized up to 340 K, and the band gap decreases as the temperature increases. While the charge distribution is not influenced until 340 K in our calculation.

Then we investigate the thermal effect on a doped polymer. When one electron is injected into a neutral chain, at absolute zero temperature, the electron will occupy the LUMO level and it will