

Study of transportation of excitons on poly 3-hexylthiophene

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In order to explain the transport and mobility of excitons, based on quantum theory, the hydrogen-like atom wave function and modification of effective charges were used to find out energy levels of poly 3-hexylthiophene (P3HT). As a result, the performance of organic solar cells can be inferred from the derived absorption character of organic material. The results are perfectly coincided with experimental data. The main absorption peak of P3HT is around 550nm, but excitons simulated by photons around 550nm can not hop to donor/acceptor (D/A) interface, which have no contribution to the Power Conversion Efficiency (PCE). Meanwhile, effective mass was used to explain the mobilities of holes. It indicates that a new structure of material which can improve the mobility of holes by enhancing the molecular conjugation and decreasing the branches.

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1. Introduction

As a renewable energy source, organic solar cells (OSCs) have been a subject of intensive studies [1-3]. Compared with inorganic solar cells, OSCs offer practical advantages in preparing flexible and lightweight devices at much lower fabrication cost due to their simple ambient-condition solution process [4,5] or the roll-to-roll coating process [6-8]. Device performance has been rapidly improved since the first report of Tang and Vanslyke, [9] and called polymer bulk heterojunction (BHJ) solar cells [10, 11]. Although the structure of BHJ is simple, the mechanism of OSCs is quite complex and can be roughly classified into three processes: 1) active materials generate excitons after absorbing photons under the light irradiation; 2) carrier transportation process and 3) carrier collection process by electrodes [12]. OSCs performance were affected by many factors such as electrical properties of polymer, [13] interactions between donor and acceptor, [14] morphology of the composite films and electrodes [15]. One of the important considerations is the balance between electrons and holes transport process. Obviously, it is need to explain the whole generation and transport process of excitons experimentally. However few theoretical deductions were work on it. Many groups [16-18] paid attention to narrowband gap materials. But the absorption of short wavelength may damage the organic layer because of the generation of radicals, which may speed up the degradation of OSCs. Moreover, although the narrowband gap materials will improve the short circuit current density

(J_{sc}) of OSCs, the low open circuit voltage (V_{oc}) cannot be neglected because of the reduced band gap [18-22]. A hypothesis is mentioned in this paper to clarify these mechanisms and explain how it enhances the performance and stability of OSCs.

2. Theory

Hydrogen-like atom wave functions [23] were used to simplify the Hamilton model instead of solving a complex wave function. The approximation method can rapidly find out the energy levels and the Hamilton parameters were listed to describe the model.

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_i \frac{Z(\delta) \cdot e^2}{r_i} + \sum_{i < j} \frac{e^2}{r_{ij}} + H_{V,J} \quad (1)$$

$$E_{V,J} = (v + \frac{1}{2})\hbar v + \frac{\hbar^2}{2I} J(J+1) \quad (2)$$

Where $-\frac{\hbar^2}{2m} \sum_i \nabla_i^2$ is the kinetic energy term,

$-\sum_i \frac{Z(\delta) \cdot e^2}{r_i} + \sum_{i < j} \frac{e^2}{r_{ij}}$ is the potential energy levels

among nucleus and electrons, and $H_{V,J}$ is the rotational

and vibrational energy. Only two adjacent monomers were considered. In these parameters, the potential energy plays the most important role. Furthermore, effective charges were used to modify the potential parameters as a shielding effect exists [24-26]. The outer electron attracted not only by the nuclei, but affected by the inner stable electrons as well. Obviously, the repulsion between electrons was weakening by the attraction between electron and nuclei which is equivalent to the reduction of the effective nuclear charge numbers. For carbon atoms, the effective charge factor δ is 0.85 for 2p orbits and it is 1 for 1s and 2s orbits.

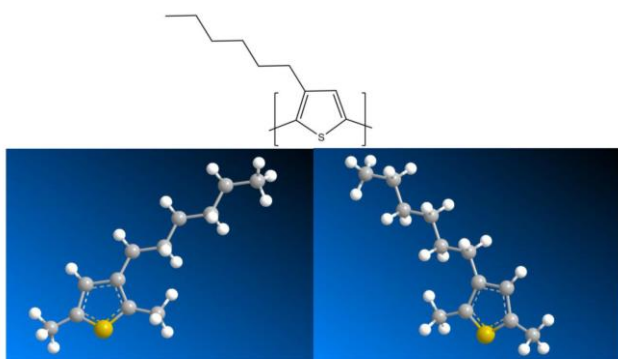


Fig. 1. Configurations of the monomer of P3HT C, H and S atoms in monomer are denoted as white, grey and yellow spheres, respectively. All of them were kept at stable state.

Monomer of P3HT molecular structure was shown in Fig. 1. The branched-chains of P3HT are connected by σ bonds. Meanwhile, the heterocyclic rings are π -cycle systems, which contribute to a conjugated system [13, 19-21]. In an ideal condition, the molecular will stay in ground state if there is no energy injection. After photon irradiate on P3HT, the molecular absorbs energy and covalence bond will become delocalized and then located on branched-chain or heterocyclic ring. By using the approximation mentioned above, energy levels difference (ΔE) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) can be found. Hence, the absorption peaks of C-H and C-S covalent system are 550 nm and 383 nm, respectively. Meanwhile, the absorption peaks of C-C and C=C systems are 631nm and 949nm, respectively. All of them were derived by equation (1) and (2). This result suggests that the branches absorb short-wavelength relative to heterocyclic rings in an absorption spectrum. In fact, the absorption of σ bond is not suitable for OSCs, because it can break the covalent bond when an electron is excited and consequently can not transits to D/A

interfaces.

3. Experimental

In order to verify the assumption, the absorption spectrum measurement of P3HT was undertaken. P3HT was purchased from Sigma Aldrich Inc., and used as received. It was dissolved in dry chlorobenzene (10mg/ml). Typically, P3HT was spin-coated on ITO. The substrates were first sonicated for 10 min twice in acetone, isopropanol, and deionized water. The as-cleaned substrate was dried with a N_2 stream, and then immediately spin-coated (60s, 1500rpm) with P3HT in glove box (the temperature and humidity were kept at 20 °C and 1% RH, respectively). All the samples were annealed at 100°C for 30 min after that. Ultraviolet-vis (UV-vis) absorption spectra were recorded on EDINBURGH FLS920P spectrophotometer (wavelength range 300–800 nm).

4. Results and discussion

Fig. 2 shows the absorption spectra of P3HT, a broad absorption band at around 560 nm can be seen corresponding to the isolated coiled P3HT chains and then gradually decreases while additional absorption peaks appear at 348 and 605 nm.

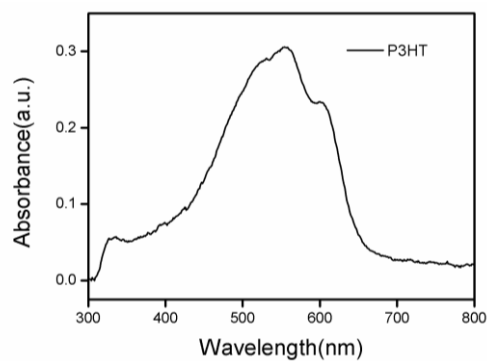


Fig. 2. Absorption spectra of P3HT.

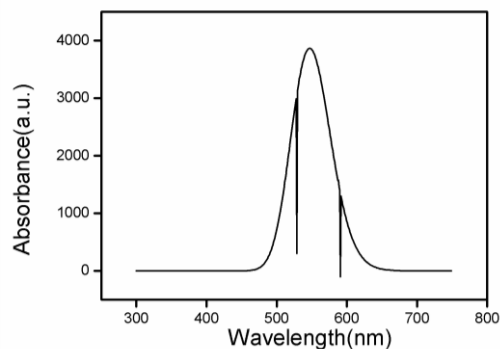


Fig. 3. Absorption spectrum analyzed by Gaussian software in an ideal condition.

In addition, the absorption spectrum fitting by the Gaussian Simulation software was also taken to analyze the results of the absorption peaks as illustrated in Fig. 3. The model was established carried under ideal conditions which means only C-H and C-C can be captured by this software, however, only a single characteristic peak (C-H absorption) was simulated. The strongest absorption at 550nm was found in the figure while the sharp decays at 590 (C-C absorption, around 600nm) and 530 nm still have no exact explanation, which may be due to the shielding effect. Table 1 shows the theoretical and experimental values of absorption peaks.

Table 1. Theoretical and experimental absorption peaks.

Theoretical (nm)	383	550	631	949
Experimental (nm)	348	560	605	N/A

According to the previous derivation, excitons are mainly generated around the absorption peaks, but most of these excitons cannot hop to D/A interfaces as mentioned before. Meanwhile, the stability of organic layer will be decreased faster by free radical damage because of the absorption on σ bonds.

The mobility should be discussed as well, according to the quantum model, an effective mass is evolved to explain the lower mobility of holes

$$f = \hbar \frac{dk}{dt} \quad (3)$$

$$a = \frac{dv}{dt} = \frac{1}{\hbar} \frac{d}{dt} \left(\frac{dE}{dk} \right) = \frac{1}{\hbar} \frac{d^2E}{dk^2} = \frac{f}{\hbar} \frac{d^2E}{dk^2} \quad (4)$$

In equation (3) and (4), f is the interaction between a carrier and the quantum system, a is the acceleration of carrier, E is the intrinsic energy of molecules, k is the momentum parameter, t is the time of the physical process. By using semi-classical theory, the effective mass is shown by equation (5)

$$m_n^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}} \quad (5)$$

As the equation 5 shows, the effective mass is relevant to the second order differential coefficient of the energy function in momentum space. Because of the uncertain relation [23,27-28]

$$\Delta x \cdot \Delta k \geq \frac{1}{2} \hbar \quad (6)$$

A Fourier transform has been used here to describe the wave function in momentum space. In equation (1), the coulomb interaction is significant while the distance is in nano-scale. If excitons are separated at the D/A interfaces,

the physical phenomenon can be described by the following equations

$$(m_e^* + m_n^*) \bar{v}_0 = m_e^* \bar{v}_1 + m_n^* \bar{v}_2 \quad (7)$$

$$\bar{v}_0 - \bar{v}_1 = -\frac{m_n^*}{m_e^*} (\bar{v}_0 - \bar{v}_2) \quad (8)$$

Where m_e^* and m_n^* are the effective mass of electrons and holes, \bar{v}_0 , \bar{v}_1 and \bar{v}_2 are average velocities of carriers. As the equation (8) shows electrons and holes diffuse in the opposite direction after excitons being dissociated. Meanwhile, the ratio of effective mass between holes and electrons is rather huge. This is consistent with reality that electrons usually have a higher mobility than holes.

In order to improve the mobility of holes, a new kind of semiconducting polymers is expected. According to equation (5), the LUMO energy level of donor must have a proper match with that of the acceptor to provide enough driving force for charge separation. Then, the organic material will enhance the molecular conjugation and reduce the length of branch chains to improve the mobility because of the red shift of auxochrome and weaker Coulomb interaction. It will benefit J_{sc} , but V_{oc} will be reduced at the same time, even photovoltaic effect cannot generate. Hence, a balance should be made in material preparation, and the derivation has proved the experiments of Liang [29]. Meanwhile, compared to P3HT, materials such as poly{[2,7-(9-(20-ethylhexyl)-9-hexylfluorene))-alt-[5,5-(40, 70-di-2-thienyl-20, 10,30-benzothiadiazole)]} (PFDTBT) [30], 2,7-silafluorene (SiF) and 4,7-di(2'-thienyl)-2,1,3-benzothiadiazole (DBT) (PSiF-DBT) [31] and other materials have been approved as better photoelectric organic donors which is consistent with the description of this manuscript.

5. Conclusions

In conclusion, this work explains the generation of excitons in P3HT and how they transport in polymer chains. The results show electrons have a faster mobility than holes. But the situation can be improved by decreasing the length of braches and enhancing the molecular conjugation according to this theory. Furthermore, experiments on these systems provide a convincing test of the validity of the model in this paper, and the proprieties of possible new semiconducting polymers are implied by the derivation.

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