

External electric field-dependent photoinduced electron transfer of Oligonaphthofurans-PC₇₀BM in BJH solar cell

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Abstract. To rely mainly on the impact of external electric field derived from the electronic coupling charge transfer rate in the change, the new theoretical method can not merely a better understanding of chemical structure the, external electric field and optoelectronic properties of donor(D)- acceptor(A) system, but also can be used for reasonable design of D-A system of novel organic solar cells. This article selects PC₇₀BM (phenyl-fullerenes-butyric acid methyl ester) (good solubility, high electron mobility, with common polymer material to take shape a fine phase separation) as this acceptor; low five different kinds of chain length of oligonaphthofurans molecules (active material of fluorescent probe molecule) as the donor, using density functional theory on the basis of the Marcus theory to calculate the electronic coupling, reorganization energy, gibbs free energy of reaction, rates of the charge recombination and the rates of exciton dissociation for this study.

1. Introduction

Organic solar cell (OSCs) materials, with many advantages and potential application values, have caught great attentions recent years [1-3]. One of promising futures in this research area, is the development of novel photoactive materials in OSCs devices, which will further lower the manufacturing cost and enhance the efficiency of the device [4,5]. From the conversion efficiency close to 1% in 1986 to consecutive refreshment of the world record (~8.3% and 9.8%) in 2010 and 2011, the OSCs have gained enormous progress rapidly and its conversion efficiency has reached the level of traditional amorphous silicon solar cells. Fluorescent materials, in most cases, possess significant absorbing efficiency in the visible region. For instance, the organic photochromic naphthopyran luminescent compounds have an importantly developing prospect in the fields of optical information storage, fluorescent switch, optical brake, et al., also have been widely used in environmental monitoring and the preparation of photosensitive materials [6,7].

In the process of complex photoelectric conversion of OSCs devices, the photoinduced excited electron transfer (ET) in photoactive materials is one of most important factors in determining its efficiency. Theoretically, Marcus ET theory is the widely used model to investigate the ET reaction, not involving the chemical bond rupture and form in this process.

Marcus model expressed energy molecules of system is how to influence the change of reaction and the molecular of adjacent structure by simple mathematical formula, theory and mathematics related theory and experimental value, calculating and explaining the electron transfer reaction to

photoinduced charge transfer rate by measurement.

Photoelectron between the donor (D) and acceptor (A) produce weak coupling and transfer, electron transfer reaction rates are related to the parameters such as alter of gibbs free energy and reorganization energy. In Marcus theory, the expression of the charge transfer rate is:

$$k = \sqrt{\frac{4\pi^3}{h^2 \lambda k_B T}} |V_{da}|^2 \exp\left(-\frac{(\Delta G + \lambda)}{4\lambda k_B T}\right), \quad (1)$$

where h is the Planck constant, λ is the reorganization energy, k_B is the Boltzmann constant, T is the temperature ($T=300K$), V_{da} is the electronic coupling matrix element between the A and the D [8], ΔG is the gibbs free energy change for the electron transfer reaction.

According to the double potential well model, the activation free energy, reorganization energy and the heat of reaction have the relationships as follows:

$$\Delta G^* = \frac{(\Delta G + \lambda)^2}{4\lambda}, \quad (2)$$

We can know the size relationship from the above formula between gibbs free energy and reorganization energy. Therefore electron transfer will have the three conditions as follows: (1) Normal area: the more exothermic reaction, activation energy is smaller, the faster the reaction rate. For the same position to λ and ΔG is gradually increasing from positive to negative parabola. There is two cases. The one is $\Delta G > 0$, the other is $\Delta G < 0$, but the both cases are $\lambda + \Delta G > 0$. So the reaction rate constant is small, but the second one could be slightly greater than the first one. (2) Incompetent base area: the reaction rate is the fastest. When ΔG become more negative, the $\lambda + \Delta G$ become more close to zero, reaching the maximum rate constant. (3) Reverse area: unlike general reaction, heat release, The more heat release, the greater the activation energy, the slower the reaction rate. If ΔG continues to become more negative, the value of $\lambda + \Delta G$ is negative. The

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activation energy of electron transfer reaction falls into Marcus inversion area.

Assigning $\lambda = \lambda_{CR}$ or $\lambda = \lambda_{CT}$, and $\Delta G = \Delta G_{CR}$ or $\Delta G = \Delta G_{CT}$, for charge reorganization or exciton dissociation, respectively. In the case of weak interaction, following Fermi's Golden Rule, the rate of electron transfer is predicted to be proportional to $|V_{da}|$ [9,10,11]. Because electronic coupling V_{da} , gibbs free energy of electron transfer reaction, reorganization energy, is determined, thus the charge transfer rate can be determined under the external electric field dependent applied.

So we can further to study the correlation properties of the excited state of light induced charge transfer rate for the oligonaphthofurans-PC₇₀BM molecular system and to further discussion the mechanism of light induced energy transfer and the charge transfer rate and so on. The typical fluorescent materials oligonaphthofurans was selected as the electron donor (D) and PC₇₀BM as the electron acceptor (A).

2. Theoretical methods

In the process of the completion of all of the quantum chemistry calculation were performed by the Gaussian 09 software [12]. The ground-state equilibrium geometries of the oligonaphthofurans-PC₇₀BM: PC₇₀BM BHJ material (isolated PC₇₀BM presented in Figure 2.1(a)) and the five oligonaphthofurans (2mer, 3mer, 4mer, 6mer, 8mer) presented in Figure 2.1(b) were optimized using density functional theory (DFT) [13] with a 6-31G(d,p) basis set and a B3LYP functional [14,15]. And then use Materials Studio 7.0 to integration for five oligonaphthofurans molecules and PC₇₀BM polymer. The electronic transitions of the oligonaphthofurans : PC₇₀BM and the geometry optimization of the lowest excited state of the isolated donor and the radical cation state were performed with time-dependent DFT (TD-DFT) [16], long-range-corrected functional (CAM-B3LYP) [17] and the 6-31G(d,p) basis set, separately. This five oligonaphthofurans: PC₇₀BM were defined as "2OP", "3OP", "4OP", "6OP", "8OP" and presented in Figure 2.1(c). By calculating the related value of the free energy, we explored the related properties of the charge transfer rate. In the cases of applying electric field (from -15×10^{-5} to 15×10^{-5} au). By selecting the B3LYP function and 6-31 g (d, p) basis set to calculate the single point to the same theoretical level [18]. Using the 3D real space analysis method to explain charge transfer and energy transfer mechanism of optical functional materials in the excited state.

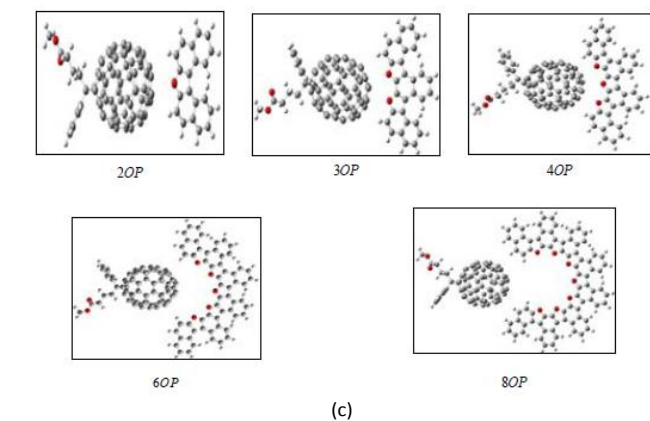
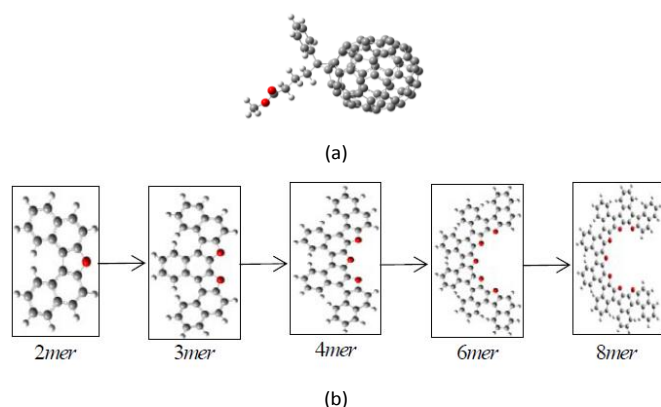


Figure 2.1: The chemical structure of (a) PC₇₀BM, (b) oligonaphthofurans, and (c) 2OP, 3OP, 4OP, 6OP, 8OP respectively.

3. Results and discussion

3.1 Excited state properties analysis

Due to the organic matter in each unit of the electron orbital energy level will directly affect the nature of the excited state, so the whole vertical absorption process of the HOMO and LUMO energy is very important. By using time-dependent density functional theory B3LYP function of 6-31 g (d, p) basis set, theory to calculate excited state properties of five kinds of macromolecular and analysis of each molecule LUMO energy levels, HOMO energy level and HOMO-LUMO energy gap [19] and five kinds of macromolecular system change with electric field.

Along with the change of the number of molecules of furan ring of five kinds of macromolecular HOMO energy level and LUMO energy levels, HOMO-LUMO energy level difference is changed accordingly and can calculate the 2OP, 3OP, 4OP, 6OP, 8OP of HOMO and LUMO energy level. The five kinds of macromolecular the frontier orbital energy level in zero electric field are shown in Figure 3.1.1, it can be seen on the premise that with the increase of macromolecular of furan ring number the HOMO and LUMO energy gap decreased with the electric field strength (HOMO increases changes greatly and the absolute value became smaller with the number of conjugated chain add. The LUMO change value is not big, as can be seen from the Figure 3.1.1). Because the reduce of the energy gap difference result in the addition of the wavelength, namely as HOMO-LUMO energy gap reduces, wavelength add, and so a red shift had taken place; HOMO-LUMO energy gap increases, the wavelength decreases, and a blue shift had taken place. The effect of chain length on HOMO, LUMO energy level difference (See Figure S1) at all kinds of electric field and also made a comparative analysis. This change rule and zero field change rule have the conformity change rule. HOMO-LUMO energy level difference is decreasing with the increases of the chain. The red shift of the excited state absorption spectra will accelerate the charge transfer.

The influence of electric field on the HOMO and LUMO almost can be ignored (See Figure S2). Taking 2OP and 6OP as examples in Figure 3.1.2(a) and 3.1.2(b), with the increase of electric field, HOMO and LUMO hardly change (the energy