Photo-Induced Polarization Inversion of Excitons in Conjugated Polymer Films*

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ABSTRACT

The study shows that, in a conjugated polymer, there exists a novel photo-induced phenomenon — a photo-induced polarization inversion, when a single-exciton is photoexcited and becomes a bi-exciton. The reason is that, in a conjugated polymer, a single-exciton displays normal polarization, whereas a bi-exciton exhibits negative polarization. The physical significance of negative polarization is explored. Photo-induced polarization inversion is an ultrafast switching process, which could be used to make photo-induced ultrafast switch devices.

Key Words: conjugated polymer, photo-induced polarization inversion, exciton, negative polarization

1. INTRODUCTION

Conjugated polymer films are the materials with a wide range of application prospects, such as to be used to make solar cells, field effect transistors, Schottky barriers, PN junctions, rapid optoelectronic devices, polymeric sensors, and polymeric lasers etc.. After the demonstration of light-emitting devices based on conjugated polymer films¹, it has been found that conjugated polymer films could also be made flat panel displays, completely flexible and colorful visual displays with large area, and portable and collapsible electronic newspapers, since the electroluminescent frequencies of the materials are in the range of visible light with various colors. In addition, polymer films are cheap in price, not heavy in weight, and easy to be processed. All these mean that conjugated polymer films will open a new channel for the technology of display and opto-electronics. Meantime, in recent years femtosecond technology has provided a powerful tool to explore new properties of excited states. And it has been found that the excited states induced by photoexcitation possess some new properties, which do not exist in the ground state. Hence, the investigation of the excited states in conjugated polymer films has become an active frontier in the interdisciplinary area of physics, chemistry and material science. Our recent studies²⁻⁸ have been focused on the area. Based on these studies, we predict here a novel phenomenon of photo-induced polarization inversion: when a single-exciton in a conjugated polymer is photoexcited and becomes a bi-exciton by absorbing one photon, the static polarization is reversed.

2. THEORETICAL METHOD

The basic physics processes of a condensed matter physics system are determined by the electron-lattice interactions and electron-electron interactions. The electron-lattice interactions H_{e-p} and the elastic energy $H_{elastic}$ of lattice in a conjugated polymer can be expressed⁹ as

$$\hat{H}_{e-p} = - \sum_{n,s} [t_0 - \alpha(u_{n+1} - u_n) + (-1)^n t_e] (\hat{C}_{n+1,s}^+ \hat{C}_{n,s} + HC) \quad (1)$$

$$H_{elastic} = \frac{1}{2} K \sum_n (u_{n+1} - u_n)^2 + \sum_n K' (u_{n+1} - u_n), \quad (2)$$

*The project supported by the National Natural Science Foundation of China under Grant No. 19874068, and the National High Performance Computing Fund of China.

where $C_{n,s}^+$ ($C_{n,s}$) is the creation (annihilation) operator of an electron on site n with spin s . The electron-electron interactions in a conjugated polymer are.

$$H_{e-e} = \frac{U}{2} \sum_n (C_{n,s}^+ C_{n,s} - \frac{1}{2})(C_{n,-s}^+ C_{n,-s} - \frac{1}{2}) + V \sum_{n,s,s'} (C_{n,s}^+ C_{n,s} - \frac{1}{2})(C_{n+1,s'}^+ C_{n+1,s'} - \frac{1}{2}). \quad (3)$$

The interactions between the electrons and an applied electric field can be written as

$$H_E = \sum_n e E n a C_{n,s}^+ C_{n,s}. \quad (4)$$

Thus the Hamiltonian of the system will be $H = H_e + H_{elastic} = H_{e-p} + H_{e-e} + H_E + H_{elastic}$. The electronic energy ε_{μ}^s and wave function $\Psi_{n,\mu}^s$ are determined by the electronic eigenequation

$$H_e \Psi_{n,\mu}^s = \varepsilon_{\mu}^s \Psi_{n,\mu}^s. \quad (5)$$

The lowest energy state is significant in physics. It demands

$$\frac{\delta \langle \Psi | H(\{u_n\}) | \Psi \rangle}{\delta u_n} \equiv 0. \quad (6)$$

Solving Eqs. (1)-(6), we can self-consistently get the electronic wave functions and charge density distributions of the lowest energy state in an external field. In the study, $t_0 = 2.5\text{eV}$, $K = 21\text{eV}/\text{\AA}^2$, $\alpha = 4.1\text{eV}/\text{\AA}$, $N = 100$ and $K' = -1.25032\alpha$ are used. For e-e interactions, we take $U=0-4\text{eV}$ and $2V \leq U$. The study shows that the change of the parameters only affects the concrete numerical values. It will not change the basic physics.

3. POLARIZATION CHARACTERISTICS OF EXCITONS IN A CONJUGATED POLYMER

With the method mentioned above, it is found that extra electron(s) and hole(s) will induce the variations of both bond-structure and electronic states in a conjugated polymer, leading to the formation of two self-trapping localized electronic states ε_{low} and ε_{high} close to the mid-gap. That is extra electron(s) and hole(s) induce a local deformation of the polymer lattice, leading to a strained field. In the meantime, the extra electron(s) and hole(s) themselves are trapped by the strain field, and the self-trapping bound state of the electron-hole, or a polaron exciton¹⁰⁻¹¹ is formed, since the bound state of electron(s) and hole(s) is also known as the exciton. In a polaron single-exciton, there is one electron in both ε_{low} and ε_{high} localized states. In a polaron bi-exciton, there are two electrons in the higher localized state ε_{high} and there is no electron in the lower localized state ε_{low} .

The charge density is a sum of squares of the absolute values of the wave functions for all the occupied states. $\rho = \sum_{\mu,s} |\Psi_{n,\mu}^s|^2$. The charge density distribution of a polaron single-exciton and a polaron bi-exciton in a conjugated polymer is depicted, respectively, in figure 1 (a) and (b).

Fig. 1 The charge density distribution of (a) single-exciton (b) bi-exciton in an external field $E=10^5\text{V/cm}$.

In figure 1, an electric field is along the abscissa direction, and the unit of the ordinate is the value of an electron charge. Fig. 1 (a) tells that a single-exciton corresponds to normal polarization. It should be noted that a bi-exciton of Fig. 1 (b), in which the positive charges drift in the opposite direction of the field and the negative charges along the field, shows negative polarization.

In order to find out the reason why the polarization of a single-exciton in a conjugated polymer is normal, whereas the polarization of a bi-exciton in a conjugated polymer is abnormal, we examine the occupied situations of electronic states for both a single-exciton and a bi-exciton, since the charge density is related to the occupied electronic states. For a single-exciton and a bi-exciton in a conjugated polymer, the same situation in occupation of electronic states is that the levels of the valence band are fully occupied, and all the levels of conduction band are vacant. The difference between a single-exciton and a bi-exciton in a conjugated polymer is the different occupations of electrons on the two localized levels close to the mid-gap. So we examine the polarization characteristics of the two localized electronic states near the mid-gap. It was also discovered that the wave function of the lower localized state ε_{low} , whose energy is a little lower than the mid-gap, corresponds to normal polarization; whereas the wave function of the higher localized state ε_{high} , whose energy is a little higher than the mid-gap, shows the negative polarization. These polarization characteristics of the two localized levels near the mid-gap can be explained by the quantum-mechanics-theory² of polarization. On the basis of the polarization characteristics of the two localized electronic states close to the mid-gap, the polarization characteristics of the excitons in a conjugated polymer can be illustrated as follows: For a single-exciton, there is one electron on both ε_{low} and ε_{high} states. The negative polarization of the ε_{high} state is offset by the normal polarization of the ε_{low} state. Therefore, the normal polarization of the single-exciton originates from the occupied valence band. This also means that the occupied valence band displays small normal polarization, as shown in Fig. 1 (a). But for a bi-exciton, there are two electrons on the ε_{high} state and there is no electron on the ε_{low} state, so the polarization of a bi-exciton should be equal to the difference between the negative polarization of the occupied ε_{high} state and the normal polarization of the occupied valence band. As a result, the biexciton shows negative polarization, as depicted in Fig. 1 (b), due to the large negative polarization of the ε_{high} state and small normal polarization of valence band.

4. PHYSICAL SIGNIFICANCE OF NEGATIVE POLARIZATION

Negative polarization sounds unusual since Landau and Lifshitz proved that "there exists only positive polarization for any material in an equilibrium state"¹². However, their demonstration is only for continuous media (classic cases) and might thus be incorrect for a quantum system. Our study shows that for a bi-exciton in a conjugated polymer, there exists indeed macroscopic negative polarization (shown in Fig. 1(b)), which originates from the negative polarization of the localized electronic state ε_{high} . It indicates that Landau's "no negative polarization theory" is correct only for classic cases, and can not cover the case where the quantum effect is involved.

Negative polarization appears to be contrary to the Coulomb's Law, but these words are also from the viewpoint of classic physics. For a quantum system there is a constraint, i.e. the orthogonality of different eigenstates. So the polarization of an eigenstate depend not only on an applied field but also on an extra restricted condition—the orthogonality of wave functions. The orthogonality of the wave functions implies that it is impossible that all the electronic states correspond to normal polarization in the presence of an electric field. The joint action of the different eigenstates' orthogonality and the Coulomb's Law will force some electronic states into negative polarization. In a word, negative polarization is a quantum effect, which originates from the orthogonality of the wave functions. This study illustrates that the high level ε_{high} corresponds to negative polarization. Negative polarization of microscopic electronic states will lead to, in some circumstances, the macroscopic negative polarization. For example, the macroscopic negative polarization of the bi-exciton in the study originates from the negative polarization of the microscopic states ε_{high} .

Negative polarization is also due to the fact that the bi-exciton in a conjugated polymer is an excited state. The polarization of ground state is always positive, since polarization is very different from the magnetization because of the absence of magnetic charge. Only for excited states, can there exist negative polarization in certain condition. It conveys that excited states can possess some novel property, which does not exist in the ground state.

5. PHOTO-INDUCED POLARIZATION INVERSION

It is demonstrated in Section 3 that a single-exciton shows normal polarization and a bi-exciton exhibits negative polarization. So when a single-exciton is photoexcited and become a bi-exciton by absorbing one photon, the

polarization in a conjugated polymer will be reversed, as shown in Fig. 2.

Fig. 2 Photo-induced polarization inversion by absorbing one photon in a conjugated polymer.

Fig. 2 illustrates there exists a novel photo-induced phenomenon—photo-induced polarization inversion. Dynamical study⁷ shows that the relaxation time of an exciton in a conjugated polymer is usually very short, only about 150 femtoseconds. Whereas, the life time of the excitons and bi-excitons in a conjugated polymer is hundreds of picoseconds. So the photo-induced polarization inversion in a conjugated polymer is an ultrafast switching process. And the phenomenon might be used to make photo-induced ultrafast quantum switch devices.

The major results of this study can be summarized as follows: Electric-field behavior of the excitons in a conjugated polymer is studied. The polarization of a single-exciton in a conjugated polymer is normal, whereas a bi-exciton in a conjugated polymer shows negative polarization. Negative polarization is of great interest both in basic physics and in technology. According to the polarization characteristics of excitons in a conjugated polymer, it is predicted here a novel photo-induced phenomenon—photo-induced polarization inversion: when a single-exciton in a conjugated polymer is photoexcited and become a bi-exciton, the polarization of excitons will be reversed. The phenomenon of photo-induce polarization inversion could be used to make photo-induced ultrafast switch devices, since the relaxation time of an exciton in a conjugated polymer is very short.

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