Circularly polarized coherent light-induced boosting of polymer solar cells photovoltaic performance

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Abstract
We report a microscopic quantum theory which can be used to study circularly polarized light (CPL) induced singlet to triplet conversions in polymer solar cells (PSCs). We demonstrate that by properly adjusting CPL irradiation parameters, the photo-created singlet excitons can be efficiently converted into non radiative triplet excitons. The maximum singlet–triplet conversion ratio might be reached when the incident CPL frequency is chosen in such a way that the resonant optical excitation occurs between singlet and triplet states. In addition, we also illustrate that with varying CPL oscillating strength, the singlet–triplet conversion patterns behave as the Rabi oscillations and the steadily maintained triplet excitons. The electron-lattice coupling leads to the self-trapping of the excitons, which enhances the coherence between the electron’s and hole’s spin oscillations. This study opens up a novel approach for enhancing and controlling the photovoltaic response of PSCs by an effective all-optical route.

In polymers, both triplet and singlet excitons may be formed. When the electron and hole constituting exciton have the same spin, the former is formed, otherwise if they possess an opposite spin, the latter is created. There are three triplet states and one singlet state. Nevertheless the real ratio of triplet to singlet states is dependent on how the exciton is formed. For instance, through photon excitation, the triplet states are optically inactive, only the singlet exciton is uniquely formed. However, the ratio can be tuned in a controllable way. Although both the triplet and singlet excitons in most applications are actively involved, they may play different roles. While highly luminescent singlet excitons are favorable for organic light emitting diodes, long-lived triplet excitons might be attractive for polymer solar cells’ (PSCs’) inner quantum efficiency (IQE). Therefore, in the polymers, promoting singlet-triplet exciton conversion might be a promising strategy for improving the IQE. To do so, several proposals, up-to-date, have been made, including using the triplet organic materials [2–4], doping the conventional ones with transition metal complex [5, 6], applying an external magnetic field [7, 8], etc. Though the problem of IQE might be partly solved by employing these techniques, from the perspective of nanodevice application, they are challenging tasks, because the defects introduced by magnetic doping reduce the mobility of the device and a strong external magnetic field can not be conveniently applied to the nano-device. Alternatively, one of our coauthors, Qin et al demonstrated experimentally that circularly polarized light (CPL) can be used to efficiently generate triplet excitons [9]. A similar scenario in polymer...
heterojunction solar cells [10] has also been reported. It opens an optical route to explore highly efficient triplet solar cells, however, the underlying microscopic mechanism still remains unclear.

Intensive investigations have been carried out to study the CPL’s effects on metals [11, 12] and quantum magnets [13–15]. Different to linearly polarized light (LLP), CPL induces the inverse Faraday effect in the irradiated medium, which acts as an effective magnetic field directed parallel to the wavevector. Floquet theory suggests that the time-dependent Schrödinger equation with periodical Hamiltonian driven by CPL could be mapped to a static eigenvalue problem [16–19], where the effect of CPL mimics a tilting effective magnetic field in the Floquet space. Interestingly, as the CPL controlling spins is a quantum coherence phenomenon, the effective magnetic field can be quite strong (1 THz ~ 50 T) in comparison with a practical bare one commonly obtained in the laboratory (~1 T). Therefore, the utilization of CPL provides a strategy to equivalently realize the strong magnetic-field effect in medium by an optical way.

In this work, we develop a theory on the quantum dynamical process of the CPL driven singlet–triplet conversions in PSCs. We reveal that with varying CPL parameters, the conversion can behave as either singlet–triplet Rabi oscillations [20] or the steadily maintained triplet excitons. Because of the weak spin–orbit couplings in polymers, the CPL induced spin state exhibits long-time coherence [20, 21]. The calculation results suggest a practical guidance for massively improve the PSCs’ IQE by using CPL.

Without loss of generality, we take cis-polyactylene (cis-PA) as the example. The prime physics revealed here can be expanded to most of the other π-conjugated polymers with strong electron-lattice couplings. The Hamiltonian of the π-electronic system under CPL irradiation is expressed as

\[ \mathcal{H}(t) = \mathcal{H}_0(t) + \mathcal{H}_{\text{cp}}(t), \]

where \( \mathcal{H}_0(t) \) is the Su–Schriffer–Heeger (SSH) Hamiltonian including the Coulomb interactions:

\[
\mathcal{H}_0(t) = -\sum_{i,s} \left( t_0 + (-1)^s t_1 - \alpha (u_{i+1} - u_i) \right) (c_{i,s}^\dagger c_{i+1,s} + \text{h.c.}) + K \sum_i (u_{i+1}^2 - u_i^2) + M \sum_i u_i^2 + U \sum_i \left( n_{i,\uparrow} - \frac{1}{2} \right) \times \left( n_{i,\downarrow} - \frac{1}{2} \right) + V \sum_i \sum_{\downarrow,\uparrow} (n_{i,\downarrow} - 1)(n_{i+1,\uparrow} - 1).
\]

The notions in equation (2) have the same meaning as in references [22, 23]. Defining the bond-length change \( \gamma_i = u_{i+1} - u_i \), our self-consistent solution of equation (2) together with the Hellman–Feynman equation \( \gamma_i = (-2\alpha/K) \left| \sum_s (c_{i,s}^\dagger c_{i,s}) - (1/N) \sum_{s'} (c_{i,s'}^\dagger c_{i,s'}) \right| \) indicates that the dimerized bond orders is the ground state. The smooth lattice configuration is obtained by further defining the alternative component of bond orders as \( \tilde{\gamma}_i = (-1)^i (2\gamma_i - \gamma_{i+1} - \gamma_{i-1}) \). Assuming the photogenerated e–h pairs occupying the spin-resolved HOMO and LUMO levels, three degenerate triplet-exciton states \( T_+ (|\uparrow\uparrow\rangle), T_- (|\downarrow\downarrow\rangle) \) and \( T_0 \left( \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \right) \) and one singlet exciton \( S \left( \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \right) \) can be obtained. In the following, except otherwise specified, we assume that \( t_0 = 1.0 \text{ eV}, t_1 = 0.2t_0, U = 1.0t_0, V = 0.67t_0, K = 15.0 \text{ eV Å}^{-2}, \alpha = 0.7\sqrt{t_0}K \). The localization of trapped photogenerated singlet exciton is shown in figure 1. The energy difference between the triplet and singlet exciton is 0.06t_0.

The interactions between CPL and the π-electron spins is written as [see supplementary material 1 (https://stacks.iop.org/NJP/22/103034/mmedia)]

\[ \mathcal{H}_{\text{cp}}(t) = \sum_i A_0 \left( e^{-i\omega t} c_{i,\uparrow}^\dagger c_{i,\downarrow} + e^{i\omega t} c_{i,\downarrow}^\dagger c_{i,\uparrow} \right), \]

where \( \omega \) and \( 2A_0 = B \) respectively denotes the frequency and amplitude (unit in \( t_0/\gamma t_0 \), with \( \gamma \) the Lande factor of electron and \( t_0 \) the Bohr magneton) of the CPL. Because the wavelength of CPL (\( c/\omega \)) is longer...
than the chain length, we assume that the CPL is uniformly applied to each site. The present CPL in equation (3) is left-handed helical.

The evolution of the electronic system is obtained by integrating the Schrödinger equation:

\[ i\hbar \dot{\Psi}_\mu(t) = \mathcal{H}^{HF}(t)\Psi_\mu(t), \]  

(4)

where \( \mathcal{H}^{HF}(t) \) is the Hamiltonian (equation (1)) under Hartree–Fock (HF) approximation and \( \Psi_\mu(t) \) is the Hartree–Fock orbital wave functions. Because the trapped-exciton associate HF orbitals are far away from the continuous bands and they are spin unpaired, the exciton can be regarded as a two-level quantum dot system. For two electrons (labeled as 1 and 2) occupying the two HF orbitals (labeled as \( a \) and \( b \)), the exciton state is written as [24]:

\[ |\Phi_{\text{EX}}(t)\rangle = \frac{1}{\sqrt{2}} \left\{ \left[ \Psi_{1\alpha}(t)\alpha_1 + \Psi_{1\beta}(t)\beta_1 \right] \left[ \Psi_{2\alpha}(t)\alpha_2 + \Psi_{2\beta}(t)\beta_2 \right] - \left[ \Psi_{2\alpha}(t)\alpha_2 + \Psi_{2\beta}(t)\beta_2 \right] \left[ \Psi_{1\alpha}(t)\alpha_1 + \Psi_{1\beta}(t)\beta_1 \right] \right\}. \]

(5)

The time-dependent fractions of the singlet and three triplet exciton components are determined by \( f_\xi(t) = \langle X|\Phi_{\text{EX}}(t)\rangle \) (\( X = S, T_0, T_+, T_- \)).

Assuming the initial state is photogenerated singlet exciton, i.e., \( f_\xi(0) = 1 \), and CPL is applied at \( t = 0.05 \text{ ps} \). The single–triplet conversion ratio (STR) is defined as \( \text{STR} = \sum_{X} f_\xi(t) \) (\( X = T_0, T_+, T_- \)). Figure 2 plots the time evolution of STR for the initial exciton being irradiated by CPL with varying (a) \( A_0 \) and (b) \( \omega \). In (a), the CPL energy is set for \( h\omega = 0.06\hbar\omega_0 \), which is resonant to singlet-triplet energy difference. It is shown that the magnitude of \( A_0 \) essentially influences the singlet–triplet conversion features. When \( A_0 \) is small (\( A_0 < 0.01\hbar\omega_0/g\mu_B \)), no singlet-triplet conversion occurs. Increasing \( A_0 \) to a relatively strong regime, such as \( A_0 = 0.05, 0.1, 0.2\hbar\omega_0/g\mu_B \), the STR initially exhibits a precursory disorderly oscillation (incoherence process). After \( t = 0.4 \text{ ps} \), the singlet-triplet ratios start to show strong coherence, which are nothing but the Rabi oscillations. The larger \( A_0 \), the faster Rabi oscillations. The largest oscillation amplitude happens at \( A_0 = 0.2\hbar\omega_0/g\mu_B \). With further increasing \( A_0 \), the coherent oscillations become vanishingly small. Accordingly, the singlet excitons are steadily converted to the triplet ones. The converted ratio reaches saturation at \( A_0 = 0.5\hbar\omega_0/g\mu_B \), where about 70% of the initial singlet excitons are converted into triplet ones. This high singlet-conversion ratio does not only originate from large \( A_0 \) essentially influences the singlet–triplet energy difference. This implies the CPL driven singlet-triplet conversion is a quantum coherence phenomenon between the light and the electronic states. The underlying physics is as follows. The photocreated singlet exciton is of \( \Delta_{ST} \) higher than the triplet excitons. After the CPL is applied, the

Figure 2. Time evolutions of singlet-triplet conversion ratios for different \( A_0 \) at \( h\omega = 0.06\hbar\omega_0 \) (a) and different \( \omega \) at \( A_0 = 0.5\hbar\omega_0/g\mu_B \) (b).
triplet level is broadened in the range of $E_T \pm \hbar \omega$. When $\hbar \omega = \Delta_{ST}$, the triplet and singlet levels are aligned and hence the singlet–triplet conversion ratio reaches its maximum.

Figure 3 illustrates time evolution of STR and fractions of triplet components $T_0$, $T_+$, and $T_-$ for $A_0 = 0.2$ (a) and $0.5 \hbar \omega / g \mu_B$ (b), respectively. Two different regimes, namely, singlet–triplet Rabi oscillation (a) and stabilized singlet-triplet conversion (b) are observed. In figure 3(a), during the interval of the precursory incoherence, the triplet components exhibit random oscillation phases and different amplitudes. For left-handed polarized CPL, the three triplet fractions satisfy $f_{T-} < f_{T0} < f_{T+}$. In the coherence regime, however, the three triplet components oscillate in phase and their amplitudes are comparable. Therefore the sum up of the three triplet components gives rise to the coherent Rabi oscillations (see black curve). In figure 3(b), singlet excitons are massively converted into triplet ones, the fractions $f_{T+}$ and $f_{T-}$ oscillate coherently with fast speed, while $f_{T0}$ is almost stable. In addition, the component $f_{T0}$ makes the largest contribution to the total STR. The STR can be as high as 70%.

To further clarify the detailed quantum features of the CPL induced dynamics, figure 4 shows time evolutions of $\tilde{y}_i$ and $s_{ip}$ ($p = x, y, z$) at $\hbar \omega = 0.06 \hbar \omega_0$ for $A_0 = 0.2$ (upper panels) and $0.5 \hbar \omega / g \mu_B$ (lower panels). In the former case, during the precursory incoherence period, the lattice-distortion envelope of the self-trapped excitons is maintained. The net spins are limited within this lattice-distortion envelope. When the dynamics transit to the coherent Rabi oscillations, the exciton undergoes the detrapping process and the net spins spread over the whole chain. Usually, singlet exciton exhibits lower binding energy and is easier to dissociate into free charges. However, the singlet free charge pairs have high possibility of e-h recombination. While the exciton is of extended state and has a certain dynamical fraction of triplet component, it can be benefit not only to charge separation but also to lowering the radiation decay. Consequently, the IQE is increased due to the singlet-triplet Rabi oscillations. In the latter case, as the achieved triplet is steadily maintained, the trapped exciton’s lattice-distortion envelope is persistent without detrapping. Meanwhile, the net spins are tightly limited in the envelope. From figures 4(b2) and (b3), one can find that $s_{ix}$ and $s_{iy}$ alternately reaches the extreme value, implying the spin is precessing in the $x - y$ plane. Without considering other spin-associate interactions, the spin precession can last for more than 1 ps. Such a scenario is equivalent to the optical control of an exciton spin state in semiconductor quantum dot [26]. With increasing $A_0$, the precessing speed becomes faster. Obviously, the triplet excitons are easier to keep trapped rather than the singlet ones. This is consistent to the knowledge that the triplet excitons are harder to be dissociated than the singlet ones. In spite of the trapping feature unfavorable to charge separation, the CPL is still an efficient and convenient way to be used to improve the photovoltaic performances: (i) the CPL generated triplet excitons are non-radiative and the spin-lattice couplings are steadily maintained, making their life time much longer; (ii) because their energy is higher than those of static ones, charge separation can easily occur at D/A interfaces. Therefore, one can expect that the PSCs would benefit from application of the CPL to improve their IQE.
We close the discussions with talking about the self-trapping effect on the singlet-triplet conversion (supplementary material 3). We find that because the e–h interaction is weak in a delocalized exciton, their HF orbitals are weakly coupled and their spins do not respond to the CPL coherently anymore. This leads to the lower coherence behaviour of the Rabi oscillations. At strong regime of $A_0$, the achieved triplet proportion is gradually decreasing as time passing by. This means although self-trapping effect in polymer solar cells plays negative role for generation of free charges, but oppositely, their spin state can be more coherently controlled by light, which makes using CPL to improve photovoltaic performance practicable.

In summary, we present a microscopic theory to study the CPL induced singlet-triplet conversion for the self-trapped excitons in PSCs. Both oscillating frequency ($\omega$) and the amplitude ($A_0$) of the CPL affect the detailed singlet-triplet conversion. Depending on the magnitude of $A_0$, the conversion behave as either the singlet-triplet Rabi oscillations or the steadily maintained triplet excitons. To reach the largest singlet–triplet conversion ratio, $\hbar\omega$ should be set resonant to the singlet–triplet energy difference. The CPL generated triplet excitons show strong self-trapping effect, and the spin maintains steady precessing in the $x$–$y$ plane. Because of their longer life time and relative higher energy, they might densely accumulate at the D/A interface of a polymer heterojunction solar cell, which contributes to the boosting of charge separation. In addition, self-trapping effect plays an important role to enhance the electron’s and hole’s spin coherence. Our results provide the theoretical foundations to optically improve PSCs’ photovoltaic performances.

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