Nonlinear Optics

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Large Optical Nonlinearity Induced by Singlet Fission in Pentacene Films**

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Abstract: *By creating two triplet excitons from one photo-excited singlet exciton, singlet fission in organic semiconductors has drawn tremendous attention for its potential applications in boosting the efficiency of solar conversion. Here, we show that this carrier-multiplication effect can also be used to dramatically improve the nonlinear optical response in organic materials. We have observed large optical nonlinearity with a magnitude of* $\chi^{(3)}$ *up to* 10^{-9} *esu in pentacene films, which is further shown to be a result of singlet fission by monitoring the temporal dynamics. The potential application of such efficient nonlinear optical response has been demonstrated with a singlet-fission-induced polarization rotation.*

Materials with large optical nonlinearity are vital for various applications, including optical switching, optical limiting, microfabrication, data storage, and bio-imaging.[1–12] Lately, organic-molecule-based nonlinear optical (NLO) materials have attracted much attention.[8–16] In the last decade, a large number of chromophores with efficient NLO response have been predicted and demonstrated by manipulating the length,[8] orbital,[11] degree of twisting,[10,13] and other degrees of freedom[7,12,14] in π-conjugated molecules. The magnitude of nonlinear susceptibility ($\chi^{(3)}$) is strongly dependent on the nonlinear polarization induced by incident photons, which can be promoted by increasing the density of excited states involving an optical transition.[6,17] So far, most studies have focused on the regime where one incident photon only excites one electron.

In this work, we show that a process of carrier multiplication, namely singlet fission (SF),[18,19] can significantly enhance the NLO response in organic molecule systems. SF is a spin-allowed process that can increase the density of excited states by creating a pair of triplet excitons ($2T_1$) from one photo-excited singlet exciton (S_1).[22] We exploit the SF-induced optical nonlinearity in pentacene films with the technique of time-resolved (TR) dual-wavelength optical Kerr effect (OKE). The measured magnitude of $\chi^{(3)}$ approaches to about 10^{-9} esu which is among the largest third-order susceptibility reported in organic molecules.[7,11] One of the potential applications of such large SF-induced optical nonlinearity is further confirmed by demonstrating an optically induced polarization rotation.

The initial purpose for studying SF processes is to break the Shockley–Queisser theoretical limit in single-junction solar cells.[20–23] The molecular structure of pentacene consists of five linearly fused benzene rings. This highly conjugated organic semiconductor is among the most efficient materials for SF discovered so far,[24–26] which has been successfully implemented to improve the efficiency of organic solar cells and photodetectors.[22,27,28] The process of SF in crystalline pentacene can be briefly described as given in Equation (1),[19,23]

$$S_0 + S_1 \leftrightarrow {}^1(TT) \leftrightarrow T_1 + T_1, \qquad (1)$$

where one singlet exciton (S_1) is converted into two free triplet excitons through an intermediate state of correlated triplet pair (${}^1(TT)$). SF in crystalline pentacene is an ultrafast process. The reported rise time of triplet population is reported to range from about 80 fs to 0.7 ps.[24,26,28–32] This extremely fast rate of carrier multiplication is beneficial for achieving an efficient ultrafast NLO response. NLO response enables photo-induced change of refractive index. To characterize the SF-induced NLO properties in pentacene films, we employ the OKE technique to monitor the nonlinearity-induced polarization variation ($\Delta\theta$) with a dual-wavelength pump–probe configuration. The samples of pentacene films with thicknesses in the range of 100–1000 nm were prepared on silica substrates through thermal evaporation. For OKE measurements, the samples are excited by visible pulses from an optical parametric amplifier (OperA Solo, Coherent) pumped by a Ti:Sapphire regenerative amplifier (Libra,

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Coherent). To avoid linear absorption, we probe the polarization rotation with the beam having photon energy of 1.55 eV (wavelength of 800 nm). Furthermore, the optically heterodyne-detected (OHD) OKE is employed to determine the sign of $\chi^{(3)}$. More details about the experiments are available in the Supporting Information.

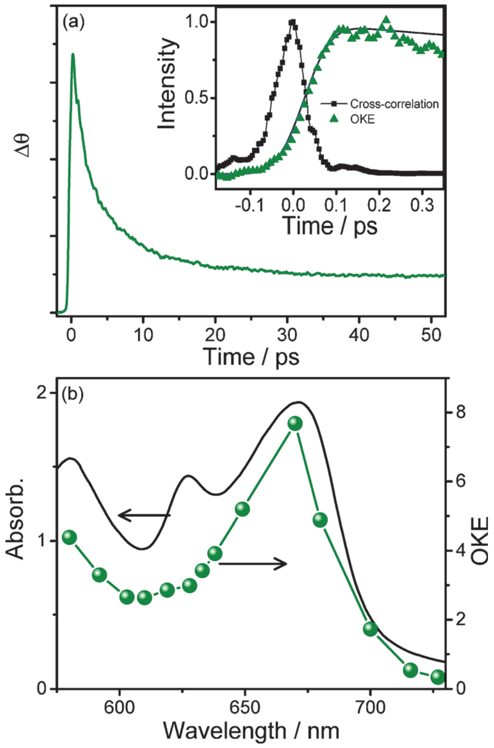

Figure 1. a) Photo-induced polarization rotation is plotted as a function of delay time with the pump at 670 nm. The excitation density is about 1 mJ cm^{-2}. Inset plots the detailed rising dynamics of the observed OKE signal together with the cross-correlation trace between the pump and probe pulses. The blue line is a fit to the data. b) The signal amplitude as a function of incident wavelength together with the absorption spectrum of the pentacene film.

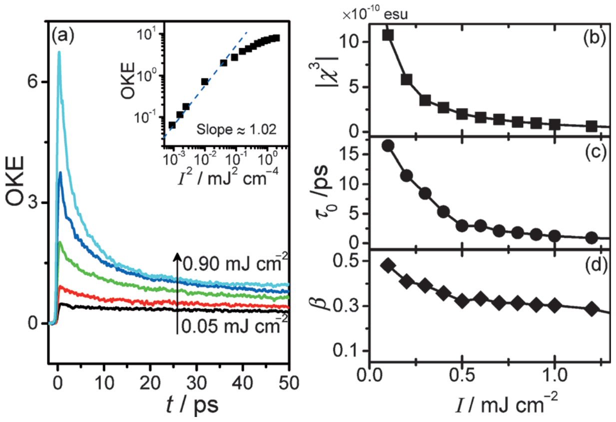

Figure 2. a) TR-OKE signals recorded with the excitation fluences of 0.05, 0.10, 0.20, 0.40 and 0.90 mJ cm^{-2}, respectively. Inset plots the signal amplitude vs square of the excitation fluence. b–d) The measured magnitude of $\chi^{(3)}$, the fitting parameters of τ_0 and β are plotted versus the excitation fluence.

Figure 1a plots a typical TR trace of $\Delta\theta$ recorded from pentacene films. The polarization of probe beam is rotated in a time scale of about 100 fs followed by a recovery process consisted of multiple exponential decay components. To trigger the SF in pentacene, the excitation is set at 670 nm being on resonance with the transition of $S_0 \rightarrow S_1$. The full-width-at-half-maximum of the TR curve is less than 5 ps, suggesting the response of SF-induced nonlinearity to be quite fast. Figure 1b gives the signal amplitude as a function of incident wavelength together with the absorption spectrum of the pentacene film. The NLO signal peaks at 670 nm and drops quickly with a further increase of the incident wavelength. These results show a high correlation between the signal amplitude and the excitonic absorption, suggesting a significant role played by the density of photo-excited singlet excitons. To evaluate the magnitude of $\chi^{(3)}$, we employ a silica cell containing CS_2 as a reference. The estimated results recorded with different excitation powers are shown in Figure 2. The magnitude of $\chi^{(3)}$ is over 10^{-9} esu with an excitation flux of 0.05 mJ cm^{-2}, which is among the highest $\chi^{(3)}$ values in organic materials measured with the similar experimental approach.[7] The signal amplitude recorded with SF is over three orders higher than that recorded under off-resonant condition (Figure 1b). These results suggest that the multiplication effect of excited carriers originated from SF is probably responsible for the obtained large value of $\chi^{(3)}$.

To confirm this assignment, we have carefully checked the temporal dynamics of NLO response in pentacene films. The inset of Figure 1a shows the onset of polarization rotation in comparison with the curve of cross correlation in our setup. The fitted dynamical curve indicates that the rising time of polarization rotation is within 100 fs, showing that the polarization of probe beam is changed by an extremely fast physical process. This time constant coincides with the temporal scale of SF process in pentacene. The generation of triplet pair is extremely fast (about 80 fs)[24,32] and highly efficient owing to the exergonic nature of SF in crystalline pentacene. The NLO response can be a result of different optical susceptibilities relevant to the states associated to the SF process, such as singlet excitons, correlated triplet pairs and free triplet excitons in pentacene films. In other words, two processes, that is, the singlet-state transition and singlet fission, may be involved in the observed NLO response. We have directly probed the nonlinear polarization at the wavelength of 670 nm to be on resonance with the singlet-state transition and compared the data with the result probed at 800 nm (see Figure S2 in the Supporting Information). The temporal dynamics of nonlinear polarization due to singlet-state transition is significantly different from the dynamics probed at 800 nm (Figure S2), suggesting that the singlet-state transition is not a major cause for the large optical nonlinearity probed at 800 nm.

Next, we perform magnetic-field-dependent OKE experiment to further confirm the role played by SF on the NLO response observed in crystalline pentacene. Such field-dependent measurements have been used as a reliable approach to confirm the presence of SF in many materials since only the processes related to triplet excitons change with magnetic field according to Merrifield's theory.[33–36] The OKE signal probed at 800 nm shows clear variations when the applied magnetic field is changed (Figure S3). This result validates the key role played by SF on the observed NLO response in pentacene. To further discriminate the NLO responses induced by singlet-state transition and SF process, OKE measurements on a control sample of anthracene film have been conducted (details can be found in the Supporting Information]. As a member of the same polyacene family, anthracene exhibits many properties that are similar to pentacene. However, SF in anthracene is highly endoergic, so that SF with photo-excitation on resonance to the transition of $S_0 \rightarrow S_1$ is negligible in anthracene.[18,37] With resonant excitation, the OKE signal probed at 800 nm in anthracene (Figure S4) comes solely from the singlet-state transition. The temporal evolution of the OKE signal in anthracene is also significantly different from that of pentacene, and the estimated magnitude of $\chi^{(3)}$ is about 2×10^{-11} esu which is nearly two orders of magnitude weaker than that of pentacene measured under similar conditions. These differences clearly indicate that the SF-induced NLO response is much larger than that induced by singlet-state transition in polyacene materials. With the above results, we can safely ascribe SF as the primary origin for the enhanced optical nonlinearity observed in pentacene films.

The recovery dynamics of OKE signal consists of multiple-exponential components, implying the complexity of processes that may be involved. For a better understanding, we perform the power-dependent measurements. Figure 2a shows the signals recorded under different excitation powers. The amplitude of OKE signal shows a disparity from the quadratic dependence at large incident powers due to saturation effect (see inset in Figure 2a). The estimated magnitude of $\chi^{(3)}$ is over 10^{-9} esu at 0.05 mJ cm^{-2} which decreases gradually and converges to a value of 2×10^{-10} esu at high intensity (Figure 2b). The recovery dynamics is also strongly dependent on the incident power (Figure 2a). The temporal evolution of OKE signal directly reflects the dynamics of nonlinear polarization, which is tightly associated with but not the same as the population dynamics of excitons. To gain more insight, we fit the recovery dynamics with a phenomenological stretched-exponential (SE) function in the form of $s(t) = Ae^{-(t/\tau_0)^{\beta}}$,[38] where τ_0 is the SE decay lifetime and β represents the distribution of decay rate with the value between 0 (board distribution) and 1 (narrow distribution). The dependences of fitting parameters (τ_0 and β) on intensity are depicted in Figure 2c and d. With increasing incident power, the time constant τ_0 gradually becomes shorter together with a reduction in β. The broad distributions of these lifetime parameters indicates that some extra channels might be involved in the recovery of polarization rotation in pentacene. These results can be ascribed to the many-body excitonic interactions. In the high-density regime, bimolecular recombination processes, such as singlet-singlet annihilation, triplet-triplet annihilation, and singlet-triplet annihilation, may become dominant in organic semiconductors.[39,40] These effects can lead to a faster relaxation of polarization rotation (Figure 2c) and the saturation of OKE signal (Figure 2a, inset).[41]

The real part of the third-order nonlinearity (Re$\chi^{(3)}$) is responsible for the power-dependent change of refractive index, which is essential for many NLO applications. To extract the value of Re$\chi^{(3)}$, we employ the technique of OHD-OKE.[42] Detail of this method is available in the Supporting Information. Briefly, a local oscillator is introduced in detection by slightly changing the angle (ϕ) of the analyzing polarizer. The value of Re$\chi^{(3)}$ can be evaluated with a phase bias configuration by measuring the signal as a function of ϕ. Figure 3a shows the signals recorded at different ϕ values with the excitation fluence of about 0.3 mJ cm^{-2}. The ϕ dependence of signal variation in pentacene films is compared with that in the reference CS_2 cell (Figure 3b). The slope of ϕ dependence of pentacene films is opposite to that of CS_2, suggesting a negative value of Re$\chi^{(3)}$ for pentacene. That is, the SF-induced NLO response in crystalline pentacene has a defocusing effect. The value of Re$\chi^{(3)}$ is then estimated to be about 3.2×10^{-10} esu which is close to the magnitude of $\chi^{(3)}$ (3.5×10^{-10} esu, Figure 3b), suggesting the major contribution to be from the real part for the photo-induced polarization rotation.

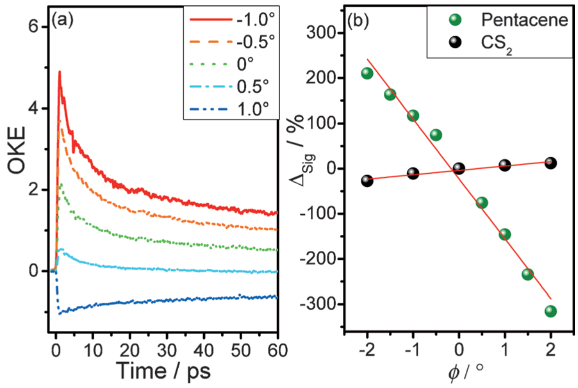

Figure 3. a) OHD-OKE signal at different heterodyne angles (ϕ) for Re$\chi^{(3)}$. b) The ϕ-dependent signals recorded from the pentacene film and the reference CS_2 cell are compared.

To test the potential application of SF-induced optical nonlinearity, we demonstrate a light-induced polarization rotation with such large SF-induced nonlinearity. We employ a configuration proposed by Agrawal's group, as schematically shown in Figure 4a,[43] with a continuous laser at 780 nm as the probe beam. Two polarizers with crossed polarizations are used to avoid the light detection by the photodiode detector. The pulsed beam with an intensity at 1 mJ cm^{-2} is applied to trigger the SF-induced nonlinearity, leading to a fast rotation of the polarization that can be monitored. A narrow slit and an optical filter are employed to exclude the pump beam from being detected, which is confirmed with the background recorded with no probe beam (Figure 4b). When the probe beam is seeded, the signal caused by polarization rotation shows as a train of pulses (Figure 4c and d). The frequency of the detected signal is controlled by that of the pump pulses (Figure 4c and d). Such light-controlled behav-

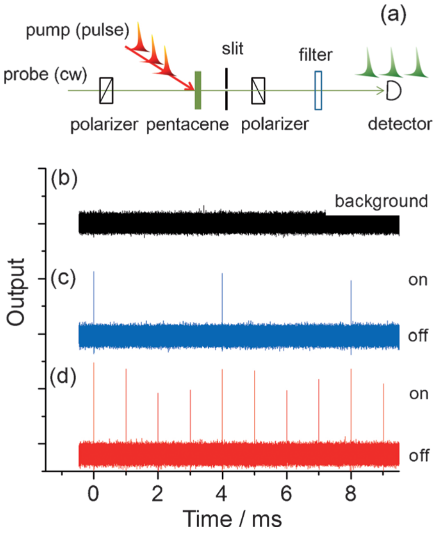

Figure 4. a) Schematic setup for demonstration of SF-induced polarization rotation. b) The noise recorded by the detector with the probe beam blocked. The optically controlled polarization rotation signals recorded with pulse excitations at 250 (c) and 1000 Hz (d), respectively.

ior may have potential applications in many NLO devices. The lasting time for each signal pulse is quite short which is actually limited by the bandwidth of the detector. The polarization rotation can be realized in a time scale of few picoseconds in the pentacene films as shown in Figures 1–3, which is close to the level achieved in the latest all-optically controlled devices.[44] The large intrinsic nonlinear susceptibility is beneficial for demonstrating future low-power devices in particularly if some photonic structures can be incorporated to enhance the local field in the constructed devices.[5,44]

In summary, we have observed large optical nonlinearity with the magnitude of $\chi^{(3)}$ up to 10^{-9} esu induced by the SF process in pentacene films. This value may be further raised in single crystals where the dipoles are better aligned. With such efficient NLO response, optically induced polarization rotation has been demonstrated. The results observed in this work indicate that the SF process could be used as an effective strategy to promote the optical nonlinearity in organic molecule systems. Considering the rapid development on the material synthesis for SF,[18,19,45,46] the magnitude of $\chi^{(3)}$ for SF-induced nonlinearity may be dramatically improved in the future. The operation wavelength for SF-induced NLO devices can be naturally extended to the infrared domain that covers the telecommunication wavelengths.

Keywords: nonlinear optics · pentacene · singlet fission · time-resolved spectroscopy

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