

The Effect of Self-Assembly on the Optical Nonlinear Absorption of Poly(3-hexyl-2,5-thienylenediethynylene)

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Optical nonlinear absorption properties of the solution in chloroform, the doped films in PMMA, the spin-coating and casting films of soluble poly(3-hexyl-2,5-thienylenediethynylene) (PHTE) were studied on a Q-switched Nd:YAG laser at 532 nm with 10 ns pulse width. It has been found that the optical nonlinear absorption properties of PHTE were affected greatly by the self-assembly effect caused by the D–A interaction strengthened π -stacking interactions among the PHTE molecules. By tuning the interaction strength among the PHTE molecules, it can show the optical bleaching effect and the optical limiting effect, respectively. These might be attributed to the self-assembly among the PHTE molecules having reduced the lifetime of the first singlet state S_1 . The special properties of PHTE will afford it important potential application in nonlinear optics.

Introduction

The optical nonlinear absorption of materials has the unique property that changing the intensity of incident radiation upon them can alter their optical absorption. It can be classified as the optical bleaching effect and the optical limiting effect. For the optical bleaching effect, the transmittance of the material will increase with the increase of the input fluence when it reaches a threshold. This property can be used in mode-locked lasers,¹ Q-switched systems,² and discrimination amplifiers.³ There are different kinds of organic and inorganic materials with an optical bleaching property.^{4–7} However, the optical limiting effect is contrary to the optical bleaching effect. So, the optical limiting materials may find their application in protecting the optical sensors and human eyes from damage caused by exposure to a sudden intense laser beam. Fullerenes^{8–11} and metallophthalocyanines^{12–15} are the most important optical limiting materials for their good optical limiting properties. In addition to these, metalloporphyrins,^{16,17} carbon nanotubes,¹⁸ diacetylenes,^{19,20} and some other organometallic compounds^{21,22} have also been reported to possess optical limiting effects. Just for its interesting properties and potential applications, optical nonlinear absorption has always drawn substantial research interest. In this article, optical nonlinear absorption properties of the soluble poly(3-hexyl-2,5-thienylenediethynylene) (PHTE) are reported.

Experimental Section

The chemical structure of PHTE is shown in Figure 1. It was prepared by self-coupling of 2,5-diethynyl-3-hexylthiophene under oxygen atmosphere with CuCl as catalyst. The polymer has been characterized by ¹H NMR, FT-IR, and UV–vis spectroscopy. Its number average molecular weight M_n was about 8000 as determined by GPC. Owing to introducing the long alkyl side group to the backbone of the polymer, it can be easily dissolved in common organic solvents, such as chloroform, THF, and toluene. This makes possible its good processibility.

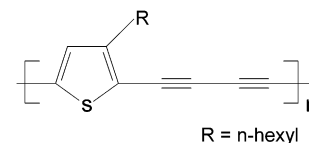


Figure 1. Molecular structure of PHTE.

The PHTE/PMMA doped films were prepared as follows: PHTE was dissolved in chloroform, and mixed with the solution of PMMA in chloroform to form a homogeneous solution. The mixed solution was cast into a PTFE mold to form a transparent film, and then the film was dried thoroughly in a vacuum. The pure PHTE films were prepared by spin-coating and casting, respectively.

Theoretical geometry optimization was conducted with AM1²³ Hamiltonian in the MOPAC package.²⁴

The UV–vis spectra were recorded on a double-beam UV–1601PC spectrometer. The emission spectrum was obtained on an F-4500 fluorescence spectrophotometer. The surface pressure–area isotherm was obtained on a KVS-5000 system. The TEM photograph of the pure PHTE film was obtained on a JEOL 2010F system. The lifetime of the excited state was measured on the system of a HORIBA NAES-1100 time-resolved spectrophotometer.

To study the optical nonlinear absorption properties, the intensity-dependent transmittance measurements were performed with a Q-switched Nd:YAG laser at the repetition rate of 10 Hz. The laser frequency was doubled to 532 nm with a 10 ns pulse width for the Gaussian mode.¹² The incident and transmitted energies were detected simultaneously by two power meters (LPE-1A), respectively. The solution sample was measured in a 1 mm quartz cell.

Results and Discussion

Figure 2 shows the UV–vis absorption spectra of the PHTE solution in chloroform and its pure film and the emission spectrum of the pure PHTE film at room temperature. From the UV–vis spectra, it can be seen that there is a high

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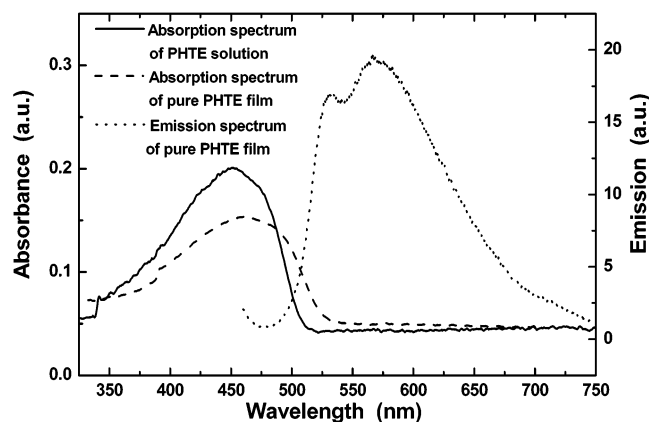


Figure 2. UV-vis absorption and emission spectra of the PHTE solution in chloroform and the pure PHTE film at room temperature.

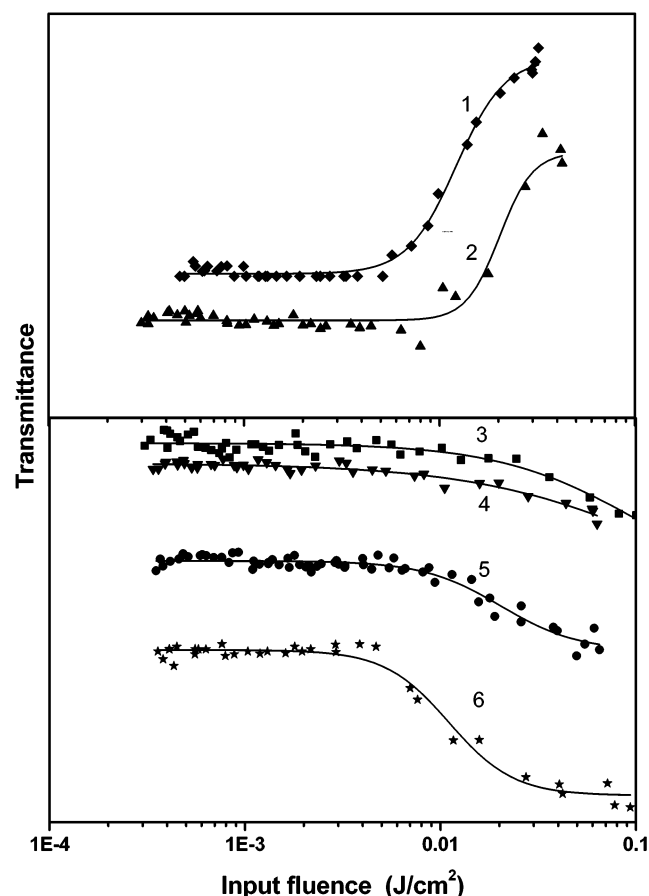


Figure 3. Optical nonlinear absorption properties of the pure PHTE films, the doped films of PHTE/PMMA, and the PHTE solution. 1: Pure PHTE casting film, $T = 0.2\%$; 2: pure PHTE spin-coating film, $T = 6.2\%$; 3: PHTE solution in chloroform, $T = 79.6\%$; 4: PHTE/PMMA-1, $T = 87.4\%$; 5: PHTE/PMMA-2, $T = 71.6\%$; 6: PHTE/PMMA-3, $T = 49.0\%$;

transmission zone at 532 nm, which is necessary to study its optical nonlinear absorption behaviors at this wavelength.

The optical nonlinear absorption properties of PHTE are shown in Figure 3. From the figure, it can be seen that, at low input fluence, the transmittance of the casting and spin-coating pure PHTE films almost constantly obey Beer's law, when the input fluence reaches a threshold (about 10^{-2} J/cm²), the transmittance of the films increases with the increase of the input fluence showing the optical bleaching effect. However, for the PHTE solution sample and its PMMA doped films (the PHTE/

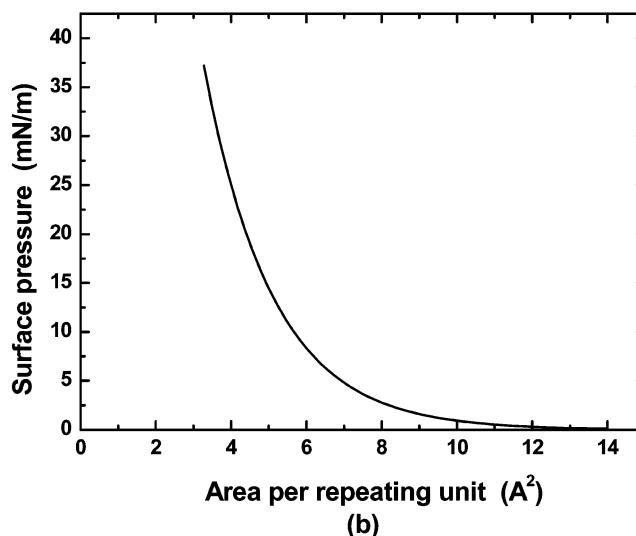
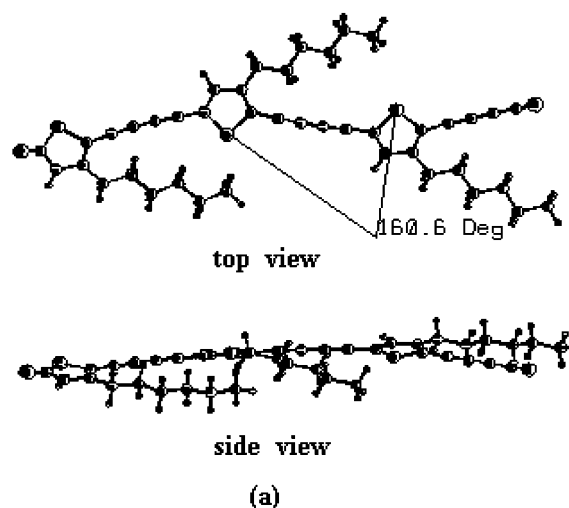


Figure 4. (a) Optimized structure of the PHTE segment. (b) Surface pressure-area isotherm of PHTE.

PMMA-1, PHTE/PMMA-2, and PHTE/PMMA-3 films contain 0.15 wt %, 0.74 wt %, and 1.19 wt % PHTE, respectively), their transmittance decreases with the increase of the input fluence after the input fluence reaches a threshold showing the optical limiting effect.

From the results shown in Figure 3, it is not difficult to understand that the interesting phenomena may have some thing to do with the interaction among the PHTE molecules.

The theoretical optimized geometry of the PHTE segment is shown in Figure 4a. It can be found that the dihedral angle between the thiophene rings in the backbone of the PHTE molecule is about 19.4° , which indicates that their coplanar property is good. The regular structure of the PHTE molecule has also been demonstrated by the surface pressure-area isotherm (Figure 4b). It is well-known that there are π -stacking interactions among conjugated polymer molecules. The regular structure of the PHTE molecule will benefit the π -stacking interactions. The electron-rich thiophene ring segments in the PHTE molecular backbone are donors (D),²⁵ and the electron-deficient diethynylene segments are acceptors (A).²⁶ The donors in one PHTE molecule will be easy to interact with the acceptors in another PHTE molecule. So the π -stacking interactions among the PHTE molecules will be further strengthened by the D-A interaction. It is not difficult to conclude that there should be strong π -stacking interactions among the PHTE molecules. The

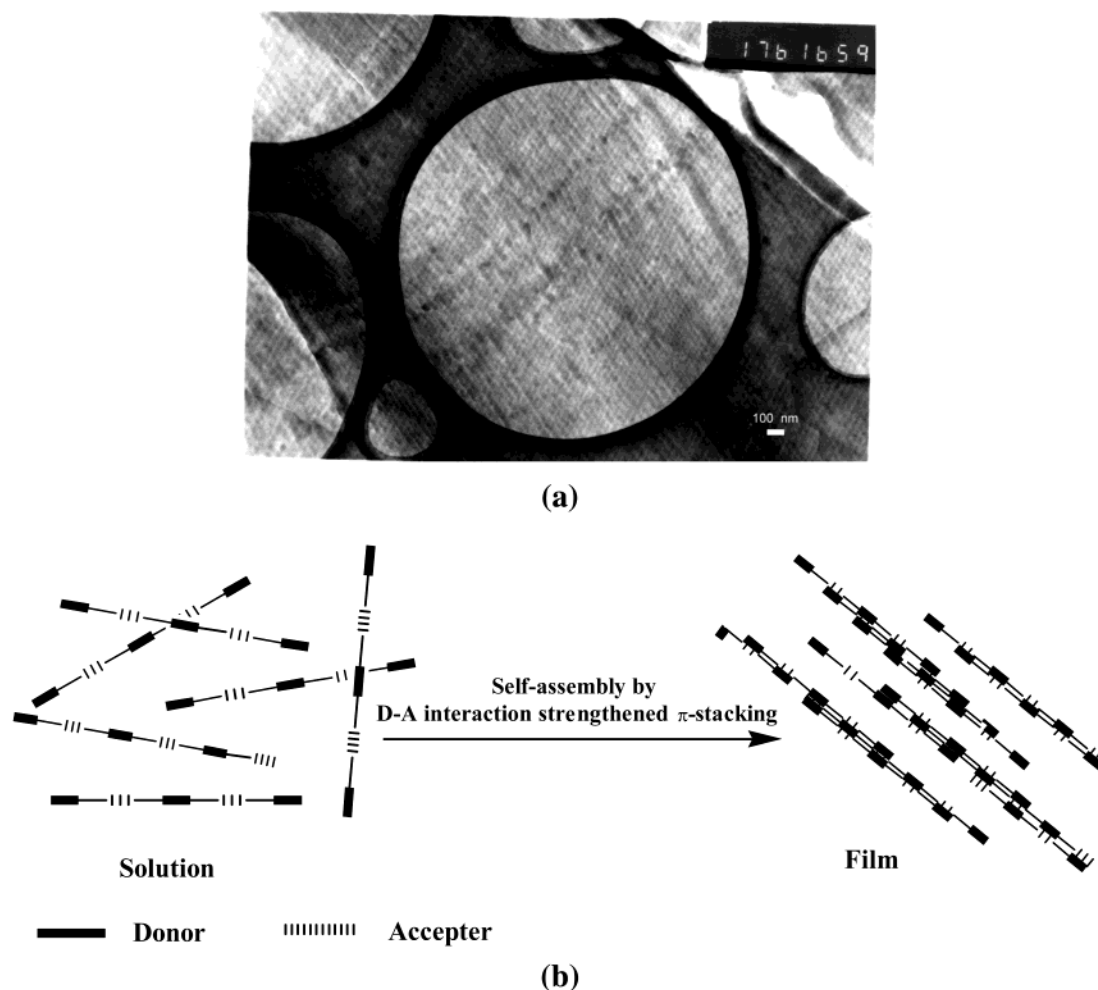


Figure 5. (a) TEM photograph of the pure PHTE film. (b) Possible self-assembly mechanism among the PHTE molecules.

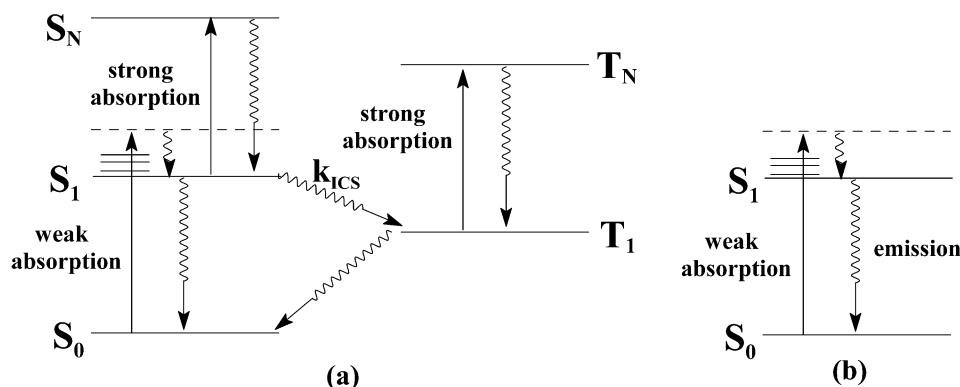


Figure 6. Molecule energy level graph for optical nonlinear absorption. (a) Optical limiting, (b) optical bleaching.

strong π -stacking interactions will lead to the self-assembly among the PHTE molecules. From the TEM photograph of the pure PHTE film (Figure 5a), the strong self-assembly does occur among the PHTE molecules to form the strip-like structures, and the possible self-assembly mechanism is shown in Figure 5b.

Just for the strong self-assembly among the PHTE molecules, we might find a proper explanation for the results shown in Figure 3 via a molecular energy level graph (Figure 6). The PHTE molecules in the ground-state S_0 absorb optical energy to be excited to the first singlet state S_1 . The molecules in the S_1 state can further absorb optical energy strongly and jump to the higher singlet state S_N or undergo intersystem crossing to the first triplet state T_1 .²⁷ The PHTE molecules in the T_1 state

absorb optical energy strongly to be excited to the higher triplet state T_N . When the PHTE molecules are in the solution and the PMMA matrix, the π -stacking interactions among them are weakened greatly. The probability for state annihilation (such as the S_0 – S_1 annihilation process) among the PHTE molecules is small. The lifetime of the S_1 state will increase. So the molecules in the S_1 state would be easy to gain a certain population. The increase of the S_1 state lifetime indicates that the nonradiative deactivation of the S_1 state is suppressed, which increases the efficiency of the intersystem crossing. For most of the organic optical limiting materials, it is the triplet excitation process that mainly contributes to the nanosecond optical limiting. So when the molecules in the S_1 state have gained a certain population, they can yield the certain population in the

TABLE 1: Lifetime of the First Singlet State (S_1) of the PHTE Samples

sample	lifetime of the S_1 state (ps)
solution in chloroform	322
spin-coating film	192
casting film	188

T_1 state required by inducing the optical limiting effect through the intersystem process during the time of the laser pulse width. The excitation process from T_1 to T_N accompanied by the strong optical absorption explains the optical limiting effect of the PHTE solution sample and the thin PHTE/PMMA doped films (Figure 6a).

However, for the pure PHTE films, the situation is quite different. Owing to the strong self-assembly among the PHTE molecules, there are strong interactions among the PHTE molecules. As a result, the excited-state annihilation process prevails. The process will shorten the lifetime of the S_1 state; thus it reduces the population of the PHTE molecules in the S_1 state and makes the T_1 state population produced by the intersystem crossing of the S_1 state not enough to induce the optical limiting effect during the time of the laser pulse width. From the lifetime of the S_1 state listed in Table 1, we can see that the lifetime of the PHTE's S_1 state in the solution is about 322 ps, while that of the film sample is less than 200 ps. It is well-known that the film sample usually possesses a longer lifetime of the S_1 state than that of the solution sample. In our experiment, it is the reverse. This indicates that the self-assembly effect has greatly reduced the lifetime of the S_1 state of the PHTE molecule in the pure polymer films. The PHTE molecules will mainly transform between the S_1 state and the S_0 state by absorption fluence and emission fluence (Figure 6b), and PHTE shows weak absorption of the emission fluence (Figure 2). The molecules of PHTE in the S_1 state and the ones in the S_0 state will maintain a dynamic balance, which leads to optical saturation.

As well-known, molecules in the casting film usually pack much closer than those in the spin-coating film; the self-assembly among the PHTE molecules in the casting film should be stronger than that in the spin-coating film. So, the lifetime of the S_1 state in the casting film should be shorter than that in the spin-coating film, which has been proved by the data listed in Table 1. Further, the optical bleaching effect of the casting film of pure PHTE will be easier to be induced than that of the spin-coating film, which has been demonstrated by results in Figure 3. The input fluence thresholds required inducing the optical bleaching effect for the pure PHTE casting and spin-coating films are 0.0021 J/cm² and 0.0082 J/cm², respectively. These further show that the optical bleaching effect is caused by the self-assembly interaction among the PHTE molecules, which has shortened the lifetime of the S_1 state.

Conclusions

Optical nonlinear absorption behaviors of the soluble PHTE were studied on a Q-switched Nd:YAG laser at 532 nm with a 10 ns pulse width. It had been found that the optical nonlinear absorption properties are greatly affected by the self-assembly among the PHTE molecules. When in the solution state and

the thin PMMA doped films, it shows the optical limiting effect. However, in the pure PHTE films, it shows the optical bleaching effect. It might be attributed to the self-assembly effect among the PHTE molecules which has reduced the lifetime of the first singlet state S_1 by the excited-state annihilation process (such as the S_0 – S_1 annihilation process) and made the T_1 state population produced by the intersystem crossing of the S_1 state not enough to induce the optical limiting effect during the time of the laser pulse width, which leads to the optical bleaching effect but not the optical limiting effect. From this interesting result, it can be seen that the optical nonlinear absorption behaviors of PHTE can be tuned easily by changing the strength of the interaction among the PHTE molecules. It can be anticipated that PHTE may find its important potential application in nonlinear optics.

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