The nonlinear optical properties of P3HT under picosecond laser irradiation*

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The nonlinear optical properties of P3HT in orthodichlorobenzene were investigated by *Z*-scan technique using second harmonic generation (532 nm) of mode-locked Nd:YAG laser in the picosecond domain. The experimental results show the magnitude of their nonlinear refraction indices was up to the order of 10^{-11} esu. The reverse saturable absorption of P3HT solution was observed and their nonlinear absorption coefficients reach up to 3.4 cm/GW. The strong optical nonlinearity of P3HT may find its new application in the photoclectric field.

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Advances in optics based technologies require efficient nonlinear optical (NLO) materials which can be used as all-optical switches, memory elements, and optical limiters, etc[1]. In the past decades, many NLO inorganic materials have been reported, including multi-quantum-well semiconductor heterostructures and metal nanoparticles, transition metal dichalcogenide (TMD) etc, which exhibit superb NLO performance[2-7]. Compared with inorganic NLO materials, the NLO properties of organic material have attracted great attention for their several predominant advantages, such as ultrafast response in the nonresonant excitation range, relative ease of production by various deposition techniques as printing or spin coating, the use of the NLO building blocks in the polymeric films suitable for waveguiding or electro-optic integration, easy structure-tailored NLO properties and so on[8]. Despite the existence of the difficulties in overcoming problems due to high linear and nonlinear optical losses, there is still high potential application in the photoelectric field. At present, much interest is concentrated on their photoelectrical application involving the characterization of their nonlinear absorption and nonlinear refraction[8-12]. Although the all-optical devices by use of the organic NLO materials have been achieved, the NLO materials exhibiting the large NLO parameter and the fast NLO response are desiderated in the application of the photonic devices[8,9]. Many efforts have been made in the pursuit of these kinds of NLO materials. Recently, several kinds of organic materials possessing excellent NLO performance have been investigated, including conjugated fluorine derivatives, organic molecules with excited-state proton transfer (ESPT) effect, organic polymers, organic semiconductors and so on[10-20]. Among these materials, poly(3-hexylthiophene) (P3HT) is one kind of the organic semiconductor-materials, which is one of the promising candidates for fabrication of the organic electronic devices such as the organic solar cell and organic field-effect transistors[21,22]. In the past decades, a lot of investigations have been focused on its electronic properties. Based on the NLO theory of molecular design, the P3HT can be predicted to possess the excellent NLO performance. However, few of them are concerned with its NLO properties except these several reports[17-20]. In this paper, we investigate the NLO properties of P3HT in orthodichlorobenzene using *Z*-scan technique under the excitation of 532 nm, 15 ps laser pulses. It was found that the nonlinear refraction of P3HT solution was up to the order of 10^{-11} esu and the P3HT exhibited a prominent reverse saturable absorption (RSA), which may lead to a wide application in the photoelectric field.

For our studies, the regioregular P3HT we used was commercially available from Sigma-Aldrich. Analytical grade polymer was used without further purification. Analytical grade orthodichlorobenzene served as solvent. For *Z*-scan measurements, a diluted solution in orthodichlorobenzene with concentration of 2 mg/mL was prepared and placed into 1-mm-thick cuvette. The linear absorption spectrum of P3HT in orthodichlorobenzene was recorded at room temperature with a UV-vis spectrometer (TU-1901). *Z*-scan technique was employed to characterize the nonlinear refraction and nonlinear absorption of P3HT. The second harmonic generation (SHG) of the Nd:YAG laser operating at 532 nm wave-

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length, 15 ps pulse width and 10 Hz repetition rate, was used to excite the sample cell with 2 mm thickness. The samples placed on a motorized translation stage were scanned along the *Z*-direction, passing through the focal point of a focused (the beam waist w_0=30 μm) laser beam. The detailed description of the *Z*-scan setup was presented in Ref.[10]. In addition, we carefully calibrated the measurement system using a liquid CS_2 as calibration standard before performing the *Z*-scan experiment. The theoretical fitting value for the *Z*-scan data for CS_2 is 1.32×10^{-12} esu, which is in close agreement with the value in Ref.[23]. Pure solvent was also examined at the same experimental condition and its nonlinear response was found to be insignificant.

The absorption spectrum of P3HT solution was shown in Fig.1. The spectral configuration was the same to that of P3HT solution in the previous report[19], confirming that the absorption of the solution in the 300—570 nm range originates from the P3HT. The broad band with maximum at 460 nm was assigned to transitions from HOMO to LUMO and the energy bandgap of P3HT was determined to be 2.70 eV.

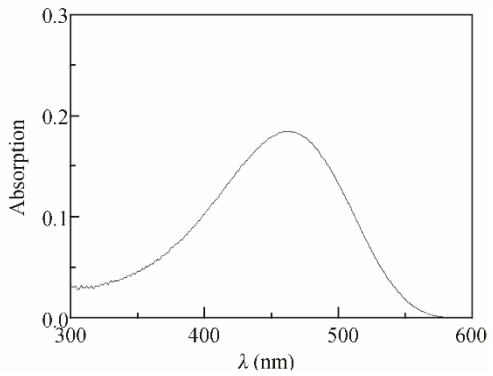

Fig.1 The absorption spectrum of P3HT in orthodichlorobenzene

Fig.2 shows typical examples of normalized transmittance against the sample position *z* from the focusing point for close aperture (CA) and open aperture (OA) *Z*-cans. Since the valley of the normalized transmittance for the CA precedes the peak as shown in Fig.2(a), the sign of the nonlinear refractive index of P3HT is negative, which suggests that P3HT is self-defocusing material at 532 nm under picosecond laser excitation. Fig.2(b) shows the OA *Z*-scan curves of P3HT solutions at different intensities, of which the straight-line configuration at the intensity of 13.8 GW/cm^2 indicates no nonlinear absorption and symmetric-valley ones imply that the reverse saturable absorption occurred at the higher intensities of 15.9 GW/cm^2, 20.4 GW/cm^2, and 23.8 GW/cm^2.

The third-order nonlinear refractive indices were determined from the simulation of CA signal in Fig.2(a). The empirically determined relation between the induced phase distortion $\Delta\Phi_0$ and the difference between normalized peak and valley transmittance ΔT_{PV} for a third order nonlinear refractive process in the absence of nonlinear absorption is given by Ref.[23] as

$$\Delta T_{PV}\approx0.406(1-S)^{0.27}|\Delta\Phi_0|, \quad (1)$$

where $\Delta\Phi_0=(2\pi/\lambda)\gamma I_0 L_{eff}$ is phase shift at focus, γ is nonlinear refractive index and I_0 is the on-axis intensity on sample, $L_{eff}=(1-e^{-\alpha L})/\alpha$ is effective length with linear absorption coefficient α and sample length L, and S is the transmitted fraction through the aperture; S=1 for open aperture (OA) and $S=1-\exp[-2r_a^2/w_a^2]$ for CA, with r_a the aperture radius and w_a the beam radius at the aperture in the linear regime. The magnitude of their nonlinear refractive indices are 1.8×10^{-11} esu, 2.4×10^{-11} esu, 4.4×10^{-11} esu and 2.7×10^{-11} esu at the input intensities of 13.8 GW/cm^2, 15.9 GW/cm^2, 20.4 GW/cm^2 and 23.8 GW/cm^2, respectively. The magnitude of the nonlinear refractive indices increased from 1.80×10^{-11} esu to 4.4×10^{-11} esu with the input intensity and then decreased to 2.7×10^{-11} esu at the intensity of 23.8 GW/cm^2.

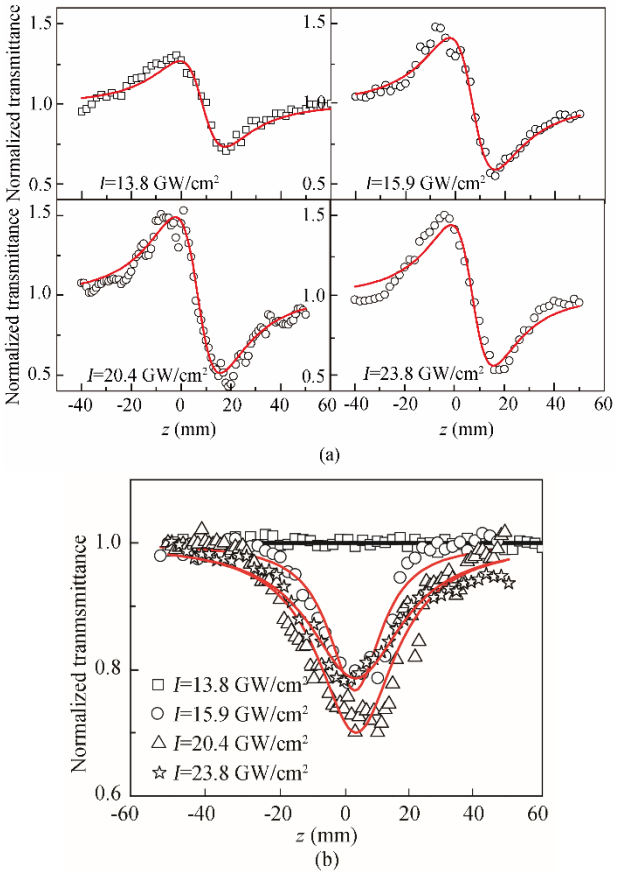

Fig.2 Normalized transmittance at different input intensities measured by the *Z*-scan: (a) CA *Z*-scan data (*S*=0.1) and (b) OA *Z*-scan data (*S*=1)

The nonlinear absorption effect should just originate from P3HT because of no observation of nonlinear absorption in the orthodichlorobenzene solvent under the excitation of 532 nm laser pulse. Moreover, the energy bandgap of P3HT is 2.70 eV and the laser pulse at 532 nm lies near the tail of the absorption band as shown in Fig.1. So it is reasonable to infer that this RSA effect may be attributed to two-photon absorption (TPA) of

P3HT. With standard *Z*-scan theory, we extract the coefficients with thin sample approximation ($L<\pi\omega^2/\lambda$)[23]

$$T(z)=\sum_{m=0}^{\infty}\frac{[-q_0]^m}{(1+z^2/z_0^2)(m+1)^{3/2}}\ , \tag{2}$$

where $q_0=I_0L_{\text{eff}}\beta_{\text{eff}}$ is the simulation parameter and β_{eff} is the effective TPA coefficient. Thus β_{eff} could be estimated by simulating the intensity dependent q_0. The TPA coefficients are 1.0 cm/GW, 3.4 cm/GW and 0.8 cm/GW at the intensities of 15.9 GW/cm^2, 20.4 GW/cm^2 and 23.8 GW/cm^2, respectively.

As for the origin of the optical nonlinearity, we present the following considerations. First, the thermo-optic effect may be neglected due to the weak linear absorption of P3HT at 532 nm, and narrow pulse width of 15 ps and low repetition rate of excitation source. Second, since the ground-state electronic and excited-state population coexist due to TPA occurrence in the process of laser excitation, the nonlinear refraction mainly originate from the combined contribution of the bound electronic and excited-state electronic in our opinion, which is supported by the variation of refractive indices with the input intensities. The P3HT solution shows a strong TPA behavior with TPA coefficient in the range from 0.8 cm/GW to 3.4 cm/GW in our experimental case. The intensity-dependent NLO refraction and the strong TPA of P3HT may allow them a wide application in the photoelectric field.

In a word, the NLO properties of P3HT in orthodichlorobenzene were investigated by *Z*-scan technique in the picosecond domain. It was found that the nonlinear refraction of P3HT solution increased first and then decreased with the input intensity increasing in our experimental case. The P3HT solutions exhibit the strong TPA and their TPA coefficient is up to 3.4 cm/GW. The intensity-dependent NLO refraction and the strong TPA of P3HT may allow them a wide application in the photoelectric field.

References

[1] Shuto Y., Watanabe T., Tomaru Satoru, Yokohama Itaru, Hikita M. and Amano Michiyuki, IEEE Journal of Quantum Electronics **33**, 349 (1997).

[2] Jongwon Lee, Mykhailo Tymchenko, Christos Argyropoulos, Pai-Yen Chen, Feng Lu, Frederic Demmerle, Gerhard Boehm, Markus-Christian Amann and Andrea Alùand Mikhail A. Belkin, Nature **511**, 65 (2014).

[3] Stefan Knoppe, Maarten Vanbel, Stijn van Cleuvenbergen, Louis Vanpraet, Thomas Bürgi and Thierry Verbiest, The Journal of Physical Chemistry C **119**, 6221 (2015).

[4] Carlos Torres-Torres, Néstor Perea-López, Ana Laura Elías, Humberto R Gutiérrez, David A Cullen, Ayse Berkdemir, Florentino López-Urías, Humberto Terrones and Mauricio Terrones, 2D Materials **3**, 021005 (2016).

[5] Peng Yao, Dawei He, Peymon Zereshki, Yongsheng Wang and Hui Zhao, Applied Physics Letters **115**, 263103 (2019).

[6] Sukanya Nasa and S.P. Purohit, Physica E: Low-dimensional Systems and Nanostructures **118**, 113913 (2020).

[7] Dalziel J. Wilson, Katharina Schneide, Simon Hönl, Miles Anderson, Yannick Baumgartner, Lukas Czornomaz, Tobias J. Kippenberg and Paul Seidler, Nature Photonics **14**, 57 (2019).

[8] Clark J. and Lanzani G., Nature Photonics **4**, 438 (2010).

[9] Li Z. Q., Hu X. Y., Zhang J. X., Yang H. and Gong Q. H., Journal of Physics D: Applied Physics **43**, 385104 (2010).

[10] G. Zhang, H. Wang, Y. Yu, F. Xiong, G. Tang and W. Chen, Applied Physics B **76**, 677 (2003).

[11] Thierry Verbiest, Sven Van Elshocht, Martti Kauranen, Louis Hellemans, Johan Snauwaert, Colin Nuckolls, Thomas J. Katz and André Persoons, Science **282**, 913 (1998).

[12] P. Aloukos, S. Couris, J.B. Koutselas, G.C. Anyfantis and G.C. Papavassiliou, Chemical Physics Letters **428**, 109 (2006).

[13] M.C. Sreenath, I. Hubert Joe and V.K. Rastogi, Optics and Laser Technology **108**, 218 (2018).

[14] Nitesh N. Ayare, Chaitannya W. Ghanavatkar, Mavila C. Sreenath, Subramaniyan Chitrambalam, Isaac H. Joeb and Nagaiyan Sekar, Journal of Photochemistry and Photobiology A: Chemistry **390**, 112327 (2020).

[15] Feng Wu, Lina Ma, Siwen Zhang, Yaohui Geng, Jiang Lü and Xiaoman Cheng, Chemical Physics Letters **519–520**, 141 (2012).

[16] Aristeidis Stathis, Ioannis Papadakis, Nikolaos Karampitsos, Stelios Couris, Georgia Potsi, Athanasios B. Bourlinos, Michal Otyepka and Radek Zboril, Chem. Plus Chem. **84**, 1288 (2019).

[17] K. Kanemoto, M. Sugisaki, M. Fujiwara, T. Karasawa and H. Hashimoto, Physica Status Solidi c **6**, S46 (2009).

[18] H. Kawahara, Y. Ueno, N. Abe, S. Kishino, K. Ema, M. Rikukawa, Y. Tabuchi and N. Ogata, Optical Review **4**, 188 (1997).

[19] J. Szeremeta, R. Kolkowski, M. Nyk and M. Samoc, The Journal of Physical Chemistry C **117**, 26197 (2013).

[20] Feng Wu, Shunlong Zhao, Siwen Zhang and Jiang Lv, Journal of Nonlinear Optical Physics and Materials **27**, 1850001 (2018).

[21] Dian Chen, Atsuhiro Nakahara, Dongguang Wei, Dennis Nordlund and Thomas P. Russell, Nano Letters **11**, 561 (2011).

[22] L. S. Grodd, E. Mikayelyan, T. Dane, U. Pietsch and S. Grigorian, Nanoscale **12**, 2434 (2020).

[23] M. Sheik-Bahae, A.A. Said, T.-H. Wei, D.J. Hagan and E.W. Van Stryland, IEEE Journal of Quantum Electronics **26**, 760 (1990).