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# Effect of electron acceptor type on nonlinear optical absorption properties in the chiral polymers based on polybinaphthyls



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### HIGHLIGHTS

• Two chiral polymers with different electron-acceptor hydroxyl and octoxy were studied at this article.

• When excited by 100 fs 800 nm laser pulses, the up-converted fluorescence were observed in two polymers.

• Under the excitation of 532 nm 38 ps pulse, two polymers presented different nonlinear absorption behavior.

• The ground-state absorption cross-section in polymer was observed to be enlarged about 10 times.

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#### ABSTRACT

Nonlinear optical absorption properties of two chiral polybinaphthyls with the same backbone but different electron acceptor hydroxyl and octoxy were studied in tetrahydrofuran solution. When excited by 100 fs 800 nm laser pulses, the up-converted fluorescence were observed and the intensities related to the different input irradiances were measured to confirm the two-photon excited fluorescence. The two-photon absorption coefficients were obtained as  $4.82 \text{ cm GW}^{-1}$  and  $12.36 \text{ cm GW}^{-1}$  with 100 fs pulses at 800 nm for two polymers, respectively. Under the excitation of 532 nm 38 ps pulse, it was found that the polymer with the side-chain of hydroxyl showed saturable absorption while the polymer with the side-chain of octoxy presented reverse saturable absorption. Their different nonlinear absorption behavior resulted from the fact that the ground-state absorption cross-section in the latter polymer was about 10 times larger than that of the former polymer while the excited-state absorption cross-section represented similar.

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## 1. Introduction

Nonlinear optical absorption properties have created considerable interest due to the outstanding applications in optical devices in recent years [1-3]. For example, reverse saturable absorption and two-photon absorption properties are being studied in the field of optical-limiters [4,5]. Saturable absorption has been extensively applied in laser physics, e.g. in mode locking and picoseconds pulse shaping [6,7]. The studies of nonlinear responses on organic polymers have attracted a lot of attentions, especially after the strategies of tuning the nonlinear optical properties by appropriate design of organic system at the molecular level have been developed [8–10]. Hales et al. [11] studied the large third-order optical nonlinearities by designing the polymethine dyes. He et al. [12] reported multiphoton absorbing properties of the materials affected by molecular designs. As a kind of organic chiral materials, optically active 2,2'-binaphthol (BINOL) and its derivatives are important C2 symmetric compounds and have often been used as starting materials for the preparation of conjugated polymers. In this work, we measured the nonlinear optical absorption properties of two chiral polymers which contain optically active binaphthol and different side-chain of hydroxyl (P<sub>1</sub>) and octoxy  $(P_2)$ . It was found that in the absorbing region at 532 nm, the different nonlinear absorption behavior had been observed with a picosecond pulse laser. And the ground-state absorption crosssection was observed to be changed in evidence. In the nonabsorbing region, two-photon fluorescence properties and twophoton absorption coefficients were studied at fs 800 nm.



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#### 2. Experiment

Two chiral polybinaphthyls  $P_1$  and  $P_2$  can be obtained by the polymerization of (R)-6,6'-dibutyl-3,3'-diiodo-2,2'-binaphthol and (R)-6,6'-dibutyl-3,3'-diiodo-2, and 2'-bisoctoxy-1,1'-binaphthyl with 4.7-diethynyl-benzo[2.1.3]thiadiazole via Pd-catalyzed Sonogashira reaction, respectively [13]. Fig. 1 shows the linear absorption spectra of two polymers in tetrahydrofuran (THF) and the inset is the molecular structure. It represents that two polymers have the same polymer backbone but different electron-withdrawn substituent. And the linear absorption spectra of two polymers are similar because of their same repeating units of the polymer backbone appearing in two polymers. The absorption bands are at 480 nm and 437 nm for P<sub>1</sub> and P<sub>2</sub> respectively. It indicates that the linear absorption peak of P1 gives a red-shift by 43 nm compared with that of P<sub>2</sub> due to the increase of  $\pi$ -conjugation. The circular dichroism spectra of P<sub>1</sub> and P<sub>2</sub> are shown in Fig. 2. It refers to the differential absorption of left and right circularly polarized light at different wavelengths and shows the phenomenon of the different absorption of molecules. In Fig. 2, the molar circular dichroism  $[\Delta \varepsilon]_{\lambda max}$  which is proportional to the differential absorbance of left and right circularly polarized light are  $-72.53~M^{-1}~m^{-1}$  (236.32 nm), 93.62  $M^{-1}~m^{-1}$  (274.35 nm) and  $-64.47~M^{-1}~m^{-1}$ (246.50 nm), 14.39  $M^{-1} m^{-1}$  (274.47 nm) for P<sub>1</sub> and P<sub>2</sub>, respectively. The inset shows the enlarged image from 350 nm to 500 nm. It indicates that there are asymmetric structures in two polymers which represent chiral polymers [14].

In the experiment, the fluorescence signals were excited by the laser at the focus of a lens with 10 cm focal length and collected by using Ocean Optics HR4000 Spectrometer. The light source in the up-converted fluorescence measurement was a mode-locked Ti: sapphire laser with the pulse width of 100 fs, the center wavelength of 800 nm, and the repetition rate of 82 MHz. An Argon-ion laser with the excitation wavelength at 488 nm was used in the excitation of the single-photon fluorescence. Z-scan technique [15] was utilized to investigate the nonlinear absorption properties of two polymers. In the Z-scan measurement, the Gaussian beam was focused on the sample by a convex lens. By translating the sample through the focus, the change in the far-field intensity pattern was monitored. This experiment was performed with the light source of the 100 fs 800 nm pulses laser and the mode-locked Nd:YAG laser (38 ps and 10 Hz).



**Fig. 1.** The linear absorption spectrum of  $P_1$  and  $P_2$ ; inset: molecular structures of chiral polybinaphthyls  $P_1$  and  $P_2$ .



Fig. 2. The circular dichroism spectra of  $P_1$  and  $P_2$ ; inset: the enlarged image from 350 nm to 500 nm for better appearance.

#### 3. Results and discussion

Fig. 3 shows the fluorescence spectra of two chiral polymers P<sub>1</sub> and P<sub>2</sub> in THF with a concentration of  $1 \times 10^{-3}$  M. The single-photon fluorescence spectra excited by 488 nm laser are shown in Fig. 3 (S<sub>1</sub>) and (S<sub>2</sub>), respectively. It exhibits a strong and narrow fluorescence band at 612 nm and 537 nm. The band's peak is red-shifted by 132 nm and 100 nm, compared with the corresponding absorption peak. The up-converted fluorescence spectra of P<sub>1</sub> and P<sub>2</sub> excited at fs 800 nm are presented in Fig. 3 (T<sub>1</sub>) and (T<sub>2</sub>), respectively. The peak position of the fluorescence band is at 617 nm and 557 nm. Comparing with the single-photon fluorescence, there are a 5 nm red shift for  $P_1$  and a 20 nm red shift for  $P_2$ . It can be considered that in each polymer, the fluorescence band remains only a little change except for intensity of the fluorescence. When choose the classic three-level molecular model to analyze the transition in different energy level, the fluorescence band could be arisen from two possible transition channels [16]. Upon excitation to the singlet state S<sub>1</sub>, the electron can undergo either a direct radiative transition to the ground state S<sub>0</sub> or experience a transition lower triplet state T<sub>1</sub> to the ground state S<sub>0</sub>. According to the absorption spectra band, if the emission band is associated with the  $S_1 \rightarrow S_0$  optical transition, it will be in the spectral range of 382–



**Fig. 3.** Single-photon spectra of  $P_1$  ( $S_1$ ) and  $P_2$  ( $S_2$ ) in THF, excited at 488 nm; upconverted fluorescence of  $P_1$  ( $T_1$ ) and  $P_2$  ( $T_2$ ), excited at fs 800 nm.

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