

Fluorescence Upconversion Properties of a Chiral Polybinaphthyl Induced by Two-Photon Absorption

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ABSTRACT: The fluorescence properties of a chiral polymer based on optically active polybinaphthyls were studied in tetrahydrofuran solution. One-photon excited fluorescence of the polymer was located in the range of ~ 596 nm and the corresponding lifetime was ~ 4.38 ns. From the excitation spectra and emission spectra excited at 800 nm, the upconversion fluorescence emission was observed. When excited by using 800 nm fs laser pulses with different input irradiances, the peak fluorescence intensity of the solution provides

square dependence with the input irradiance power, giving an evidence for two-photon excited fluorescence. Furthermore, open aperture Z-scan measurements were performed at different irradiation intensities to confirm two-photon absorption property of the solution at 800 nm excitation. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2867–2870, 2012

Key words: upconversion fluorescence; two-photon absorption; one-photon absorption; Z-scan; chiral polybinaphthyls

INTRODUCTION

Two-photon absorption (TPA), which is based on the simultaneous absorption of two photons in a single event,¹ has created considerable interest in recent years for their potential technological applications. Organic polymers with TPA and two-photon excited fluorescence (TPF) play an important role in various applications, such as optical power limiting,² all-optical switching and signal processing,³ three-dimensional (3D) optical data storage,⁴ and photodynamic therapies.⁵ TPA is the most intuitive upconversion process and organic polymers with frequency upconversion performance have been used in several aspects including two-photon frequency-upconverted lasing^{6,7} and two-photon fluorescence imaging microscopy.⁸ As one of the most important C₂ symmetric organic compounds, the chiral polymer based on optically active polybinaphthyls are currently of interest, due to their multifunctional properties, such as fluorescence chemosensors for sensitive detection of metal ions or chiral molecules recognition,^{9,10} asymmetric catalysts¹¹ by controlling the chiral organic groups, and linker structure at a well-defined molecular level. Previous researches have been carried out at two-photon properties of the polybi-

naphthyl. Drucker and McClain¹² reported the TPF properties of naphthalene and 2, 2'-binaphthyl. Zhang and Pu¹³ showed the synthesis and investigation of chiral polybinaphthyls with two-photon absorbing chromophores. Their efforts of studying polybinaphthyls were on molecular design and researches of TPF. To use the optically active organic polymer for photonics based device, the properties of two-photon pumped upconversion fluorescence on the chiral polymer should be studied effectively. In this work, we present our experimental observations on one-photon and two-photon excited fluorescence of a chiral polybinaphthyl. Comparison of the excitation spectra and the emission spectra excited in resonance and unresonance region, TPF of the chiral polybinaphthyl remains the same shape as that obtained by one-photon absorption. By using 800 nm fs laser pulses, the peak fluorescence intensities of spectra were measured at different input irradiances and open aperture (OA) Z-scan measurements were performed to confirm TPF property.

EXPERIMENT

A typical Pd-catalyzed Sonogashira reaction condition was applied to the synthesis of the chiral polymer. The polymerization was carried out by (*R*)-6, 6'-dibutyl-3,3'-diiodo-2,2'-binaphthol with 4,7-diethynyl-benzo[2,1,3]thiadiazole in the presence of a catalytic amount of tetrakis(triphenylphosphine) palladium(0) and copper iodide with triethylamine

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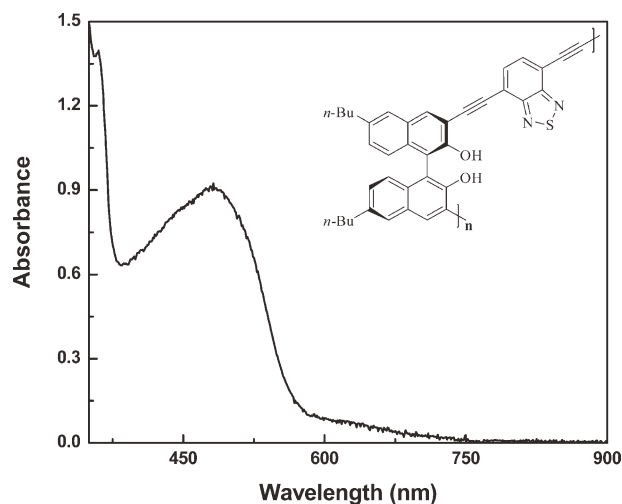


Figure 1 Linear absorption spectra of the polymer in THF; inset: the molecular structure of the chiral polymer.

under nitrogen in 56.2% yield.⁹ M_w , M_n , and the polydispersity index of the polymer were determined by gel permeation chromatography using polystyrene standards in tetrahydrofuran (THF) and the values of them are 10,260, 9960, and 1.03, respectively. The gel permeation chromatography result of the polymer shows the moderate molecular weight. The chiral conjugated polymer shows good solubility in some common solvents, such as toluene, THF, CHCl_3 , and CH_2Cl_2 , which can be attributed to the nonplanarity of the twisted polymer backbone and the flexible *n*-butyl group substituents. Figure 1 displays the linear absorption spectra of the polymer in THF and the inset shows the molecular structure. The wavelength of maximum absorbance is 480 nm. In the experiment, the excitation and emission spectra of the polymer were measured with a Fluorescence Spectrophotometer (970CRT). The detection of fluorescence lifetime imaging was based on a time-correlated single photon

counter and scanned by a 405 nm ps diode laser (Edinburgh Instruments, EPL405). For both open-aperture Z-scan¹⁴ and TPF measurement, a mode-locked Ti:sapphire laser was used as the light source. The pulse duration was 100 fs, repetition frequency was 82 MHz, and excitation wavelength was 800 nm, respectively. The laser beam was focused on the sample by a lens with 10 cm focal length. TPF signal was excited at the focus of the lens and collected by using Ocean Optics HR4000 Spectrometer. The detailed description of the Z-scan setup and TPF measurement was presented in Ref. 15.

RESULTS AND DISCUSSION

Figure 2(a) shows the fluorescence excitation spectra of the chiral polymer in THF for emission at 596 nm, which is the peak wavelength of fluorescence emission spectra. Figure 2(b) gives the results of fluorescence lifetime image excited at 405 nm. The concentration of the solution was 1.8×10^{-5} M. In Figure 2(a), it exhibits that the excitation spectra has a strong and narrow fluorescence at 546 nm in resonance region and a small band at 800 nm in unresonance region. As can be seen from Figure 2(b), the fluorescence decay of the polymer excited at ps 405 nm can be fitted by biexponential under experimental condition and the expression is given by:

$$F(t) = \sum_i \alpha_i \exp\left(-\frac{t}{\tau_i}\right) \quad (1)$$

where α_i is a preexponential factor representing the fractional contribution to the time-resolved decay of the component with a time constant τ_i . The results fitted by the biexponential is $\tau_1 = 4.416 \pm 0.065$ ns (99%), $\tau_2 = 1.361 \pm 0.029$ ns (1%), and the average fluorescence lifetime of the polymer is 4.38 ns. This

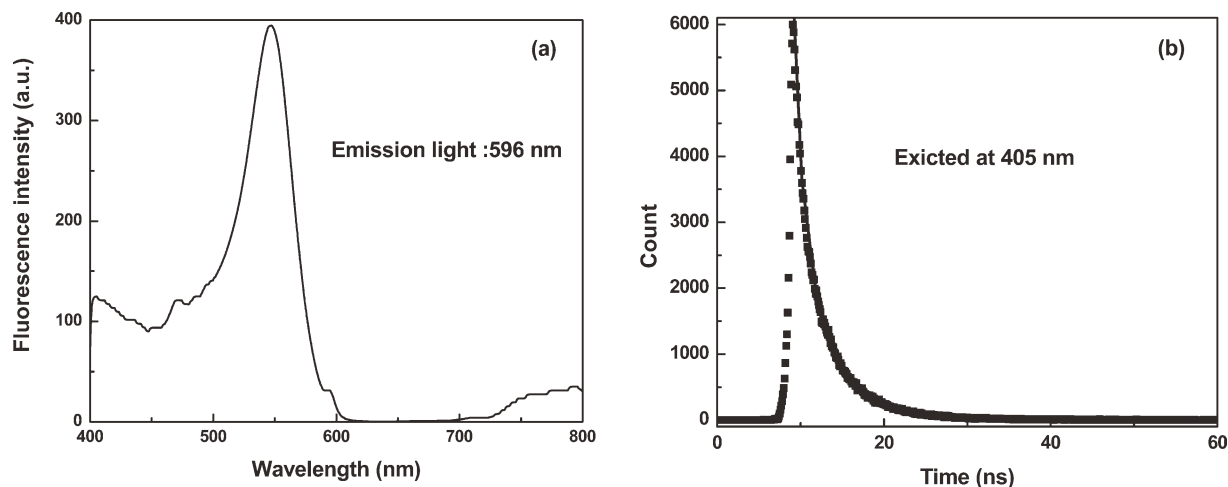


Figure 2 (a) Fluorescence excitation spectra of the chiral polymer for emission at 596 nm. (b) The fluorescence lifetime image was excited at 405 nm. The solid line is the fitting curves.

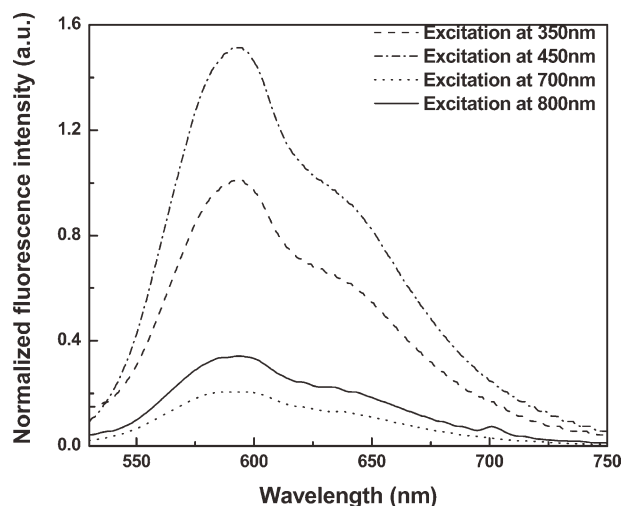


Figure 3 Normalized fluorescence emission spectra excited at 350, 450, 700, and 800 nm, respectively.

is an indication of several excitation decay channels exist in the polymer system for multiexponential character showed in the fluorescence decay.

The fluorescence emission spectra excited at 350, 450, 700, and 800 nm are showed in Figure 3. The peak position of the spectra is at 596 nm and the Stokes shift of the polymer is 116 nm. The fluorescence emission spectra excited in unresonance region remain the same shape as that excited in resonance region, i.e., the same emission processes from the excited states to the ground state were involved. On comparison of the spectra in Figures 2 and 3 excited at 800 nm, the upconversion fluorescence emission was observed.

In the interest of studying the upconversion fluorescence properties of the chiral polymer in this work, we excite the polymer by using 800 nm fs laser pulses. Figure 4(a) shows fluorescence spectra observed in the range of 554–665 nm for several excitation levels, $P_0 = 60\text{--}305$ mW, and the polymer of the solution was prepared at a higher concentration (2×10^{-3} M) and excited at fs 800 nm. The corresponding peak fluorescence intensity (dots) are plotted in Figure 4(b) and superimposed by an empirical square fit (solid trace). The two dots in Figure 4(b) corresponding with the input irradiation intensities 260 and 305 mW represent the decrease of fluorescence intensity, which is concerned with the polymer photodegradation at high laser pumping energy.¹⁶ It is indicated that the upconversion fluorescence observed by Spectrometer was induced by the process of TPA. As there is a considerable Stokes shift between the pump wavelength $\lambda_0/2$ for two-photon excited fluorescence and the upconversion fluorescence spectra wavelengths, the excited molecules have to relax to the lowest excited state of the complex rovibrational energy levels, which has been observed in fluorescence lifetime image in Figure 2(b), before they start to emit.

Moreover, we use OA Z-scan measurements to confirm TPA property of the polymer at 800 nm excitation. Z-scan technique is an effective tool to measure the nonlinear refractive index and nonlinear absorption coefficient. It has been used widely in material characterization.¹⁴ The nonlinear refraction in solid and liquid samples can be rapidly measured by using closed aperture (CA) Z-scan measurements, which uses self-focusing or self-defocusing phenomena in optical nonlinear materials.¹⁷ In CA Z-scan measurements, the transmittance of a tightly focused Gaussian beam through a finite aperture in the far field is measured by a detector, which is a function of the sample position z with respect to the focal plane. A typical peak–valley (valley–peak) transmittance curve is obtained when the nonlinear refraction of the medium is negative (positive). Removing the aperture in the far field, it is possible to perform nonlinear absorption measurements. In the OA Z-scan experiments, the curves are symmetric with respect to the focal point ($z = 0$), where they exhibit a minimum transmittance in the case of reverse saturable absorption and a maximum for the saturable absorption. Obviously, the multiphoton absorption can also be easily measured by using the OA Z-scan configuration. The normalized transmittance for OA Z-scan experiment is given by

$$T(z, s = 1) = \Sigma[-q_0(z, 0)]^m / (m + 1)^{3/2}, (q_0(0) < 1) \quad (2)$$

where $q_0(z, 0) = \beta_{\text{eff}} I_0 L_{\text{eff}} / (1 + z^2/z_0^2)$; $z_0 = k\omega_0^2/2$ is the diffraction length of the beam, β_{eff} is the effective absorption coefficient, ω_0 is the beam waist radius at the focus point, $k = 2\pi/\lambda$ is wave vector, and I_0 is the intensity of the laser beam at focus $z = 0$, $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$ is the effective thickness of the sample, α is the linear absorption coefficient and L is the

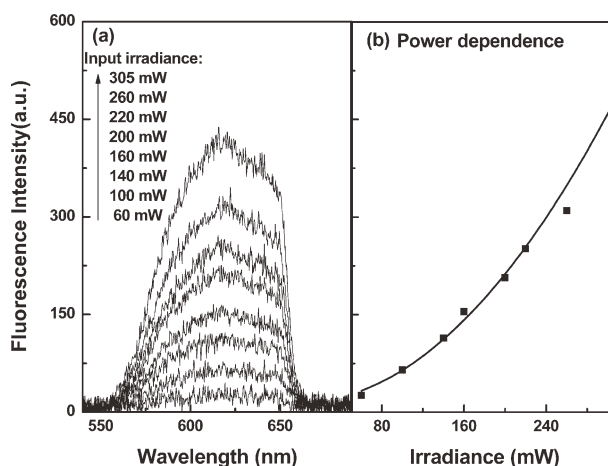


Figure 4 (a) Fluorescence spectra excited at fs 800 nm under several excitation levels. (b) The corresponding peak fluorescence intensity as a function of P_0 was plotted by the dots. The solid line is a square fit to the data.

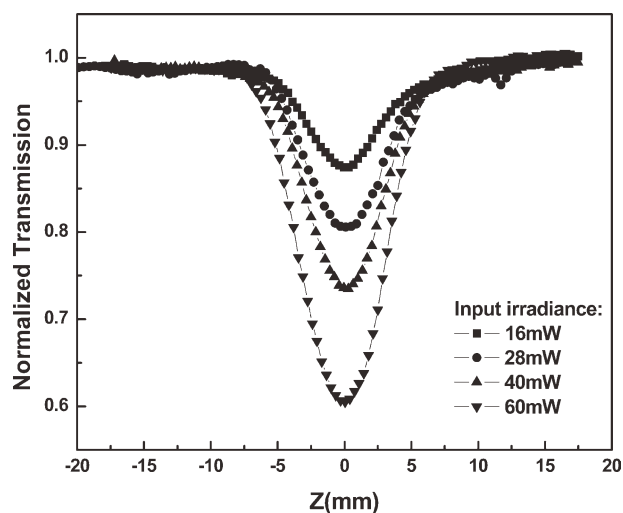


Figure 5 OA of the polymer in THF at different input irradiation intensity.

thickness of the sample. At the focus of the lens, $z = 0$, there is $q_0 = \beta_{\text{eff}} I_0 L_{\text{eff}}$, if the higher order terms are ignored, we can get the formula about the normalized peak and valley transmittance ΔT divided by I_0 :

$$\Delta T/I_0 = \beta_{\text{eff}} L_{\text{eff}} 2^{-1.5} \quad (3)$$

It indicates that $\Delta T/I_0$ has to be independent of the input irradiation intensity I_0 in the case of TPA.

In the experiment, Figure 5 shows the data of OA of the polymer in THF with $z_0 = 3.2$ mm and different input irradiation intensity: $P_0 = 16, 28, 40$, and 60 mW. In Figure 5, it is observed that the transmittance of the polymer reduces with the increasing light intensity and shows an enhancement with the decreasing light intensity. The values of $\Delta T/P_0$ under the different input irradiance were calculated to be 0.0079, 0.0071, 0.0067, and 0.0069. It indicates that $\Delta T/P_0$ or $\Delta T/I_0$ do not change along with the input irradiance, that is to say, the effective absorption coefficient β_{eff} of the polymer excited by using fs 800 nm keeps invariant under the different input irradiance. This result suggests that the nonlinear optical absorption property measured by OA Z-scan technique is related to TPA and the upconversion fluorescence of the polymer induced by TPA was confirmed.

CONCLUSION

In summary, fluorescence properties of the chiral polymer based on optically active polybinaphthyls excited by one-photon and two-photon excitation were studied in the experiment. One-photon excited fluorescence was measured in the range of ~ 596 nm and the corresponding average lifetime excited at ps 405 nm was ~ 4.38 ns. As to the small band at 800 nm in unresonance region in the excitation spectra, we

excited the polymer by using 800 nm fs laser pulses with different input irradiances. The peak fluorescence intensity of the solution excited by fs 800 nm provides square dependence on the input irradiance power, giving a direct evidence for TPF. Then, OA Z-scan measurements are performed at different irradiation intensity to confirm TPF property of the polymer at 800 nm excitation. This work opens new opportunities for the potential applications of polybinaphthyls in two-photon imaging and sensitization. Results on the transmittance change versus excitation irradiance and strong two-photon induced fluorescence demonstrate that polybinaphthyls are attractive for application in optical limiting and two-photon upconversion lasing. Moreover, due to larger stokes shift (116 nm) and long lifetime ($\tau_{\text{average}} = 4.38$ ns), the efficient two-photon induced fluorescence emission is particularly beneficial to bioimaging by reducing the background light scattering and autofluorescence as well as useful for tagging of specific cellular components in TPA induced fluorescence microscopy.

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References

- Goeppert Mayer, M. *Ann Phys* 1931, 9, 273.
- Ehrlich, J. E.; Wu, X. L.; Lee, I. Y. S.; Hu, Z. Y.; Röckel, H.; Marder, S. R.; Perry, J. W. *Opt Lett* 1997, 22, 1843.
- Victor, M.; DeLong, K. W.; Stegeman, G. I.; Saifi, M. A.; Andrejco, M. J. *Opt Lett* 1989, 14, 1140.
- Corredor, C. C.; Huang, Z. L.; Belfield, K. D. *Adv Mater* 2006, 18, 2910.
- Jorgensen, P. K. M.; Ogilby, P. R. *J Am Chem Soc* 2001, 123, 1215.
- He, G. S.; Zhao, C. F.; Bhawalkar, J. D.; Prasad, P. N. *Appl Phys Lett* 1995, 67, 3703.
- He, G. S.; Yuan, L. X.; Cui, Y. P.; Li, M.; Prasad, P. N. *J Appl Phys* 1997, 81, 2529.
- Sanchez, E. J.; Novotny, L.; Xie, X. S. *Phys Rev Lett* 1999, 82, 4014.
- Huang, X. B.; Meng, J.; Dong, Y.; Cheng, Y. X.; Zhu, C. J. *J Polym Sci Part A: Polym Chem* 2010, 48, 997.
- Liu, Y.; Zhang, S.; Miao, Q.; Zheng, L.; Zong, L.; Cheng, Y. *Macromolecules* 2007, 40, 4839.
- Fan, Q. H.; Li, Y. M.; Chan, A. S. C. *Chem Rev* 2002, 102, 3385.
- Drucker, R. P.; McClain, W. *Chem Phys Lett* 1974, 28, 255.
- Zhang, H. C.; Pu, L. *Tetrahedron* 2003, 59, 1703.
- Sheik-Bahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Van Stryland, E. W. *IEEE J Quant Electr* 1990, 26, 760.
- Varnavski, O.; Leanov, A.; Liu, L.; Takacs, J.; Goodson, T. J. *Phys Chem* 2000, 104, 179.
- Bochkarev, N. N.; Donchenko, V. A.; Zemlyanov, A. A.; Zemlyanov, A. A.; Kabanov, A. M.; Kartashev, D. V.; Kibitkin, P. P.; Matvienko, G. G.; Stepanov, A. N. *Russ Phys J* 2005, 48, 4.
- He, T. C.; Zhang, L.; Yin, Y. F.; Cheng, Y. G.; Ding, L.; Mo, Y. *J Phys Lett A* 2008, 372, 3937.