Wavelength dependence and figures of merit of ultrafast third-order optical nonlinearity of a conjugated 3,3′-bipyridine derivative

Qiying Chen, Edward H. Sargent, Nicolas Leclerc, and André-Jean Attias

The wavelength dependence and figures of merit of the third-order optical nonlinearity of a conjugated 3,3′-bipyridine derivative, a designed nondipolar structure of the donor–acceptor–acceptor–donor type, are reported. *Z* scans reveal positive nonlinear refractive-index changes for wavelengths longer than the one-photon absorption wavelength. Although the value of nonlinear Kerr coefficient n_2 decreases from $6.0(\pm 0.2) \times 10^{-6}$ cm^2/GW at 750 nm to $4.6(\pm 0.7) \times 10^{-6}$ cm^2/GW at 1550 nm, the value of nonlinear absorption β decreases from 0.084 cm/GW at 750 nm to a negligible value at 1550 nm, giving rise to excellent nonlinearity-to-loss figures of merit at telecommunications wavelengths. © 2003 Optical Society of America

OCIS codes: 190.4710, 190.4400, 320.7110.

1. Introduction

Nonlinear optical materials are needed in the wavelength ranges 750–800 nm for biomedical applications and 1300–1600 nm for telecommunications applications.[1–3] Third-order nonlinear optical (NLO) phenomena permit all-optical switching and signal processing. In transmission-based devices, materials are required to have large nonlinear refractive indices accompanied by minimal absorption losses.[4–6] Figures of merit quantify the NLO efficiency/transparency ratio to facilitate evaluation of the suitability of materials for all-optical switching and signal processing in transmission mode.[6,7] In applications such as nonlinear-absorption-based ultrafast optical limiters, optically defined waveguides, Bragg grating inscription, and laser micromachining,[7,8] nonlinear absorption is desired. The spectral dependence of optical nonlinearity and of its ultrafast response (picosecond or less) is therefore of great interest. Many previous reports of results at single wavelengths were published; a long-time-duration pulse was used, and information on the wavelength dependence of the third-order optical nonlinearity was often missing. We have found no report so far to discuss the third-order optical nonlinearity of organics and polymers at the important telecommunication wavelength of 1550 nm.

Motivated by this dearth of spectral information, we report the NLO properties and figures of merit of a 3,3′-bipyridine derivative characterized in the visible and near-infrared regions. π-Conjugated organic compounds are a promising class of third-order NLO material because of their potentially large third-order susceptibilities associated with fast response time[4,7] in addition to their variety and processibility. We designed the molecule explored herein to optimize nonlinear performance, and a derivative of similar molecular structure[6] was found to possess a nonresonant Kerr coefficient whose value was comparable to the largest value published so far measured with longer pulses.[5]

2. Experimental Details

We employed a picosecond Ti:sapphire amplified system (Fig. 1), which consisted of four parts: (1) a femtosecond Ti:sapphire seed oscillator (Vitesse from

---

When this research was performed, Q. Chen (qiying.chen@nrc.ca) and E. H. Sargent were with the Department of Electrical and Computer Engineering, University of Toronto, 10 King's College Road, Toronto, Ontario M5S 3G4, Canada. Q. Chen is now with the Integrated Manufacturing Technologies Institute, National Research Council of Canada, 800 Collip Circle, London, Ontario N6G 4X8, Canada. N. Leclerc and A.-J. Attias are with the Laboratoire de Chimie des Polymères, Unite Mixte de Recherche, 7610, Centre National de la Recherche Scientifique, Université Pierre et Marie Curie, 4 Place Jussieu, F-75252 Paris Cédex 05, France.

Received 4 April 2003; revised manuscript received 3 September 2003.
0003-6935/03/367235-07$15.00/0

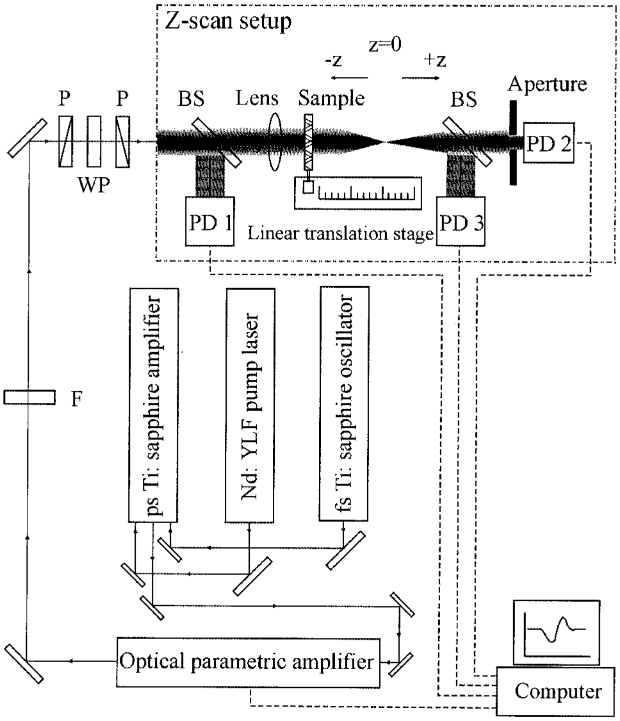

Fig. 1. Experimental setup for Z-scan measurement: F, filter; P's, polarizers; WP, λ/2 plate; BS's, beam splitters; PD1–PD3, photodetectors.

Coherent, Inc.; output wavelength, 800 nm; pulse width, <100 fs; repetition rate, 80 MHz; power, 300 mW), pumped by a 1.4-W Verdi diode laser from Coherent, Inc.; (2) a pump laser (*Q*-switched Nd:YLF laser; 527DP-S from Quantronix Corporation; 527 nm, 150–220 ns, 1 kHz, 15 W); (3) a picosecond Ti: sapphire regenerative and multipass amplifier (Titan-DP2-2 from Quantronix Corporation; 800 nm, ~3.5 ps, 1.8 W); and (4) an optical parametric amplifier (traveling-wave optical parametric amplification system from Light Conversion). The optical parametric amplifier's output coming from parametric superfluorescence within the nonlinear crystal β-barium borate at a pulse width of 3.3 ps and a repetition rate of 1 kHz was split into two components, one acting as a pump beam and the other, which had an intensity of <10% of the first beam, acting as the reference beam (PD1). After the focusing lens, two photodetectors (PD2 and PD3) simultaneously measured the closed-aperture (with an aperture just before the detector of aperture transmittance $S = 0.015$) and open-aperture ($S = 1$) Z scans when the sample moved in the vicinity of the laser waist through a linear translation stage.

3. Results and Discussion

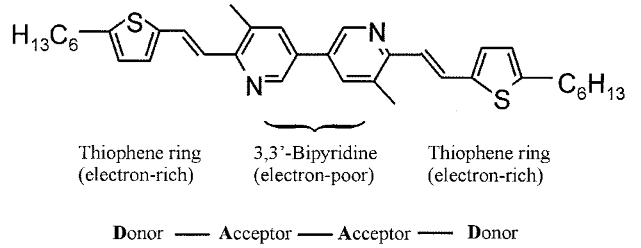

Fig. 2. Molecular structure of 6,6′-bis(5-hexyl-2-thienyl vinylene)-3,3′-bipyridine.

The conjugated material described in this paper is 6,6′-bis(5-hexyl-2-thienyl vinylene)-3,3′-bipyridine. The molecular structure and the absorption spectrum of its dichloromethane solution (molar concentration, 0.05 mM) are shown in Figs. 2 and 3, respectively. The strategy for designing the molecules was reported in Ref. 6, and a new synthetic route[9] was developed by modification of the route reported in a previous paper.[10] The molecule exhibits a nondipolar donor–acceptor–acceptor–donor (D–A–A–D) structure in which the 3,3′-bipyridine core acts as the acceptor group (A–A) and the donor group (D) is a thiophene ring. In general there are two main peaks in the absorption spectrum, one near 225–260 nm and another, low energy, peak from 320 to 450 nm. The oscillator strength can be estimated from Eq. (1) (Refs. 11 and 12):

$$f = 1.88 \times 10^{-9} \int \varepsilon(\nu)\mathrm{d}\nu, \tag{1}$$

and the transition dipole moments from

$$|\mu|^2 = 2.17 \times 10^6 f\lambda, \tag{2}$$

where ε is the molar extinction coefficient [L mol^{-1} cm^{-1}], ν is wave number 1/λ, and the dipole moments are expressed in Debye units.

The large molar extinction coefficients (ε > 60,000 L mol^{-1} cm^{-1}; Fig. 3, inset) of the strong and intense low-lying absorption band are indicative of a highly π-conjugated system. The optical properties are related to the donor/acceptor strength and the structure of the end substituent.[6,9,10] The derivative

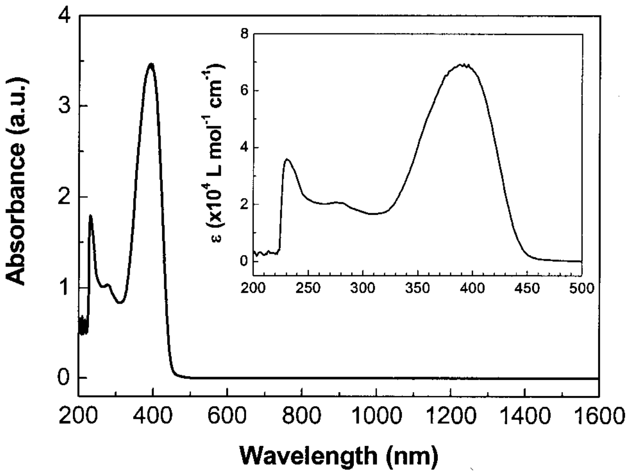

Fig. 3. Absorption and molar extinction coefficient spectra of 6,6′-bis(5-hexyl-2-thienyl vinylene)-3,3′-bipyridine in dichloromethane.

shows a low cutoff wavelength (lower than 450 nm) and exhibits an optical transparency at the second-harmonic wavelengths of the telecommunication wavelengths (1.3 and 1.55 μm). Following the spectrum of the molar extinction coefficient, the values of the oscillator strength and the transition dipole moment [D] of the lowest-energy peak in the linear absorption spectra can be calculated as 0.74 and 7.9, respectively. The values of the molar extinction coefficient, oscillator strength, and transition dipole moment here are in the same range as those reported by Colditz *et al.*[13] for unsubstituted oligothiophenes with two to six thiophene rings and by Keuren *et al.*[12] for substituted oligothiophenes. The values of the oscillator strength and the transition dipole moment here are larger than 0.10–0.55 and 4.0–7.7, respectively, for oligothiophene derivatives.[12] The larger oscillator strength (and larger transition dipole moment) reflects a greater overlap of ground and excited-state wave functions. By varying the number and type of substituents it is possible to shift the bandgaps, increase the oscillator strength, and enhance the NLO properties compared with those of unsubstituted polythiophene. It was also reported that the increased transition dipole is related to the fact that the substituents occupy end positions on the chain.

In materials that exhibit a third-order nonlinearity, index of refraction n and nonlinear absorption coefficient $\alpha(I)$ can be expressed as

$$n = n_0 + n_2 I, \tag{3}$$

$$\alpha(I) = \alpha_0 + \beta I, \tag{4}$$

where n_0 is the linear part of the index and where n_2 [cm^2/W] is the nonlinear optical Kerr coefficient. α_0 is the linear absorption coefficient and β is the two-photon absorption coefficient.

For a temporal Gaussian pulse with an incident Gaussian spatial profile, the on-axis transmission has been shown as a function of sample position relative to the lens's focal point to be[14,15]

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q(z)]^m}{(m+1)^{3/2}}, \qquad |q| < 1, \tag{5}$$

where

$$q(z) = \frac{I_1 L_{\mathrm{eff}} \beta}{1 + (z^2/z_0^2)}, \tag{6}$$

in which I_1 is the peak on-axis irradiance. Confocal parameter z_0 is simply $\pi \omega_0{}^2/\lambda$, where ω_0 is the beam waist at the lens focus. The effective sample length, L_{eff}, takes into account linear absorption coefficient α_0:

$$L_{\mathrm{eff}} = \frac{[1 - \exp(-\alpha_0 L)]}{\alpha_0}, \tag{7}$$

where L is the sample thickness.

For a small third-order nonlinear loss and for a pulse of Gaussian temporal shape, the normalized transmittance can be described by[7]

$$T(z) = 1 - \frac{\beta I_0 L_{\mathrm{eff}}}{2\sqrt{2}} \frac{1}{1 + z^2/z_0^2}, \tag{8}$$

where I_0 is the peak on-axis irradiance with the sample at focus ($z = 0$). The value of β can be obtained from a theoretical fit performed on the experimental data of the open-aperture measurement.

Nonlinear refractive index n_2 can be obtained from a closed-aperture Z-scan measurement. To obtain the nonlinear refraction in the presence of nonlinear absorption, a simple division of the curves obtained from the two Z scans (closed–open) gives a curve that closely approximates what would be obtained with a closed-aperture Z scan of a material that possesses the same Δn but with $\Delta\alpha = 0$. When far-field condition $d \gg z_0$ is satisfied, the normalized transmittance can be described as[14]

$$T(z, \Delta\Phi_0) \approx 1 - \frac{4\Delta\Phi_0 x}{(1 + x^2)(9 + x^2)}, \tag{9}$$

where $x = z/z_0$. $\Delta\Phi_0$ is the phase change and $\Delta\Phi_0 = 2\pi\Delta n L_{\mathrm{eff}}/\lambda$. Numerical fitting to the experimental data with $\Delta\Phi_0$ and z_0 as variables will give the values $\Delta\Phi_0$ and z_0, from which values of Δn and subsequently n_2 [cm^2/W] can be deduced.

Useful figures of merit that quantify the NLO efficiency/transparency ratio are[6,16,17]

$$W = \frac{n_2 I}{\alpha_0 \lambda}, \tag{10}$$

$$T = \frac{\beta\lambda}{n_2}. \tag{11}$$

Z-scan measurement was performed first on a 1-mm-thick quartz cuvette filled with pure dichloromethane solvent, followed by measurement of the dichloromethane solution of the derivative (concentration, 2.0×10^{-2} mol L^{-1}) in the same type of cuvette. By minimizing the solvent's contribution to the net signal through careful selection of the pulse energy, one can achieve reliable measurements, and extrapolation to the solute n_2 value can be achieved by use of the relation $n_{2\mathrm{sol}} = g n_2 + (1 - g) n_{2\mathrm{solvent}}$, where g is the molar fraction.[17,18] The beam waist at lens focus ω_0 was measured to be 16 μm, and confocal parameter z_0 was calculated to be 1.1 mm. In the model of Sheik-Bahae *et al.*,[15] if the sample length is small enough that changes in the beam diameter within the sample that are due either to diffraction or to nonlinear refraction can be neglected, the medium is regarded as thin. For linear diffraction, this implies that $L \ll z_0$, whereas for nonlinear refraction $L \ll z_0/\Delta\Phi(0)$. In most cases, the second criterion is automatically met because $\Delta\Phi$ is small. For the experimental conditions in this study at different wavelengths, these criteria were satisfied. Figure 4 shows the open- and closed-aperture *Z*-scan curves of

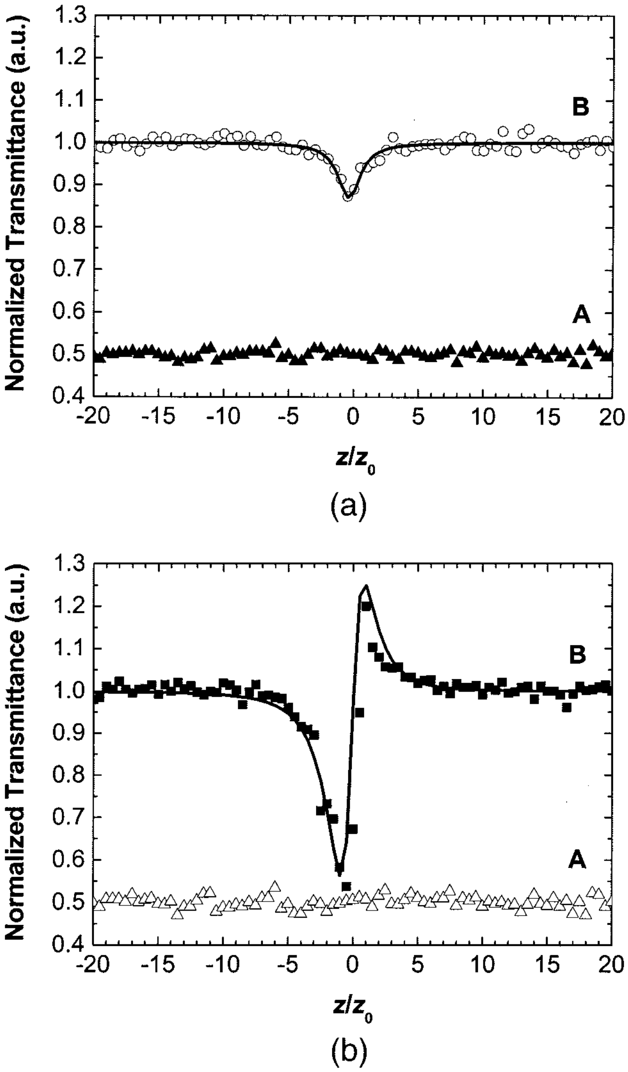

Fig. 4. Nonlinear transmission as a function of distance for both open- and closed-aperture scans measured at 750-nm wavelength: (a) open-aperture Z-scan data, (b) closed-aperture data. Data sets A and B correspond to background measurement (pure dichloromethane in the cuvette) and measurement of the solute in dichloromethane in the cuvette after removal of the background contribution, respectively. For visual convenience, the data for background measurements have been scaled to 50%. Theoretical fittings of the open- and closed-aperture data for B are shown by solid curves.

the background (solvent and cuvette windows, curves A) and the solute in dichloromethane after removal of the background contribution (curves B) measured at 750 nm. Inasmuch as no valley or peak was found from the closed-aperture Z-scan curve of the background, the upper limit of the n_2 value for dichloromethane can be estimated to be 7×10^{-7} cm^2/GW, whereas n_2 for quartz is 2×10^{-7} cm^2/GW (Ref. 4) and the thickness of each of the two cuvette windows is 1 mm. The open-aperture curve of the solute in dichloromethane in Fig. 4(a) shows a valley, indicating nonlinear absorption ($\beta = 0.084$ cm/GW). Nonlinear least-squares fitting yields $\Delta\Phi_0 = 2.8$. Following the relation $\Delta\Phi_0 = 2\pi\Delta n L_{\text{eff}}/\lambda$, it is possible to obtain the refractive-index change at the focal point, $\Delta n = 3.34 \times 10^{-4}$, and Kerr coefficient $n_2 = 6.0(\pm 0.2) \times 10^{-6}$ cm^2/GW.

Table 1. Dependence on Wavelength of Nonlinear Refractive Index n_2, Nonlinear Absorption β, and Figures of Merit of the Sample

	Wavelength (nm)		
Parameter	750	1200	1550
n_2 ($\times 10^{-6}$ cm^2/GW)	6.0 ± 0.2	3.7 ± 0.59	4.6 ± 0.7
β (cm/GW)	0.084	0.049 ± 0.010	<0.01
W	>300	>410	>600
T	1.05	1.59	<0.15

Values of n_2 and β at wavelengths 750, 1200, and 1550 nm are listed in Table 1. The W values were calculated from $I_{\max} = 50$ GW/cm^2, the maximum peak intensity before the onset of irreversible change or damage in the material, which represents the maximum nonlinear phase shift that can be achieved with the material. At these wavelengths, n_2 decreases from $6.0(\pm 0.2) \times 10^{-6}$ cm^2/GW at 750 nm to $4.6(\pm 0.7) \times 10^{-6}$ cm^2/GW at 1550 nm, whereas β decreases from 0.084 to less than 0.01 cm/GW at 1550 nm, estimated from the uncertainty in the open-aperture measurement. The nonlinear absorptions at wavelengths 750 and 1200 nm are attributable to multiphoton processes in view of the relationship between photon energy and transition energy. As the material exhibits extremely small one-photon absorption α_0 for wavelengths longer than 450 nm, low limits of W values can be estimated with $W \gg 1$.

Because of nonlinear absorption at wavelengths 750 and 1200 nm, the T values are 1.05 and 1.59, respectively. An upper bound for T (<0.15) at 1550 nm can be estimated from the β value and shows a nonresonant nonlinearity with good figures of merit. It is important in evaluating third-order optical nonlinearity to consider the possibility of thermal effects. Absorption necessarily results in heat transfer to the irradiated material, potentially changing the properties of the material. When there is a linear relationship between laser irradiation and the refractive index, an effective third-order nonlinearity will result, with a negative n_2. With the absorption peaks located in the UV region, there is negligible linear absorption for 3,3′-bipyridine derivatives at wavelengths longer than 450 nm, such that thermal effects are avoided. In closed-aperture Z-scan curves the distance between peak and valley (peak–valley separation, ΔZ_{p-v}), as a function of z_0, usually reflects the origin of the NLO process. In the model of Sheik-Bahae *et al.*, $\Delta Z_{p-v} \cong 1.7\, z_0$.[15] In NLO processes of thermal origin, usually $\Delta Z_{p-v} > 1.7\, z_0$. From the closed-aperture Z-scan curve of the D–A–A–D chromophore in Fig. 4, $\Delta Z_{p-v} \cong 1.7\, z_0$, suggesting that the optical nonlinearity measured here is not of thermal origin.

Previous research has shown that the third-order NLO response of NLO molecules can be described by a three-level model[19–24] in which three states, i.e., the ground state, a one-photon excited state, and a two-photon excited state, are needed to describe the second hyperpolarizabilities γ. A full three-level model involves at least nine terms, which are not completely independent of one another. A sum-over-states analysis of γ derived from perturbation theory indicated that three classes of terms dominate the third-order NLO response. In particular, it was shown that in the static limit

$$\gamma \propto -\left(\frac{\mu_{ge}{}^{4}}{E_{ge}{}^{3}}\right) + \sum_{e'} \left(\frac{\mu_{ge}{}^{2}\mu_{ee'}{}^{2}}{E_{ge}{}^{2}E_{ge'}}\right) + \left[\frac{\mu_{ge}{}^{2}(\mu_{ee} - \mu_{gg})^{2}}{E_{ge}{}^{3}}\right], \tag{12}$$

where g labels the ground state, e and e' label the two excited states, and μ and E are the dipole matrix elements and the transition energy, respectively, between the labeled states. Hence the three-state expression for γ consists of three terms: the first one, negative; the second one, a two-photon term; and the third one, a dipolar term.

Our approach to molecular design was to reduce the ground-state aromatic character by incorporating a thiophene ring as the donor group in the π-conjugated system on the one hand and a symmetrical D–A–A–D π-conjugated bridge on the other hand to enhance the nonresonant n_2 value. Hein *et al*. reported that the n_2 values for thiophene oligomers (nT, where n is the number of thiophene rings $n = 6$–2) lie in the range (from -3.5 to 4.9) $\times 10^{-15}$ cm^2/W measured by laser pulses of pulse width 30 ps at wavelength 532 nm.[25]

A detailed comparison of the enhancement of the optical nonlinearity of a D–A–A–D structure with relevant symmetric molecules and asymmetric push–pull molecules can be found in Ref. 6. The figures of merit for the D–A–A–D structure here show improvement over the values for these relevant molecule structures with $W > 300$ and $T < 0.3$. The figures of merit for the D–A–A–D structure here are also better than those values for some promising nonlinear organic materials, i.e., Disperse Red 1–poly(methyl methacrylate) ($W \sim 0.2$ and $T \sim 10$),[26] substituted poly(p-phenylene vinylene) solutions ($1.6 < T < 4.7$),[18] and solid-state guest–host blends of poly(2-methoxy,5-(2′-(ethyl)-hexyloxy)-p-phenylene vinylene) with poly(methyl methacrylate) ($W = 1.7$ and $T = 0.6$),[27] which possess large negative n_2 and β values because the laser wavelengths lie between the one- and two-photon absorption edges of the materials. The nonresonant n_2 values here are also significantly larger than those for some well-known nonlinear crystals, for example, (0.19–2.0) $\times 10^{-6}$ cm^2/GW for $LiNbO_3$:MgO, $KTiOAsO_4$, $KTiOPO_4$, β-BaB_2O_4, and LiB_3O_5.[28] The inclusion of an electron-rich thiophene ring that produces a dramatic enhancement of n_2 can be qualitatively explained in the three-state model on the basis of a large increase in the $e \rightarrow e'$ transition dipole moment ($\mu_{ee'}$) and an increase in the $g \rightarrow e$ transition dipole moment (μ_{ge}). This result could be associated with the lower delocalization energy of the thiophene conjugating moiety and the symmetric charge transfer in the excited state from the terminal electron-rich thiophene ring to the electron-poor pyridine ring, leading to an increase in electron delocalization in the first excited state.

The optical Kerr effect, known as the intensity-dependent refractive index that results from the third-order NLO process, originates from a variety of physical mechanisms.[3] Optical transitions that give rise to optical nonlinearity are closely related to the energy eigenstates of the system. These eigenstates can be associated with bound electronic motion, molecular vibrations, or molecular rotations of the system. Electronic transitions involve the largest energy separation, rotational transitions, the smallest. One or more of these excitations may contribute to the optical Kerr effect. The Z-scan technique is sensitive to all these nonlinearities; however, it cannot simply be used by itself to distinguish these nonlinear processes or separate fast from slow nonlinearities. In general, the various contributions differ in response time, magnitude, and frequency dependence. The nonlinearity associated with the electronic transitions give the fastest response time (<10 fs), which can be regarded as instantaneous. The nonlinearity associated with rotational motion of molecules, however, has a response time in the picosecond range.[29–37] The orientational Kerr effect involves transitions between rotational energy levels of a molecule. After the optical field polarizes the molecule and results in an induced dipole moment, the induced dipole interacts with the applied field and aligns itself along the direction of polarization. This molecular reorientation (rotation) causes birefringence in an isotropic solution in which the molecules were randomly oriented, and no birefringence exists at the beginning. The light-induced molecular orientation is regarded as the most effective mechanism to produce the optical Kerr effect in transparent organic liquids on a nanosecond time scale,[32,37,38] in which molecules are exposed to the light field for longer time with a longer pulse duration (nanoseconds), and more orientational motion of the molecules may result in its larger contribution to the optical nonlinearity. The reorientational response time of a molecule depends on its mass: The heavier the molecule, the slower the reorientational process. Take CS_2, a reference sample, as an example: CS_2 has a reorientational response time $\tau \approx 1$–2 ps.[3,33] Kiyohara *et al*.[29] and Kamada *et al*.[30,31] reported the molecular dynamics of thiophene homologues (C_4H_4X, $X = $ O, S, Se) with reorientation lifetimes for furan (O), thiophene (S), and selenophene (Se) of 0.9, 2.0, and 3.2 ps, respectively, from their experimental results. Considering the fact that the molecular weight (Mw) of 3,3′-bipyridine derivative (Mw 541) is much larger than those of CS_2 (Mw 76) and thiophene homologues (Mw 68-131), we can expect the response time for the 3,3′-bipyridine derivative to be larger than that of the pulse width (~3.3 ps). So, when molecules are exposed to a light field, less orientational motion of the molecules may contribute to the measured n_2 values that are solely attributed to purely electronic Kerr effects. The reorientational Kerr effects of 3,3′-bipyridine derivative are under investigation.

4. Conclusions

Third-order optical nonlinearity of a conjugated 3,3′-bipyridine derivative with enhancement of nonlinearity by its symmetrical donor–acceptor–acceptor–donor structure was investigated and found to possess positive ultrafast nonlinearity in the wavelength range 750–1550 nm with nonresonant nonlinearity at 1550 nm. The dependence on wavelength of nonlinear refractive index and nonlinear absorption in the visible and the near-infrared regions is important for biomedical and communications applications, respectively.

References

1. R. W. Waynant and M. N. Ediger, eds., *Electro-Optics Handbook* (McGraw-Hill, New York, 2000).
2. M. G. Shim, B. C. Wilson, E. Marple, and M. Wach, "Study of fiber-optic probes for *in vivo* medical Raman spectroscopy," Appl. Spectrosc. **53,** 619–627 (1999).
3. G. I. Stegeman, "All-optical switching," in *Handbook of Optics IV: Fiber Optics & Nonlinear Optics*, 2nd ed., M. Bass, J. M. Enoch, E. W. V. Stryland, and W. L. Wolfe, eds. (McGraw-Hill, New York, 2001), Chap. 21.
4. G. I. Stegeman and W. E. Torruellas, "Nonlinear materials for information processing and communications," Phil. Trans. R. Soc. London Ser. A **354,** 745–756 (1996).
5. B. L. Lawrence, M. Cha, J. U. Kang, W. Torruellas, G. Stegeman, G. Baker, J. Meth, and S. Etemad, "Large purely refractive nonlinear index of single crystal *P*-toluene sulphonate (PTS) at 1600 nm," Electron. Lett. **30,** 447–448 (1994).
6. F. Cherioux, A.-J. Attias, and H. Maillotte, "Symmetric and asymmetric conjugated 3,3′-bipyridine derivatives as a new class of third-order NLO chromophores with an enhanced nonresonant, nonlinear refractive index in the picosecond range," Adv. Funct. Mater. **12,** 203–208 (2002).
7. S. Kershaw, "Two-photon absorption," in *Characterization Techniques and Tabulations for Organic Nonlinear Optical Materials*, M. G. Kuzyk and C. W. Dirk, eds. (Marcel Dekker, New York, 1998), pp. 515–654.
8. A. M. Streltsov and N. F. Borrelli, "Study of femtosecond-laser-written waveguides in glasses," J. Opt. Soc. Am. B **19,** 2496–2504 (2002).
9. N. Leclerc, I. Serieys, and A.-J. Attias, "6-(Arylvinylene)-3-pyridinylboronic esters. Versatile building blocks for conjugated chromophores via Suzuki cross-coupling," Tetrahedron Lett. **44,** 5879–5882 (2003).
10. N. Lemaitre, A.-J. Attias, I. Ledoux, and J. Zyss, "New second-order NLO chromophores based on 3,3′-bipyridine: tuning of liquid crystal and NLO properties," Chem. Mater. **13,** 1420–1427 (2001).
11. N. Mataga and T. Kubota, *Molecular Interactions and Electronic Spectra* (Marcel Dekker, New York, 1970).
12. E. V. Keuren, H. Möhwald, S. Rozouvan, W. Schrof, V. Belov, H. Matsuda, and S. Yamada, "Linear and third order nonlinear optical properties of substituted oligothiophenes," J. Chem. Phys. **110,** 3584–3590 (1999).
13. R. Colditz, D. Grebner, M. Helbig, and S. Rentsch, "Theoretical studies and spectroscopic investigations of ground and excited electronic states of thiophene oligomers," Chem. Phys. **201,** 309–320 (1995).
14. M. Sheik-Bahae, A. A. Said, and E. W. Van Stryland, "High sensitivity, single beam n_2 measurement," Opt. Lett. **14,** 955–957 (1989).
15. M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, "Sensitive measurement of optical nonlinearity using a single beam," IEEE J. Quantum Electron. **26,** 760–769 (1990).
16. G. I. Stegeman, E. M. Wright, N. Finlayson, R. Seaton, and C. T. Seaton, "Third order nonlinear integrated optics," J. Lightwave Technol. **6,** 953–970 (1988).
17. M. Samoc, A. Samoc, B. Luther-Davies, Z. Bao, L. Yu, B. Hsieh, and U. Scherf, "Femtosecond Z-scan and degenerate four-wave mixing measurements of real and imaginary parts of the third-order nonlinearity of soluble conjugated polymers," J. Opt. Soc. Am. B **15,** 817–825 (1998).
18. H. S. Nalwa and S. Miyata, eds., *Nonlinear Optics of Organic Molecules and Polymers* (CRC Press, Boca Raton, Fla., 1997).
19. B. M. Pierce, "A theoretical analysis of the third-order nonlinear optical properties of linear cyanines and polyenes," in *Nonlinear Properties of Organic Materials IV*, K. D. Singer, ed., Proc. SPIE **1560,** 148–161 (1991).
20. C. W. Dirk, L.-T. Cheng, and M. G. Kuzyk, "A simplified three-level model describing the molecular third-order nonlinear optical susceptibility," Int. J. Quantum Chem. **43,** 27–36 (1992).
21. A. F. Garito, J. R. Heflin, K. Y. Yong, and O. Zamani-Khamiri, "Recent studies on the nonlinear optical properties of conjugated linear chains and rigid rod polymers," in *Nonlinear Optical Properties of Organic Materials*, G. Khanarian, ed., Proc. SPIE **971,** 2–10 (1988).
22. S. R. Marder, J. W. Perry, G. Bourhill, C. B. Gorman, B. G. Tiemann, and K. Mansour, "Relation between bond-length alternation and second electronic hyperpolarizability of conjugated organic molecules," Science **261,** 186–189 (1993).
23. S. R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J. L. Brēdas, and B. M. Pierce, "A unified description of linear and nonlinear polarization in organic polymethine dyes," Science **265,** 632–635 (1994).
24. S. R. Marder, W. E. Torruellas, M. Blanchard-Desce, V. Ricci, G. I. Stegeman, S. Gilmour, J.-L. Brēdas, J. Li, G. U. Bublitz, and S. G. Boxer, "Large molecular third-order optical nonlinearities in polarized carotenoids," Science **276,** 1233–1236 (1997).
25. J. Hein, H. Bergner, M. Lenzner, and S. Rentsch, "Determination of real and imaginary part of $\chi(3)$ of thiophene oligomers using the Z-scan technique," Chem. Phys. **179,** 543–548 (1994).
26. R. Rangel-Rojo, S. Yamada, H. Matsuda, and D. Yankelevich, "Large near-resonance third-order nonlinearity in an azobenzene-functionalized polymer film," Appl. Phys. Lett. **72,** 1021–1023 (1998).
27. Y. Lin, J. Zhang, L. Brzozowski, E. H. Sargent, and E. Kumacheva, "Nonlinear optical figures of merit of processible composite of poly(2-methoxy, 5-(2′-(ethyl)hexyloxy)-*p*-phenylene vinylene) and poly(methyl methacrylate," J. Appl. Phys. **91,** 522–524 (2002).
28. H. P. Li, C. H. Kam, Y. L. Lam, and W. Ji, "Femtosecond Z-scan measurements of nonlinear refraction in nonlinear optical crystals," Opt. Mater. **15,** 237–242 (2001).
29. K. Kiyohara, K. Kamada, and K. Ohta, "Orientational and collision-induced contribution to third-order nonlinear optical response of liquid CS_2," J. Chem. Phys. **112,** 6338–6348 (2000).
30. K. Kamada, M. Ueda, K. Ohta, Y. Wang, K. Ushida, and Y. Tominage, "Molecular dynamics of thiophene homologues in-

vestigated by femtosecond optical Kerr effect and low frequency Raman scattering spectroscopies," J. Chem. Phys. **109,** 10948–10957 (1998).

31. K. Kamada, M. Ueda, T. Sakaguchi, K. Ohta, and T. Fukumi, "Femtosecond optical Kerr study of heavy atom effects on the third-order optical nonlinearity of thiophene homologues: purely electronic contribution," Chem. Phys. Lett. **263,** 215–222 (1996).
32. D. Paparo, L. Marrucci, G. Abbate, E. Santamato, M. Kreuzer, P. Lehnert, and T. Vogeler, "Molecular-field-enhanced optical Kerr effect in absorbing liquids," Phys. Rev. Lett. **78,** 38–41 (1997).
33. P. P. Ho and R. R. Alfano, "Optical Kerr effect in liquids," Phys. Rev. A **20,** 2170–2187 (1979).
34. D. McMorrow, W. T. Lotshaw, and G. A. Kenney-Wallace, "Femtosecond optical Kerr studies on the origin of the nonlinear responses in simple liquids," IEEE J. Quantum Electron. **24,** 443–454 (1988).
35. Y. J. Chang and E. W. Castner, Jr., "Fast response from 'slowly relaxing' liquids: a comparative study of the femtosecond dynamics of triacetin, ethylene glycol, and water," J. Chem. Phys. **99,** 7289–7299 (1993).
36. Y. J. Chang and E. W. Castner, Jr., "Femtosecond dynamics of hydrogen-bonding solvents. Formamide and *N*-methylformamide in acetonitrile, DMF, and water," J. Chem. Phys. **99,** 113–125 (1993).
37. Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984), pp. 291–293.
38. R. W. Boyd, *Nonlinear Optics* (Academic, Boston, Mass., 1992), pp. 178–179.