Ultrafast nonresonant third-order optical nonlinearity of a conjugated 3,3′-bipyridine derivative from 1150 to 1600 nm

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A conjugated 3,3′-bipyridine derivative, an apolar structure of donor–acceptor–acceptor–donor (D–A–A–D) type was designed and characterized for third-order optical nonlinearity using Z-scan technique in the wavelength range of 1150–1600 nm. Z-scan spectra reveal a positive Kerr coefficient across this wavelength range with $n_2 = (4.6 \pm 0.7) \times 10^{-6}$ cm²/GW at 1550 nm accompanied by negligible nonlinear absorption for wavelength around 1550 nm, indicating ideal figures of merit for applications in ultrafast all-optical switching. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1584517]

Nonlinear optical processes have received considerable attention for applications in a variety of optoelectronic and photonic devices. Third-order nonlinear optical (NLO) phenomena are of interest in optical switching and signal processing.[1,2] For fast photonic applications with low-power sources, nonlinear media must simultaneously satisfy three main requirements: large nonlinear refractive index (n_2) at the operating wavelength, typically in the range 1.3–1.6 μm; minimal absorption losses due to one- or multiphoton absorption (hence precluding the use of resonant nonlinearity); and ultrafast nonlinear refractive index response and relaxation times (picoseconds or less).[3,4] π-Conjugated organic compounds have emerged as a promising class of third-order nonlinear optical materials because of their potentially large third-order susceptibilities associated with fast response time,[5–9] in addition to their variety and processibility.

Large values of molecular polarizability γ and third-order nonlinear optical susceptibility $\chi^{(3)}$ have previously been reported.[6,10] However, few organic materials reported to date provide suitable nonlinearity in the near infrared region. In many cases, the nonlinear refractive index n_2 ($n = n_0 + n_2 I$, n_0, linear part of the refractive index and I, incident light intensity) is often enhanced through one- or two-photon resonant transitions, when the absorption peak wavelength of the material lies sufficiently close to one or half of the operating wavelength. Such resonant enhancement of n_2 is accompanied by absorption losses, commonly given by $\alpha = \alpha_0 + \beta I$, where α_0 is the linear absorption coefficient and β is the nonlinear absorption coefficient. The NLO efficiency/transparency tradeoff (n_2/α) at a specific wavelength is therefore of primary importance for assessing the suitability of a material for all-optical integrated devices. This parameter is usually evaluated through two figures of merit:[3,6] $W = n_2 I / \alpha_0 \lambda$, and $T = \beta \lambda / n_2$. According to the requirements mentioned above, it is necessary to achieve $W \gg 1$ and $T \ll 1$.

In this letter we report the nonlinear properties and figures of merit of a 3,3′-bipyridine derivative characterized over the range 1150–1600 nm.

The conjugated material investigated in this letter is 6,6′-bis(5-hexyl-2-thienylvinylene)-3,3′-bipyridine with the molecular structure shown in Fig. 1. For infrared applications, nonresonant NLO molecules' one-photon absorption peak λ_{max} must lie sufficiently far into the UV-blue range to avoid two-photon transitions ($\lambda_{max} \ll \lambda/2$, where λ is the laser wavelength). The strategy for designing molecules according to these requirements has been reported in Ref. 11, and a new synthetic route has been developed[12] by modifying the one reported in previous articles.[13] The molecule exhibits an apolar structure donor–acceptor–acceptor–donor (D–A–A–D), in which the 3,3′-bipyridine core acts as the acceptor group (A–A) and the donor group (D) is a thiophene ring. The absorption spectra of the material dissolved in dichloromethane in the visible and near-infrared wavelength range are shown in Fig. 2, where the inset shows the range of 190–500 nm. The sample is absorbing over the range of 225–450 nm with the absorption peak located at 390 nm. There is essentially no absorption for wavelength longer than 450 nm.

The tunable laser for the measurement came from a picosecond Ti:sapphire amplified system, which consisted of four parts: femtosecond Ti:sapphire seed oscillator (Vitesse, Coherent Inc., output wavelength 800 nm, pulsewidth <100 fs, repetition rate 80 MHz, power 300 mW, pumped
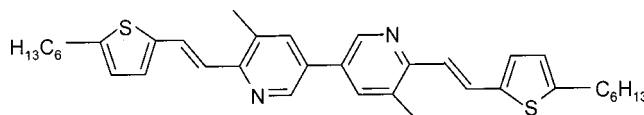

FIG. 1. Molecular structure of 6,6′-bis(5-hexyl-2-thienylvinylene)-3,3′-bipyridine investigated in this study.

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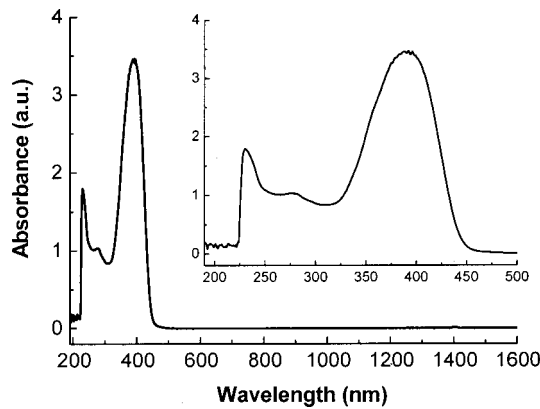
FIG. 2. Absorption spectra of 6,6′-bis(5-hexyl-2-thienylvinylene)-3,3′-bipyridine in dichloromethane.
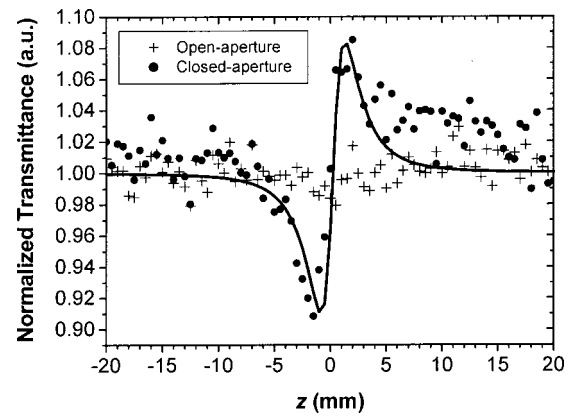

FIG. 3. Z-scan curves of the sample measured at the wavelength 1550 nm (power 0.8 mW): (+), open-aperture data; (•), closed-aperture data. The theoretical fitting of the measured closed-aperture data is shown as the solid line.

by a 1.4 W Verdi diode laser, Coherent Inc.), pump laser (Q-switched Nd:YLF laser, 527DP-S, Quantronix Corp., 527 nm, 150–220 ns, 1 kHz, and 15 W), picosecond Ti:sapphire regenerative and multipass amplifier (Titan-DP2-2, Quantronix Corp., 800 nm, ∼3.5 ps, and 1.8 W), and the optical parametric amplifier [traveling wave optical parametric amplification system (Topas), Light Conversion]. The Topas output came from the parametric superfluorescence within the nonlinear crystal BBO at pulsewidth 3.3 ps and repetition rate 1 kHz with good optical pulse spectra properties for both the signal and idler pulses over the entire tuning range. The signal and idler beams from Topas were separated using a wavelength separator. In the setup, an attenuation stage consisting of a set of cross-polarized polarizers with a $\lambda/2$ waveplate in the middle was employed to adjust the output power. Z scan and its interpretation are described in Refs. 14 and 15. The output from Topas was split into two components, one acting as a pump beam and the other, which has an intensity of <10% of the first beam, acting as the reference beam. After the focusing lens, two photodetectors simultaneously measured the closed-aperture (with an aperture just before the detector of aperture transmittance $S=0.015$) and open-aperture Z scans ($S=1$) when the sample moved in the vicinity of the laser waist through a linear translation stage.

For a temporal Gaussian pulse with an incident Gaussian transverse spatial profile, the on-axis transmission as a function of sample position relative to the lens focal point is[15]

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

where

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

in which I_1 is the peak on-axis irradiance. z_0 is the Rayleigh range of the beam, equal to $\pi \omega_0^2/\lambda$, where ω_0 is the beam waist at the lens focus. The effective sample length L_{eff}, which takes into account the linear absorption coefficient, α_0, can be expressed as $L_{\text{eff}} = (1 - e^{-\alpha_0 L})/\alpha_0$ with sample length L. The value of β can be obtained from a theoretical fitting performed on the experimental data of the open-

aperture measurement while the nonlinear refractive index n_2 can be obtained from the closed-aperture measurement.

By tuning the output wavelength of Topas, we measured Z-scan curves of the dichloromethane solution of the material (concentration 2.0×10^{-2} mole L^{-1}) in a quartz cuvette with laser power of 0.8 mW and obtained the spectra of nonlinear refractive index and nonlinear absorption in the wavelength range of 1150–1600 nm. Before measuring this sample, the system was calibrated using a standard CS_2 solution in a quartz cuvette (optical length 1 mm, same for all cuvettes used in this study) as reference. Measurement on the pure solvent sample in the cuvette was also performed under the same measuring conditions to verify that the valley peak in the Z-scan curves originated from the material, not from the solvent or cuvette. The measurement was carried out consecutively at a wavelength interval of 50 nm. Figure 3 shows the Z-scan curves (open and closed aperture) of the sample measured at 1550 nm. The theoretical fitting results of n_2 and β are given in Fig. 4. At 1550 nm, the open-aperture curve does not show any valley or peak indicating that no nonlinear absorption exists ($\beta=0$). Nonlinear least-square fitting with $\Delta\Phi_0$ and z_0 as variables yields $\Delta\Phi_0=0.58$ and $z_0=1.2$ mm. 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 $\Delta n = 1.43 \times 10^{-4}$ and Kerr coefficient $n_2 = (4.6 \pm 0.7)$
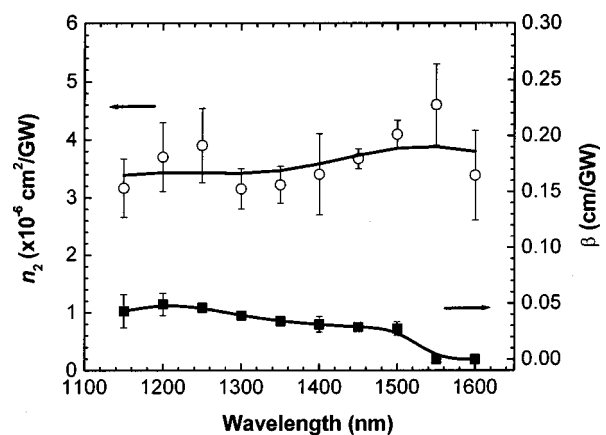

FIG. 4. Spectra of nonlinear refractive index n_2 and nonlinear absorption β of the sample in the wavelength range of 1150–1600 nm. Solid lines are guides for the eye.

$\times 10^{-6}$ cm^2/GW. In this wavelength region, the n_2 values lie between $(3.2$ and $4.6)\times 10^{-6}$ cm^2/GW while the β values decrease from about 0.05 cm/GW near 1150 nm to essentially zero for wavelength above 1550 nm. The nonlinear absorption at wavelength near 1150 nm could be attributable to multiphoton processes in view of the relationship between photon energy and transition energy. Since the material exhibits negligible one-photon absorption α_0 throughout this infrared region, the W values are ideal, i.e., $W \gg 1$. Due to nonlinear absorption for wavelengths near 1150 nm, the T values near 1150 nm are marginal. However, T values are satisfactory near 1550 nm ($T=0$).

Experiments on different π-conjugated push–pull and symmetric 3,3′-bipyridine derivatives showed significant differences in the nonlinear optical response depending on the molecular structural variations.[11] It has been proved that reducing 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, enhance the nonresonant n_2 value. The detailed comparison on the enhancement of optical nonlinearity of D–A–A–D structure with other molecular structures can be found in Ref. 11. 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 of LiNbO$_3$:MgO, KTA, KTP, BBO, and LBO.[16] The inclusion of an electron-rich thiophene ring producing a dramatic enhancement of n_2 can be qualitatively explained in a three-state model, on the basis of: (i) a large increase in the $e \rightarrow e'$ transition dipole moment ($\mu_{ee'}$), (ii) an increase in the $g \rightarrow e$ transition dipole moment (μ_{ge}), where g labels the ground state, and e and e' the two excited states, μ_{ij} is the dipole matrix element between the labeled states. 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.

In summary, third-order optical nonlinearity of a conjugated 3,3′-bipyridine derivative with the enhancement of nonlinearity by its symmetrical donor–acceptor–acceptor–donor (D–A–A–D) structure is investigated and found to possess ultrafast nonresonant nonlinearity around 1550 nm with excellent figures of merit. The study of the third-order optical nonlinearity over a wide infrared wavelength range gives clues as to structure–property relationships and, in the range 1300–1600 nm, is pertinent to applications in optical signal processing in communication systems.

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