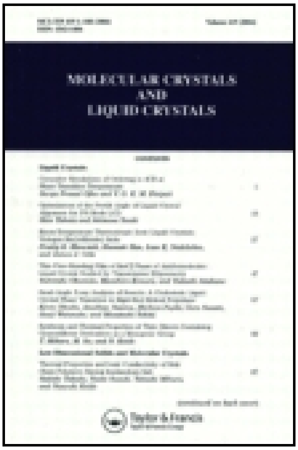

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Third-Order Nonlinear Optical Properties of a Stable Radical Species with Nitronyl Nitroxide Group

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Third-Order Nonlinear Optical Properties of a Stable Radical Species with Nitronyl Nitroxide Group

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We report third-order nonlinear optical properties of a stable radical species, 2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (PTIO). The nonresonant values of second hyperpolarizabilities measured by femtosecond Z-scan method at 780-857 nm were found to be negative. Wavelength dispersion of the hyperpolarizabilities is discussed referring to the theoretical predictions.

Keywords: third-order optical nonlinearity; nitronyl nitroxide; second hyperpolarizability

INTRODUCTION

Structure-property correlation of organic nonlinear optical (NLO) materials has attracted much attention due to future applications for photonics. In particular, a number of efforts have been made for elucidating the structure-property correlation of organic third-order NLO material, which has not been established. Exploring new potential molecular system for the third-order NLO materials and elucidating the mechanism of the nonlinear response are of importance, which lead one not only to establishing the structure-property correlation but also to better understanding of the interaction between matters and electromagnetic fields.

Molecules with nitronyl nitoxide (NN) group form unconventional class of photoactive molecules. The molecules are stable radical species and contain delocalized unpaired electrons. The delocalized radical system is considered to provide unique magnetic and optical properties. Awaga and Maruyama studied magnetic property of some NN derivatives and found *p*-nitrophenyl NN (NPNN) exhibits ferromagnetic phase at low temperature [1]. Nicoud *et al.* investigated the second-order optical nonlinearity of NPNN and discussed the correlation between NLO and magnetic properties [2]. For third-order NLO property, very recently, Yamada *et al.* made theoretical studies on several NN derivatives and reported that NN group may have negative static second hyperpolarizabilities γ and the nonlinearity is expected to be easily modified by substituting side groups[3, 4]. However, experimantal investigation of the third-order NLO properties of NN derivatives have never been reported to our best knowledge.

In this paper we report the third-order NLO properties of a phenyl NN derivatives, 2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (PTIO, inset of Figure 1). The near- and non-resonant γ values of PTIO are measured by Z-scan method with femtosecond pulses at the wavelengths from 780 to 857 nm. The wavelength dispersion of γ and comparison with static γ values obtained by theoretical calculations are discussed.

EXPERIMENTAL

Z-scan method is a sensitive single-beam technique developed by Sheik-bahae *et al*.[5] By using Z-scan method, one can determine sign, as well as magnitude, of both the real and imaginary parts of γ.

The femtosecond laser pulses used for the measurements were generated by Ti:sapphire regenerative amplifier operated at the repetition rate of 20 kHz, seeded by Ti:sapphire oscillator. Typical pulsewidth of the femtosecond pulses was 150 fs. Advantage of using femtosecond pulses for Z-scan method is simplification of nonlinear optical processes contributing to the observed response. Possibility of contribution from slow processes such as molecular orientational and thermal processes can be ruled out because they negligibly contribute to observed response during the femtosecond pulse duration.

The output beam from regenerative amplifier was divided with beam splitter and the small portion of the beam (~7 mW) was focused by lens and used for the measurement. The radial intensity profile was sufficiently close to the Gaussian shape. The radius of the beam and typical intensity at beam waist were 18.2 μm and 0.42 TW/cm^2, respectively. The beam passing an aperture placed after quartz sample cell was detected with a silicon photodiode and the signal was analyzed by a lock-in amplifier synchronized with femtosecond pulses. Long-time fluctuation of laser intensity was monitored by another lock-in amplifier also synchronized with the laser pulses.

Sample path length is 1 mm, which was in the same order of the Rayliegh range (z_R = 0.68 mm) of this setup. The path length can be regarded as optically 'thin' because the phase variation due to the nonlinear optical effect was very small in Z-scan experiment [5]. Methanol solution of PTIO was used for the measurements. PTIO (Tokyo Kasei) was used as received.

RESULTS AND DISCUSSION

UV-Visible Absorption Spectrum

Figure 1 shows UV-visible absorption spectrum of PTIO in methanol. In longer wavelengths, a weak (ε = 630 $M^{-1} cm^{-1}$) and broad absorption band centered 583 nm are observed. This band is shifted to longer wavelengths in benzene and is attributed to n-π* transition. The band consists of two peaks which are more prominent in benzene solution. The two peaks probably arise from weak splitting of the energy level of the two oxygen n orbitals[6]. The two bands in short wavelengths

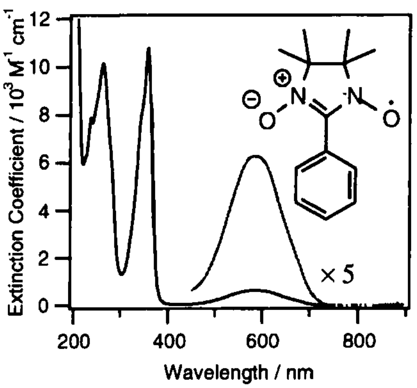

FIGURE 1 UV-visible absorption spectrum of PTIO in methanol.

(359 nm, ε = 11000 $M^{-1}cm^{-1}$; and 268 nm, ε = 10100 M^{-1} cm^{-1}) are considered to be due to π-π* transitions.

Z-scan traces

Z-scan experiments were performed in the wavelength range from 780 to 857 nm where no one-photon absorption is observed. Typical close-aperture Z-scan traces of PTIO/methanol solution (0.45 M) are shown in Figure 2. From the principle of Z-scan method, PTIO/methanol solution gives a *peak-valley* trace, exhibiting negative nonlinearity of the solution. On the other hand, pure methanol produces a weak *valley-peak* trace, which means methanol has positive nonlinearity. By subtracting the trace of pure solvent from that of the solution, the net Z-scan trace for PTIO are obtained, which indicates that PTIO has negative γ at the wavelengths.

From the peak-valley difference of normalized transmittance, $\Delta T_{p\text{-}v}$, of close-aperture traces, nonlinear refractive index change n_2 is obtained. Hence, γ can be determined from n_2 with considering density and local field correction. Figure 3 shows wavelength dispersion of the γ's. It should be noted that the minus direction of vertical axis is oriented upward in Figure 3. No detectable two-photon absorption signal was observed by open-aperture experiments in the same wavelength range. Absolute values of γ are evalu-

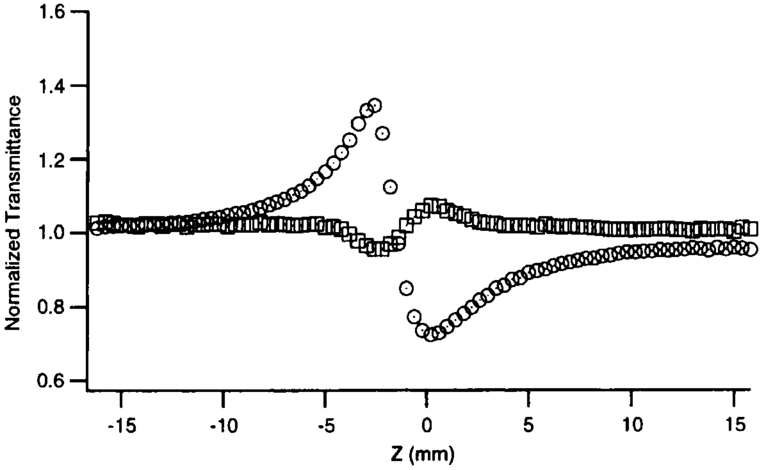

FIGURE 2 Z-scan traces of PTIO/methanol solution (O) and methanol (□).

ated by comparing with the known γ value of a high-refractive index glass (FD2)[7]. Within the observed wavelength range, γ is always negative, but the absolute value decreases with increasing wavelength. The relatively large value in shorter wavelength is considered to arise from one-photon resonance to n-π* band.

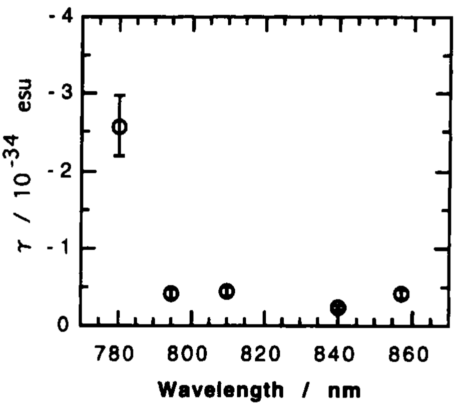

FIGURE 3 Dispersion of γ of PTIO.

Estimation of static γ

Theoretical consideration predicts that sign of static γ value can be negative for high polarizable centrosymmetric molecules. As NN moiety belongs to C_{2v} symmetry, γ_{xxxx} (the component along the O-N-C-N-O axis) can be negative. INDO coupled Hatree-Fock calculations for several PTIO derivatives reveal that static γ_{xxxx} is the largest component in absolute value and is negative for each derivatives[4]. The present result obtained by Z-scan experiment also indicates that near- and non-resonant γ's are negative values [4]. However, on considering consistency between the theoretical prediction and the experimental results, presumable inversion of sign of γ should be taken into account. From the sum-over-state (SOS) expression, γ for Z-scan process, i. e. $\gamma(-\omega; \omega, -\omega, \omega)$, can resonate at the wavelengths of one- and two-photon absorption. Sign of γ is inverted about the resonant wavelengths due to energy denominator in the SOS expression. For instance, if γ value is positive at wavelengths shorter than a resonant wavelength, it is negative at longer wavelengths. Our present result suggests that γ value is negative at wavelengths longer than that of one photon resonance. Therefore static γ value is still negative as long as there is no two-photon absorption in the wavelengths longer than 857 nm. Unfortunately, two-photon allowed levels of PTIO are still unknown, so we cannot definitively conclude the consistency between the theory and the experimental results. Further studies on the two-photon allowed levels of NN-contain γ molecules are needed to solve the problem.

Comparison with polyenes and cyanins

The observed absolute γ values for PTIO are in the order of 10^{-35}~10^{-34} esu. These values are one or two order larger than those of molecules with similar size unsaturated chain (2,5-dimethyl-2,4-hexadiene, $\gamma = 4.9 \times 10^{-36}$ esu;

$(H_3C)_2N$  $N^+(CH_3)_2\ Cl^-$,0.53×10^{-36} esu; measured by THG method at 1908 nm)[8]. Comparison of γ obtained between different methods and wavelengths is very difficult; nevertheless, the γ of PTIO is considered to be larger than those of the molecules. This relatively large absolute value of γ presumably originates from charge transfer character of NN group.

CONCLUSION

In this paper, we reported the third-order NLO properties of PTIO, one of stable radical species with NN group, for the first time to our best knowledge. The γ values were measured by femtosecond Z-scan method and were found to be negative and in the order of 10^{-35}~10^{-34} esu in absolute value. The negative values of γ are of interest in terms of comparison with theoretical prediction as well as applications for tuning nonlinearity, but further study on two-photon allowed level is needed to clarify the consistensy.

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