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Third-order Optical Nonlinearities of Asymmetric Carbocyanine Dyes

Hidetsugu IKEDA, Toshio SAKAI, and Kenji KAWASAKI
Central Research Laboratories, Idemitsu Kosan Co., Ltd., 1280 Kami-izumi, Sodegaura, Chiba 299-02

Asymmetric carbocyanine dyes were synthesized and their third-order optical nonlinearities in solutions were investigated by using degenerate four-wave mixing technique. Large third-order hyperpolarizabilities of electronic origin up to 10^{-28} esu were observed and the advantage of asymmetric structures was demonstrated.

Nonlinear optics (NLO) is expected to play a significant role in future technology of optical signal processing (e.g. frequency up-conversion, electro-optic modulation, or optical switching) and optical computing. Second-order optical nonlinearities have been comparatively well studied in spite of the rareness of non-centrosymmetric materials. The origin of the second-order optical nonlinearities in organic conjugated molecules is fairly well explained by distortion of π-electrons induced by an electron donating group (donor) and an accepting group (acceptor), in other words the anharmonic oscillation of distorted π-electrons.1) According to this molecular design, many organic molecules have been investigated2) and the assignment of optimizing their crystalline structures or morphology of doped polymers, including phase-matchability, has been made a certain progress as the future device of harmonic generators. On the other hand, third-order optical nonlinearities have been less studied, though it should be inevitable for ultra-fast optical switching devices such as optical Kerr cell or optical bistable plate. Most of the interest so far in the third-order NLO materials has concentrated around the electron-conducting polymers e.g. polythiophenes,3) poly-p-phenylene-vinylenes,4) or polydiacetylenes,5) and intermolecular charge transfer (CT) salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF).6,7) The obtained NLO coefficients for these materials, however, were macroscopic susceptibilities which were not suitable for molecular designs of better NLO materials. Therefore the fundamental studies on the relationship between molecular structures and the third-order optical nonlinearities should be done in small molecules because the sufficient molecular designs for the third-order NLO materials have never been found yet.8) For example some efforts to find substitution effects have been made in chlorophenols9) and nitroanilines,8) however no simple relationship between substituents' position and the third-order hyperpolarizabilities has been found.

Hermann has investigated the third harmonic generation (THG) in symmetric carbocyanine dyes10) and demonstrated a drastic enhancement of $\gamma(-3\omega; \omega, \omega, \omega)$ with increasing conjugation length. This result revealed that the effective delocalization of π-electrons occurred by an introduction of cationic charge into polyenic chain and enhanced $\gamma(-3\omega; \omega, \omega, \omega)$ since the reported $\gamma(-3\omega; \omega, \omega, \omega)$ for 3,3'-diethylthiatricarbocyanine methylsulfate was larger than that of retinol11) in two orders of magnitude while both of them have 5 double bonds. Rustagi et al.12) have carried out the theoretical calculations of the third-order hyper-

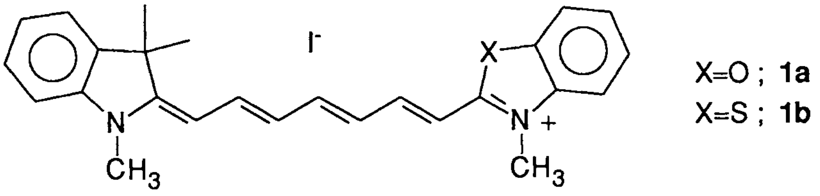

Fig. 1. Molecular structures of asymmetric carbocyanine dyes.

polarizabilities in cyanine dyes and pointed out the importance of anharmonic oscillation of π-electrons. In the previous paper,[13] we have also demonstrated that an introduction of donor or acceptor into polyenic chains, i.e. asymmetric structures, enhanced $\gamma(-\omega; \omega, -\omega, \omega)$. In the present paper, we have synthesized asymmetric carbocyanine dyes, which are expected to induce an anharmonic oscillation of π-electrons and to give large $\gamma(-\omega; \omega, -\omega, \omega)$, and investigated their third-order optical nonlinearties by using degenerate four-wave mixing (DFWM).

The molecular structures of asymmetric carbocyanine dyes are depicted in Fig. 1. They were synthesized according to the literature method,[14] where N-methyl-2-(6-acetanilido-1,3,5-hexatrienyl)-benzoxazolium (or benzothiazolium) iodide were prepared as a intermediate followed by a condensation with 1,3,3-trimethyl-2-methyleneindoline.

DFWM was used to evaluate $\gamma(-\omega; \omega, -\omega, \omega)$ values of the dyes. The experimental setup in detail was described elsewhere.[13] The second harmonics (532 nm) of a Q-switched Nd:YAG laser was used as a light source. It should be noted that thermal grating was avoided by the cross-polarization configuration and thus the obtained $\gamma(-\omega; \omega, -\omega, \omega)$ was of electronic origin. A sample dissolved in dimethylsulfoxide (DMSO) at the concentration about 10^{-3} mol/l was placed in a 1-mm-thick quartz cell. $\gamma(-\omega; \omega, -\omega, \omega)$ values were obtained by the pump-beam intensity dependence of the phase conjugated reflectivity from the comparison with the value for CS_2 [$\chi^{(3)}(-\omega; \omega, -\omega, \omega)=1.6 \times 10^{-12}$ esu].[15]

The obtained $\gamma(-\omega; \omega, -\omega, \omega)$ values for the dyes are listed in Table 1 together with the visible absorption maxima (λmax) in DMSO solutions. Asymmetric structures have small effect on λmax because the λmax values of asymmetric dyes located between symmetric ones, of which λmax values in DMSO solutions were observed as 750 nm, 700 nm, and 770 nm for 1,1',3,3,3',3'-hexamethyl-2,2'-indotricarbocyanine iodide, 3,3'-diethyl-2,2'-oxatricarbocyanine iodide, and 3,3'-dimethyl-2,2'-thiatricarbocyanine iodide, respectively. Benzothiazole derivative (**1b**) produced a bathochromic shift of 40 nm compared with the corresponding benzoxazole one (**1a**). Large $\gamma(-\omega; \omega, -\omega, \omega)$ values of 10^{-28} esu were observed in asymmetric carbocyanine dyes. The $\gamma(-\omega; \omega, -\omega, \omega)$ of **1b** would be converted to the third-order susceptibility of $\chi^{(3)}(-\omega; \omega, -\omega, \omega)=3 \times 10^{-8}$ esu for a 0.1 mol/l solution, which was comparable to that of BEDT-TTF/I_3 [$\chi^{(3)}(-\omega; \omega, -\omega, \omega)=5 \times 10^{-8}$ esu],[6] the largest $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ ever investigated. One should be careful for resonance enhancement when comparing $\gamma(-\omega; \omega, -\omega, \omega)$ values since $\gamma(-\omega; \omega, -\omega, \omega)$ was enhanced in some orders of magnitude when measuring wavelength was within an absorption band. The resonance enhancement is determined mainly by an energy detuning ($\Delta\omega$) between the transition energy to the first excited state and a laser photon. The absorption spectrum of **1b** was

Table 1. Third-order hyperpolarizabilities at 532 nm and visible absorption maxima

Molecules	λmax(log(ε)) / nm	$\gamma(-\omega; \omega, -\omega, \omega)$ / esu
1a	720 (5.2)	3.0×10^{-28}
1b	760 (5.1)	5.4×10^{-28}

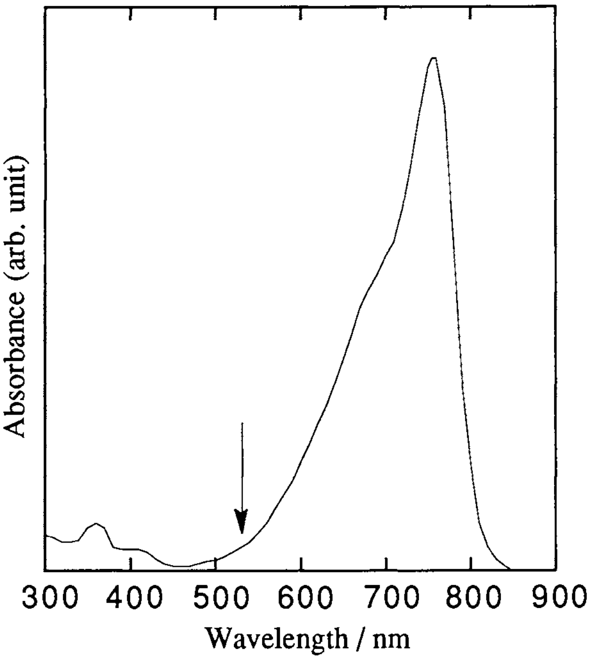

Fig. 2. Visible absorption spectrum of **1b**.
The arrow in the figure shows the laser wavelength (532 nm).

depicted in Fig. 2. The measuring wavelength (532 nm) was located at the edge of the large absorption band ($\Delta\omega$=0.70 eV) and thus the observed $\gamma(-\omega; \omega, -\omega, \omega)$ was less influenced by the resonance enhancement. The $\gamma(-\omega; \omega, -\omega, \omega)$ value of **1b** was larger than that of the corresponding symmetric dye, 3,3'-diethyl-2,2'-thiatricarbocyanine iodide [$\gamma(-\omega; \omega, -\omega, \omega)$=6.4 x 10^{-30} esu, $\Delta\omega$=0.51 eV] obtained from the DFWM measurement.[16)] This result suggests an advantage of asymmetric structures for optical nonlinearities, while the linear optical properties (λmax) has not changed largely compared with the corresponding symmetric dyes as mentioned above. The $\gamma(-\omega; \omega, -\omega, \omega)$ value of **1b** was larger than that of **1a**, though $\Delta\omega$ of **1b** was larger than that of **1a** and thus the $\gamma(-\omega; \omega, -\omega, \omega)$ of **1b** was less enhanced resonantly compared with that of **1a**. This phenomenon was attributed to the difference in electron donating property between oxygen and sulfur. The strong electron donating property of oxygen formed a local CT in oxazole ring preferably than along the main conjugated chain.

In conclusion, an introduction of asymmetric structure to cyanine dyes has enhanced $\gamma(-\omega; \omega, -\omega, \omega)$ in a few orders of magnitude to give the very large $\gamma(-\omega; \omega, -\omega, \omega)$ of 10^{-28} esu. Though heterocycles in carbocyanine dyes have some effects on γ (−ω; ω, −ω, ω), they were relatively small.

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