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Large third-order optical nonlinearity realized in symmetric nonpolar carotenoids

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We show that a very large enhancement of third-order optical nonlinearity (γ) of π-conjugated molecules can be realized without a major redshift of the absorption spectrum that disturbs optical transparency in the visible region. By changing the number (n) of C=C bonds of β carotene ($n=11$) from 7 to 15, a remarkable 3.4-fold increase in the γ value was observed when $n=15$ relative to that of β carotene. This enhancement of γ mainly originates from three-photon resonance of a lowest optically allowed excited state. The controversial higher-lying essential state is not important for generating the large value of γ.

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Large optical nonlinearity has attracted much attention for applications in optical devices. The configuration and conformation of carotenoids, which is a typical π-conjugated molecule, are well characterized compared to π-conjugated polymers; therefore, the mechanism that produces the large optical nonlinearities in carotenoids have been extensively studied.[1–10] For example, it has been shown that introduction of polar functional groups into carotenoids is a promising way to enhance their optical nonlinearity.[9,10] This increase in the magnitude of the optical nonlinearity, however, has the unfortunate side effect of losing optical transparency in the visible wavelength region. The work described here is motivated by finding other strategies that simultaneously improve the magnitude of the optical nonlinearity and such serious side effects of losing transparency.

In this Rapid Communication, we show that the third-order optical nonlinearity of carotenoids can be greatly enhanced by merely adding more C=C conjugated double bonds (n) to β carotene. The optical nonlinearity of the homologs of β carotene (symmetric nonpolar carotenoids, see Fig. 1) can be comprehensively described with a three-state model comprising the ground state S_0 ($1\,{}^1A_g^-$: classified on the basis of the C_{2h} point symmetry), the one-photon allowed state S_2 ($1\,{}^1B_u^+$), and the higher-lying one-photon forbidden state, S_m ($m{}^1A_g^-$), which is a controversial state that has been claimed to be essential for creating the large optical nonlinearity in carotenoids.[3,6–9] Our theoretical analyses show that the large optical nonlinearity in the nonpolar symmetric carotenoids can be achieved without the S_m state. Rather the enhancement of the optical nonlinearity in these carotenoids mainly results from the three-photon resonance of the transition from S_0 to S_2. In the case of the asymmetric polar carotenoids the same three-state model is applied to account for the third-order optical nonlinearity,[9] but in this case the origin of the enhancement is due to the strong electronic coupling between the S_2 and S_m states. Thus changing n gives another way to dramatically enhance the third-order optical nonlinearity in carotenoids without sacrificing optical transparency in the visible region.

The β-carotene homologs were synthesized and purified as described in a previous report.[11] They were doped into polystyrene films, which were spin coated onto a fused silica substrate. The carotenoid's concentration was determined from its maximum absorption. Stylus profilometry showed that the film thickness was typically between 0.04–0.06 μm. Third harmonic generation (THG) maker fringes were measured at each excitation wavelength.[7,8] A pulsed Nd:yttrium aluminum garnet (YAG) laser pumped optical parametric oscillator (Spectra-Physics, MOPO-PO, Quanta-Ray Pro 250–10) was used as the light source. The fringes were analyzed in the manner of van Beek *et al.*[8] in order to determine the second molecular hyperpolarizability (γ) and its phase. The $\chi^{(3)}$ value of the fused silica substrate was taken as 1.4×10^{-14} esu and used as a reference.[12]

Figures 1(a)–1(e) show the absorption spectrum of each homolog in the polymer matrix. The main absorption peaks in the spectra are due to the transitions to the S_2 state. The energy of the S_2 state decreases as n increases.[13] Figs.

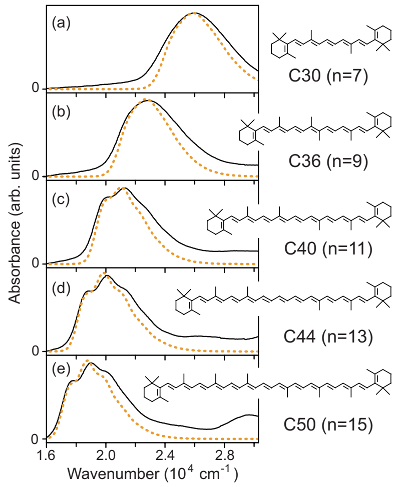

FIG. 1. (Color online) The experimental (solid line) and simulated (dotted line) absorption spectra of (a) C30, (b) C36, (c) C40, (d) C44, and (e) C50, respectively. The chemical structure of each homolog is shown in the inset with their respective conjugation lengths n.

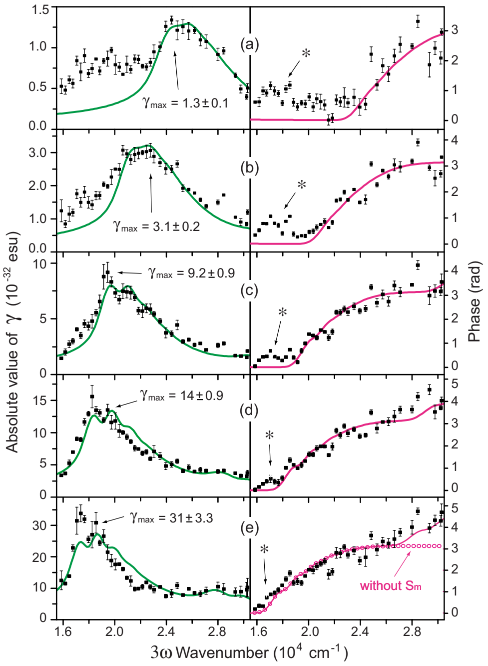

FIG. 2. (Color online) The experimental (square dots) and simulated (solid line) γ and phase spectra of (a) C30, (b) C36, (c) C40, (d) C44, and (e) C50, respectively. The left-hand side shows the γ spectrum, while the right-hand side shows the phase spectrum. The symbol (*) indicates the experimental artifact (Refs. 14 and 15). The simulated phase spectrum of C50 without including the S_m state is shown in Fig. 2(e) by the open circles.

2(a)–2(e) show the γ and phase spectra of each homolog. One can clearly see the strong enhancement of $\gamma_{\max}$ (the γ measured at the peak[14]) from 1.3×10^{-32} to 31×10^{-32} esu as n increases from 7 to 15. The latter value is 3.4 times higher than that of β carotene (9.2×10^{-32} esu), which itself shows one of the largest optical nonlinearities ever reported.[1,9] This is an unexpectedly large increase as a result of just extending the number of conjugated C=C double bonds in a typical nonpolar symmetric carotenoid such as β carotene.

Previously such large optical nonlinearity has been generated by the introduction of electron donors and/or acceptors at the ends of the conjugation chain.[1,2,9,10,16] Marder *et al.*[9] have reported that large enhancement of $\gamma_{\max}$ can be achieved by introducing strong electron acceptors. They prepared several polar carotenoids having different functional groups. Their $\gamma_{\max}$ values increased as the wavelength of the linear absorption maxima ($\lambda_{\max}$) of their derivatives were much more strongly redshifted, as shown in Fig. 3(a), in contrast to the homologs we used in the present study. Here we have also plotted our results of $\gamma_{\max}$ as a function of $\lambda_{\max}$. The values of $\gamma_{\max}$ of our homologs are proportional to $(\lambda_{\max})^{10.3}$, while those of Marder *et al.*'s samples are proportional to $(\lambda_{\max})^{6.6}$. Notably the sharper increase in γ provides the transparency over the wide spectral region. Therefore our finding has potential benefits for applications in devices.

Samuel *et al.*[17] reported a similar range of the optical nonlinearity using *m*-phenylene-vinylene-type oligomers. In their study, γ values, which were comparable to our results,

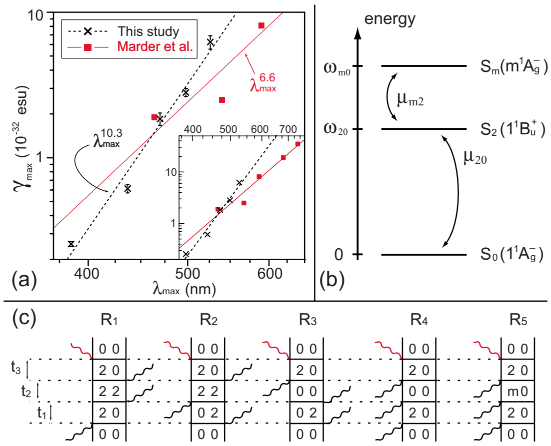

FIG. 3. (Color online) (a) Log-log plot of the $\gamma_{\max}$ values of the homologs and of the Marder's asymmetric polar carotenoids (Ref. 9) as a function of $\lambda_{\max}$. Our values of $\gamma_{\max}$ are rescaled to theirs by taking account of the local-field correction factor, which in their paper was taken as unity. The inset shows their data in the range above 650 nm. (b) The energy diagrams of the homologs used in the simulations. ω_{20} and ω_{m0} are the S_2-S_0 and S_m-S_0 transition frequencies, respectively. μ_{20} and μ_{m2} are the coupling strengths of S_2-S_0 and of S_2-S_m, respectively. (c) The double-sided Feynman diagrams of the THG process used in our simulations. Here 0, 2, and m indicate the S_0, S_2, and S_m states, respectively. Black and gray (or red online) wavy lines indicate ω and 3ω photons, respectively.

were realized in quite large oligomers ($n=50-100$), in contrast to number of theoretical predictions that the cubic nonlinearity would be more rapidly increased with respect to n. They ascribed this inconsistency to the molecular structure of their sample, i.e., a *cis* linkage, existed in π-conjugated double bonds, diminishes the electron delocalization. Therefore the β-carotene homologs can be regarded as a more idealistic π-conjugated system for studying optical nonlinearity because they have no bond discontinuities within their polyenic chain.

In order to clarify the mechanism that gives rise to the large optical nonlinearity in the present homologs, we have made theoretical simulations based on time-dependent perturbation theory. In this theoretical framework, any time-domain or frequency-domain spectroscopic signal can be calculated using a set of response functions. Since these response functions describe the time evolution of the molecule's polarization, frequency-domain optical spectra can be derived from the half-Fourier transform of the response functions.[18] Thus a correct description of the response functions for the THG process should be sufficient to allow the γ and phase spectra to be calculated.

Figures 3(b) and 3(c), respectively, show an energy diagram of the homologs and double-sided Feynman diagrams of the THG process, which remain under the following two conditions: (1) The first photon always makes coherence between the S_2 and S_0 states because only the S_2 state can be accessed from S_0 due to symmetry considerations. (2) The ground-state population must always be created after the final interaction because the emitted 3ω photon must fulfill the resonance condition. Based on the density-matrix formalism, after the coherence between the S_0 and S_2 states ($|2\rangle\langle 0|$ or

$|0\rangle\langle 2|$) is created by the first interaction, the populations of the S_2 ($|2\rangle\langle 2|$) and the S_0 ($|0\rangle\langle 0|$) states are created by the pathways R_1–R_4. Those populations then proceed to make again coherence between the S_2 and S_0 states [$|2\rangle\langle 0|$ or $|0\rangle\langle 2|$, see Fig. 3(c)]. Then this coherence reaches the S_0 population ($|0\rangle\langle 0|$) by the final interaction. On the other hand, the pathway R_5 is a *population free* process. By this pathway, after the first interaction, the S_2-S_0 coherence ($|2\rangle\langle 0|$) is generated and then the second interaction generates S_m-S_0 coherence ($|m\rangle\langle 0|$). After the third photon has interacted with the system the density matrix will again form coherence between S_2 and S_0 ($|2\rangle\langle 0|$) because the subsequent interaction (emission of 3ω photon) will then generate the ground-state population.

Using a Brownian oscillator model,[18,19] the mathematical expressions of the response functions R_1–R_5 are given by

$$S^{(3)}_{\mathrm{THG}}(t_3,t_2,t_1)=\sum_{i=1}^{5}R_i(t_3,t_2,t_1), \tag{1a}$$

$$R_1=R_4=|\mu_{20}|^4\exp[-i\omega_{20}(t_1+t_3)]\exp[-g(t_1)-g(t_3)], \tag{1b}$$

$$R_2=R_3=|\mu_{20}|^4\exp[i\omega_{20}(t_1-t_3)]\exp[-g^*(t_1)-g(t_3)], \tag{1c}$$

$$\begin{aligned}R_5={}&|\mu_{20}|^2|\mu_{m2}|^2\exp[-i\omega_{20}(t_1+t_3)-i\omega_{m0}t_2]\\&\times\exp[-g(t_1)-g(t_2)-g(t_3)].\end{aligned} \tag{1d}$$

Here $g(t)$ is a line-broadening function.[19] The parameters in these equations are defined in the caption of Fig. 3. We have ignored any correlations between the three time durations t_1, t_2, and t_3 (fast modulation limit[18]). The response functions R_1–R_5 assume that the collective nuclear coordinate between any two states can be satisfactorily represented by the coordinate between the S_0 and S_2 states. The linear absorption spectra were calculated as described previously.[19,20] The second hyperpolarizability γ with its phase term $e^{i\psi}$ can be obtained from

$$\begin{aligned}\gamma e^{i\psi}\propto{}&-\int_0^\infty dt_3\int_0^\infty dt_2\int_0^\infty dt_1[S^{(3)}_{\mathrm{THG}}(t_3,t_2,t_1)\\&-S^{(3)*}_{\mathrm{THG}}(t_3,t_2,t_1)]e^{i3\omega t_3}e^{i2\omega t_2}e^{i\omega t_1}.\end{aligned} \tag{2}$$

The results of these simulations are shown in Figs. 1 and 2. The parameters used in the simulations are summarized in Table I. The simulations of the absorption spectra are in good agreement with the experimental ones (Fig. 1). The small discrepancy at the low-energy wavelength edge is due to reflections at the surface of the film (a correction for these reflections has not been applied).[21] Although another optically allowed excited state appears on the higher-energy side of the S_2 state in the spectrum of C50 (see the peak around 30 000 cm^{-1}), this state can be ignored because of the lack of its contribution to the nonlinear optical response. The simulated γ and phase spectra also show good agreement with the experimental data.[15]

We can see the presence of the S_m state in the β-carotene homologs and the dependence of its energy level on n. The phase spectra are particularly sensitive to contributions from the S_m state. The phase spectra of C30 and C36 can be reproduced using only two states, i.e., the S_0 and S_2 states [see Figs. 2(a) and 2(b)]. In these cases the contribution of the S_m state is quite small in our energy region of interest because the two-photon resonances with the S_m state will occur far above our experimental energy region (e.g., 33 000 cm^{-1} for C36). In the case of the other three carotenoids, the contributions of the S_m state must be considered [see Figs. 2(c)–2(e)] because the phase still increases from π in the spectral range of above 26 000 cm^{-1}. A simulated phase spectrum of C50 without including the contribution of the S_m state is shown in the right-hand panel of Fig. 2(e).

TABLE I. The parameters used for the theoretical simulations. We have assumed ω_B=200 cm^{-1} and γ_B=200 cm^{-1} for every homolog (Ref. 20). λ_B, ω_B, and γ_B are, the coupling strength, the central frequency, and the linewidth of a lower-frequency Brownian oscillator, respectively. Δ_{in} and Γ_{HWHM} (where HWHM stands for half-width at half maximum) are the inhomogeneous broadening and the linewidth of a higher-frequency Brownian oscillator, respectively. They have been defined in Ref. 19 (We have omitted the solvation reorganization energy described in this reference in order to set ω_{20} to the value of the conventional 0–0 excitation energy.) Note that ω_{m0} and μ_{m2}/μ_{20} of C30 cannot be determined because the two-photon resonance at its S_m state is outside of our experimental frequency range.

Parameters	C30	C36	C40	C44	C50
ω_{20} (10^4 cm^{-1})	2.39	2.10	1.94	1.82	1.72
ω_{m0} (10^4 cm^{-1})		2.20	2.03	1.93	1.86
μ_{m2}/μ_{20}		0.55	0.55	0.65	0.75
Δ_{in} (cm^{-1})	500	450	300	290	290
λ_B (cm^{-1})	650	550	490	420	370
Γ_{HWHM} (cm^{-1})	5	4	4	7	8

A similar three-state model can also be used to take account of the large optical nonlinearity of the asymmetric polar carotenoids.[9,22] In this case the electronic coupling of the S_2 and S_m states plays a crucial role in generating the large optical nonlinearity. On the other hand, the strong enhancement of $\gamma_{\max}$ in the present set of carotenoids comes from a simple three-photon resonance to the S_2 state. The contribution of the two-photon resonance to the S_m state to the magnitude of $\gamma_{\max}$ is less than 20% even in C50, in which the largest value of μ_{m2} is observed (see Table I).

Our detailed theoretical analyses have clarified the nature of the S_m state, which has been a controversial issue in the interpretation of the THG spectrum of a π-conjugated molecule,[6–8] e.g., its energy location and/or the strength of its coupling to the S_2 state. The S_m state is determined to be located slightly ($\sim$1000 cm^{-1}) above the S_2 state and to be weakly coupled ($\mu_{m2}/\mu_{20}\sim 0.6$) to the S_2 state. The S_m state accounts for the nonzero small γ values in the high-energy spectral region of the γ spectra, which still remain above the S_2 resonance (above 22 000 cm^{-1} in the C50s spectrum, for example). The S_m state does not have a large contribution to the $\gamma_{\max}$ value (less than 20%) as stated above. We thus conclude that the strong enhancement of $\gamma_{\max}$ in the nonpolar carotenoids comes from a simple three-photon resonance of the S_2-S_0 transition. It should be noted that our result is derived from the systematic study on the dispersion of γ with respect to the length of the pure-polyenic conjugated chain. There have been a number of studies that claim the importance of the "essential" state,[1–8,16,23] but the effect of the essential state on the relationship between the dispersion of γ and the length of pure-polyenic structure is still uncertain. Our present study provides comprehensive information on the dependence of the character of the essential state on the length of pure-polyenic structure and shows that in this case the essential state is of minor importance.

This simple mechanism of the three-photon resonance enhancement of γ in the symmetric nonpolar carotenoids by increasing n has the advantage that it can enlarge the optical nonlinearity dramatically while retaining optical transparency in the visible region. It should be emphasized that our finding does not diminish the importance of introducing polar functional groups to a polyenic chain in order to induce large optical nonlinearity since this method can also be applied to relatively short carotenoids with low values of n. Rather the strong coupling of the S_2 and S_m states seems more suitable to get closer to the fundamental limit of the magnitude of γ described in recent reports.[16,23] In this context, there may be a possibility in the future that one can realize much larger γ values, together with the same range of wide transparency of the present carotenoids, by increasing μ_{m2}.

In summary, we have shown that a very large enhancement of γ of the nonpolar symmetric carotenoids can be obtained by increasing n a rather small amount. A systematic study about the dependence of the γ and phase spectra of a group of β-carotene homologs on n have led us to the detailed understanding of the THG response of these carotenoids. Our theoretical simulations based on time-dependent perturbation theory were able to show that a three-state model consisting of S_0, S_2, and S_m is sufficient for accurately describing the THG process in the homologs used in the present study as well as the data previously obtained with some asymmetric polar carotenoids.[9] It was shown that the controversial higher-lying essential state, S_m, is not important for generating the large value of $\gamma_{\max}$ in our nonpolar symmetric carotenoids. Moreover the strong enhancement of $\gamma_{\max}$ in the case of β-carotene homologs mainly originates from three-photon resonance of the S_2 state. Thus changing n provides another way to greatly enhance optical nonlinearity in carotenoids without having to introduce polar constituents.

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[14] The largest γ value of C50 is actually 34×10^{-32} esu and is located at around 17 300 cm^{-1}. This γ value is, however, anomalously enhanced compared with the simulated result. The disagreement is accounted for the effect of the experimental artifact, which has been marked in the phase spectra (Ref. 15). For this reason, we consider that the experimental $\gamma_{\max}$ of C50 is located at 18 550 cm^{-1} (31×10^{-32} esu), at which the simulated γ spectrum also has its maximum.

[15] In the phase spectra, an experimental artifact is observed at the same energy region in every homologue. The origin of this artifact is not clear. However, we believe that it is an artifact because at the energy at which it is located the homologues do not have any absorption and so the phase angle would be expected to be zero.

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