Hyper-Rayleigh scattering of thiophene-incorporated polyene chromophores with π-configuration locking

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Abstract

The hyper-Rayleigh scattering (HRS) technique is used to determine and compare the first hyperpolarizabilities (β) of thiophene-incorporated polyene chromophores with and without a configuration locked trans-triene bridge. To ensure the purity of the HRS signal, special attention is paid to its dependence on the fundamental intensity and the spectral content of the scattered radiation including the two-photon absorption induced fluorescence. From the HRS results, it is found that the configuration-locked trans-triene bridge enhances the β values of the chromophores studied. The β-enhancement is more pronounced when the electron acceptor $CHC(CN)_2$ in the chromophores is replaced with $C_2(CN)_3$. © 1997 Elsevier Science B.V.

1. Introduction

Conjugated organic chromophores capped with electron donor and acceptor groups are known to have good electro-optical (E-O) properties such as large second-order optical susceptibility. These molecules also have low dielectric constants and display a large optical damage threshold. For these reasons, much research activity has been made on these molecules to search for possible applications in second harmonic generation, frequency conversion and E-O modulation [1,2]. The second-order optical susceptibility of such an organic material is intrinsi-

cally related to the molecular first hyperpolarizability β. Organic chromophores with large and stable β are thus very important for the development of non-linear optical (NLO) devices.

It has been shown that a large nonlinearity can be achieved either by employing hetero-aromatic rings in chromophores, whose aromatic stabilization energy is lowered upon charge separation [3,4], or by using an extended polyene π-bridge system capped by strong electron acceptors [5]. The incorporation of these chromophores into polymer matrices and subsequent alignment of these guest/host systems using an externally applied electric field have led to large electro-optic coefficients ($r_{33} = 45-55$ pm/V) at 1.3 μm [6,7]. These r_{33} values are larger than the value of 31 pm/V for commercially available $LiNbO_3$.

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However, the long-term alignment stability of these E-O polymer systems was limited due to the low inherent thermal stability of these chromophores for temperatures up to 175°C, which also prevents them from being processed and poled at higher temperatures. Thus, in addition to optimizing the molecular β value in the design and synthesis of NLO chromophores [5,8–11], attention must also be paid to their thermal stability so that they will survive material processing and device fabrication [12,13]. Recently, Shu et al. developed a facile approach to the synthesis of NLO chromophores with enhanced thermal stability [14,15]. This synthetic method takes advantage of using the thiophene ring and the triene as efficient conjugating moieties to ease charge separation. It also incorporates conjugated ethylenic bonds into a 6-membered ring system to provide the configuration-locked geometry of trans-triene, thereby preventing the thermally induced cis–trans isomerization process [14,15].

Hyper-Rayleigh scattering (HRS) has been shown to be a useful technique for characterizing the chromophore β values [16–23]. It is more straightforward than the electric field induced second harmonic generation (EFISH) technique. Furthermore, it can also be applied to ionic chromophores, octopolar molecules [21], polymers and proteins [18], to which the EFISH technique cannot be applied. Recently, HRS from some molecules excited by 1.064 μm radiation has been found to be accompanied by two-photon absorption (TPA) induced fluorescence [24–26]. Consequently, the β value, which is determined by the usual HRS technique without making appropriate corrections for contribution from the TPA induced fluorescence, could be too large. The TPA induced fluorescence can be discriminated by using a femtosecond laser with a pulse width much shorter than the fluorescence lifetime (usually nanoseconds), and ultra-fast gating electronics [27]. Alternatively, a long-wavelength laser such as the Raman–Stokes shifted line at 1.907 μm can be used to eliminate the TPA induced fluorescence [28]. However, these techniques suffer from either complex experimental apparatus [27] or reduced scattering efficiency and hence signal to noise [28]. Without invoking any of these methods, we have shown how one can correct for the TPA induced fluorescence in our previous studies [25,26].
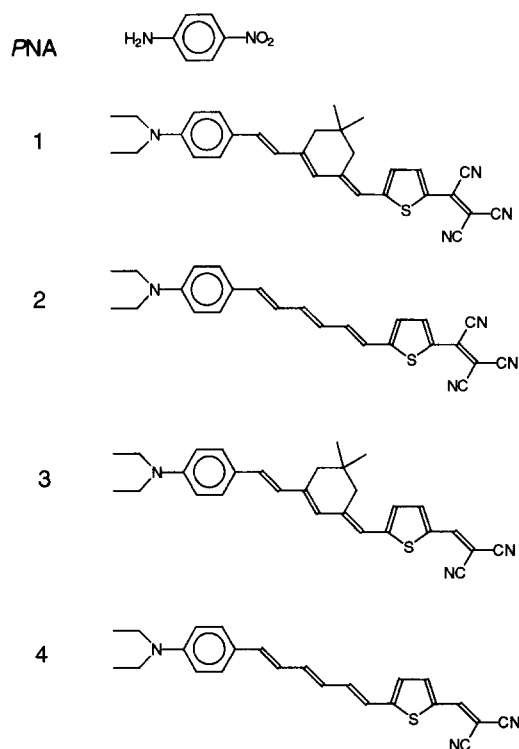

Fig. 1. Chemical structures of the five chromophores studied in this work.

In this Letter, the β values of some structurally related thiophene-incorporated polyene chromophores (Fig. 1), which we synthesize according to the facile approach described above for enhanced thermal stability, are measured and compared using the HRS technique. From the comparison, the effect of the configuration-locked trans-triene bridge on the nonlinear optical properties of the thiophene-incorporated polyene chromophores becomes better understood.

2. Experimental

Chromophores 1–4 (Fig. 1) were synthesized according to the reported procedures [14,15]. The chromophore solutions were prepared by first dissolving the chromophores in dioxane solvent and then successively diluted to proper concentrations. Para-nitroanaline (pNA) dioxane solutions were also prepared by the same procedure and used as external

standards. To remove undissolved particulates, all solutions were filtered through a 0.25 μm filter.

A Q-switched Nd:YAG 1064 nm laser (Continuum Surlite I) generating 8 ns pulses at 10 Hz was used as the light source of the HRS experiment. Rotating a computer-controlled half-wave plate between a pair of polarizers varied the incident laser intensity. After passing through high-pass filters to block unwanted short-wavelength flash light, the laser beam was then focused on the sample in a glass cylindrical cell (radius 1.25 cm) by a $f = 20$ cm lens. An aspheric lens at a scattering angle of 90° collected the scattered light. The collected light was first passed through an interference band-pass filter (centered at the 532 nm wavelength, bandwidth 3 nm) and two low-pass filters, to ensure the passage of only the 532 nm light, and finally focused onto a photomultiplier tube (PMT) with a $f = 7$ cm lens. The electrical signal from the PMT, first integrated by a boxcar integrator, was digitized and then transmitted to a personal computer for data processing. During the experiment, the incident laser energy was kept below 2 mJ/pulse, a level well below the dielectric breakdown threshold. Every data point was the average of 300 laser shots. To ensure the spectral purity of the HRS signal, attention was paid to its dependence on not only the fundamental intensity but also the spectral content of the scattered radiation including the TPA induced fluorescence. The former was examined by measuring the scattered intensity at 532 nm as a function of the half-wave plate angle [29], and the latter was examined by measuring the TPA induced fluorescence spectrum. The TPA induced fluorescence spectrum was recorded in a manner identical to the HRS experiment except that a monochromater replaced the interference filter.

3. Results and discussion

The HRS intensity $I_{2\omega}$ from a two-component solute–solvent system at low chromophore concentration is proportional to the square of the incident laser intensity I_ω [16–25]:

$$I_{2\omega} = G\left(N_s\langle \beta_s^2\rangle + N_c\langle \beta_c^2\rangle\right)I_\omega^2 . \tag{1}$$

In this equation $\langle \ \rangle$ stands for an orientational average. Subscripts s and c stand for solvent and chro-

mophore, respectively. N refers to the number density. G is a constant related to the scattering geometry, local field correction factors at ω and 2ω and other instrument factors. For a one-dimensional chromophore (or solvent), the molecular first hyperpolarizability tensor can assume only one major component $\beta_{c,zzz}$ (or $\beta_{s,zzz}$). Consequently, $\langle \beta_c^2\rangle$ and $\langle \beta_s^2\rangle$ can be expressed as

$$\langle \beta_c^2\rangle = k\beta_{c,zzz}^2 \equiv k\beta_c^2 ,$$

and

$$\langle \beta_s^2\rangle = k\beta_{s,zzz}^2 \equiv k\beta_s^2 , \tag{2}$$

where k is a constant related to the average of the product of the direction cosines.

In order to ascertain the two-photon scattering process experimentally, the incident laser intensity I_ω is expressed as a function of the half-wave plate rotation angle ϕ,

$$I_\omega = I_0 \sin^2(2\phi + \alpha) , \tag{3}$$

where I_0 is the maximum intensity and α is the start angle of the half-wave plate rotation. The $I_{2\omega}$ versus the half-wave plate angle ϕ can thus be expressed as

$$I_{2\omega} = I\left[\sin^4(2\phi + \alpha)\right] + b , \tag{4}$$

where

$$I \equiv Gk\left(N_s \beta_s^2 + N_c \beta_c^2\right)I_0^2 . \tag{5}$$

In Eq. (4) b is added to account for the dc intensity offset. Fig. 2 shows the measured $I_{2\omega}$ intensity (circles) at 532 nm versus the half-wave plate angle for chromophore 2 in dioxane. The solid line is generated with Eq. (4) using a dc intensity offset of 0.087. As shown in the figure the experimental data are well fitted to Eq. (4) for chromophore 2, an observation also true with all the other chromophores. Thus, all of the signals detected at 532 nm are due to the two-photon scattering process, which includes both HRS and TPA induced fluorescence.

A linear dependence is obtained when the I of Eq. (5) is plotted against N_c. Thereupon, the intercept and the slope of the fitted straight line, given respectively by $GkN_s \beta_s^2 I_0^2$ and $Gk\beta_c^2 I_0^2$, can, in principle, be used to determine β_c. We use, however, the pNA in dioxane solution, with a known β_c' value of 16.9×10^{-30} esu [30], as an external stan-
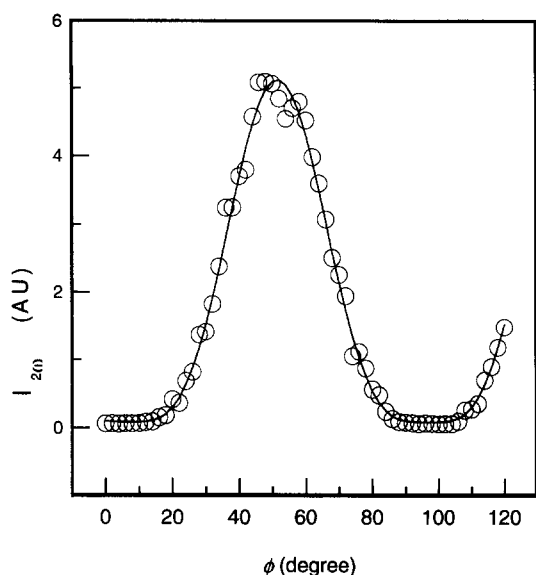
Fig. 2. A plot of the HRS intensity measured at 532 nm (circles) vs. the half-wave plate angle for chromophore 2 in dioxane. The solid line is theoretical, Eq. (4).
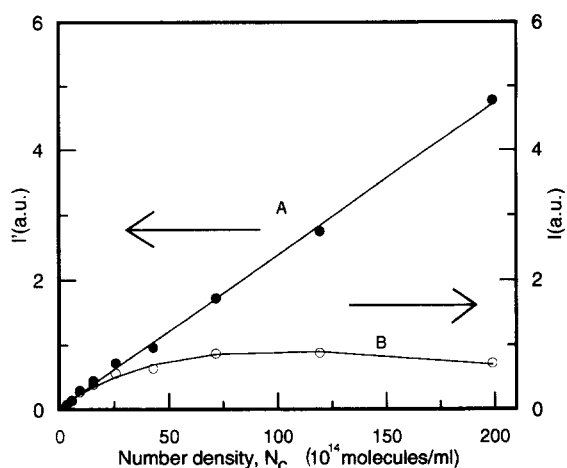

Fig. 3. Plots of corrected I' and uncorrected I vs. the number density of chromophore 3 in dioxane. The solid lines represent the theoretical fit to the experimental data points.

dard to determine the β_c value of the unknown chromophore. This method is referred to as the external standard method (ESM) and its details has been reported elsewhere [23,25]. From the ESM, the hyperpolarizability of the unknown chromophore β_c is found to be [23,25]:

$$\beta_c = \beta_c'\sqrt{m_c/m_c'} \ . \tag{6}$$

Here, m_c and m_c' are the fitted slopes of the I versus N_c plots for the sample chromophore and the external standard solution, respectively (cf. Eq. (5)).

When the HRS signal is partially absorbed by the chromophores, a correction to the HRS intensity is needed to correctly obtain the β_c value of the absorbing chromophore. We have made the intensity correction according to the equation

$$I' = I\exp(\epsilon N_c l) \ , \tag{1'}$$

where ϵ (1 mol^{-1} cm^{-1}) is the extinction coefficient of the chromophore solution at the second harmonic wavelength and l is the effective path length that the $I_{2\omega}$ light travels in the partially absorbing solution. Shown in the B curve of Fig. 3 is the HRS intensity (I in the right Y-scale) of chromophore 3 in dioxane solution as a function of N_c, uncorrected for the absorption effect. After removing the absorption effect, a linear plot of I' (in the left Y-scale) versus N_c

is obtained, and the β_c value of the unknown chromophore can thus be determined following the same procedure as that of the non-absorption case described above.

Fig. 4 shows the narrow HRS (532 nm) and broad TPA induced fluorescence spectra of pNA, and chromophores 1, 2, 3 and 4 (without correcting for
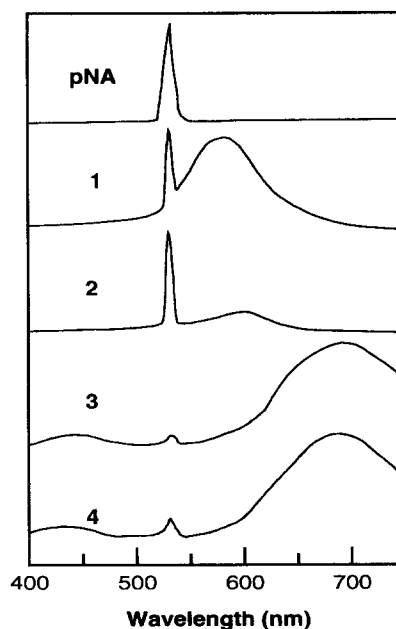

Fig. 4. Two-photon absorption induced fluorescence spectra and HRS signals for pNA, and chromophores 1, 2, 3 and 4, whose chemical structures are given in Fig. 1.

Table 1
Linear and nonlinear optical properties of chromophores pNA, 1, 2, 3 and 4

Chromophore	λ_{max} (nm)	β_c $(10^{-30}$ esu)	β_0 $(10^{-30}$ esu)
pNA	354	16.9 [a]	8.4
1	686	−1504	582
2	678	−1410	523
3	560	−1125	88
4	546	−1500	59

[a] From Ref. [30], which was measured by EFISH technique.

self-absorption). The TPA induced fluorescence spectra are found to have some substructures which, being unrelated to the data of interest, have been smoothed out. Note the variation in the of fluorescence peak position for the chromophores studied. In comparison with the sharp HRS spikes, the fluorescences of pNA and chromophore 2 observed around 532 nm are weak, whereas those of chromophores 1, 3 and 4 are strong. The contribution of fluorescence to the HRS data is removed using the procedure illustrated in Ref. [26]. After removing fluorescence contribution, m_c and m'_c are separately determined as per Eq. (5). They are then used in Eq. (6) to calculate the β_c values of chromophores 1, 2, 3 and 4, which are found to be 1504×10^{-30}, 1410×10^{-30}, 1125×10^{-30} and 1500×10^{-30} esu, respectively.

Summarized in Table 1, for all the chromophores studied, are the linear absorption maximum λ_{max} and the first hyperpolarizability β_c, measured with the 1.064 μm fundamental wavelength, and its dispersion-free counterpart β_0. All the β_c values are measured in the lower concentration range so that the intermolecular interaction has been excluded [23]. The errors of the measured β_c values are approximately 5%. The β_0 values are calculated from the β_c values by removing the one- and two-photon resonance enhancement factors under the two-level approximation without considering damping. We note that although the β_c values of chromophores 3 and 4 are close to those of chromophores 1 and 2, their β_0 values are much smaller than those of chromophores 1 and 2. This occurs because replacing the electron acceptor $C_2(CN)_3$ with $CHC(CN)_2$ shifts the electronic energy levels upstream by almost 130 nm so that the excited states (or λ_{max} as per Table 1)

become less detuned from the 532 nm excitation and hence more correction for resonance enhancement in determining β_0. Further examination of the variation of β_0, as well as λ_{max}, with the chromophore structure (Fig. 1) is given in the following.

We first look at the effect of locking the π-configuration triene with a 6-membered ring. As shown in Table 1, both the λ_{max} and β_0 values of chromophore 1 are larger than those of chromophore 2. This is understandable since incorporating a 6-membered ring to lock the trans-triene significantly improves the degree of planarity and the electron delocalization efficiency of the π-configuration system. By the same token, both the λ_{max} and β_0 values of chromophore 3 are larger than those of chromophore 4. The increases in both β_0 and λ_{max} inevitably result in the so-called nonlinearity-transparency trade-off, unfortunately. Along with the gain in nonlinearity, chromophore 1 (3) has its linear absorption red-shifted relative to the nonlinear-optically less active chromophore 2 (4), and the red-shift may preclude its utilization in some nonlinear frequency conversion applications due to an increased absorption of the converted frequencies.

The effect of replacing the electron acceptor $CHC(CN)_2$ with $C_2(CN)_3$ on nonlinearity, to be discussed now, is much stronger than the effect of π-configuration locking mentioned above. Note in Table 1 the marked increases in both the λ_{max} and β_0 values of chromophore 1 with respect to those of chromophore 3, as well as those of chromophore 2 with respect to 4. The indication is thus strong that the strength of acceptor $C_2(CN)_3$ (chromophores 1 and 2) is much greater than that of $CHC(CN)_2$ (chromophores 3 and 4). Their relative strength depends, however, on the structure of the remaining part of the chromophore, and the dependence is understandable. For chromophores with π-configuration locking (i.e., 1 and 3) the ratio of the β_0 value of the chromophore with $C_2(CN)_3$ to that of the chromophore with $CHC(CN)_2$ is 6.6 according to the data given in Table 1. For chromophores without π-configuration locking (i.e., 2 and 4) the β_0-ratio is higher, 8.8. Given the structures of the chromophores studied these β_0-ratios are in qualitative agreement with the finding reported earlier. For example, with the NO_2 group of pNA replaced by the acceptors of present concern, Cheng et al. obtained a

value of 1.4 for the ratio of β_0 weighted by the dipole moment (μ) [31]. When the triene of chromophores 2 and 4 is replaced by a conjugated π-bond, the μ-weighted β_0-ratio increases to 3.5, and further extension of the π-configuration at the end of the chromophore opposite to the acceptor leads to a μ-weighted β_0-ratio closer to ours, 5.7 [32,33]. We conclude that for an extended π-electron delocalization the effect of the electron acceptor $C_2(CN)_3$ on nonlinearity can be much stronger than the acceptor $CHC(CN)_2$. The less extended the delocalization, the closer their relative strength.

4. Conclusions

Four thiophene-incorporated polyene chromophores with and without a configuration-locked trans-triene bridge for enhanced thermal stability have been synthesized. Their dispersion-free first hyperpolarizabilities (β_0) were determined with the HRS technique, using pNA in dioxane as an external standard. Special attention is paid to the TPA induced fluorescence spectrum in order to remove its contribution to the observed HRS signal, which is also corrected for one- and two-photon resonance enhancements under the two-level approximation without considering damping. It is found from the HRS results that the configuration locked trans-triene bridge enhances the β_0 values of the thiophene-incorporated polyene chromophores. Furthermore, the effect of the electron acceptor $C_2(CN)_3$ on enhancing the β_0 value is much stronger than that of the acceptor $CHC(CN)_2$. This is in line with the observation that the π-configuration of the chromophores studied is rather extended.

Acknowledgements

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