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First-order hyperpolarizability of oligo-acene derivatives by hyper-Rayleigh scattering

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Abstract

First-order hyperpolarizabilities β for a series of oligo-acene derivatives were estimated as a function of the conjugation length by means of the hyper-Rayleigh scattering (HRS) technique. Satisfactory data acquisition and analyses gave the hyperpolarizabilities $(17 \pm 2) \times 10^{-30}$ and $(68 \pm 8) \times 10^{-30}$ esu for naphthalene-2,3-dialdehyde and anthracene-2,3-dialdehyde, respectively. The pure β value of tetracene-2,3-dialdehyde (OA4) could not be determined because of multiphoton absorption induced fluorescence superimposed on the HRS signal. A large β value ($\approx 180 \times 10^{-30}$ esu) is expected for OA4 by extrapolating the conjugation length dependence on β . © 1997 Elsevier Science B.V.

1. Introduction

Studies of nonlinear optical effects have received considerable attention due to their potential applicability to the direct manipulation of optical fields, e.g. second-harmonic generation. Conjugated molecules are becoming the materials for optical applications since they present several advantages compared to inorganic materials [1,2]. Their nonlinear responses are often larger and faster due to electron polarization. These optical nonlinearities combined with the versatility of synthetic chemistry, allows the optimization of the nonlinear response.

The principal requirement for the materials which exhibit a macroscopic second-order susceptibility is that they have a non-centrosymmetric structure. This

structure can be achieved by the use of the Langmuir-Blodgett (LB) technique. A suitable molecule for LB films has been an amphiphile consisting of a hydrophilic moiety and usually a hydrophobic long alkyl chain. Therefore, the long alkyl chain used as the hydrophobic moiety separates every monolayer in cumulated multilayer films without any interaction between the monolayers. Is there any other hydrophobic moiety suitable for the amphiphile and possibly for interactive mediation between layers? This is the first objective of this Letter. There have been a few amphiphilic π -conjugated molecules which form a stable monolayer on a water subphase, but the effective transfer of the monolayer onto a substrate has not yet been established [3-9]. We have considered oligo-acene amphiphiles. The multilayer consisting of such a hydrophobic conjugated system will hopefully allow appreciable interlayer interaction and then demonstrate strong correlation between the detectable electronic properties and the number of the monolayers. In order to obtain the optimized macroscopic nonlinear optical response of our oligo-acene derivatives, as a first step, a better understanding of the relationship between molecular structure and its molecular hyperpolarizability is required.

In the present study, we have applied the hyper-Rayleigh scattering (HRS) method to the measurement of the molecular hyperpolarizabilities for a series of oligo-acene dialdehydes as a function of increasing π conjugation length to determine β of these molecules.

2. Experimental

The series of oligo-acene molecules (OA n) used in this study (Fig. 1) are naphthalene-2,3-dialdehyde (OA2), anthracene-2,3-dialdehyde (OA3) and tetracene-2,3-dialdehyde (OA4). All the OA nmolecules were synthesized by one-pot consecutive condensation of o-phthalaldehyde (Aldrich) as a starting dialdehyde with an appropriate amount of 2,5-dimethoxytetrahydrofuran (Aldrich) which is converted in situ to a reactive 1,4-dioxobutane in aqueous acetic acid solution containing a catalytic amount of piperidine [10]. After reflux for 24 h, the reaction mixture was cooled and left until a precipitate appeared. The OA2 and OA3 were purified by sublimation at 130° and 220°C, respectively, under 0.1 Torr. The OA4 was purified by recrystallization from acetic acid. These products were identified by IR, NMR and UV-VIS spectroscopy. 4-Nitroaniline (Wako pure chemicals) is used as a standard molecule to check the reliability of the present HRS measure-



Fig. 1. Molecular structures used in this study.

ment. Other chemicals (Wako pure chemicals) are used without further purification.

Until now, the electric-field induced secondharmonic generation (EFISH) technique has been mainly adopted for the determination of the molecular optical hyperpolarizability β of a species in solution [11,12]. In this case, one requires knowledge about local field factors, in addition to information about the ground-state dipole moment. Another technique for determining β (HRS) measurement [13,14]. This light scattering, which results from fluctuations in the orientation or number density of the molecule in question, has been recently applied for the determination of molecular hyperpolarizabilities. The main advantage of HRS over EFISH is that the applicability is extended over all the molecules including dipolar, octopolar [15] and ionic species [16] and β is determined directly, with no information on the molecular dipole moment μ required, which should be independently measured in the case of EFISH.

A Q-switched Nd³⁺:YAG laser (repetition rate 10 Hz, pulse width 10 ns and wavelength 1064 nm) was used as an excitation source. The incident light intensity, less than 1 mJ, was controlled by neutral density filters and a set of linear polarizers. The fundamental laser beam was focused on the center of the 4 cm path quartz cell containing the sample solution. The light scattered perpendicular to the incident beam was collected with a concave mirror and two lenses and was detected by a photomultiplier tube (Hamamatsu Photonics, R-329-05) through a 3 nm bandwidth, 532 nm interference filter and a long-wavelength-pass filter. The incident light intensity was monitored by the detection of a small fraction of the 1064 nm fundamental with a photodiode. Signals from both the photomultiplier and the photodiode were integrated with a gated boxcar averager (Stanford Research SR-250). The layout of our experimental HRS apparatus was described elsewhere [17].

The HRS signal intensity can be written as Eq. (1), reflecting the solute and solvent contributions [13,14]:

$$I_{2\omega} = G(N_{\text{solvent}} \beta_{\text{solvent}}^2 + N_{\text{solute}} \beta_{\text{solute}}^2) I_{\omega}^2, \qquad (1)$$

where N, β , I_{ω} and $I_{2\omega}$ are the molecular number density, the first-order hyperpolarizability, and the

fundamental and scattered second harmonic light intensities, respectively. The constant, *G*, includes local field factors, the optics geometry and instrumental factors. The quadratic coefficients of I_{ω} are determined as a function of the incident fundamental light intensity and a linear relationship between the quadratic coefficients and the N_{solute} gives the β_{solute} , using the known value of β_{solvent} . Our measurement and analysis were calibrated by a standard sample, 4-nitroaniline in methanol. The EFISH measurements by Oudar and Chemla [18] and Stähelin et al.[19] gave 34.5×10^{-30} and 32×10^{-30} esu, respectively. A consistent value of 31×10^{-30} esu was obtained for 4-nitroaniline in methanol by the present HRS measurement.

Electronic absorption spectra were recorded with a Shimadzu UV-3100PC UV-visible absorption spectrophotometer. Fluorescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer.

3. Results and discussion

3.1. First-order hyperpolarizability of oligo-acene molecules

The UV–VIS absorption spectra of the OA n in chloroform are shown in Fig. 2. Considerable redshift of the absorption bands was observed as the conjugation length increased from OA2 to OA4. The spectra include intense absorption bands in the UV or near-UV region and weak bands in the longerwavelength region.



Fig. 2. UV–VIS absorption spectra for (1) OA2, (2) OA3 and (3) OA4 in CHCl $_3$.



Fig. 3. (a) The relationship between observed HRS signal for OA3 in chloroform and the incident fundamental light intensity. (b) The quadratic coefficient obtained from the curves in (a) versus the number density of OA3 at room temperature.

Fig. 3a shows the plots of the HRS intensity $(I_{2\omega})$ versus the fundamental intensity I_{ω} for OA3 in CHCl₃. The quadratic coefficients obtained from a least-squares fitting of the $I_{2\omega}-I_{\omega}$ relations were plotted against the number density of the solute, as shown in Fig. 3b. From the slope and the intercept a value of $(68 + 8) \times 10^{-30}$ esu was obtained for β (OA3), taking β (chloroform) = -0.45×10^{-30} esu [20]. In a similar manner, a value of $(17 \pm 2)x10^{-30}$ esu for the β of OA2 was estimated. Although the present oligo-acene derivatives have aldehyde groups as electron acceptors and have no conventional strong electron donating group, these β values are relatively high. The oligo-acene moiety could function as an electron donating group and the proper hybridization and longer extensions of the aromatic conjugation to aldehyde groups may be the reason for the effectiveness of the accepting groups. OA4 was expected to have large β value. However, a proper β (OA4) value could not be determined by the present HRS method since multiphoton absorption induced fluorescence was unfortunately superim-



Fig. 4. Fluorescence spectra of OA2, OA3 and OA4 under the excitation wavelengths of 241, 265 and 322 nm, respectively. The plotted line is the wavelength dependence of the scattered light intensity of OA4.

posed on the HRS signal, as will be discussed in the next section.

A pure HRS signal should show a sharp peak centered at 532 nm, consistent with frequency doubling of the incident fundamental light (1064 nm). Fig. 4 shows the wavelength dependence of the scattered light intensity from OA4 through several 3 nm bandwidth interference filters, at 490, 510, 532, 550 and 570 nm. Strong scattered light was detected even out of 532 nm and, moreover, the intensity increases along with the conventional fluorescence spectrum under excitation at 322 nm. The fluorescence spectra of OA2 and OA3 are also shown in Fig. 4. A large red-shift was observed as the conjugation length increased and especially, the OA4 emits at ~ 550 nm, close to the HRS signal. Quadratic dependencies of the fluorescence intensities on the incident fundamental light were found in all the observed wavelength regions. We have to conclude that the strong multiphoton absorption induced fluorescence of OA4 screens the HRS signal to be collected. Unfortunately, it is impossible to extract the small HRS signal from much larger contribution of the fluorescence. Actually, the absorption tail of OA4 is found to come down the 532 nm region.

3.2. Conjugation length dependence on β

It is, however, worth examining a relationship between β and the conjugation length among a series of molecules in the field of nonlinear optical materials [21–23,25]. Many experimental studies have been performed on various kinds of conjugated molecular systems. Using standard time-dependent perturbation theory (or static perturbation theory), useful information about size effects and scaling laws can be obtained with the Unsöld approximation [24]. That is, the β value is proportional to a power of the conjugation length, which can be described as the number (*n*) of double bonds in a molecule. When two double bonds are counted for each benzene unit, the present oligo-acene derivatives include 4 double bonds for OA2, 6 for OA3 and 8 for OA4. The β value should be proportional to a power of the conjugation length in the case of oligo-acene. A linear dependence between log(β) and log(*n*) is characterized by the following equation:

$$\log(\beta) = p \log(n) - q.$$
⁽²⁾

Here, p = 3.4 was evaluated by applying Eq. (2) to the obtained β values of OA2 and OA3. It is reported that the exponent p is end-group dependent and their values appear to be inversely related to the combined donor-acceptor strength or magnitude of the hyperpolarizability [25]. The large exponent obtained seems to be due to the absence of an electron donating group. Phenylpolyene or retinal derivatives with weak donor and acceptor sites show a p of 3.3-3.5 [22,25], consistent with the case of the oligo-acene derivatives used here. By extrapolation along the line, the β value of OA4 can be estimated to be ~ 180×10^{-30} esu (Fig. 5).

Among the reported results on the conjugation length dependence of β , oligomeric polyphenylene which consists of a similar aromatic π -conjugated system, shows contrasting results. For oligo-phenylene, extending the aromatic conjugation leads to a substantial reduction in nonlinearity. The main difference between these systems is planarity of their



Fig. 5. Conjugation length dependence of the first hyperpolarizability of OA2, OA3 and OA4. The extrapolation of this line gives β a value of 180×10^{-30} esu.

molecular structures. It is well known that the neighboring benzene rings may rotate on the linkage of oligo-phenylene and that a non-zero torsional angle between two π systems will lead to an increase of the transition energy and a reduction of the extinction coefficient of the $\pi - \pi *$ transition [26]. In contrast, oligo-acenes have a planar structure. Therefore, charge delocalization over the whole molecule becomes easier which results in an increase of oscillator strength. Effective delocalization of charge and full participation of the π system causes a larger nonlinear property. These results indicate that in addition to the increased numbers of polarizable and hyperpolarizable electrons and the reduced energy gap, structural features of a extended π system such as planarity also play an important role in the enhancement of β .

4. Conclusions

Large first hyperpolarizabilities of the oligo-acene derivatives were evaluated by the hyper-Rayleigh scattering method. A value of ~ 180×10^{-30} esu for OA4 was estimated by an extrapolation in the relationship between β and conjugation length. The aldehyde groups at the 2 and 3 positions of the oligo-acene work effectively as an electron acceptor for the high β values. The present study on oligoacene derivatives, quite different from the conventional strategy for nonlinear optical organic materials, donor- π -acceptor, will encourage the exploration of new materials with, not only a high susceptibility but also additional properties. We have preliminarily found that OA4 forms a monolayer on a water-air interface by the Langmuir-Blodgett technique and that the monolayers could be cumulated on a quartz glass substrate [27]. The OA4 is an amphiphile with no long alkyl chain suitable for monolayer or multilayer formation. Taking into account of our success in the preparation of noncentrosymmetric Z-type multilayer films of OA4, the present oligo-acene derivatives are concluded to become one of the promising candidates for secondorder nonlinear optical materials.

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