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The first-order molecular hyperpolarizability and thermal stability of charge-transfer azo diol and azo aldimine

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Abstract

Nonlinear optical chromophores with nitro acceptors have been designed and synthesized. The first-order hyperpolarizability of the chromophores was determined using hyper-Rayleigh scattering; the decomposition temperature was determined using DSC and the absorption spectra of the compounds were measured. The nonlinear optical properties of the chromophores were discussed; the first-order hyperpolarizabilities of chromophores **3** and **4** come from their two-dimensional structure, the length of the conjugation bridge and intramolecular proton transfer. The strong dihydroxyl donor of chromophores **1** and **2** expanded the first-order hyperpolarizabilities, the measured β_{HRS} values of chromophores **1** and **2** at 1064 nm are 211×10^{-30} esu and 177×10^{-30} esu, respectively. These NLO-chromophores exhibit higher decomposition temperature in the range of 290–330 °C.

Keywords: Azo chromophores; Hyper-Rayleigh scattering; Thermal stability; Nonlinear optical property

1. Introduction

Second-order nonlinear optical materials have attracted much attention because of potential utilization in photonic applications. Due to their high molecular hyperpolarizabilities, organic materials display a number of significant nonlinear optical properties and hence are emerging as possible materials for the next generation telecommunication technologies, optical information processing, and storage [1–5]. It has been generally accepted that donor and acceptor terminal groups separated by a delocalization π-conjugated system exhibit large first-order hyperpolarizabilities [6–8]. Donor–acceptor charge-transfer molecules have been used to manufacture efficient photonic switches and gates; much effort has concentrated on the optimization of the typical "push–pull" structure.

In this paper, we report a systematic study of the structure–nonlinearity relationship and nonlinearity–transparency–thermal stability trade-off for several charge-transfer azo compounds containing a nitro group, a fixed donor group and different conjugated systems. The chemical structure of the synthesized chromophores are listed in Table 1. Two types of chromophores are reported here:

- wherein the chromophore employed the bihydroxyl-nitro group and which displayed large optical nonlinearity and was able to form NLO-active polyimides via the Mitsunobu reaction of diol and diimide;
- a two-dimensional azo imine chromophore containing both intramolecular charge transfer and intramolecular proton transfer and which showed obvious blue-shifted absorption compared with a chromophore of similar chain length.

The results indicate that the combination of different types of conjugation bridge provides a new opportunity for NLO-materials. These chromophores exhibited good

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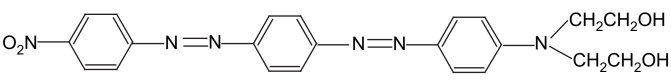
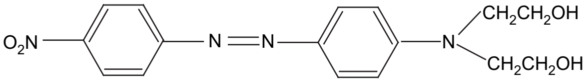
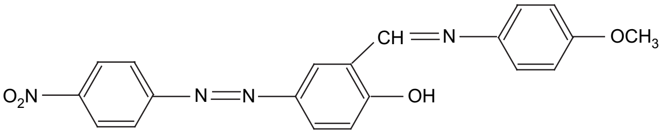
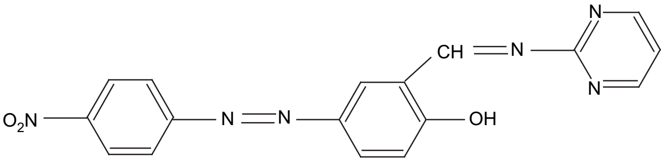
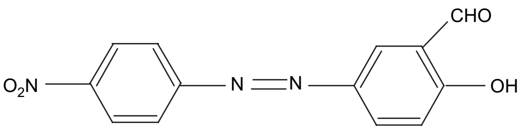
Table 1
Experimentally determined β-values and the maximum absorption wavelength of chromophores

Chromophores	Chemical structures of NLO-chromophores	λ_{max} (nm) in THF	β_{HRS} (10^{-30} esu)
1		514.0	211
2		486.8	177
3		364.0	94
4		363.0	87
5		362.2	66

transparency at both telecommunication wavelengths 1300 nm, and 1550 nm and in their second harmonic and also displayed nonlinearity–transparency–thermal stability trade-off for nonlinear optical application.

2. Experimental

2.1. Materials

N,*N*-Di-(2-hydroxyethyl)aniline, aminopyrimidine and *p*-anisidine were purchased from Aldrich. All the regents and solvents involved in synthesis were analytically pure and used as received without further purification.

2.2. Characterization

Chemical structures of NLO-chromophores were synthesized and fully characterized by Fourier transform infrared spectra (FT-IR), UV–vis and ^{1}H NMR spectroscopy with a Brucker 300 spectrometer and the data are in full agreement with the structures assigned. Differential scanning calorimetry (DSC) curves and thermal degradation temperature were

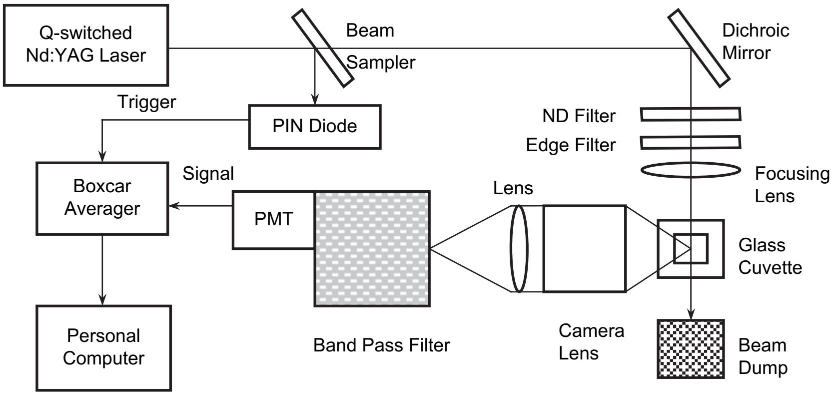
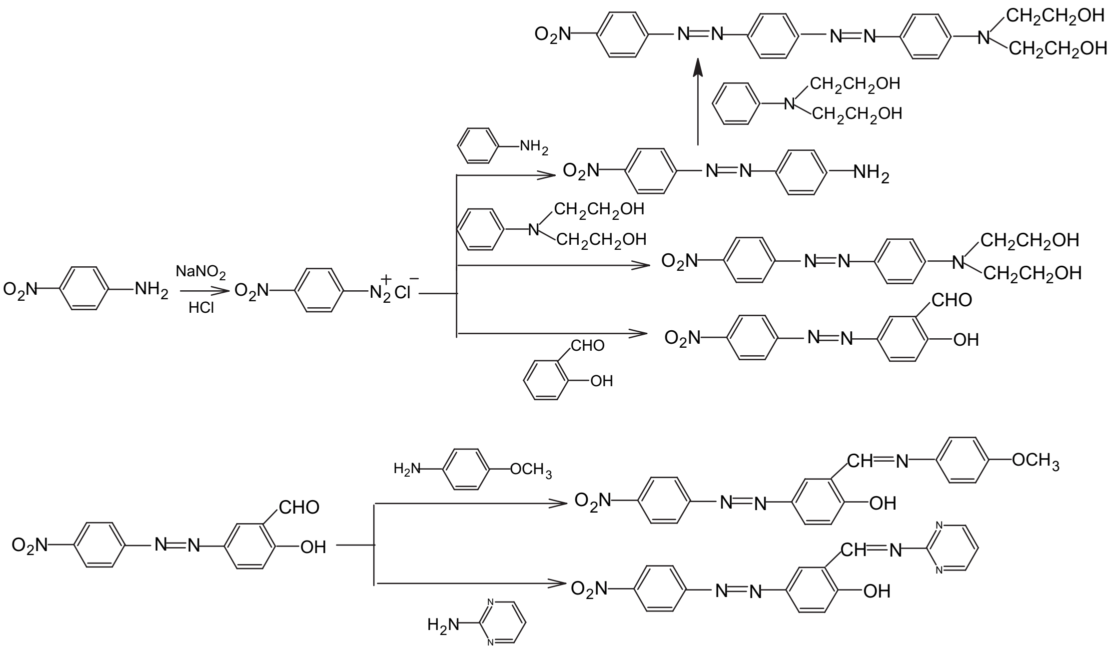


Fig. 1. Experimental set up for hyper-Rayleigh scattering in solution.



Scheme 1. Synthesis of the NLO-chromophores.

obtained with SDT Q600 thermogravimetric analyzer at a heating rate of 20 °C/min under nitrogen atmosphere.

2.3. HRS apparatus

The set up for hyper-Rayleigh scattering measurements in molecules is shown in Fig. 1. Laser pulses at fundamental wavelength of 1064 nm were obtained from a mode lock Nd:YAG laser (Quantel YG901C, producing 35 ps pulses up to 100 mJ with a 10 Hz repetition rate). After filtering out any residual flash lamp light with a high-pass filter, the fundamental light was focused onto the sample cell by using a long focal length plano-convex lens ($f = 1200$ mm). To keep away from any unwanted nonlinear processes such as stimulated Raman scattering, stimulated Brillouis scattering and dielectric breakdown, the laser pulse (≤ 10 mJ) was focused at 150 mm after passing through the sample cell. The harmonic radiation from the solution was collected by an efficient condenser system and was passed through a 3 nm FWHM interference filter centred at 532 nm. Gated integrators were used to retrieve actual values for the intensities of the incident and second-order scattered light pulses. The output signal from a photomultiplier tube (Hamamatsu CR114) was sampled by a boxcar signal averager (Stanford Research Sys. SR250), and all experimental data points were background subtracted and averaged over 1000 laser pulses.

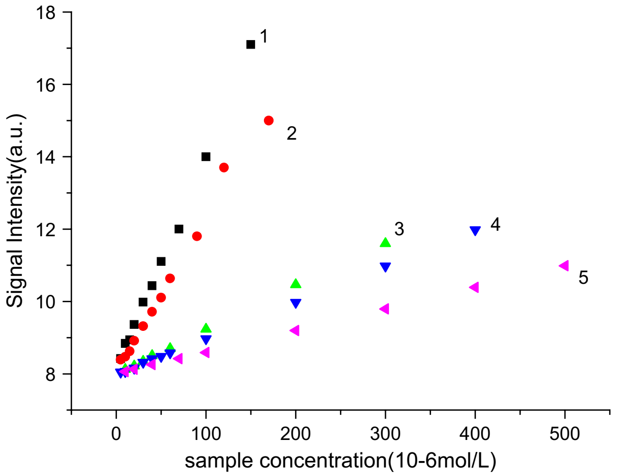


Fig. 2. Plot of HRS signal versus sample concentration of chromophores **1–5** in THF.

To confirm the performance of our experimental apparatus, the β-value of PNA, which was usually taken as standard material in HRS experiment, and quardratic power dependence of signal were measured. The results are in good agreement with those reported before [9,10].

Control compound *para*-Nitroaniline (PNA) was purchased from Aldrich and purified by recrystallization from water. Solutions were freshly prepared in tetrahydrofuran for samples. Spectrograde methanol and tetrahydrofuran were used for the preparation of solutions.

Table 2
Thermal degradation temperature and melting point of chromophores

Chromophores	m.p. (°C)	ΔH (J/g)	T_d (°C)
1	243.09	41.81	302.36
2	209.50	88.39	291.93
3	231.93	74.71	330.45
4	235.25	64.90	297.19
5	198.06	95.77	301.71

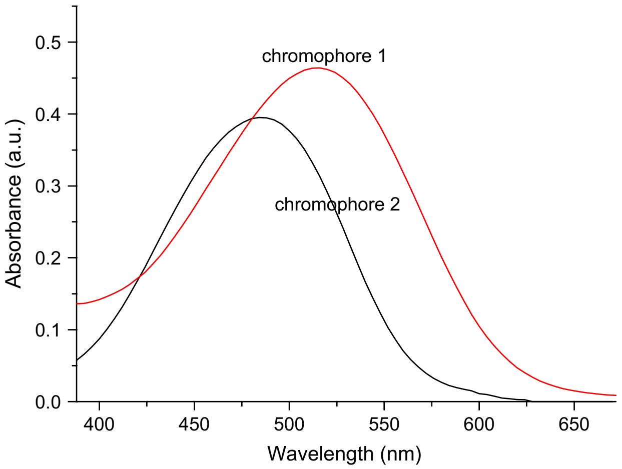


Fig. 3. UV–vis spectrum of the chromophores **1** and **2** in THF.

HRS experiment was performed as follows. A portion of the spectrograde solvent (1 ml) was placed in the sample cuvette. Aliquots (5–10 μl) of a solution of the dye were then added, and the signal recorded after each addition. A minimum of three replications of each experiment was required to provide data suitable for analysis.

3. Results and discussion

3.1. Synthesis of chromophores

Scheme 1 depicts the synthetic route of the NLO-chromophore. Azo compounds were synthesized by diazo coupling, in which arenediazonium salts reacted with salicylaldehyde and di-(2-hydroxyethyl)aniline, respectively in an ice-bath. Azo imines were synthesized by Schiff base condensation, in which an equimolar amount of azo aldehyde reacted with aromatic amine in boiling ethanol.

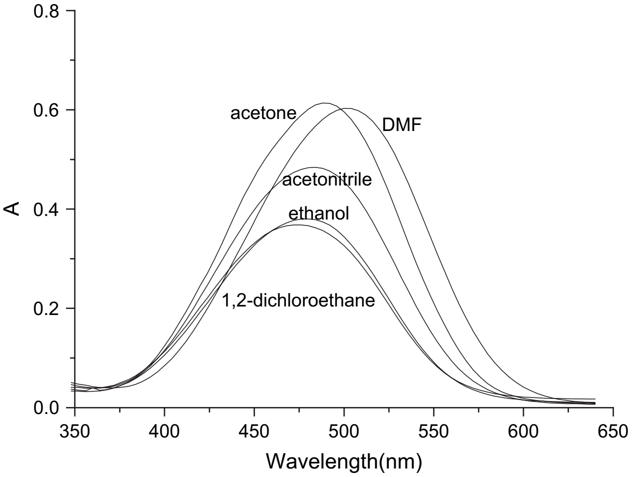


Fig. 4. UV–vis spectrum of chromophore **1** in different solvents. Up to down: acetone, DMF, acetonitrile, ethanol, 1,2-dichloroethane.

Azo compounds bring two or three substituted aromatic rings into conjugation with a donor group and nitro acceptor group, which are strong NLO-chromophores.

3.2. Hyper-Rayleigh scattering

The incoherent second-order nonlinear light scattering in a macroscopically isotropic molecular liquid has emerged as a widely applicable technique for the experimental determination of the first-order hyperpolarizability of nonlinear optical molecules in solution. The technique has become widely known as hyper-Rayleigh scattering (HRS) [11,12]. Over the last 10 years, HRS has been used as a tool to determine the β-value of the organic chromophores in solution [13–20].

The hyper-Rayleigh scattering method is capable of measuring a wider range of molecules including octupolar and ionic compounds in solution. First-order hyperpolarizabilities of compounds **1–5** in THF were measured using the HRS technique with respect to the one observed for PNA, a reference compound frequently used in determination (Fig. 2). The internal reference method (IRM) eliminates the need for local-field correction factors. The incoherent detected signal intensity, at twice the fundamental pump frequency, is directly related with the first hyperpolarizability $\beta(2\omega;\omega,\omega)$. In HRS, the measured signal, the second harmonic intensity, $I(2\omega)$, is given by [11,17,21–23]:

$$I(2\omega)=G\left(N_s\beta_s^2+N_c\beta_c^2\right)I^2(\omega)\exp\left(-\varepsilon^{2\omega}\mathrm{Cl}\right) \quad (1)$$

where G is a proportionality constant, related to a fixed geometrical aspect of detection and to the solvent local-field parameter, N designates the number density of the solvent (subscript "s") or chromophore solute (subscript "c"). β is the first-order hyperpolarizability of the solvent or material, respectively. $I(\omega)$ is the intensity of the incident laser at the fundamental frequency. The observable product, $G\beta_c^2$, is often called the quadratic coefficient, which can be determined by least-squares fitting of the experimental data.

Comparison between the amplitudes of the scattered signal by a sample and that from the reference compound, in identical signal collection conditions for the same parameter G, allows one to determine the first-order hyperpolarizability of the molecule in its particular solvent environment. Values of β are estimated relative to that of PNA as standard. Measurement of the quadratic coefficient for a substance, for which β is known, effectively determines the collection efficiency factor, G, in Eq. (1), and allows it to be solved directly for β in the cases of interest. The β-value for **1–5** NLO-chromophores are given in Table 1.

3.3. Thermal stabilities of chromophores

The synthesized chromophores present high melting point, which can be seen by DSC analysis. TGA shows the good thermal stability of the designed compounds. The samples were heated in a pan at a rate of 20 °C/min to give the melting point and the decomposition temperature, which are listed in

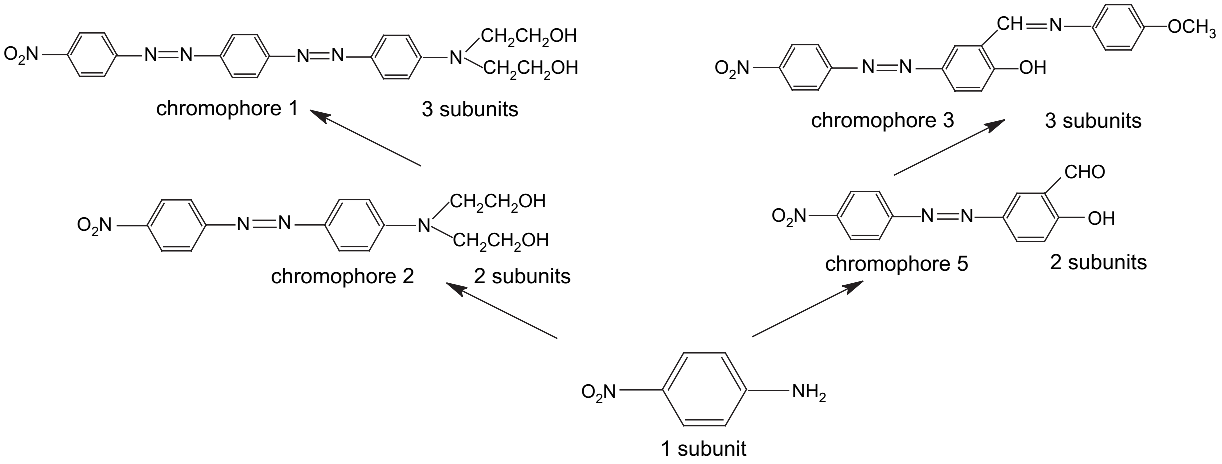


Fig. 5. Structures of the NLO-chromophores and their corresponding subunits.

Table 2. Great thermal stability and high melting point are much desirable for device applications. The NLO-chromophore show higher decomposition temperature between 291 and 330 °C, which makes it a good chromophore for the incorporation into high temperature glass polymer. The decomposition temperature of chromophores **1** and **2** wase decreased due to the bihydroxyl group in their structures, which makes chromophores more susceptible to sublimation at high temperatures. Two-dimensional multipolar chromophore **3** was thermally stable up to 330 °C under a nitrogen atmosphere.

3.4. Linear and nonlinear optical properties

UV−vis absorption spectra of the NLO-chromophores **1** and **2** are shown in Fig. 3. The maximum absorption wavelength of chromophores **1** and **2** appear at 514 nm and 486.8 nm, respectively, due to the π−π* transition of the conjugation bridge. Chromophores **3** and **4** displayed obviously blue-shifted absorption whose conjugation bridges were much longer in comparison with chromophore **2**. The blue-shifted absorption can be partially accounted for by the poorer co-planarity and the limitation of the intramolecular charge transfer between two-dimensional multipolar chromophores **3** and **4**.

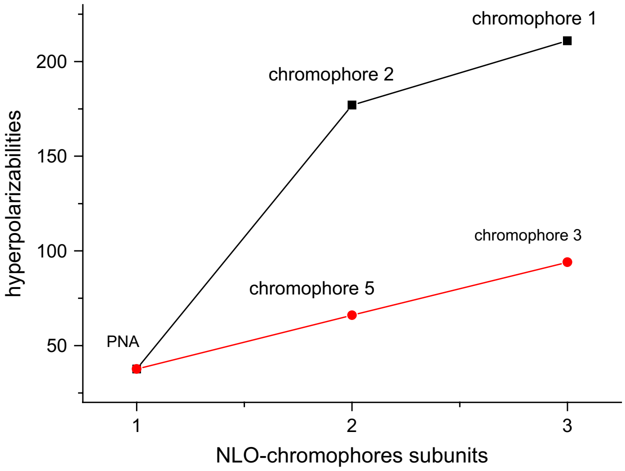


Fig. 6. Relationship between first hyperpolarizabilities (× 10^{-30} esu) of NLO-chromophores and their subunits.

Fig. 4 depicts the solvent dependence of the UV−vis absorption spectrum of chromophore **1**, which shows the solvatochromic effect in different solvents. In particular, the effect of solvent on position, shape, or intensity of the absorption bands of a molecule can be determined from the UV−vis spectrum.

Since these NLO-chromophores can be considered to be made up of some dipolar molecules (Fig. 5) we have also measured these "subunits" and taken the ratio of the hyperpolarizabilities of the chromophores and their dipolar subunits (Fig. 6). The relationship between the NLO-chromophores and their subunits can be discussed. First, the chromophores are much larger than their corresponding subunits; the ratio of the hyperpolarizabilities of the chromophores and their subunits is found to be between 1.2 and 4.7. Second, longer conjugated bridge lead to longer absorption wavelengths of the chromophores compared to the subunits.

Since the length of the conjugation bridge was much longer, chromophores **3** and **4** displayed larger NLO-property in comparison with the corresponding chromophore **5**. The strong donor−acceptor and effective intermolecular charge transfer expanded the β-values of chromophores **1** and **2**.

It is interesting that two types of intramolecular hydrogen bonds (either N−H···O or N···H−O) exist in chromophores **3** and **4**. In the aldimine compounds made from salicylaldehyde derivatives both types of hydrogen bonds were found [24,25]. The tautomeric equilibrium of Schiff bases in solid state and in solution has been a subject of considerable interest (Fig. 7). However, the enol−keto tautomerism has effect to enlarge molecular hyperpolarizability because of the intramolecular proton transfer associated with a change in π-electron configuration. The charge transport occurs through overlapping intramolecular π orbitals with proton transfer.

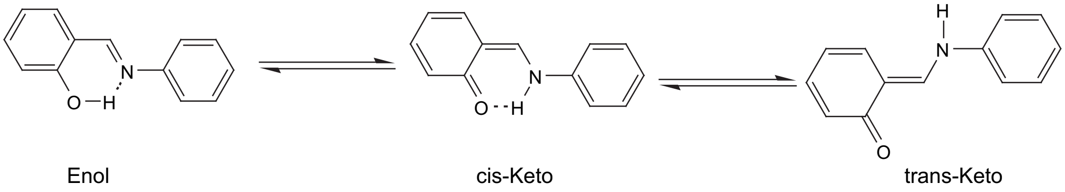


Fig. 7. The tautomeric equilibrium of Schiff bases.

4. Conclusions

In this work, some NLO-chromophores containing nitro acceptor have been synthesized by diazo coupling and Schiff base condensation. The first-order hyperpolarizability of the chromophores was measured by hyper-Rayleigh scattering for sample solutions having a linear relationship between the signal intensity versus number density. The decomposition temperature was determined with differential scanning calorimetry, and the linear absorption spectra were measured. Especially, the first-order hyperpolarizabilities of chromophores **3** and **4** come from their two-dimensional structure, the length of the conjugation bridge and the intramolecular proton transfer. The strong dihydroxyl donor and effective intermolecular charge transfer of chromophores **1** and **2** expanded the first-order hyperpolarizabilities; the measured β_{HRS} values of chromophores **1** and **2** at 1064 nm are 211×10^{-30} esu and 177×10^{-30} esu, respectively. These NLO-chromophores exhibit higher decomposition temperature in the range of 290−330 °C. In summary, it is important to consider optical nonlinearity−transparency−thermal stability trade-off in design of the NLO-materials.

Acknowledgements

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