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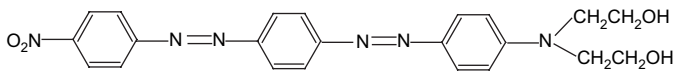
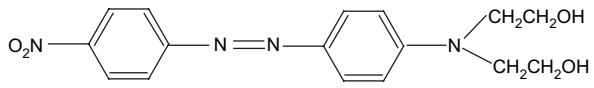
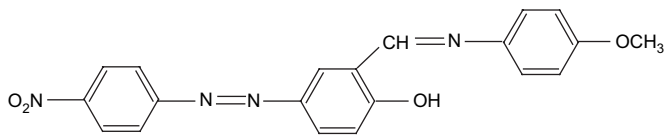
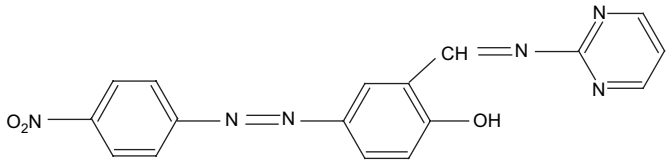
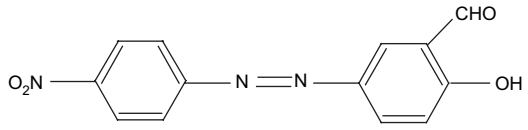
Table 1
Experimentally determined β-values and the maximum absorption wavelength of chromophores

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

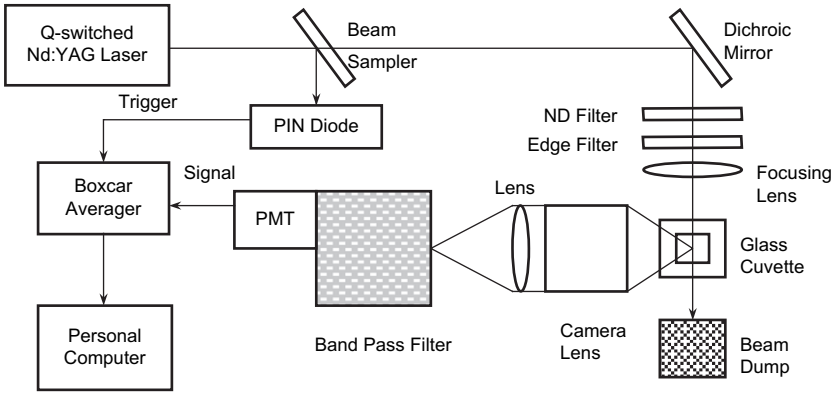


Fig. 1. Experimental set up for hyper-Rayleigh scattering in solution.