



Impact of electronegative character on ultrafast nonlinear optical absorption of azine derivatives

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ABSTRACT

Two azine derivatives (NO(Cl) and NS(Cl)) with different electronegative central core were prepared and spectroscopically characterized. Their ultrafast third-order nonlinear optical (NLO) responses were investigated using open aperture Z-scan and optical limiting method with 190 fs laser pulses at 515 nm. The frontier molecular orbitals and energy gaps of samples were obtained through quantum chemical calculation. Transient absorption spectra demonstrated that the origin of strong NLO absorption of two molecules was attributed to excited-state absorption. A simplified three-energy-level model was used to determine their photo-physical parameters. Our results show that the stronger the electronegative cationic groups is, the stronger the NLO absorption performs. The azine compounds have large excited-state lifetime and large ratio of singlet excited-state absorption cross-section to that of ground state cross-section (~ 20.2), indicating it is a candidate material for future ultrafast optical limiters.

1. Introduction

Nonlinear optical (NLO) materials have been attracted too much attention due to its giant potential application for all-optical switching, sign processing, data storage and optical limiting [1–4]. Organic materials have been regarded as extraordinary appreciative NLO materials for fast response speed, low cost, structural controllable and large NLO coefficients [5,6]. So far, many methods, such as enlarging π conjugation lengths [7–9], metal complexation [10–12], designing donor-acceptor structure [13,14], intramolecular charge or energy transfer process involving [15–17], increase frontier molecular orbital occupied ratio of main nonlinear functional group [18,19] and so on, are used to improving the NLO properties of organic materials. However, it is a great challenge to achieving practicality in photoelectric devices for structural complexity of materials. Many efforts are still expectable to devote to exploring the relationship of microscopic structure and macroscopic NLO properties for designing preeminent NLO materials.

Azine derivatives have one-dimensional linear resonant structures, which can be used for solar cell dyes and fluorescence probe for heavy metal ions [20]. So far, a lot of efforts have been devoted to the

synthesis and characterization of fluorescent properties of azine derivatives [21,22]. As for NLO properties, several literatures have reported the third-order NLO properties of azine compounds and their derivatives in picosecond and nanosecond regime [23,24]. Those previous reports demonstrated that symmetrical and unsymmetrical azine compounds experienced strong reverse saturable absorption and self-focusing effect. The NLO mechanism of azine compounds was contributed to the excited-state nonlinearity. Moreover, the third-order nonlinear absorptions would change from reverse saturable absorption (RSA) to saturable absorption (SA) with increasing percentage of the phenoxazinium in the PMMA films under nanosecond and picosecond regime [25]. However, few literatures have reported the NLO responses of these materials in femtosecond regime. Recently, we have reported that such material performed strong nonlinear RSA in femtosecond scale condition [26]. However, the relationship of structure and NLO properties for azine derivatives is remain unknown in femtosecond regime.

Therefore, we proceed in-depth research on NLO properties of azine derivatives based on preliminary work. Herein, we have synthesized two azine molecules with different electronegative character on the core. The NLO responses of two molecules were investigated through Z

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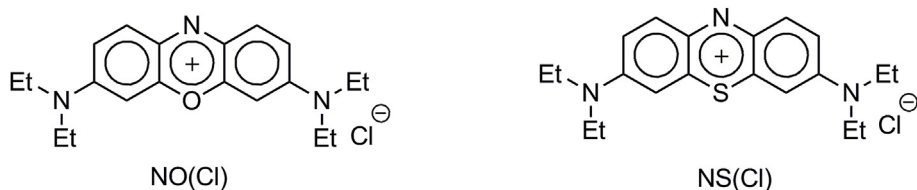


Fig. 1. Molecular structures of NO(Cl) and NS(Cl).

scan, transient absorption spectrum and optical limiting measurements. The frontier molecular orbitals and energy gaps of molecules were estimated through density functional theory. Our results have shown that organic cation groups act as major role in NLO responses of azine derivatives and the increase of electronegative character of the electron acceptor on the core is responsible for the increase of the excited-state absorption values of the two molecules. Our optical limiting experiments show that such compounds can be used to be good candidates for ultrafast optical limiters.

2. Experimental methods

2.1. Samples preparation and spectroscopic characterization

Two azine derivatives were prepared according to the literature [21,27]. The ^1H NMR value of the structures are consistent with the reported data. The molecular structure of the samples are illustrated in Fig. 1. Ground state absorption spectra of two azine derivatives were recorded with a Shimadzu UV1800 spectrophotometer.

2.2. Nonlinear optical measurements

In Z-scan technique, the light source was an optical parametric amplifier (ORPHEUS, Light Conversion) which generated 20 Hz, 190 fs, 515 nm laser pulses. The spatial and temporal distribution of the pulse was nearly a Gaussian profile. The experimental setup was similar to the one in Ref. [28]. The concentration of NO(Cl) and NS(Cl) solution was 6×10^{-4} mol/L and 1×10^{-3} mol/L, respectively. Two samples solution were injected into 2 mm thickness quartz cell, which moved along the z-axis with respect to the focal point of a 200 mm focal lens. All beams were measured by using energy detectors (Rjp-765 energy probe) linked to an energy meter (Rj-7620 ENERGY RATIO METER, Laser probe). The experimental data were collected through a GPIB interface. The experimental system was calibrated using benchmark Kerr liquid CS_2 .

In transient absorption measurement, the light source was a regeneratively amplified Yb: KGW fiber laser system (Light Conversion, PHAROS-SP) which produced 1 mJ pulses centered at 1030 nm with a repetition rate of 6 kHz and 190 fs (FWHM). The optical parametric amplifier (OPA, ORPHEUS, Light Conversion) output was tuned to 650 nm wavelength as the pump beam. The white-light probe pulse was produced by focusing a 1030 nm laser pulse into a 2 mm thick Ti: sapphire plate. The beam waist radius of pump and probe beam were nearly 1 mm and 100 μm in the sample solution, respectively. The effective temporal resolution of the measurement system is approximately 300 fs. Further details can be found in Ref. [26]. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Ground state absorption spectra

The ground state absorption spectra of two molecules were shown in Fig. 2. The maximum absorption wavelength of NO(Cl) and NS(Cl) was 650 nm and 665 nm, respectively. In comparison with 4a (Br) in Ref. [26], we found that the halogen anion has no influence on the absorption spectra. When the oxygen atom was replaced by sulfur atom,

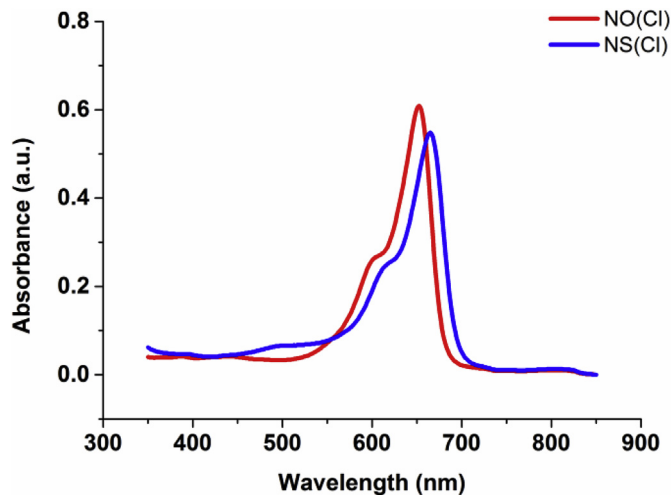


Fig. 2. The red line and blue line represent the ground state absorption spectra of NO(Cl) and NS(Cl), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the absorption band of NS(Cl) was redshifted by about 15 nm. In order to reveal the differences of their photo-physical properties, various parameters of two molecules were estimated by density functional theory (DFT). In strong polar organic solvent DMF, the two molecules are ionized into free ion and become dissociative azine derivatives cation and Cl anion rather than neutral molecules. As a result, the Cl anion has very little influence on molecular orbitals and the calculated system is logical. The CPCM (the polarizable conductor mode) includes a better approximation of outlying charge effects, is one of the most used and reliable continuum solvation procedures. Especially for ionic organic molecules, the CPCM is the best choice [29,30]. Therefore, the ground states of two molecules were fully optimized by DFT//B3LYP/6-31 + g²//CPCM(DMF) and the orbital energy were optimized by DFT//B3LYP/6-311 + g^{**}//CPCM(DMF). The frontier molecular orbital distributions and energy levels for two molecules were shown in Fig. 3 and the energy values of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) and HOMO-LUMO gaps for NO⁺(a) and NS⁺(b) were summarized in Table 1. All calculations were performed by using the Gaussian 09 program package [31]. The possession percentage of each component occupied in frontier molecular orbitals of NO⁺ and NS⁺ were summarized in Table 2 and Table 3, respectively. In these two azine compounds, from Tables 2 and 3, the contribution of HOMO is located in dimethylamino and central core, while the contribution of LUMO is located in central core. Therefore, when excited by laser sources, the dimethylamino group acted as electron donor and the central core acted as electron acceptor, composed as D-A structures. The electron transfer process can effectively improve NLO properties of materials [32]. In addition, the selected parameters for the vertical excitation (UV-Vis absorptions) of NO(S)⁺ based on the optimized ground state geometries in DMF were summarized in Table 4. From Table 4, the ground state absorption spectrum of sulfur-containing NS(Cl) is redshifted in comparison with that of oxygen-containing NO(Cl), which is consistent with the measured absorption spectra.

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