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Third-order nonlinear optical properties of the phenothiazinium chlorides at 532 nm

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ABSTRACT

A series of phenothiazinium chlorides, which have good solubility in polar solvents and good thermal stability, were evaluated in dimethyl sulfoxide solution for third-order nonlinear optical properties at 532 nm using a nanosecond and picosecond Z-scan technique. The title compounds exhibit strong reverse saturable absorption and nonlinear refraction. The third-order nonlinear optical properties were obtained under irradiation with either a nanosecond or picosecond laser. The nonlinear mechanism is revealed as excited-state nonlinearity by a picosecond pump-probe response experiment for one of the compounds. The absorption and emission maxima, Stokes shift and quantum yield are also reported.

1. Introduction

Organic materials possessing a large third-order nonlinear optical (NLO) response have attracted much attention over the past two decades, mainly due to their potential applications in various fields [1–6]. Most reports on third-order NLO materials focus on large π-conjugated molecules [7,8], or molecules bearing conjugated electron-donor (D) and/or electron-acceptor (A) groups. The design of third-order nonlinear materials used to be based on the classic valence bond (VB) conjugated structures [9–13]. However, the relationship between third-order NLO properties and molecular features, such as conjugation, charge transfer and polarization, is still a challenging field [14]. More effective methods are needed in the design of potential third-order NLO materials.

Compounds with zwitterionic structures or potential diradical character were recently suggested for the selection of third-order NLO materials. It is believed that the existence of intermediate diradical character and zwitterionic character in the molecule and the large coupling between these two VB resonance forms are responsible for large γ' values [15,16]. The third-order NLO properties of di(benzofuranonyl)methanolate (**BM4*i*4*i***, Fig. 1) film gave an exciting result with the imaginary part of the third-order NLO coefficient $\chi_I^{(3)} = -0.83 \times 10^{-7}$ esu [17,18]. Nonsymmetric squaraine compounds with directional charge transfer character were recently designed for second harmonic generation research [19]. Materials with resonance structures were selected for NLO research owing to their potential large fluctuation of electrons or large polarizable π-bridge. Current research, such as investigations on **BM4*i*4*i*** [17,18], croconates [20] and squaraine compounds [19], show the general character of resonance structures serving as NLO materials as follows: the organic molecule has more than two stable conjugated resonance structures, electron donor and/or acceptor groups participate in the resonance, and resonance structures can be well consistent with the classical VB structures. Considering the complexities of third-order NLO properties, more experimental examples are needed to explore the role of resonance stabilization and delocalized structures in predicting third-order NLO properties of materials.

In our previous work, benzo[a]phenoxazinium salts were prepared which displayed strong reverse saturable absorption (RSA) with a third-order NLO coefficient $\chi^{(3)} = 0.42–1.20 \times 10^{-11}$ esu and the second hyperpolarizabilities $\gamma' = 2.75–7.29 \times 10^{-29}$ esu under irradiation with a nanosecond laser beam at 532 nm [21]. These

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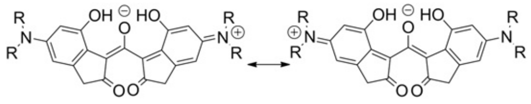


Fig. 1. Resonance structures of **BM4i4i**.

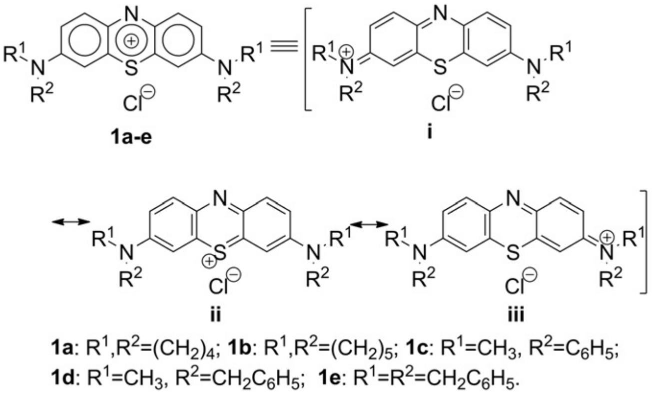


Fig. 2. Resonance structures of phenothiazinium chlorides.

results provided the impetus to find further potential candidates by examining simple resonance structures. However, benzo[a]phenoxazinium salts are partially dissociated to the free base and corresponding acids in neutral solvents under high dilution, which might affect the future device research.

The research of phenothiaziniums and their analogues has focused on antimalarial drugs [22], photosensitisers [23] and solar cells [24]. In this paper, five phenothiazinium chlorides (Fig. 2) were examined for third-order NLO properties. The delocalized D-π-D structure of phenothiazinium (**1**) can be expressed by three stable resonance structures (**i-iii**) involving the amino groups. The presence of large polarizable conjugated π-electron systems in these aromatic heterocycles and potential electron fluctionality serve the requirements of promising third-order NLO materials. The third-order NLO properties of phenothiazinium chlorides will be discussed in the following sections in detail.

2. Experimental section

2.1. Materials

3,7-Di(pyrrolidinyl)phenothiazinium chloride (**1a**), 3,7-di(piperidinyl)phenothiazinium chloride (**1b**), 3,7-bis(methyl(phenyl) amino)phenothiazinium chloride (**1c**), 3,7-bis(benzyl(methyl) amino)phenothiazinium chloride (**1d**) and 3,7-bis(dibenzylamino) phenothiazinium chloride (**1e**) were obtained from our previous work [25].

Table 1
Absorption and emission data of **1a**–**e** in methanol solution.

Compds.	λ_{max} (abs) (nm) [25]	lg ε (L mol^{-1} cm^{-1}) [25]	λ_{max} (em) (nm)	Stokes shift (nm)	Φ^a
1a	660	5.1	688	28	0.06
1b	667	4.3	697	30	0.01
1c	652	4.1	ND^b	ND^b	ND^b
1d	655	4.6	684	29	0.04
1e	654	5.0	684	30	0.03

[a] Values were obtained in methanol solution by the peak height and cresyl violet was used as standard.

[b] Fluorescent response cannot be detected.

2.2. Instruments

TGA analyses were performed on a Thermo-Gravimetric/Differential Thermal Analyzer (TG/DTA 6300, SII NanoTechnology Inc.). UV–vis spectra were recorded on a Perkin–Elmer λ-17 spectrometer using a 10 mm square quartz cell. Fluorescence spectra were investigated on a Shimadzu RF-5300PC spectroscope.

The third-order NLO properties were measured by the Z-scan technique [26]. A Nd:YAG 532 nm laser (EKSPLA) with a pulse width of 4 ns (fwhm) and repetition rate of 10 Hz was used for nanosecond Z-scan measurements, while a Q-switched Nd:YAG 532 nm laser (EKSPLA) with a pulse width of 19 ps (fwhm) and repetition rate of 2 Hz was used for picosecond Z-scan measurements. The nanosecond Z-scan test of the title compounds (**1a**–**e**) was measured in 2 mm cell with the incident energy of the laser beam is 6.6 μJ, while the picosecond Z-scan test was measured in 2 mm cell with the incident energy of the laser beam is 0.6 μJ. Two Rj-7620 Energy Ratiometers were employed as the detectors. The thickness of the sample cell was 2 mm. The solution was placed in a high-precision mobile platform moving along the incident light direction (Z). The Z-scan curve, the transmittance as a function of the sample position, could then be obtained.

In the picosecond pump-probe experiments, a Q-switched Nd:YAG laser (EKSPLA), which delivers 21 ps (fwhm) single pulse at 532 nm with 10 Hz repetition rate, was used. The pump-probe experimental setup was a standard arrangement, and the probe peak irradiance was approximately 8% of the pump irradiance [27].

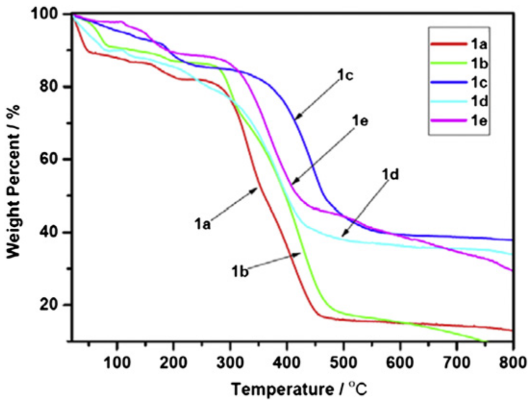


Fig. 3. The thermal stability of the compounds **1a**–**e**.

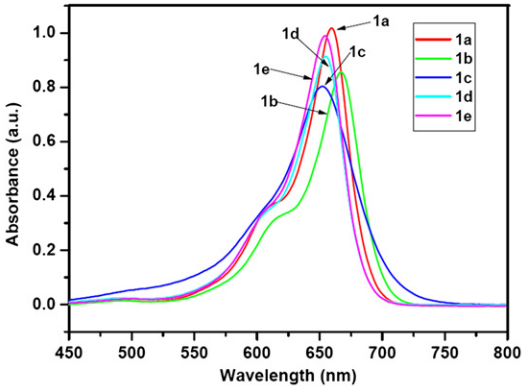


Fig. 4. Absorption spectra of phenothiazinium chlorides (**1a**–**e**) in CH_3OH ($c = 1.0 \times 10^{-5}$ mol L^{-1}).

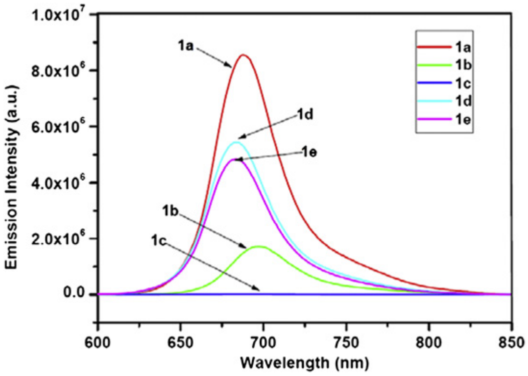


Fig. 5. Emission spectra of phenothiazinium chlorides (**1a**–**e**) in CH_3OH ($c = 1.0 \times 10^{-5}$ mol L^{-1}).

A variable delay was introduced into the probe path, and the two pulses were recombined at the sample cell (2 mm thickness) at a small angle. The probe beam waist was three times smaller than that of the pump. The small angle between the beams and the fact that the probe spot size was considerably smaller than the pump, which ensured that the probe could test a uniformly excited region of material in the 2 mm cell. The polarization of the pump beam was set perpendicular to that of the pump beam to avoid interference. The change of the probe beam intensity as a function of time delay was recorded after the pump beam.

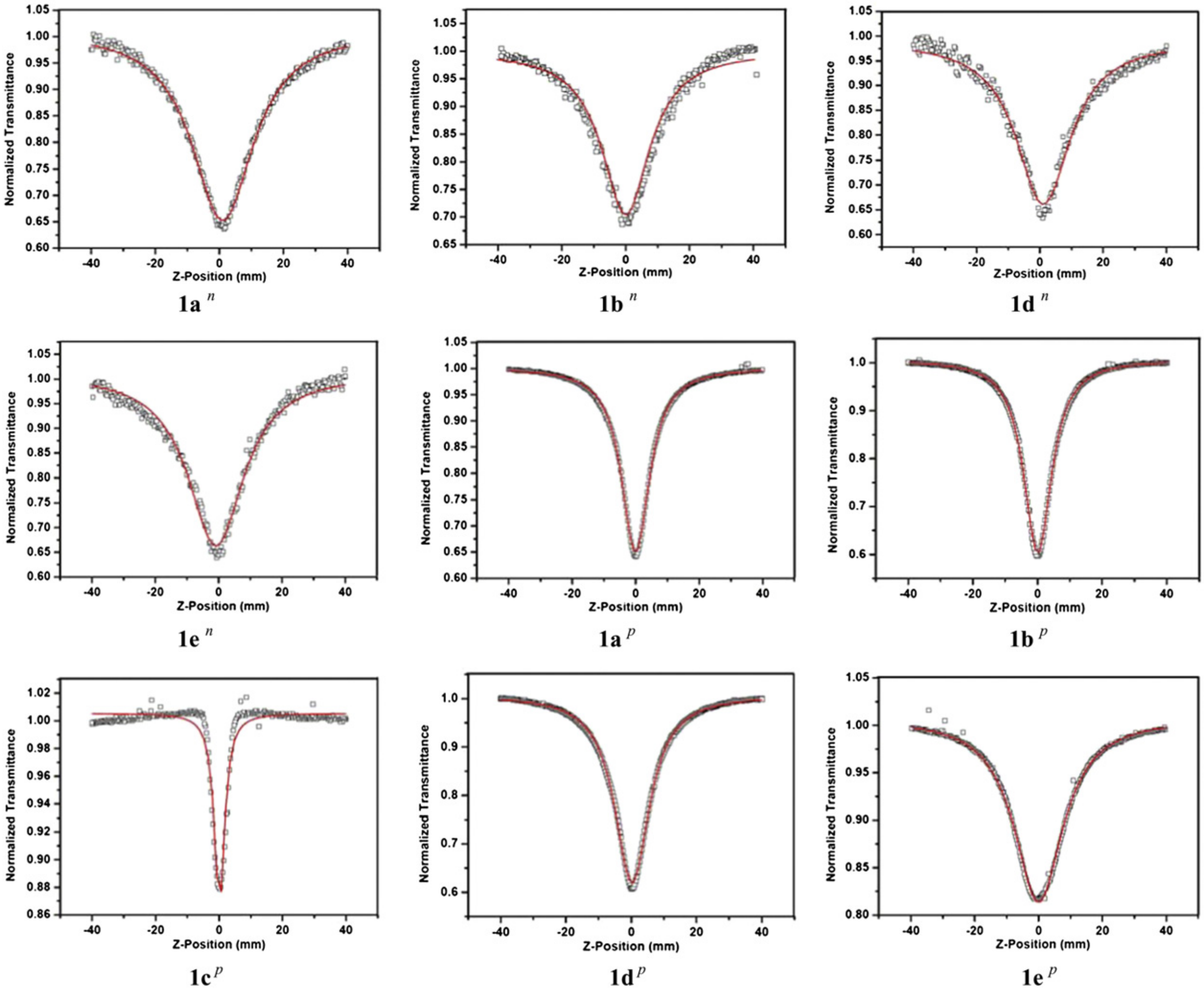
3. Results and discussion

3.1. Solubility and thermal stability

The phenothiazinium chlorides (**1a**–**e**) have good solubility in most polar solvents, such as water, chloroform and methanol. Fig. 3 shows the TGA curves for phenothiazinium chlorides (**1a**–**e**) in a nitrogen environment at a scan rate of 10 °C min^{-1}. The compounds are thermally stable up to approximately 300 °C, which is very good for such organic compounds with a low molecular weight. The good solubility and high thermal stability both show that these title compounds are promising for their application in devices.

3.2. Absorption and emission spectra

The absorption and emission maxima, Stokes shift and quantum yields were measured for **1a**–**e** in methanol solution and the data are summarized in Table 1. The compounds exhibit absorption maxima in the range 652–667 nm (Fig. 4). There is only small variation in the absorption maxima with different side groups. The longest absorption is observed for compound **1b**, which is a consequence of the good electron donating properties of this unit.

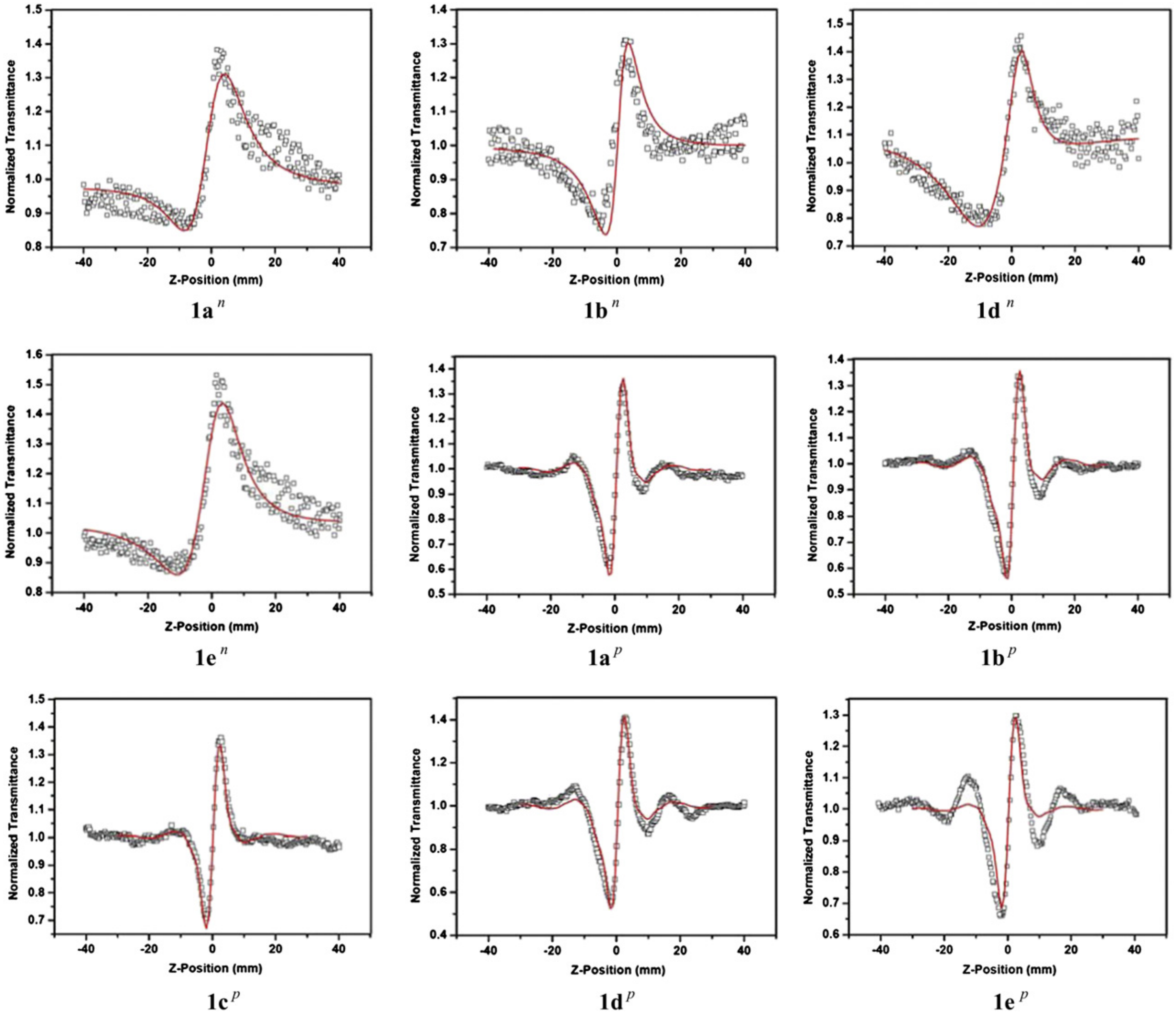


1a ^{n} 1b ^{n} 1d ^{n}

1e ^{n} 1a ^{p} 1b ^{p}

1c ^{p} 1d ^{p} 1e ^{p}

Fig. 6. Z-scan data of opened aperture (^{n} nanosecond, ^{p} picosecond).



1a ^{n} 1b ^{n} 1d ^{n}

1e ^{n} 1a ^{p} 1b ^{p}

1c ^{p} 1d ^{p} 1e ^{p}

Fig. 7. Z-scan data of refractive part (Data are the ratio of the closed aperture transmittance divided the open aperture transmittance, ^{n} nanosecond, ^{p} picosecond.).

Compound **1a** which contains the pyrrolidine units has a shorter wavelength maxima than that of compound **1b**. Compounds **1c**–**e**, which have a bulky benzene ring, have similar wavelength absorption at approximately 654 nm, which is slightly shorter than those of compounds **1a** and **1b**. All the compounds have almost no absorbance at 532 nm, which ensures low intensity and small temperature change for the third-order NLO test with the 532 nm laser [28].

The emission maxima are in the range 684–697 nm (Fig. 5), which follow a similar pattern to the absorption maxima. No fluorescence emission was observed in compound **1c**, and it is obvious that the fluorescence is negated by the p-π conjugation of the nitrogen atom and the benzene group. The quantum yields, measured in methanol solution are low and range from 0.01 for compound **1b** to 0.06 for compound **1a**. Compound **1a** which has the most rigid structure provides the highest quantum yield. The Stokes shifts of compounds **1a**–**e** are at approximately 29 nm owing to the excited and ground state similarity.

3.3. NLO properties

3.3.1. Z-scan results

Dimethyl sulfoxide (DMSO) was used as solvent, since it is relatively involatile. In order to obtain the second hyperpolarizability γ', the concentration of the compounds were maintained at 3.13×10^{-4} mol L^{-1} in DMSO solution. The nonlinearity of pure DMSO solvent was also measured under the same conditions and no signal could be obtained. So the nonlinearity of solvent could be ignored under both nanosecond and picosecond laser beam irradiation [29]. All the figures indicate that the compounds have strong third-order NLO properties. The trough of normalized transmittance shown in Fig. 6 indicates that the laser pulse experience RSA. A positive sign of refractive nonlinearity has been observed in Fig. 7, which indicates a self-focusing behavior.

The nonlinear absorption component was evaluated under an open aperture. Since light transmittance (T) is a function of the sample's Z position (with respect to the focal point at $Z=0$), the nonlinear absorption ($\alpha = \beta\ (I_i)$) and linear absorption (α_0) can be described by the classical eq. (1), where α and α_0 are linear and effective third-order NLO absorptive coefficients. τ is the time, and L is the optical path [30,31].

$$T(Z) = \frac{\alpha_0}{\sqrt{\pi}\beta I_i(Z)\left(1-e^{-\alpha_0 L}\right)} \int_{-\infty}^{\infty} \times \ln\left[1+\beta I_i(Z)\frac{1-e^{-\alpha_0 L}}{\alpha_0}e^{-\tau^2}\right]\mathrm{d}\tau \quad (1)$$

From Fig. 7, the compounds also exhibit strong nonlinear refraction at 532 nm. The nonlinear refractive data are the ratio of the closed

Table 2
The third-order NLO properties of **1a**–**e** in DMSO solution.

Compds.	T_0[a]	Laser	n_2 (10^{-17} m^2 W^{-1})	β_{eff} (10^{-10} m W^{-1})	$\chi^{(3)}_R$ (10^{-11}esu)	$\chi^{(3)}_I$ (10^{-11}esu)	$\chi^{(3)}$ (10^{-11}esu)	γ' (10^{-29}esu)
1a	79%	ns [n]	5.35	4.06	4.16	1.34	4.37	6.10
1b	76%	ns [n]	5.08	4.21	3.95	1.39	4.18	5.85
1c	64%	ns [n]	ND[b]	ND[b]	ND[b]	ND[b]	ND[b]	ND[b]
1d	67%	ns [n]	6.30	4.44	4.90	1.46	5.11	7.13
1e	65%	ns [n]	6.36	4.42	4.95	1.46	5.16	7.20
1a	69%	ps [p]	0.35	0.22	0.27	0.73	0.28	0.39
1b	67%	ps [p]	0.37	0.25	0.29	0.83	0.30	0.42
1c	40%	ps [p]	0.40	0.10	0.31	0.03	0.31	0.43
1d	64%	ps [p]	0.43	0.25	0.33	0.82	0.34	0.48
1e	57%	ps [p]	0.34	0.12	0.26	0.04	0.26	0.37

[n] With nanosecond laser beam at 6.6 μJ.
[p] With picosecond laser beam at 0.6 μJ.
[a] With 3.13×10^{-4} mol L^{-1} in DMSO solution.
[b] RSA phenomenon cannot be detected in nanosecond Z-scan measurement.

aperture transmittance divided the open aperture transmittance. The trough and peak occur at equal distances from the focus. Besides, the trough-peak separation(ΔZ_{V-P}) and the difference between normalized transmittance values at trough and peak positions (ΔT_{V-P}) are found to fit to a set of equations, $\Delta Z_{V-P} = 1.72\pi\omega_0^2/\lambda$, $n_2^{eff} = \lambda a_0 \Delta T_{V-P}/[0.812\pi I(1-e^{-\alpha L})$ which are derived for a third-order NLO process [32]. An effective third-order nonlinear refractive index n_2 can be derived from the ΔT_{V-P}, where α_0 is the linear coefficient, L is the sample thickness, I is the peak irradiation intensity at focus, and λ is the wavelength of the laser.

From the β and n_2 values, the effective third-order NLO susceptibility $\chi^{(3)}$ values of the title compounds can be calculated according to the equations: $\chi_I^{(3)} = 9 \times 10^8 \epsilon_0 n_0^2 c^2 \beta/(4\omega\pi)$, $\chi_R^{(3)} = c n_0^2 n_2/(80\pi)$, $\chi^{(3)} = [(\chi_I^{(3)})^2 + (\chi_R^{(3)})^2]^{1/2}$ [26].

The second hyperpolarizabilities γ' of the compounds were obtained by $\gamma' = \chi^{(3)}/[N((n_0^2+2)/3)^4]$ [33], where N is the density of molecules in the unit of number of molecules per cm^3 and n_0 is the linear refractive index of the dimethyl sulfoxide($n_0 = 1.4783$). The detailed parameters of the NLO properties of the title compounds were collected in Table 2.

From Table 2, the third-order NLO susceptibility $\chi^{(3)}$ and second hyperpolarizabilities γ' of the phenothiazinium chlorides(**1a**–**e**) are up to 10^{-11} and 10^{-29} esu under nanosecond laser irradiation at 532 nm, respectively. The third-order NLO properties of the compounds range in the same order of magnitude under the same laser beam irradiation due to their structural similarity. Under the nanosecond laser beam, **1a** has a slightly larger value than **1b** in the third-order NLO susceptibility $\chi^{(3)}$ and the second hyperpolarizability γ', which indicates that the strain of the 5-membered pyrrolidine ring is beneficial for the third-order NLO properties. The $\chi^{(3)}$ and γ' of phenothiaziniums **1d**–**e** are better than those of **1a**–**b** under nanosecond laser irradiation, illustrating that bulky benzyl amino substitutent also enhances the third-order NLO properties under the same conditions.

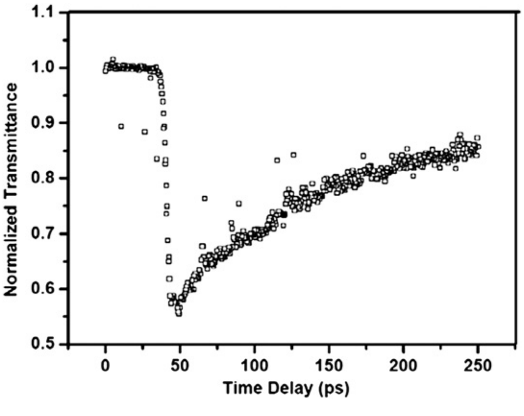


Fig. 8. Pump-probe result of **1b**.

There is an order of magnitude decrease in the third-order NLO coefficients under picosecond laser beam irradiation. Phenothiazinium salts **1c** and **1e** exhibit weak performance on nonlinear refraction under the picosecond laser beam, resulting in the relatively weak third-order NLO susceptibilities $\chi^{(3)}$ and second hyperpolarizabilities γ'.

Compound **1c** does not show any third-order NLO response under the nanosecond laser beam, whereas it performs well under irradiation with the picosecond pulse beam. It is obvious that the p-π conjugation between the phenyl group and nitrogen atom results in a different response in the nanosecond and picosecond Z-scan techniques. We assume that the different characteristics of nanosecond and picosecond laser beam, such as frequceny and energy, make the different third-order NLO response of the phenothiaziniums.

The high values of $\chi^{(3)}$ and γ' indicate that the resonance structures have large polarizability and potential electron fluctionality which meet the requirements for third-order NLO materials.

3.3.2. Pump-probe measurement

In order to gain an insight into the nonlinear origin of these compounds, picosecond time-resolved pump-probe experiments have been performed at 532 nm on **1b**. The experimental curve is shown in Fig. 8. Initially, the absorption of the solution increases as a function of time in a manner consistent with the temporal integration of the pump pulse; the instant drop of the probe is dominant due to the excited single state absorption which has a larger cross section than that of the ground state. Once the pump pulse has passed through the sample, the initial response is followed by recovery and the appearance of a long low transmission tail. This behavior is consistent with induced absorption in the first excited singlet state that increases as the excited state is populated and then diminishes as the population in that state relaxes to the ground state. So the nonlinear mechanism of the compound is the typical observed for the excited-state nonlinearity [28].

4. Conclusions

Five phenothiazinium chlorides were evaluated for third-order nonlinear optical properties at 532 nm using a nanosecond and picosecond Z-scan technique in dimethyl sulfoxide solution. The results reveal that four compounds exhibit RSA and nonlinear refraction with third-order NLO susceptibilities $\chi^{(3)} = 4.18–5.16$

$\times 10^{-11}$ esu and the second hyperpolarizabilities $\gamma' = 5.85–7.20 \times 10^{-29}$ esu under nanosecond laser beam irradiation; and all compounds show RSA and nonlinear refraction with $\chi^{(3)} = 0.26–0.34 \times 10^{-11}$ esu, $\gamma' = 0.37–0.48 \times 10^{-29}$ esu under picosecond laser beam irradiation. The picosecond pump-probe response of the compound **1b** implies that the nonlinear mechanism is excited-state nonlinearity. Moreover, the compounds possess good thermal stability and good solubility in most polar solvents. The results show that they are potential candidates for NLO devices.

Acknowledgements

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