Dyes and Pigments 91 (2011) 489–494

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Third-order nonlinear optical properties of symmetric phenoxazinium chlorides with resonance structures at 532 nm

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ARTICLE INFO

Article history:
Received 17 January 2011
Received in revised form
31 March 2011
Accepted 1 April 2011
Available online 8 April 2011

Keywords:
Phenoxazinium chloride
Third-order NLO
Resonance structure
Z-scan
NLO material
Functional dyes

ABSTRACT

A series of symmetric phenoxazinium chlorides, which have good solubility in polar solvents and good thermal stability, were evaluated in acetonitrile solution for third-order nonlinear optical properties at 532 nm using nanosecond and picosecond *Z*-scan techniques. The title compounds exhibit strong reverse saturable absorption and nonlinear refraction. The third-order nonlinear optical properties under nanosecond laser beam irradiation and picosecond laser beam irradiation were obtained. The nonlinear mechanism is revealed as excited-state nonlinearity by a picosecond pump-probe response experiment for one of the compounds.

1. Introduction

Novel materials endowed with a high nonlinear optical (NLO) response are required in many fields of material science as they find potential applications in optical limiting [1], photodynamic therapy [2] and three-dimensional memories [3]. Organic third-order NLO materials are taken much attention, since it is possible to design their chemical structures and they have been reported to possess relatively large nonlinearities and fast response time [4–6]. Molecules with large π-conjugation systems, such as phthalocyanine [7], porphyrins [8,9], azobenzene [10] etc, have attracted considerable interests. However, the relationship between the chemical structures and the third-order nonlinear optical properties is still a challenge for the researchers.

From the recently reported NLO materials such as BM4i4i [11,12], croconates [13] and squaraine compounds [14], it was found that the conjugated molecules with resonance structures would be the good selections for the third-order NLO materials. In our previous work, the candidates with resonance structures [15,16] were proposed for the new third-order NLO materials. Benzo[a]phenoxazinium salts [15] and phenothiazinium salts [16] which have been examined to show good NLO performance have enhanced the design idea. Benzo[a]phenoxazinium salts display strong reverse saturable absorption (RSA) and nonlinear refraction with 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 nanosecond laser beam at 532 nm, while the phenothiazinium salts exhibit a better performance 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 the same condition. On the basis of the structure similarity of phenoxazinium and phenothiazinium, we have resynthesized several symmetric phenoxazinium and evaluated their third-order NLO properties. Here, we report our findings, which might be helpful information to the related fields.

Five symmetric phenoxazinium chlorides (Fig. 1) with resonance structures were synthesized to examine for third-order NLO properties. The delocalized D–π–D structure of phenoxazinium chlorides (**1**) can be expressed by three stable resonance structures

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doi:10.1016/j.dyepig.2011.04.004

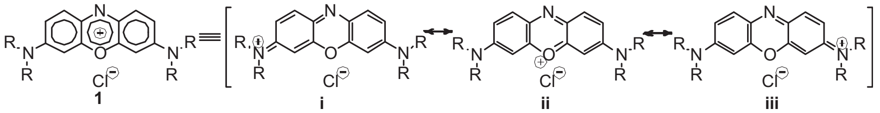


Fig. 1. Resonance structures of phenoxazinium chlorides.

(**i**–**iii**) and the amino groups well participate in the resonance. The presence of large polarizable conjugated π-electrons in the aromatic heterocycles and potential electron fluctionality well meet the requirements of promising third-order NLO materials.

2. Experimental

2.1. Materials

3,7-Bis(diethylamino)phenoxazinium chloride (**1a**), 3,7-bis(dipropylamino)phenoxazinium chloride (**1b**), 3,7-di(pyrrolidinyl) phenoxazinium chloride (**1c**), 3,7-di(piperidinyl)phenoxazinium chloride (**1d**), 3,7-dimorpholinophenoxazinium chloride (**1e**) (Fig. 2)were synthesized by the reported method. Their structures are consistent with the reported values by ^{1}H NMR analysis [17,18].

2.2. Instrument

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 [19]. 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 21 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 6.3 μJ, while the picosecond *Z*-scan test was measured in 2 mm cell with the incident energy of the laser beam is 0.4 μJ. Two Rj-7620 Energy Ratiometers were employed as the detectors. The solution was placed in a high-precision mobile platform moving along the incident light direction (*Z*). Then *Z*-scan curve, the transmittance as a function of the sample position, could be obtained. In the picosecond pump-probe experiments, a Q-switched Nd:YAG laser (EKSPLA) that 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.

3. Results and discussion

3.1. Solubility and thermal stability

The symmetric phenoxazinium chlorides (**1a**–**e**) have excellent solubility in most polar solvents, such as water, chloroform, methanol, which affords them potential applications in device research. Fig. 3 shows the TGA curves for phenoxazinium chlorides (**1a**–**e**) in a nitrogen environment at a scan rate of 10 °C min^{-1}. From the Fig. 3, the compounds (**1a**–**b**) are thermally stable up to approximately 250 °C, while the thermal stable temperatures of compounds (**1c**–**e**) are around 340 °C. It is notable that the compounds with the alkyl chain amines in side groups have relatively poor thermal stability comparing to the compounds with cyclic amines. The compound **1c** that has pyrrolidine ring in the side group owns the best thermal stability, which may be attributed to the rigid structure of the pyrrolidine. Overall, phenoxazinium chlorides (**1a**–**e**) possess good thermal stability for organic compounds with a low molecular weight, which gives them the prospect for the device research.

3.2. Structure study with DFT calculation

To demonstrate an inside view of the symmetrical phenoxazinium cation, the structures were fully optimized by using Density Functional theory (DFT) method with B3LYP [20]. The basis set used was 6–31G*. Based on the optimized structures and with the same basis set, vibrational frequencies were calculated. All predicted vibrational spectra had no imaginary frequency, which implied that the optimized geometries were locating at the local lowest point on the potential energy surface [21]. All the calculations were performed by using Gaussian 98 program package [22].

The typical molecular orbitals of phenoxazinium cation (**1a**$^+$) are given in Fig. 4. The graphics of bonding orbitals clearly demonstrated that the bonding electrons are mainly located in the aromatic phenoxazinium skeleton and the wings of these structures, which means the intramolecular electron transfer is easy. The conjugations between the two nitrogen atoms and phenoxazinium skeleton are contributed by the orbitals of HOMO-2 and HOMO-5. Comparably, the antibonding orbitals are mostly located in the central part of the molecular. The symmetrical structure with two amino groups only makes the slight difference for each molecular

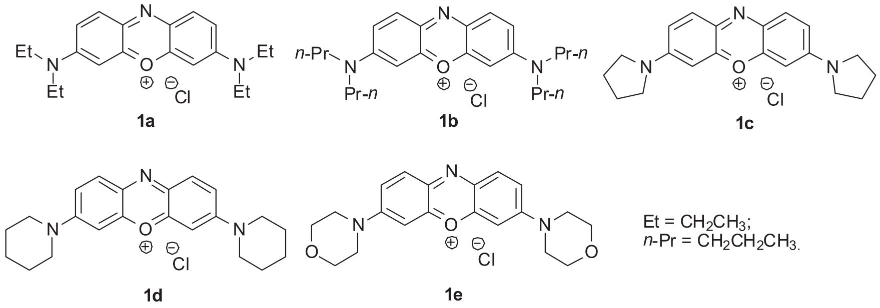


Fig. 2. Structures of phenoxazinium chlorides (**1a**–**e**).

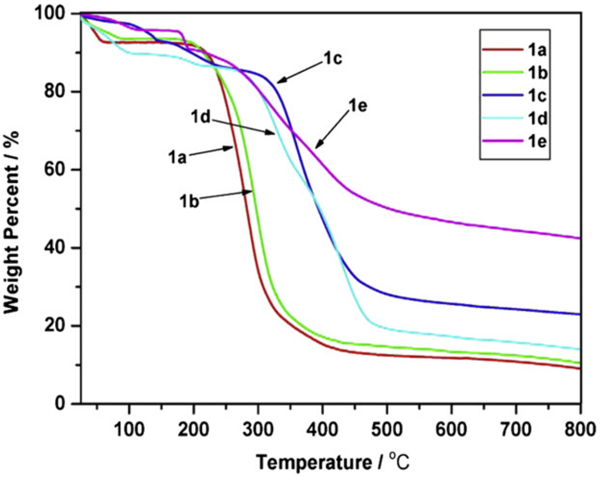


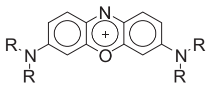
Fig. 3. The thermal stability of the compounds **1a**–**e**.

orbital. The calculated HOMO (eV) and LUMO (eV) energies of phenoxazinium cations (**1a**$^+$–**e**$^+$) are listed in Table 1, and energy gaps (E_{HL}) are quite small in the range of 2.422–2.485 eV. The small energy gap enables the electron transit easily, which is the essential cause of the excellent nonlinear properties.

3.3. Absorption spectra

Comparing to the benzo[a]phenoxazinium salts [15] and phenothiazinium salts [16], the symmetric phenoxazinium chlorides (**1a**–**e**) show slight blue shift ranging in 643–652 nm (Fig. 5). There is only small variation with different side groups in the absorption maxima. The longest absorption is observed for compound **1d**, which is a consequence of the good electron donating properties of this unit. It is obvious that **1c** which contains pyrrolidine has shorter wavelength maxima than that of compound **1d**. 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 532 nm laser beam [23].

Table 1
Calculated HOMO (eV) and LUMO (eV) energies of phenoxazinium cations (**1a**$^+$–**e**$^+$).



1a$^+$~e$^+$

Entry	Compounds	–R, –R	HOMO (eV)	LUMO (eV)	ΔE_{HL}(eV)
1	**1a**$^+$	C_2H_5–, C_2H_5–	–8.440	–5.968	2.472
2	**1b**$^+$	n–C_3H_7–, n-C_3H_7–	–8.344	–5.897	2.447
3	**1c**$^+$	–$(CH_2)_4$–	–8.429	–5.944	2.485
4	**1d**$^+$	–$(CH_2)_5$–	–8.333	–5.903	2.430
5	**1e**$^+$	–$(CH_2)_2O(CH_2)_2$–	–8.598	–6.176	2.422

3.4. Z-scan results

Acetonitrile (CH_3CN) was used as solvent. The nonlinearity of pure CH_3CN 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 [24,25]. In order to obtain the second hyperpolarizability γ', the concentration of the compounds were maintained at 1.79×10^{-4} mol L^{-1} in CH_3CN solution. All the figures indicate that these compounds have strong third-order NLO properties. The trough of normalized transmittance shown in Fig. 6

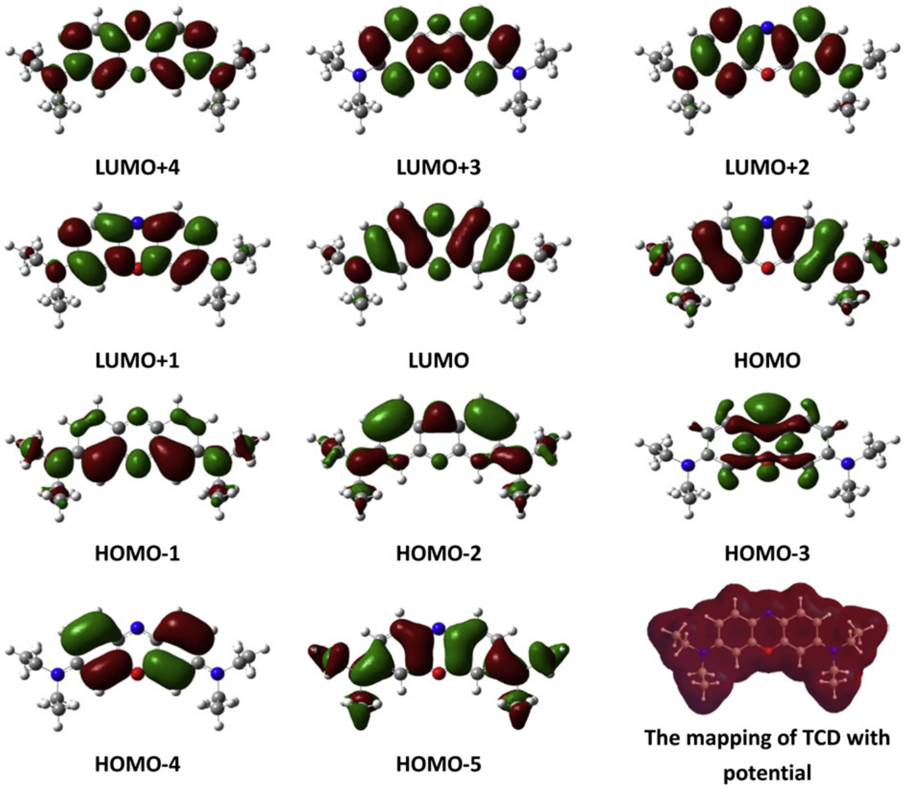


Fig. 4. Molecular orbitals and the mapping of Total Charge Density (TCD) with potential of phenoxazinium cation (**1a**$^+$).

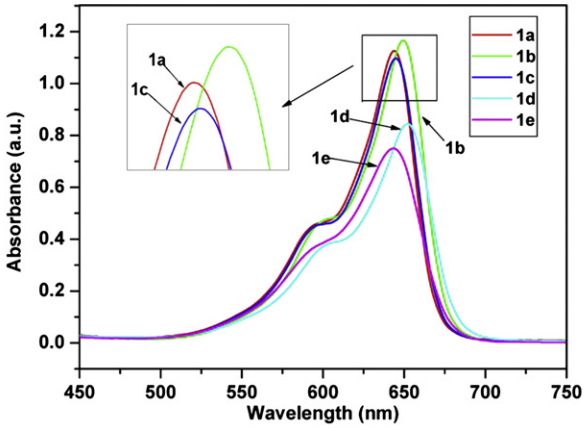
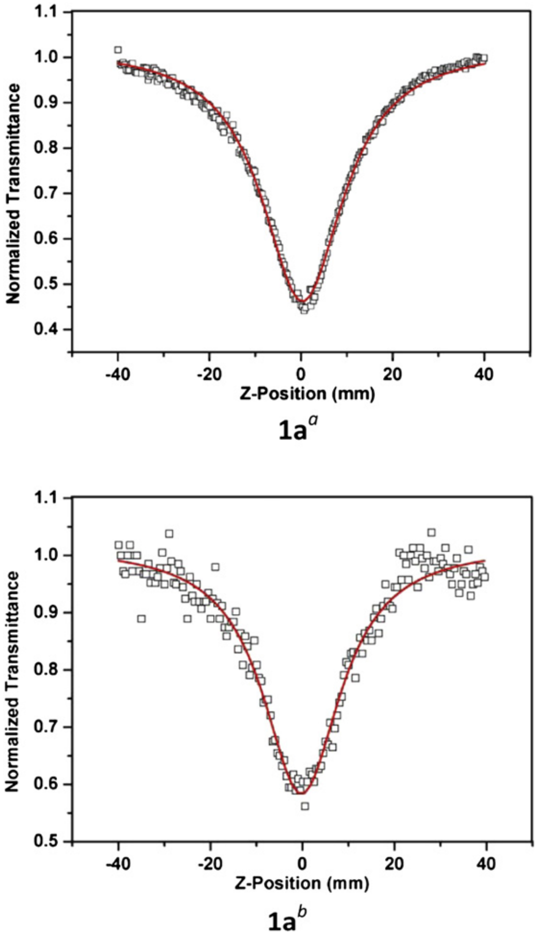


Fig. 5. Absorption spectra of symmetric phenoxazinium chlorides (**1a**–**e**) in CH_3CN ($c = 1 \times 10^{-5}$ mol L^{-1}).

indicates that the laser pulses experience strong RSA. A positive sign of refractive nonlinearity has been observed in Fig. 7, which indicates a self-focusing behavior.

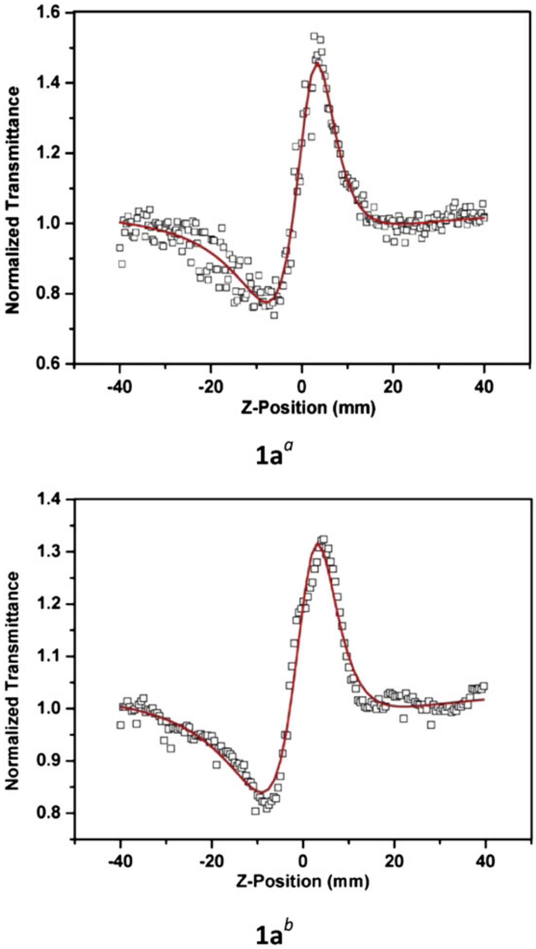
The nonlinear absorption component was evaluated under an open aperture. Since light transmittance (T) is a function of the sample's Z position (with respect to the focal point at $Z = 0$), the nonlinear absorption ($\alpha = \beta\ (I_i)$) and linear absorption (α_0) can be described by the classical eq (1), where α_0 and α are linear and effective third-order NLO absorptive coefficients. τ is the time, and L is the optical path [26–28].



$1a^a$

$1a^b$

Fig. 6. *Z*-scan data of opened aperture for **1a** (^{a} nanosecond, ^{b} picosecond).



$1a^a$

$1a^b$

Fig. 7. *Z*-scan data of refractive part for 1a that are the ratio of the closed aperture transmittance divided the open aperture transmittance (^{a} nanosecond, ^{b} picosecond).

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

From the Fig. 7, the compounds also exhibit strong nonlinear refraction at 532 nm. The nonlinear refractive data are the ratio of the closed 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, $\Delta Z_{V-P} = 1.72\pi\omega_0^2/\lambda$, $n_2^{\mathrm{eff}} = \lambda a_0 \Delta T_{V-P}/[0.812\pi I(1 - e^{-\alpha L})]$ which are derived for a third-order NLO process [26,29]. 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: $X_I^{(3)} = 9 \times 10^8 \varepsilon_0 n_0^2 c^2 \beta/(4\omega\pi)$, $X_R^{(3)} = c n_0^2 n_2/(80\pi)$, $X^{(3)} = [(X_I^{(3)})^2 + (X_R^{(3)})^2]^{1/2}$ [19,26]. The second hyperpolarizability γ' of the compounds was obtained by $\gamma' = X^{(3)}/[N((n_0^2 + 2)/3)^4]$ [25,26], where N is the density of

Table 2
NLO properties of **1a**–**e** in CH_3CN solution.

Entry	Compds.	T_0	Laser	n_2 (10^{-17} m^2 W^{-1})	β_{eff} (10^{-10} m W^{-1})	$X_R^{(3)}$ (10^{-11} esu)	$X_I^{(3)}$ (10^{-11} esu)	$\chi^{(3)}$ (10^{-11} esu)	γ' (10^{-29} esu)
1	**1a**	66%	ns[a]	7.83	7.25	6.96	2.73	7.48	15.9
2	**1b**	67%	ns[a]	7.05	6.76	6.27	2.54	6.76	14.3
3	**1c**	64%	ns[a]	9.68	7.81	8.61	2.94	9.10	19.3
4	**1d**	61%	ns[a]	6.84	5.71	6.08	2.15	6.45	13.7
5	**1e**	64%	ns[a]	6.48	3.82	5.76	1.44	5.94	12.6
6	**1a**	61%	ps[b]	0.436	0.446	0.388	0.168	0.423	0.898
7	**1b**	64%	ps[b]	0.347	0.417	0.308	0.157	0.346	0.734
8	**1c**	62%	ps[b]	0.402	0.455	0.357	0.172	0.396	0.840
9	**1d**	59%	ps[b]	0.400	0.428	0.356	0.161	0.391	0.830
10	**1e**	47%	ps[b]	0.570	0.432	0.507	0.162	0.532	1.13

[a] With nanosecond laser beam at 6.3 μJ.
[b] With picosecond laser beam at 0.4 μJ.

molecules in the unit of number of molecules per cm^3 and n_0 is the linear refractive index of the CH_3CN ($n_0 = 1.53$). The detailed parameters of the NLO properties of the title compounds were tabled as follows.

From Table 2, the third-order NLO susceptibility $\chi^{(3)}$ and second hyperpolarizabilities γ' of the phenoxazinium chlorides(**1a**–**e**) are up to 10^{-11} and 10^{-28} esu under nanosecond laser beam 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. There is more than an order of magnitude decrease in the third-order NLO coefficients under picosecond laser beam irradiation. We assume that the different characteristics of nanosecond and picosecond laser beam, such as frequency and energy, make the different third-order NLO response of the phenoxaziniums.

The data obtained for the symmetric phenoxazinium chlorides are one order of magnitude larger than those obtained for the benzo[a]phenoxazinium salts [15] under nanosecond laser beam at 532 nm, while they are almost two times larger than the phenothiazinium salts [16] under both nanosecond and picosecond laser beam.

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

3.5. 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 **1a**. 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 excited-state nonlinearity [23].

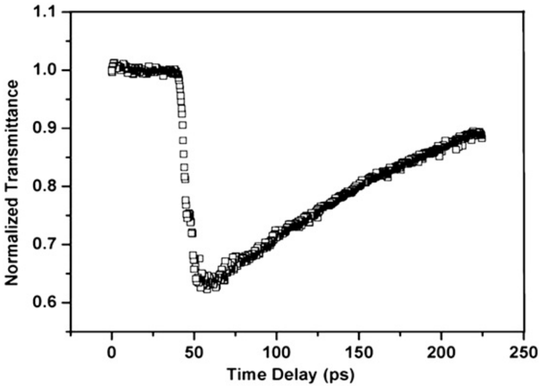


Fig. 8. Pump-probe results for the compound **1a**.

4. Conclusion

Five phenoxazinium chlorides were evaluated in acetonitrile solution for third-order nonlinear optical properties at 532 nm with nanosecond and picosecond *Z*-scan techniques. The results reveal that the compounds exhibit strong RSA and nonlinear refraction with third-order NLO susceptibilities $\chi^{(3)} = 5.94–9.10 \times 10^{-11}$ esu and the second hyperpolarizabilities $\gamma' = 1.26–1.93 \times 10^{-28}$ esu under nanosecond laser beam irradiation and $\chi^{(3)} = 3.46–5.32 \times 10^{-12}$ esu, $\gamma' = 0.73–1.13 \times 10^{-29}$ esu under picosecond laser beam irradiation. The compounds possess good thermal stability and good solubility in most polar solvents. The picosecond pump-probe response of the compound **1a** implies that the nonlinear mechanism is excited-state nonlinearity. The results show that they are potential candidates for NLO devices. Moreover, the phenoxazinium chlorides (**1a**–**e**) can be easily self-assemble because they are made up of cation and anion, and the impact of self-assemble on third-order nonlinear optical properties can be studied in further research.

Acknowledgments

We thank the financial support from National Natural Science Foundation of China (20876101, 21071105), Natural Science Fund (BK2009113) and Natural Science Fund for Colleges and Universities (08KJB430013) in Jiangsu Province.

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