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The synthesis and third-order nonlinear optical properties of resonance Benzo[a]phenoxazinium salts

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ABSTRACT

The third-order nonlinear optical properties of a series of resonance benzo[a]phenoxazinium salts in acetic acid solution were studied using the Z-scan technique employing a Nd:YAG nanosecond laser at 532 nm. The compounds displayed strong reverse absorption with third-order nonlinear optical coefficients of 0.42–1.20 × 10^{-11} esu and second hyperpolarizabilities of 2.75–7.29 × 10^{-29} esu, respectively. Quantum chemical calculations showed that the compound with more stable highest occupied molecular orbital energy also displayed highest second hyperpolarizability.

1. Introduction

Third-order nonlinear optical (NLO) materials have attracted considerable interest in the last two or so decades, owing to their potential application in photonic technologies such as ultrafast optical communications, computing, data storage, all-optical switching and image processing [1–4]. The synthesis of novel molecules with large macroscopic optical non-linearity continues to attract attention [5]. Various types of organic compound have been shown to display large third-order susceptibility $\chi^{(3)}$ [6–9] and it is generally accepted that substantially conjugated, donor/acceptor compounds of diradical character are important aspects for third-order NLO materials [6,10–12].

However, the relationship between third-order NLO properties and molecular structure, such as conjugation, charge transfer and polarization, remains unresolved [13]. Usually, there are two approaches to achieving good third NLO potency, namely via the optimization of a π-bridge structure for donor and/or acceptor pairs and via the optimization of donor and/or acceptor pairs for given π-bridges [14]. Recently, significant progress has been made in the development of third-order NLO chromophores based on high efficient donor and/or acceptor pairs [15–17], although π-bridge structure–property relationships have not yet been fully explored. The third-order NLO properties of di(benzofuranonyl)methanolate (BM4i4i) indicate that significant coupling between valence bond (VB) resonance forms was responsible for the observed large second hyperpolarizability γ' value [12,18,19]. Few examples have been reported of the resonance structure of NLO materials except for the resonance structures of nonsymmetric squaraines [20]. More experimental examples are required to validate the selection of resonance compounds for third-order NLO materials.

Fig. 1 shows the structure of 5,9-diaminobenzo[a]phenoxazinium. The delocalized D–π–D structure of benzo[a]phenoxazinium **1** can be expressed by the stable resonance structures **2**–**4** [21–24]. The presence of large polarizable conjugated π-electrons in the aromatic heterocycle and corresponding potential electron fluctuant ability meet the requirements for a promising third-order NLO material.

Benzo[a]phenoxaziniums have been utilised as fluorescent probes for amino acids, heavy metal ions and biomolecules [25–27], few have been employed as NLO materials [28]. This paper concerns the synthesis and the third-order NLO properties of 5-((3-chlorophenyl)amino)-9-(diethylamino)benzo[a]phenoxazinium salts.

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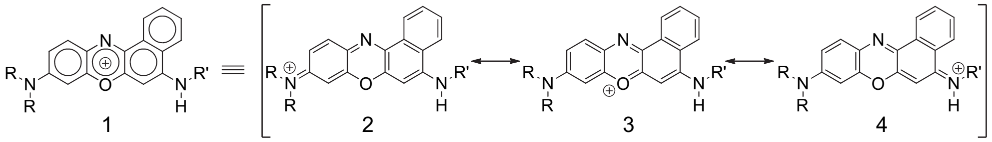


Fig. 1. Resonance structures of benzo[a]phenoxazinium salt.

2. Experimental section

2.1. Materials

Starting materials were purchased from TCI (Shanghai) Development Co., Ltd. or Sinogharm Chemical Reagent Co., Ltd. and used directly. Synthetic grade solvents were obtained commercially and used without further purification.

2.2. Instruments

Melting points were measured on an X-4 microscope electro thermal apparatus (Taike, China) and the results are uncorrected. IR spectra were recorded on a Nicolet 5200 FT-IR instrument using solid samples dispersed in KBr pellets. The elemental analyses were performed with a Vario El-III elemental analyzer. Mass spectra were obtained on Waters ZQ 2000. UV–vis absorption spectra were recorded at room temperature in quartz cells of 1 cm path length using a TU-1800 SPC spectrophotometer. Fluorescence spectra were recorded at a HORIBA Jobin-Yvon Fluorolog 4 Tau-3 spectroscope. ^{1}H NMR spectra were obtained on Bruker-300 or Varian-400 NMR spectrometer, DMSO-*d*6 or $CDCl_3$ were used as solvents, and tetramethylsilane was used as the internal standard.

To measure the optical non-linearity, open/close aperture Z-scan measurements were performed at 532 nm with a pulse width of 4 ns and a repetition rate of 10 Hz from a Nd:YAG laser (EKSPLA), the laser beam with approximately 15 μJ pulse energy was focused on the solution in 2-mm cell by a lens of 10-cm focal length, after the sample was collected by a photodiode detector connected with a Boxcar integrator, the data acquisition was automated [29–32]. **8a-f** were dissolved in acetic acid solution at the concentration of 1.0×10^{-4} mol L^{-1}, and no aggregation was observed at this concentration.

2.3. Synthesis

2.3.1. 9-(Diethylamino)benzo[a]phenoxazin-7-ium nitrate (**6**)

The procedure followed the published procedure that used *N,N*-diethyl-4-nitrosoaniline hydrochloride (**5**) and 2-naphthol [33]. The product was directly used in the next stage of the synthesis without purification.

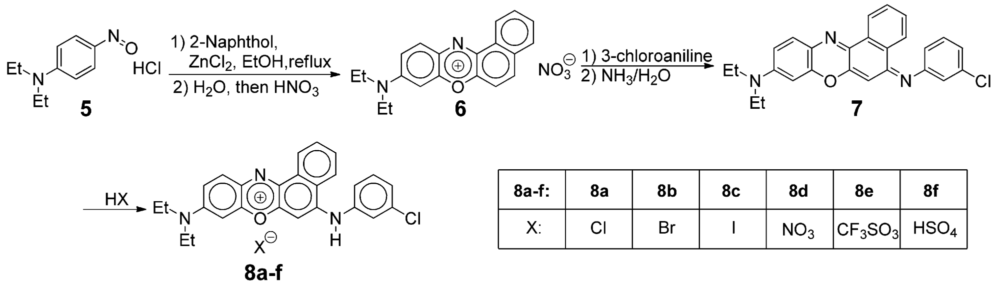
2.3.2. 5-((3-Chlorophenyl)imino)-N,N-diethyl-5H-benzo[a]phenoxazin-9-amine (**7**)

9-(Diethylamino)benzo[a]phenoxazin-7-ium nitrate (**6**) (1.00 g, 2.7 mmol) and 3-chloroaniline (1.03 g, 8.1 mmol) were dissolved in ethanol (40 mL) and the mixture was heated under reflux for 72 h with stirring. After cooling to room temperature, the residue obtained by filtration was dissolved in 40 mL water, and aqueous ammonia was added slowly while stirring until the pH reached ~9.0. The mixture was stirred for 3 h at room temperature and filtered; the solid was dried under vacuum and purified by silica column chromatography eluted with chloroform to afford a dark green powder. Yield: 41%, mp: 171–173 °C; IR (KBr pellet, cm^{-1}): 2972, 2928(alkyl-CH), 1639, 1579, 1446(benzo[a]phenoxazinium skeleton), 1157(C–N); ^{1}H NMR (300 MHz, *$CDCl_3$*) *δppm*: 8.60 (m, 2H, 2 × Ar-H), 7.65 (m, 2H, 2 × Ar-H), 7.50 (d, $J = 9.0$ Hz, 1H, Ar-H), 7.31 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.08 (d, $J = 8.2$ Hz, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 6.84 (d, $J = 7.4$ Hz, 1H, Ar-H), 6.56 (d, $J = 9.1$ Hz, 1H, Ar-H), 6.28 (d, $J = 11.9$ Hz, 2H, Ar-H), 3.41 (q, $J = 7.0$ Hz, 4H, 2 × CH_2), 1.22 (t, $J = 7.0$ Hz, 6H, 2 × CH_3); Calc. for $C_{26}H_{22}ClN_3O$: C 72.97; H 5.18; N 9.82. Found: C 72.71; H 5.21; N 9.85; TOF-MS(EI): *m/z* 427.1453 $[M]^+$, Calc for *m/z* 427.1453 $[M]^+$.

2.3.3. General procedure for the preparation of benzo[a]phenoxazinium salts (**8a–f**)

5-((3-Chlorophenyl)imino)-N,N-diethyl-5H-benzo[a]phenoxazin-9-amine (**7**) (22.8 mg, 0.053 mmol) was dispersed in $CHCl_3$ (10 mL) and ethanol (10 mL) and the appropriate acid (0.1 mmol) was added. The mixture was stirred for 0.5 h at room temperature, the solvent was removed by rotary evaporation under reduced pressure until 5–7 mL solvent remained in the flask; diethyl ether (40 mL) was added with stirring. After filtration, the product was washed with ether and dried under vacuum overnight.

*2.3.3.1. 5-((3-Chlorophenyl)amino)-9-(diethylamino)benzo[a]phenoxazin-7-ium chloride (**8a**).* Green power, yield: 78%, mp: 184–185 °C; IR (KBr pellet, cm^{-1}): 2971, 2867(alkyl-CH), 1639, 1574, 1446(benzo[a]phenoxazinium skeleton), 1160(C–N); ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm}: 9.74 (m, 1H, Ar-H), 8.84 (d, $J = 5.9$ Hz, 1H, Ar-H), 7.89 (m, 3H, 3 × Ar-H), 7.68 (m, 2H, 2 × Ar-H), 7.43 (m, 2H, 2 × Ar-H), 7.08 (s, 1H, Ar-H), 6.85 (s, 1H, Ar-H), 6.62 (s, 1H, Ar-H), 3.66–3.57 (m, 4H, 2 × CH_2), 1.36 (t, $J = 6.7$ Hz, 6H, 2 × CH_3); Calc. for



8a-f:	8a	8b	8c	8d	8e	8f
X:	Cl	Br	I	NO_3	CF_3SO_3	HSO_4

Fig. 2. Synthesis of benzo[a]phenoxazinium salts **8a–f**.

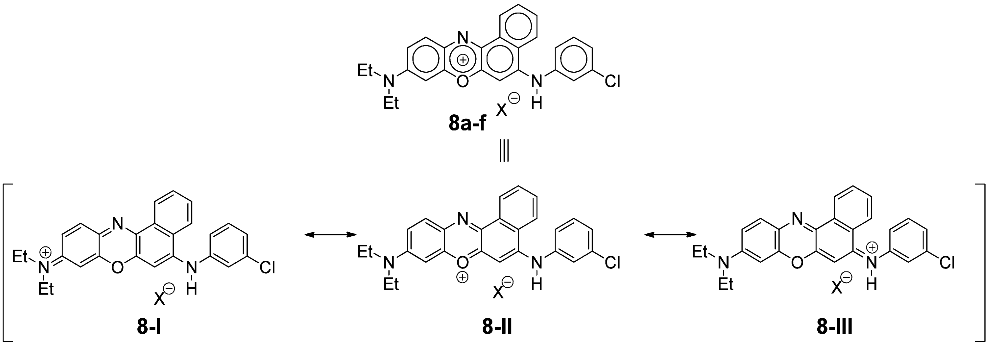


Fig. 3. Resonance structures of benzo[a]phenoxazinium salts **8a**–**f**.

$C_{26}H_{23}Cl_2N_3O\cdot2.5H_2O$: C 61.30; H 5.54; N 8.25. Found: C 61.23; H 5.13; N 8.10.

*2.3.3.2. 5-((3-Chlorophenyl)amino)-9-(diethylamino)benzo[a]phenoxazin-7-ium bromide (**8b**).* Green powder, yield: 83%, mp: 210–212 °C; IR (KBr pellet, cm^{-1}): 2971, 2926, 2867(alkyl-CH), 1639, 1573, 1443(benzo[a]phenoxazinium skeleton), 1160(C–N); ^1H NMR (400 MHz, DMSO-*d6*) δ_{ppm}: 8.84 (d, $J = 7.8$ Hz, 1H, Ar-H), 8.66 (d, $J = 9.8$ Hz, 1H, Ar-H), 8.01 (m, 3H, 3 × Ar-H), 7.92 (m, 2H, 2 × Ar-H), 7.71–7.60 (m, 2H, 2 × Ar-H), 7.50 (m, 2H, 2 × Ar-H), 7.08 (s, 1H, Ar-H), 6.82 (s, 1H, Ar-H), 3.72–3.68 (m, 4H, 2 × CH_2), 1.23 (t, $J = 6.6$ Hz, 6H, 2 × CH_3); Calc. for $C_{26}H_{23}ClBrN_3O\cdot2.5H_2O$: C 56.38; H 5.10; N 7.59. Found: C 56.38; H 4.70; N 7.37.

*2.3.3.3. 5-((3-Chlorophenyl)amino)-9-(diethylamino)benzo[a]phenoxazin-7-ium iodide (**8c**).* Black powder, yield: 76%, mp: 207–209 °C; IR(KBr pellet, cm^{-1}): 2972, 2926(alkyl-CH), 1639, 1573, 1443(benzo[a]phenoxazinium skeleton), 1160(C–N). ^1H NMR (400 MHz, DMSO-*d6*) δ_{ppm}: 8.88 (d, $J = 7.8$ Hz, 1H, Ar-H), 8.67 (d, $J = 7.8$ Hz, 1H, Ar-H), 8.02 (d, $J = 7.4$ Hz, 1H, Ar-H), 7.94 (m, 3H, 3 × Ar-H), 7.68–7.55 (m, 2H, 2 × Ar-H), 7.46 (m, 2H, 2 × Ar-H), 7.06 (s, 1H, Ar-H), 6.81 (s, 1H, Ar-H), 3.73–3.69 (m, 4H, 2 × CH_2), 1.25 (t, $J = 7.0$ Hz, 6H, 2 × CH_3); Calc. for $C_{26}H_{23}ClIN_3O\cdot4H_2O$: C 49.73; H 4.98; N 6.69, Found: C 49.52; H 4.67; N 6.54.

*2.3.3.4. 5-((3-Chlorophenyl)amino)-9-(diethylamino)benzo[a]phenoxazin-7-ium nitrate (**8d**).* Black green powder, yield: 90%, mp: 135–136 °C; IR(KBr pellet, cm^{-1}): 2972, 2928(alkyl-CH), 1640, 1574, 1448(benzo[a]phenoxazinium skeleton), 1159(C–N); ^1H NMR (400 MHz, $CDCl_3$) δ_{ppm}: 8.91 (m, 1H, Ar-H), 8.82 (d, $J = 7.9$ Hz, 1H, Ar-H), 7.91–7.71 (m, 3H, 3 × Ar-H), 7.60 (m, 1H, Ar-H), 7.54 (m, 1H, Ar-H), 7.45 (m, 1H, Ar-H), 7.42–7.32 (m, 1H, Ar-H), 7.11 (m, 1H, Ar-H), 6.89 (s, 1H, Ar-H), 6.63 (s, 1H, Ar-H), 3.64–3.62 (m, 4H, 2 × CH_2), 1.33 (t, $J = 6.9$ Hz, 6H, 2 × CH_3); Calc. for $C_{26}H_{23}ClN_4O_4\cdot2H_2O$: C 59.26; H 5.16; N 10.63. Found: C 58.96; H 4.82; N 10.34.

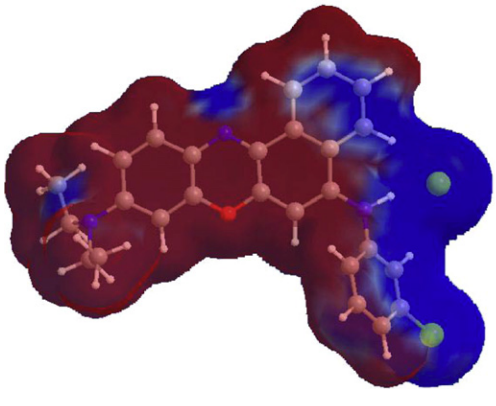


Fig. 4. Optimized geometry and the total NBO Charge Density of **8a(III)** at B3LYP/6-31G*.

*2.3.3.5. 5-((3-Chlorophenyl)amino)-9-(diethylamino)benzo[a]phenoxazin-7-ium trifluoromethanesulfonate (**8e**).* Brown powder, yield: 84%, mp: 203–204 °C; IR(KBr pellet, cm^{-1}): 2972, 2928 (alkyl-CH), 1642, 1580, 1445(benzo[a]phenoxazinium skeleton), 1156(C–N); ^1H NMR (300 MHz, DMSO-*d6*) δ_{ppm}: 8.88 (d, $J = 8.0$ Hz, 1H, Ar-H), 8.66 (d, $J = 8.0$ Hz, 1H, Ar-H), 8.10–7.99 (m, 1H, Ar-H), 7.93 (m, 2H, 2 × Ar-H), 7.63 (m, 2H, 2 × Ar-H), 7.52 (m, 3H, 3 × Ar-H), 7.09 (s, 1H, Ar-H), 6.83 (s, 1H, Ar-H), 3.72–3.69 (m, 4H, 2 × CH_2), 1.23 (t, $J = 6.7$ Hz, 6H, 2 × CH_3); Calc. for $C_{27}H_{23}ClF_3SN_3O_4\cdot0.5H_2O$: C 55.24; H 4.12; N 7.16. Found: C 55.36; H 3.96; N 7.06.

*2.3.3.6. 5-((3-Chlorophenyl)amino)-9-(diethylamino)benzo[a]phenoxazin-7-ium hydrosulfate (**8f**).* Green powder, yield: 83%, mp: 130–131 °C; IR(KBr pellet, cm^{-1}): 2974, 2928(alkyl-CH), 1641, 1575, 1445(benzo[a]phenoxazinium skeleton), 1158(C–N); ^1H NMR (300 MHz, DMSO-*d6*) δ_{ppm}: 8.92 (d, $J = 8.2$ Hz, 1H, Ar-H), 8.69 (d, $J = 8.2$ Hz, 1H, Ar-H), 8.04 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.97 (m, 2H, 2 × Ar-H), 7.71–7.60 (m, 2H, 2 × Ar-H), 7.59–7.45 (m, 3H, 3 × Ar-H), 7.13 (s, 1H, Ar-H), 6.88 (s, 1H, Ar-H), 3.71–3.68 (m, 4H, 2 × CH_2), 1.24 (t, $J = 6.7$ Hz, 6H, 2×CH_3); Calc. for $C_{26}H_{24}ClSN_3O_5\cdot4.5H_2O$: C 51.44; H 5.48; N 6.92. Found: C 51.73; H 5.20; N 7.01.

3. Results and discussion

3.1. Synthesis and structure

3.1.1. Synthesis

Fig. 2 shows the synthetic procedure. To remove the zinc chloride which might affect the following procedure and properties of the target compound, the 9-(diethylamino)benzo[a]phenoxazin-7-ium nitrate (**6**) was prepared from N,N-diethyl-4-nitrosoaniline hydrochloride (**5**) and 2-naphthol by two steps. The stable free base

Table 1
Calculated HOMO (eV) and LUMO (eV) energies of **8-III**.

Compounds	X	LUMO (eV)	HOMO (eV)	ΔE_{HL} (eV)
8a	Cl	−3.523	−5.249	1.726
8b	Br	−3.541	−4.844	1.303
8c	I	−3.670	−4.559	0.889
8d	NO_3	−3.560	−5.379	1.819
8e	CF_3SO_3	−3.498	−5.884	2.386
8f	HSO_4	−3.678	−5.814	2.136

5-((3-chlorophenyl)imino)-N,N-diethyl-5H-benzo[a]phenoxazin-9-amine (**7**) was obtained by the reaction of 6 and 3-chloroaniline followed by the treatment of ammonia, then treated with the corresponding acids to form 5-((3-Chlorophenyl)amino)-9-(diethylamino)benzo[a]phenoxazin-7-ium salts (**8a**–**f**). FT-IR spectra of **8a-f** were exhibited characteristic bands of 1639, 1579, 1446 cm^{-1}, which are contributed to the structure skeleton, and C–N stretching vibrations appear at 1157 cm^{-1}. The ^{1}H NMR chemical shifts of aromatic proton of **7** (6.25–8.75 ppm) were fully changed to 6.50–9.75 ppm, it is clear that the proton from the acids fully changed the properties of the π-conjugated system.

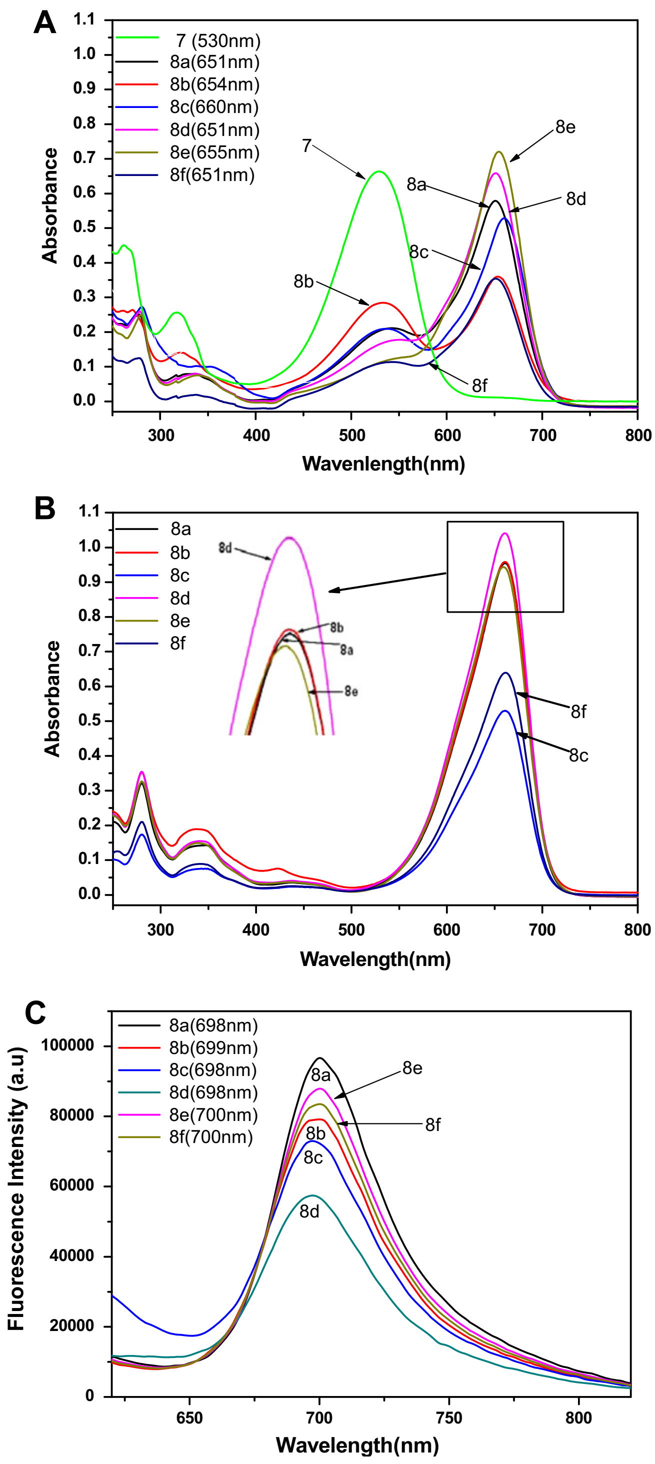


Fig. 5. Absorption spectra of dyes **8a**–**f** in chloroform (A) and acetic acid (B), emission spectra of dyes **8a**–**f** in acetic acid (C).

3.1.2. *Structure study with DFT calculation*

As mentioned in the introduction part, there are three resonance structures for the benzo[a]phenoxazinium salts **8a**–**f** (Fig. 3). In order to evaluate the relative stability of the three resonance structures, their equilibrium geometries were calculated using DFT method with B3LYP [34]. The basis set used was 6–31G* for C, H, N, O, F, S, Cl and Br atoms, and LANL2DZ for I atom[35]. Based on the optimized structures and with the same basis set, vibrational frequencies were calculated. All predicted vibrational spectra have no imaginary frequency, which implied that the optimized geometries were locating at the local lowest point on the potential energy surface [36]. All the calculations were performed by using Gaussian 98 program package [37]. The results show that **8-III** are the most stable structures, in which the anions are near N–H, and it can be explained by the p–π conjugation between the lone-pair electron located in nitrogen atom and the π electron in 3-chlorobenzene. The total NBO Charge Density with potential of **8a(III)** is given in Fig. 4 together with the optimized geometry. It is clear that the positive charge is located in the central conjugated heterocycles. Table 1 lists the calculated HOMO and LUMO energies of the most stable structures, **8a**–**f(III)**.

3.2. *Absorption and emission spectra*

The UV–vis absorption spectra of **8a**–**f** with concentrations of 1.0 × 10^{-5} mol L^{-1} in chloroform are shown in Fig. 5. Two absorption peaks between 500 and 750 nm were present around 530 and 655 nm. According to Fig. 5A, the free base **7** happened to have the maximum peak at 530 nm, it is obvious that **8a**–**f** was partially dissociated to the free base **7** and corresponding acids in high diluted neutral solvents. Acetic acid was selected as the solvent to prohibit the ionization equilibrium, the 530 nm peak was disappeared as expected and there is only one peak between 500 and 750 nm present at 660 nm (Fig. 5B). The more than 100 nm red shifts from **7** to **8a**–**f** indicated the proton strongly enhanced the conjugation of delocalized π electron system. Fig. 5C shows the emission spectra of these compounds in acetic acid. The emission peaks were located around 700 nm when the samples were excited at 500 nm. However, the observed quantum yields were very low. The absorption and emission properties of **8a**–**f** are listed in Table 2.

3.3. *NLO properties*

The nonlinear coefficients of the dyes were measured by the Z-scan technique [39,40]. In our experiments, the properties of dyes in acetic acid solution (approximately 1 × 10^{-4} mol L^{-1}) were investigated with 532 nm laser pulses using the Z-scan technique.

Table 2
The absorption and emission spectra properties of benzo[a]phenoxazinium salts **8a**–**f**.

Compounds[a]	λ_{max}(abs) (nm)	lg ε (L·mol^{-1} cm^{-1})	λ_{max}(em) (nm)	Stokes shift (nm)	Φ[b]
8a	661	4.87	698	37	<0.01
8b	661	4.91	699	38	<0.01
8c	661	4.70	698	37	<0.01
8d	661	4.93	698	37	<0.01
8e	661	4.96	700	39	<0.01
8f	661	4.75	700	39	<0.01

[a] Acetic acid was used as solvent.

[b] Absolute fluorescence quantum yields were measured by reported method [38].

The sample was moved forward or backward along the direction of the laser beam around the focus ($Z = 0$). The transmittance was simultaneously recorded by an energy meter with or without an aperture in the far field of lens as the function of sample position. The non-linearity of pure acetic acid solvent was also measured under the same conditions as the above, but no signal could be obtained, so the non-linearity of solvent could be ignored.

Fig. 6 shows the normalized transmittances measured with an open aperture, which is used to describe a third-order NLO absorptive process. All transmittances are symmetric with respect to the focus ($Z = 0$) where they have minimum transmittances, indicating an induced absorption, i.e. reverse saturated absorption.

Due to the presence of nonlinear absorption, the pure nonlinear refractive property should be assessed from the division of the normalized closed-aperture data by the open aperture data. The NLO refractive properties of compounds **8a**–**f**, shown in Fig. 7, were obtained by the division of the closed-aperture data by the corresponding open aperture data shown in Fig. 6. We can see a valley-peak shape, which was representative of positive nonlinear refractive index($n_2 > 0$) and a self-focusing effect, as shown in Fig. 7, and the difference between the normalized transmittance values at valley and peak positions($\Delta T_{\text{p-v}}$) was related to the effective third-order NLO refractive index $n_2(\text{m}^2 \cdot \text{W}^{-1})$

NLO processes are governed by the nonlinear susceptibility ($\chi^{(3)}$) of NLO materials. The larger the $\chi^{(3)}$ value, the better the material's NLO properties. In accordance to the observed γ and NLO absorption coefficient(β) values, the modulus of the effective $\chi^{(3)}$ can be calculated [40–43]. The nonlinear susceptibility $\chi^{(3)}$ of **8d** was determined to be 1.2×10^{-11} esu, which is almost six times larger than that of some metallophthalocyaines [44]. With the value of $\chi^{(3)}$, the value of second-order hyperpolarizabilities could be obtained by: $\gamma' = \chi^{(3)}/N_c[(n_0^2 + 2)/3]^4$. Where N_c is the number density of molecules and n_0 is the linear refractive index of solvent. Here, the solvent is acetic acid and the n_0 is 1.3716. All NLO

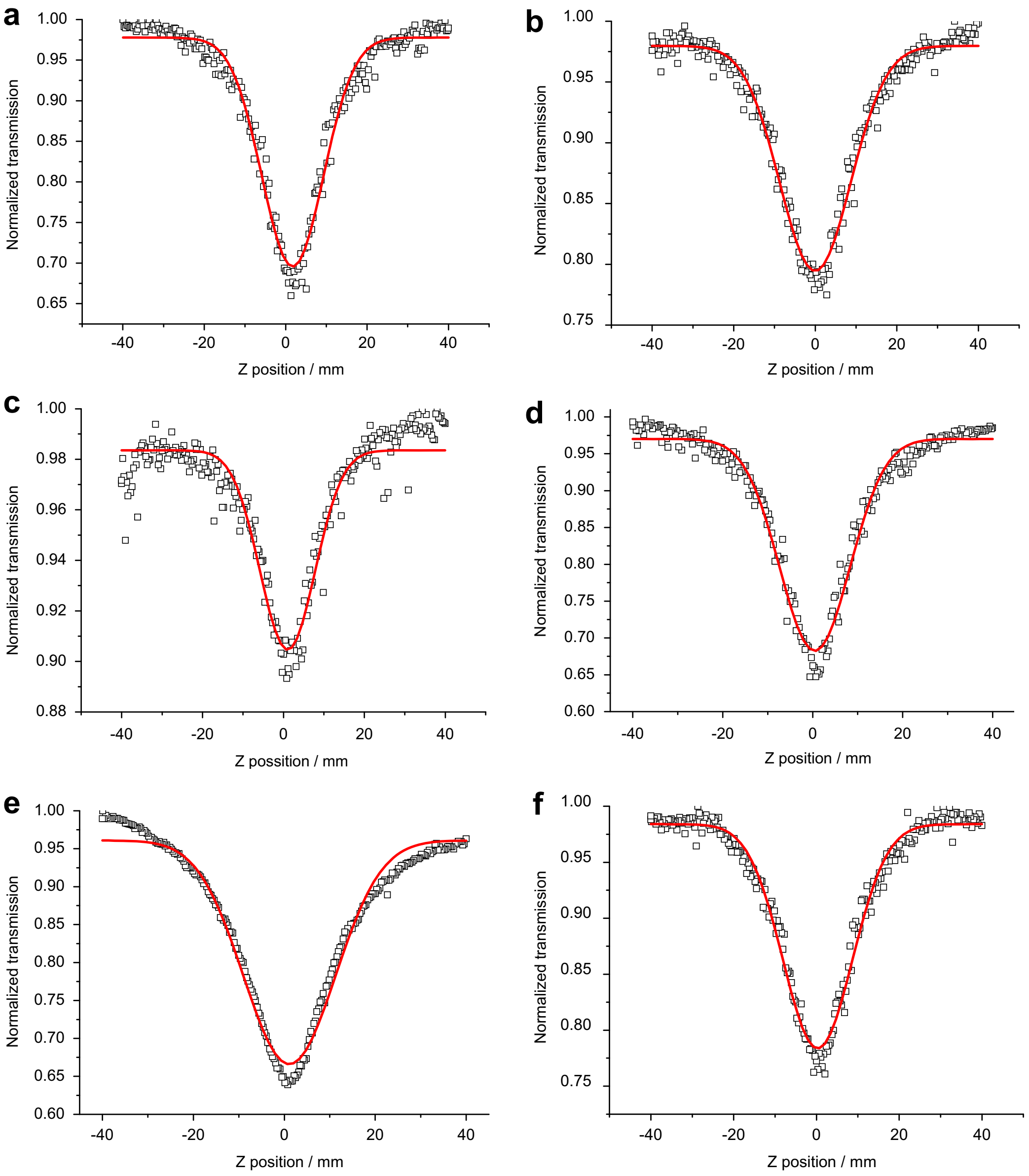


Fig. 6. Z-scan data of opened aperture.

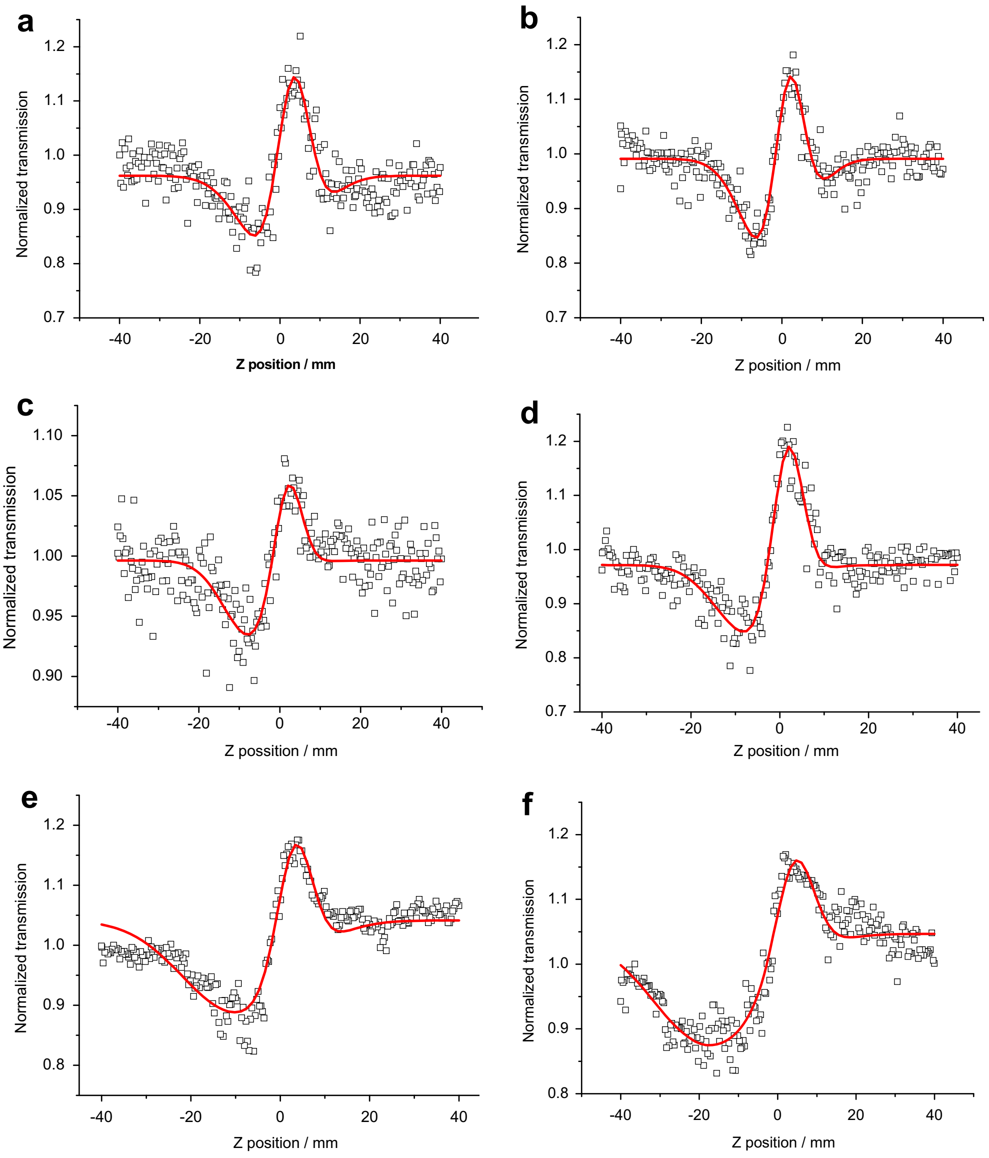


Fig. 7. Z-scan data of refractive part.

properties of compounds **8a**–**f** are summarized in Table 3 according to the formula from previous literature [39].

For the compounds **8a**–**f**, γ′ (**8c**)< γ′ (**8b**)< γ′ (**8a**)< γ′ (**8f**)< γ′ (**8d**)< γ′ (**8e**), whereas the energies of the highest occupied molecular orbital (HOMO), E_H(**8c**) > E_H(**8b**) > E_H(**8a**) > E_H(**8d**) > E_H(**8f**) > E_H(**8e**), we noted that the increase in γ′ within compounds **8a**–**f** is somewhat related to the HOMO energy (Table 1), which depends upon the anion. Indeed, the more stable HOMO energy is, the larger γ′ value is.

4. Conclusions

A series of novel resonance benzo[a]phenoxazinium salts were designed and synthesized by multi-step reactions, and their structures were confirmed by FT-IR, UV–vis, ^{1}H NMR and elemental analyses. Z-scan measurements indicated that these salts possessed large third-order NLO coefficients, and the anions influenced their NLO properties, the more stable HOMO energy is, the larger γ′ value is. Such novel salts are expected to be potential candidates for

Table 3
NLO properties of **8a**–**f** in acetic acid.

Compounds	T_0	C (mol·L^{-1})10^{-4}	β (m·W^{-1})10^{-11}	n_2 (m^2·W^{-1})10^{-18}	$\chi^{(3)}{}_R$ (esu)10^{-12}	$\chi^{(3)}{}_I$ (esu)10^{-12}	$\chi^{(3)}$ (esu)10^{-12}	γ (esu)10^{-29}
8a	0.73	1.08	15.4	11.6	9.05	5.06	10.4	5.71
8b	0.78	0.98	9.84	10.9	8.49	3.24	9.09	5.50
8c	0.72	0.90	4.88	4.96	3.86	1.61	4.18	2.75
8d	0.74	1.00	16.4	13.7	10.7	5.39	12.0	7.12
8e	0.70	0.87	17.5	11.6	8.99	5.78	10.7	7.29
8f	0.70	0.95	11.6	11.2	8.72	3.59	9.43	5.89

optical limiting, optical switching and other fast photonic applications.

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