Theoretical studies on NLO properties of push-pull multi-cycle electro-optical polymer intermediates including thiophene ring

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The second-order nonlinear optical susceptibilities β_{ijk}, β_μ and third-order non-linear optical susceptibilities γ_{ijkl}, $\langle\gamma\rangle$ of a series of the novel push-pull multi-ring electro-photo polymer intermediates have been calculated. The influences of molecular structure, donor, acceptor and the frequency of external field on β and γ, and the relationship between γ and the number of thiophene rings (i.e. conjugated chain length) have been studied using INDO/SCI methods combined with sum-over-state (SOS) formula. The calculated results show that γ is proportional to 2.69 power of the chain length of the conjugated molecular bonds when the length is not quite long.

Keyword   Push-pull multi-cycle electro-photo polymer intermediates, second-order nonlinear optical susceptibility, third-order nonlinear optical susceptibility, ZINDO-SOS

Introduction

Nonlinear optical phenomenon refers to the fact that the value of the induced polarization of the media does not satisfy a linear relationship to the intensity of the electric field imposed under the effect of sufficiently strong electric field. Researches on the NLO materials have become one of the subjects that many experimental and theoretical chemists are interested in.[1,2] They can affect the frequency of the external field and change the phase angle of the light wave. These properties make them become more and more important in the fields of optical information processing such as optical communication, optical computer, optical devices and dynamic images. The organic NLO materials possess many superior NLO characteristics. Specifically, molecule-based NLO materials offer ultrafast response time, lower dielectric constants, better processability characteristics (e.g., amenability to thin-film fabrication), and enhanced nonresonant NLO responses relative to the traditional inorganic solids. In general good NLO properties of the optical materials are determined by the good NLO properties of the molecules of which they consist. It is required that the molecule should have high second and third-order nonlinear optical susceptibilities β and γ, which are determined by the molecular micro-structure. This kind of problem can be studied by quantum chemistry methods.[3-21] Due to the large charge transfer in the thiophene derivatives, it is potential to be new NLO material connected to the bones of multi-cycle electro-optical polymers.[22-26]

In this paper several thiophene derivatives with big β and γ have been designed based on ample study of the influences of molecular structure, donor and acceptor, external field frequency and the length of conjugation bonds on β and γ.

1 Theoretical methods

When external electrical field is imposed on a non-conductive, nonmagnetic media and the molecules of the media are polarized, the dipole vector μ_i can be ex-

pressed as:

$$\mu_i = \mu_i^0 + \alpha_{ij}E_j + \gamma_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_i + \cdots (1)$$

where μ_i is the dipole vector along the ith molecular axis, β_{ijk} the second order nonlinear optical susceptibility and γ_{ijkl} the third order nonlinear optical susceptibility.

Usually three kinds of quantum chemistry methods

are used to calculate the NLO susceptibilities: sum-over-state (SOS) method, finite field (FF) method and coupled perturbation Hartree-Fock method. SOS method is herein, and sum-over-state (SOS) formalism for the second order nonlinear optical susceptibility β_{ijk} and the third order nonlinear optical susceptibility γ_{ijkl} is induced using the perturbation theory combined with density matrix method.[27,28]

$$\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2) = \hbar^{-2}\Sigma_P {\sum_{m,n}}' < g \mid \hat{\mu}_i \mid m > < m \mid \overline{\mu_j} \mid n > < n \mid \hat{\mu}_k \mid g >$$
$$\times (\omega_m - \omega_\sigma)^{-1}(\omega_n - \omega_2)^{-1} \tag{2}$$

$$\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \hbar^{-3}\sum_P [{\sum_{m,n,q}}' < g \mid \hat{\mu}_i \mid m > < m \mid \overline{\mu_j} \mid n > < n \mid \overline{\mu_k} \mid q$$
$$> < q \mid \hat{\mu}_l \mid g > \times (\omega_m - \omega_\sigma)^{-1}(\omega_n - \omega_2 - \omega_3)^{-1}(\omega_q - \omega_3)^{-1} - {\sum_{m,n}}'$$
$$< g \mid \hat{\mu}_i \mid m > < m \mid \hat{\mu}_j \mid g > < g \mid \hat{\mu}_k \mid n > < n \mid \hat{\mu}_l \mid g >$$
$$(\omega_m - \omega_\sigma)^{-1}(\omega_n - \omega_3)^{-1}(\omega_n + \omega_2)^{-1}] \tag{3}$$

In these equations, $\omega_\sigma = \sum\omega_x$, $\overline{\mu_i}$ is the component i of the fluctuation electric dipole moment operator, $\overline{\mu_i} = \hat{\mu}_i - < g\mid\hat{\mu}_i\mid g >$, which in fact, for the cases at hand, is simply $\hat{\mu}_i$. $\sum_P$ in Eq. (2) infers to a sum over the six permutations of the pairs $(-\omega_\sigma,\hat{\mu}_i)$, $(\omega_1,\hat{\mu}_j)$, and $(\omega_2,\hat{\mu}_k)$ and in Eq. (3) to a sum over the 24 permutations of the pairs $(-\omega_\sigma, \hat{\mu}_i)$, $(\omega_1,\hat{\mu}_j)$, $(\omega_2,\hat{\mu}_k)$, and $(\omega_3,\hat{\mu}_l)$. The primes on the sums indicate the exclusion of the ground state g, and ω_m is the circular, electronic transition frequency between the mth excited state, with wavefunction $\mid m >$, and the ground state.

Theoretically, all SCF + CI methods can be used to calculate the physical values in Eq. (2) and Eq. (3). ZINDO-SOS method was used due to its special efficiency in calculating the UV-vis spectrum of conjugated organic molecules.[12-14] First the molecular structures was optimized using ZINDO method and the molecular orbits was calculated using INDO-SCF. Then the ground state and excited states through configuration interaction (CI) method were obtained as well as the transition energies

between two states and corresponding oscillator strengths, i.e. the electron spectrum. Finally the β_{ijk} and γ_{ijkl} were calculated using the program designed by ourselves.

In calculation the axis z was set to be perpendicular to the plane of phenyl ring, with its direction along the direction of molecular permanent dipole moment. β is a third order tensor. β_μ is the vector component in the dipolar direction of β, which is usually measured by the electric-field-induced second order-harmonic generation (EFISH) measurements. In order to compare with the experimental results, β_μ was calculated with the equation as follows:

$$\beta_\mu = (\mu_x\beta_x + \mu_y\beta_y + \mu_z\beta_z)/(\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \tag{4}$$

where $\beta_i = \beta_{iii} + 1/3\sum_{i\neq j}(\beta_{jii} + \beta_{iji} + \beta_{iij})$ $i,j = (x,y,z)$ (5)

$<\gamma>$ is calculated by Eq. (6):

$$<\gamma> = \frac{1}{5}[\sum_i\gamma_{iiii} + \frac{1}{3}\sum_{i\neq j}(\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji})] \quad i,j = x,y,z \tag{6}$$
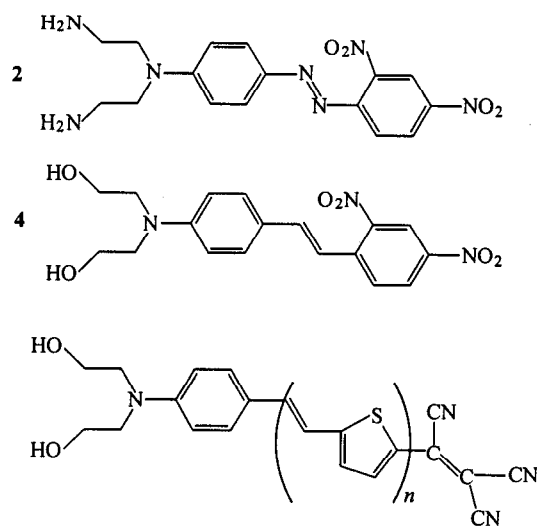
where γ_{ijkl} is a forth order tensor.

2 Results

2.1 Designing idea
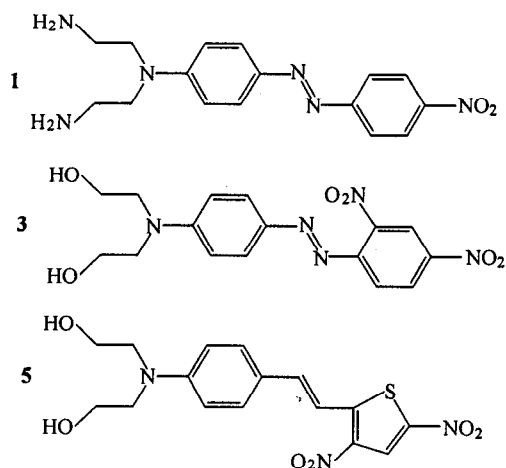
The molecular structures are designed and numbered as follows:

1

2

3

4

5

6

n =1,2,3,4,5

6 *n*=1; **7** *n*=2; **8** *n*=3; **9** *n*=4; **10** *n*=5

In this paper the molecules were designed and studied based on molecule **1**. By changing the push-pull substituents in the molecules and the molecular bone structures, their influences on β, γ were studied. Further the π conjugated bond was elongated to study its influence on γ.

2.1.1   Since molecule **1** has relatively high β and γ, molecules designed in this paper are based on it.

2.1.2   Molecule **2**: a nitro group is introduced to molecule **1** to study the influence of electron-withdrawing group on β and γ.

2.1.3   Molecule **3**: In order to attach the NLO molecule to the backbones of polymers such as polyurethane, polyimides and polyester, two hydroxy groups substitute the amino groups in molecule **2**.

2.1.4   Molecule **4**: Azo group is substituted by vinyl group, thus to compare the influences of the derivatives of diphenylvinyl and azobenzene on β and γ.

2.1.5   Molecule **5**: Thiophene ring has lower delocalized energy than that of phenyl ring (thiophene ring : 121.3 kJ/mol; phenyl ring: 150.6 kJ/mol), so it is expected that under external field the charge transferring is much more easier in thiophene ring than in

phenyl ring. The substitution of the phenyl ring with the thiophene ring in diphenylvinyl can increase the charge transfer in the molecule, thus the nonlinear optical response of the material can be enhanced. Molecule **5** was designed accordingly.

2.1.6   Molecule **6**: By introducing the tri-cyanovinyl group to the molecule, the conjugated areas were elongated in the molecule and several electronwithdrawing groups (– CN group) were also introduced to the molecule, thus enabling it to have superior nonlinear optical response.

2.1.7   Molecules **7—10**: On the basis of molecule **6**, by increasing the units of vinylthiophene the influence of the length of conjugated bonds on γ was studied.

2.2 Geometric structure optimization

The geometric structures of molecules were optimized using AM1 method. The axis z was set to be perpendicular to the molecular plane, and axis z was approximately along the direction of the permanent dipole moment of the molecule. The optimized results showed that the molecules designed in this paper were all of

trans form, with their main structures analogous to the structure of molecule **1**. The optimized structures are shown in Fig. 1 with molecule **1** as an example.
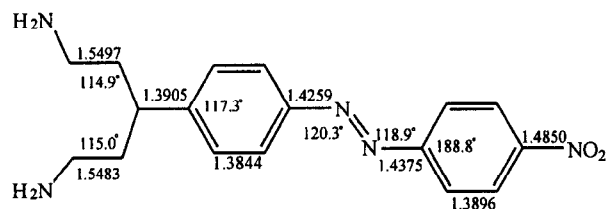

Fig. 1 Optimized geometry of molecule **1**.

2.3 Electronic spectra

On the optimized structures the electronic spectra of the 10 molecules were calculated using INDO/CI method. The results are listed in Table 1. The results are in good agreement with the experimental values (see Table 1). Table 1 lists only the wavelengths (λ) and oscillator strength (f) of a few important excited states. The whole ultraviolet spectrum is shown in Fig. 2 with molecule **5** (HBDT) as an example.

Table 1 Calculated and observed UV-Vis spectra of molecules

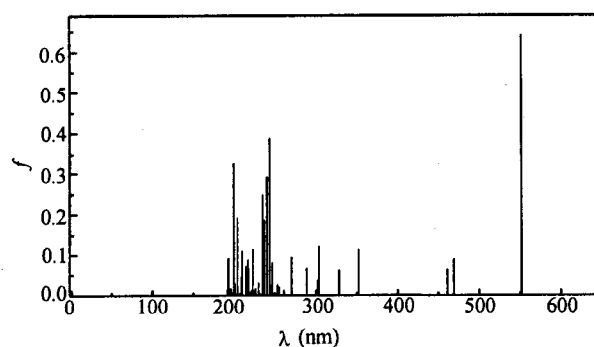| Comp.	λ_{cal1} (nm)	f_1	λ_{cal2} (nm)	f_2	λ_{cal3} (nm)	f_3	λ_{exp}^{23} (nm)
1	451	0.9806	208	0.7444			460,209
2	477	0.7427	230	0.6751			
3	406	0.4145	223	0.5297			
4	424	0.5039	217	0.7203			
5	550	0.6402	244	0.3881	200	0.3274	530,276,200
6	525	1.1261	197	0.4063			
7	586	1.5498	228	0.5953	221	0.4240	
8	617	1.9140	220	0.4209			
9	631	2.2175	366	0.4349			
10	634	2.6472	453	0.6090			

Fig. 2 UV-Vis spectrum of molecule **5**.

2.4 Second-order and third-order nonlinear optical susceptibilities

In the SOS expression of β_{ijk} and γ_{ijkl} it should include the full set of the nonperturbation system eigenfunctions, but in actual calculation it must be truncated. The related theoretical work[12-14] has been reported before. The numbers of excited states should be studied respectively according to different molecules. Taking molecule **5** (HBDT) for an example, the numbers of excited states were selected from 1 to 50 to calculate β_{ijk}

and β_μ, γ_{ijkl} and $\langle \gamma \rangle$ after each selection, then plot β_μ and $\langle \gamma \rangle$ against the numbers of excited states (Fig. 3A, Fig. 3B) to obtain converged values. β_μ and $\langle \gamma \rangle$ values of the other molecules are obtained in the same way. As shown in Fig. 3A and Fig. 3B, the values are fairly well converged when selecting about 36 excited states. Take β as a shortcut for converged $|\beta_\mu|$ and γ for converged $\langle \gamma \rangle$. β and γ are related with external field frequency. To compare with the experimental results,[23,24] λ = 1.907 μm was used when calculating β. β_0 is the value of β at 0 frequency (ω = 0) and β and β_0 are listed in Table 2A. Similarly, λ = 1.064 μm was used when calculating γ. γ_0 is the value of γ at 0 frequency (ω = 0) and γ and γ_0 are listed in Table 2B.

Table 2A Values of β (10^{-28} esu), $\mu\beta$ (10^{-46} esu)

Comp.	β_{cal}	$\mu\beta_{cal}$	β_{0cal}	$\mu\beta_{0cal}$	$\mu\beta_{exp}^{23}$
1	3.814	50.04	1.190	15.61	
2	5.542	69.00	1.184	14.74	
3	0.589	4.19	0.315	2.24	
4	1.324	7.31	0.258	1.42	
5	9.276	57.88	0.772	4.82	84.43
6	26.900	211.41	0.940	7.39	

Table 2B   Values of μ (De), γ $(10^{-32}$ esu), γ_0 $(10^{-34}$ esu)

Comp.	1	2	3	4	5	6	7	8	9	10
μ	13.12	12.45	7.11	5.52	6.24	7.82	11.80	10.76	11.60	13.37
γ_{0cal}	0.019	0.418	0.227	0.114	0.246	0.278	0.547	1.487	2.153	2.910
γ_{cal}	0.274	0.490	0.123	0.105	1.550	2.068	6.738	9.680	13.864	14.902
$\gamma_{exp}^{23,24}$				3.93						
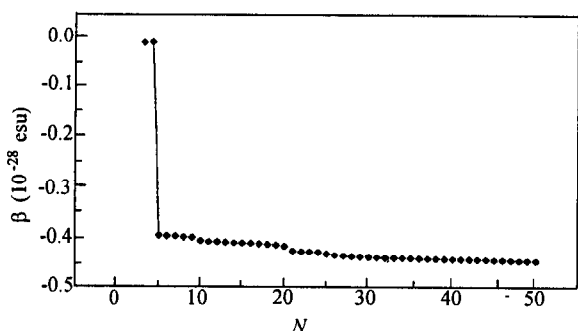
Fig. 3A β values plotted against numbers of excited states for molecule **1**.
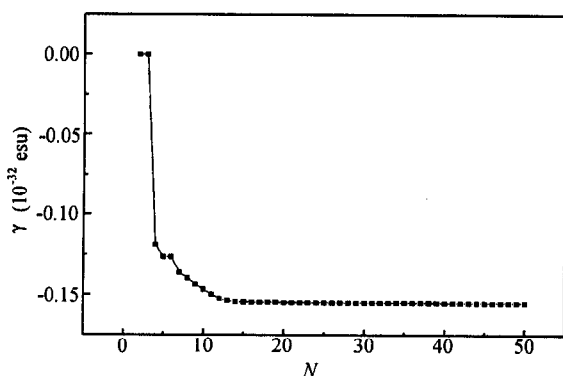
Fig. 3B γ values plotted against the numbers of excited states for molecule **1**.

3 Discussion

3.1 Substitituents' influences on β and γ

3.1.1 Acceptor's influence on β

Molecule **2** was designed by introducing an electron-withdrawing group -NO_2 to the meta position of nitrobenzene in molecule **1**. Table 2A and Table 2B show that $\beta_2 > \beta_1$, $\gamma_2 > \gamma_1$(subscript 1 and subscript 2 refer to molecules **1** and **2**, respectively). It can be inferred that intermolecular charge transfer can be further enhanced by introducing more electron-withdrawing groups to the right side of the molecule, thus the values of β and γ of the molecule can be increased.

3.1.2 Donor's influence on β and γ

According to the sequence of the electronic contributing abilities of the donors, -NH_2 should have stronger electronic contributing ability than -OH. Table 2A and Table 2B show that $\beta_2 > \beta_3$, $\gamma_2 > \gamma_3$. Stronger donors can also enhance the charge transferring in the molecule, thus increase the values of β and γ. But sometimes we have to "sacrifice" the values of β and γ for a more important purpose. In this paper, -OH instead of -NH_2 was introduced for the purpose of attaching the NLO active sectors to the backbones of polymers such as polyimide, polyurethane and polyester.

3.1.3 Influence on β and γ of the change of molecular backbone

Based on molecule **3**, introducing vinyl group to substitute the azo group between the two benzene rings (molecule **4**) was to study the influence of changing the molecular backbone on β and γ. Table 2A and Table 2B show that $\beta_4 > \beta_3$, $\gamma_4 > \gamma_3$. It can be inferred that the intermediate of diphenylvinyl polymer has better NLO properties than the intermediate of azobenzene polymer.

Molecule **5** was designed by substituting the phenyl ring with a thiophene ring in molecule **4**. Table 2A and Table 2B show that $\beta_5 > \beta_4$, $\gamma_5 > \gamma_4$. There is a great increment of the β and γ values of molecule **5** compared with molecule **4**. This can be readily explained by the fact that thiophene ring has lower delocalization energy than the phenyl ring, thus the π electrons in the thiophene are much easier to transfer than those of the phenyl ring under external field, inducing large second and third order NLO susceptibities. In order to illustrate that, the charge distribution was calculated in molecules **4** and **5**. Fig. 4 shows the ground state and crucial excited state charge distribution of molecules **4** and **5**. The charge on the phenyl ring connecting to -NO_2 in

molecule **4** is 0.217 in ground state and 0.352 in excited state. The charge transfer is $\Delta Q = 0.352 - 0.217 = 0.135$. The charge on thiophene ring in molecule **5** is 0.230 in ground state and 0.562 in excited state. The charge transfer is $\Delta Q = 0.562 - 0.230 = 0.332$. There is more charge transfer in molecule **5** than in molecule **4**, therefore molecule **5** has bigger β and γ values. The dipole moments of molecules **4** and **5** were also calculated. The dipole moment of molecule **4** in the ground state is $\mu_g = 5.52$, and in the excited state is $\mu_e = 12.28$, and the difference between μ_g and μ_e is $\Delta\mu = 6.76$. The dipole moment of molecule **5** in the ground state is $\mu_g = 6.24$, and in the excited state is $\mu_e = 13.98$. As shown in Table 1, the difference between μ_g and μ_e is $\Delta\mu = 7.74$. $\Delta\mu_5 > \Delta\mu_4$ and $f_5 > f_4$, $\lambda_5 > \lambda_4$. According to the calculation by SOS formula, oscillator strength (f) is in direct ratio to the square of the transition moment and λ is in inverse ratio to ω_{ng}, thus β and γ values of molecule **5** should be bigger than those of molecule **4**.
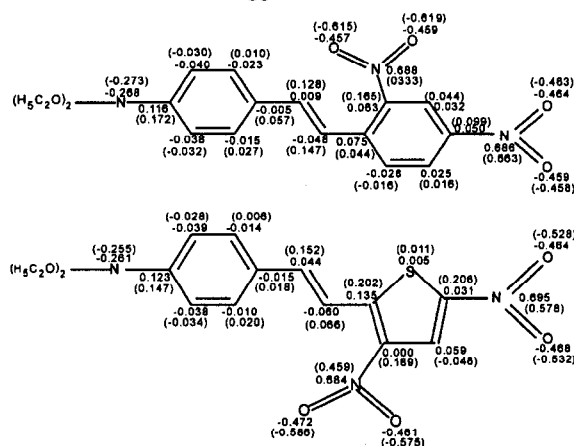

Fig. 4   Mulliken charge populations of the ground state and the excited state (in parentheses) of molecule **4** and **5**.

3.1.4 Influence of tricyanovinyl group on β and γ

Molecule **6** was designed by introducing tricyanovinyl group. Table 2A and Table 2B show $\beta_6 > \beta_5$, $\gamma_6 > \gamma_5$. There is a considerable increase of β and γ of molecule **6** than molecule **5**. Theoretically, a novel NLO molecule **6** with big NLO susceptibilities was obtained which can be attached to the backbones of polymers such as polyimide, polyurethane and polyester.

3.2 Two-state approximation

If only the ground state and the most important ex-

cited state are included in the SOS expression of β_{ijk}, the famous two-state approximate formula of β_μ can be obtained as:

$$\beta_\mu = \frac{3e^2\hbar^2}{2m}\frac{Wf\Delta\mu}{[W^2 - (2\hbar\omega)^2][W^2 - (\hbar\omega)^2]} \quad (7)$$

where ω is the frequency of the laser field; and $W = \hbar\omega_{ng}$ is the transition energy from ground state to excited state; f, the oscillator strength of the transition; and $\Delta\mu$, the difference of dipole moments between the excited state and ground state.

If

$$\beta_0 = \frac{3e^2\hbar^2 f\Delta\mu}{2mW^3} \quad (8)$$

β_0 is called as static second-order nonlinear optical susceptibility.

Then

$$\beta_\mu = \frac{\beta_0 W^4}{[W^2 - (2\hbar\omega)^2][W^2 - (\hbar\omega)^2]} \quad (9)$$

β_0 is independent of external electric field (as expressed in Eq. (8)), so it can reflect the intrinsic nature of the molecule better. Usually β_μ is obtained by experiments, then β_0 was calculated through Eq. (9).

β_0 can also be calculated using SOS expression of β_{ijk} in Eq. (2). It need only let $\omega = 0$ in calculation. The β_0 values calculated by the two approaches are listed in Table 3. The results are in excellent agreement. It shows that "the most important excited state" really contributes to β_0 principally, and the two-state model is a good approximation.

3.3 Dispersion

β and γ values are related to external frequency, and it is called as dispersion. This paper studied the dispersion too.

The relationship of γ and external frequency ω was studied with molecule **5** as an example. The results are shown in Table 4 and Fig. 5. Table 4 shows that γ increases when ω increases. γ will become infinitely large when ω is near the resonant frequencies. Resonant frequencies mean that ω or 2ω equals to ω_{ng}. At resonant frequencies, the denominator becomes 0, so γ becomes infinite large. When ω exceeds resonant frequencies, γ decreases as ω increases. The wavelength of the most

important excited state of molecule **5** is 550 nm, and the transition energy is 18181 cm^{-1}, so resonance occurs at

18181 cm^{-1}(2.25 eV), as indicated in Table 4 and Fig. **5**.

Table 3 β_0 and $\mu\beta_0$ values of molecules **1—6** obtained by two methods

Comp.	Calculated values from the SOS formula		Calculated values from two-state formula	
	β_0 (10^{-28} esu)	$\mu\beta_0$ (10^{-46} esu)	β_0 (10^{-28} esu)	β_0 (10^{-46} esu)
1	1.190	15.61	1.436	18.84
2	1.184	14.74	1.397	17.39
3	0.315	2.24	0.399	2.84
4	0.258	1.42	0.319	1.76
5	0.772	4.82	0.874	5.45
6	0.940	7.39	0.881	6.92

In order to study the relationship between ω and molecular structure, we select ω different from resonant frequency. For molecule **5**, $\hbar\omega$ is selected as 1.17 eV, i.e., 9399 cm^{-1}, which falls in the non-resonant sector.

Table 4 Values of γ in different electric field frequences for molecule **5**

$\hbar\omega$ (eV)	$\hbar\omega$ (cm^{-1})	γ (10^{-33} esu)
0	0	2.457
0.31	2500	2.550
0.93	7500	6.254
1.10	8832	11.55
1.17	9399	15.50
1.35	10900	16.89
1.55	12500	20.12
1.80	14519	45.61
2.00	16132	274.2
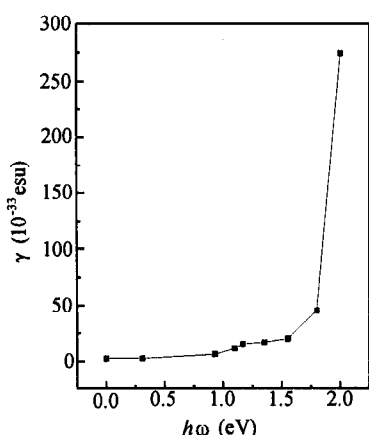
Fig. 5 Relationship between γ and different electric field frequencies.

Fix ω_n in Eq. (3) and let $\omega_\sigma = \omega$, $\omega_1 = \omega$, $\omega_2 = -\omega$, $\omega_3 = \omega$. We can see when ω increases, the denominators $(\omega_m - \omega_\sigma)$, $(\omega_n - \omega_2 - \omega_3)$, $(\omega_q - \omega_3)$, $(\omega_n - \omega_3)$, all decrease, so γ value increases.

3.4 Relation between γ and the length of conjugated bonds

In order to study the relationship between third order NLO susceptibilities and the length of the conjugated bonds, molecules **7—10** were designed by increasing the number of the vinylthiophene units, thus extending the length of the conjugated bonds. The calculated data listed in Table 2 show that γ increases when the length of the conjugated bonds increases. i.e., $\gamma_{10} > \gamma_9 > \gamma_8 > \gamma_7 > \gamma_6$. The NLO properties of the molecule are greatly enhanced when the length of the conjugated bonds increases. This can be explained that when the length of the conjugated bonds increases, ω_m decreases but ω remains unchanged, thus the denominators in Eq. (3) become smaller, so γ value increases. Since $\gamma(0; 0, 0, 0)$ is independent of external field, it can reflect the intrinsic nature of the molecule, so we should take static third order NLO susceptibities into consideration. Define N_π as the sum of C = C bonds and C—C bonds in the conjugated area of molecule, plot the line of $\log\gamma(0; 0, 0, 0)$ against $\log N_\pi$ for molecules **6—10** and obtain a line, as shown in Fig. 6. The relation between $\gamma(0; 0, 0, 0)$ and N_π can be expressed as:

$$\log\gamma(0; 0, 0, 0) = 2.69\log N_\pi + A$$

Fig. 6 shows that $\log\gamma(0; 0, 0, 0)$ is 2.69th power of N_π.
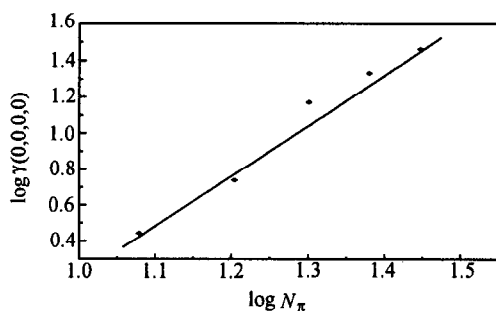
Fig. 6   Relationship between $\gamma(0,0,0,0)$ and N_π.

References

1.   Prasad, P.N.; Williams, D.J., *Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, 1991.

2.   Kanis, D.R.; Ratner, M.A.; Marks, T.J., *Chem. Rev.*, **94**, 195(1994).

3.   Bartlett, R.J.; Purris III, G.; Sekino, H., *J. Chem. Phys.*, **84**, 2726(1986).

4.   Pierce, B.M., *J. Chem. Phys.* **91**, 791(1989).

5.   Bishop, D.M., *Rev. Mod. Phys.*, **62**, 343(1990).

6.   Morley, J.O.; Paugh, D., *J. Chem. Soc. Faraday Trans.*, **87**, 3021(1991).

7.   Karna, S.P.; Dupuis, M., *J. Comput. Chem.*, **12**, 407(1991).

8.   Pierre, M.; Baldeck, P.L.; Block, D.; Georhes, R.; Trommsdorff, H.P.; Zyss, J., *Chem. Phys.*, **156**, 103 (1991).

9.   Kanis, D.R.; Marks, T.J.; Ratner, M.A., *Int. J. Quantum Chem.* **43**, 61(1992).

10. Hammoutene, D.; Boucekkine, G.; Boucekkine, A.; Berthier, G., *J. Mol. Struct.* (*Theochem*), **106**, 93 (1993).

11. Lazzerett, P.; Malagoli, M.; Turci, L.; Zanasi, R., *J. Mol. Struct.*, (*Theochem*), **288**, 255(1993).

12. Li, J.; Feng, J.K.; Sun, C.C., *Chem. Phys. Lett.*, **203**, 560(1993).

13. Li, J.; Feng, J.K.; Sun, C.C., *Int. J. Quantum Chem.*, **52**, 673(1994).

14. Li, J.; Feng, J.K.; Sun, C.C., *J. Phys. Chem.*, **98**, 8636(1994).

15. Nalwa, H.S., *Mater. Lett.*, **33**, 23(1997).

16. Albert, I.D.L.; Morley, J.O.; Pugh, D., *J. Phys. Chem. A*, **101**, 1763(1997).

17. Glaser, R.; Chen, G.S., *Chem. Mater.*, 928(1997).

18. Ecans, C.C.; Beucher, M.B.; Masse, R.; Nicoud, J. F., *Chem. Mater.*, **10**, 847(1998).

19. Lesley, M.J.G.; Woodward, A.; Taylor, N.J.; Marder, T.B., *Chem. Mater.*, **10**, 847(1998).

20. Dlucas, A.I.; Martin, N.; Sanchez, L.; Seone, C., *Tetrahedron*, **54**, 4655(1998).

21. Angeles. M.; Herranz, N.; Martin, L.; Sanchez, J. Carin, *Tetrahedron*, **54**, 11651(1998).

22. Rao, V.P.; Jen, A.K-Y.; Wang, K.Y.; Drost, K.J., *Tetrahedron Lett.*, **34**, 1747(1993).

23. Wang, J.; Zhai, J.; Zhou, J.; Zhao, Y.; Shen, Y, *Chinese Journal of Polymer Science*, **174**, 359(1999).

24. Wang, J.; Shen, Y.Q.; Shi, Z.W., *Journal of Materials Science*, to be accepted.

25. Alex, K-Y.; Rao, V.P.; Wong, K.Y.; Drost, K.J., *J. Chem. Soc.*, *Chem. Commun.*, 90(1993).

26. Mignani, G.; Leising, F.; Meyrueix, R.; Samson, H., *Tetrahedron Lett.*, **31**, 4743(1990).

27. Bishop, D.M., *Adv. Quantum Chem.*, **25**, 1(1994).

28. Orr, B.J.; Ward, J.F., *Mol. Phys.*, **203**, 513(1971).