Design of Second-Order Nonlinear Optical Molecules Exhibiting Improved Nonlinearity-Transparency Trade-off and Large Nonlinearity

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The nonlinear second-order optical susceptibilities (β) of a series of multi-branched molecules with triphenylbenezene as π center have been calculated by means of a combination of intermediate neglect of differential overlap Hamiltonian with the configuration interaction (INDO/SDCI) method combined with sum-over-states expression (SOS). The results show that the β values are increased by replacing benzene rings with thiophene rings in the branches, as well as by increasing the donating and accepting strength of the three terminal substituents. The properties of the intermolecular charge transfer were studied through the calculation of charge changes between the ground and the main excited states and the frontier orbitals of these molecules. The results also indicate that these molecules investigated here possess improved transparency-nonlinearity properties.

Keywords   triphenylbenzene crux, nonlinearity-transparency, INDO/SDCI-SOS

Introduction

The study on new organic compounds with high second-order optical nonlinearities has attracted increasing interest during the past two decades in view of their applications in various fields such as telecommunications, optical data storage and information processing,[1] and has ranged over a variety of different molecular structures,[2-18] starting from the typical donor-acceptor substituted π-conjugated push-pull configuration to organometallic complexes and multipolar molecules. However, it is well known that the dipolar molecules have certain limitations such as the difficulty associated with aligning the dipoles noncentrosymmetrically in the solid state to achieve maximum bulk effect [$\chi^{(2)}$]. An alternative approach to overcome this difficulty would be to use the octupolar compounds. Lehn, Zyss and coworkers have opened a pioneering route towards octupolar molecules.[19] They obtained potentially large β[20] and γ,[21] but at the expense of significantly reduced transparen-cy in the visible region.[22] In order to achieve an improved nonlinearity-transparency trade-off, Jérémie Brunnel and coworkers synthesized a series of nanoscale propeller-shaped molecules whose design was based on the grafting of three extended blades bearing an electron-withdrawing or an electron-releasing tip on triphenylbenzene crux.[23] Meanwhile, some researchers[24] considered that due to the electron excessivity, thiophene ring bridge acted as an auxiliary donor and increased the donor ability, thus could enhance the NLO responsibility. Based on these studies, we designed a series of molecules with triphenylbenzene as π center and some thiophene-substituted-phenyl derivatives (shown in Fig. 1). On the basis of INDO/SDCI-SOS calculation, it was obtained that the thiophene-substituted derivatives have enhanced second-order optical nonlinearites compared with the benzene rings bridge molecules, furtheremore, they kept good transparency, which is important for the application in practice. This indicates that the thiophene-substituted bridge molecules with tripheylbenzene as π center are good candidates for the NLO materials.

Methodology

A quantitative description of molecular NLO response is derived from a power-series expansion of the molecular polarization upon interaction with an oscillating external electromagnetic field in Eq. (1)

$$P_i = \sum_j \alpha_{ij}E_j + \sum_{j \le k}\beta_{ijk}E_jE_k + \sum_{j \le k \le l}\gamma_{ijkl}E_jE_kE_l + \cdots \quad (1)$$

With normal values of E, the quadratic and cubic terms in Eq. (1) can be neglected, and only linear optical behavior is observed. The coefficient α_{ij} is known as the *linear molecular polarizability* and is related to the refractive index of the material. However, under conditions
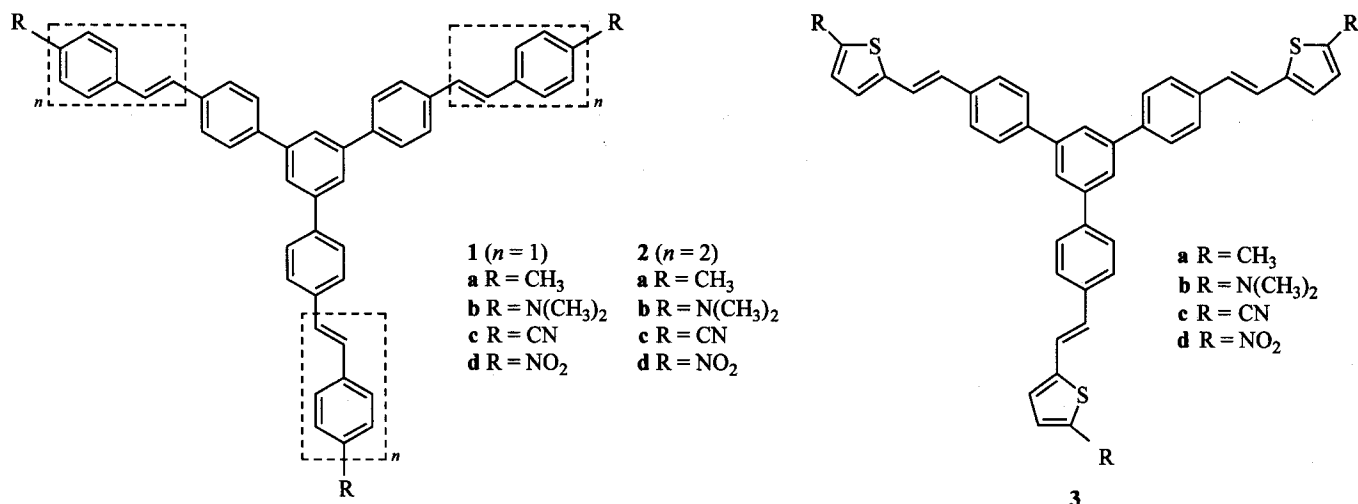
Fig. 1 Designed molecules for investigation.

where E approaches the magnitude of atomic field strengths, such as in a laser beam, the $\sum \beta_{ijk}E_jE_k$ and $\sum \gamma_{ijkl}E_jE_kE_l$ terms in Eq. (1) become important and it is these which give rise to quadratic (second-order) and cubic (third-order) NLO effects, respectively. The coefficients β_{ijk} and γ_{ijkl} are termed molecular hyperpolarizailities.

In this paper, based on the optimized geometry with AM1 quantum chemical method, the molecular spectroscopy was obtained using INDO/SDCI, and combined with SOS formula [Eq. (2)], the second-order optical susceptibilities β_{ijk} was calculated.

$$
\begin{aligned}
\beta_{ijk} + \beta_{ikj} = \frac{1}{4\hbar^2} \Bigg\{ &\sum_{\substack{n \neq n' \\ n' \neq g \\ n \neq g}} \Bigg[\left(r_{gn'}^i r_{n'n}^j r_{gn}^k + r_{gn'}^k r_{n'n}^i r_{gn}^j \right) \times \left(\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - \omega)} \right) + \\
&\left(r_{gn'}^i r_{n'n}^j r_{gn}^k + r_{gn'}^j r_{n'n}^k r_{gn}^i \right) \times \left(\frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)} + \frac{1}{(\omega_{n'g} + 2\omega)(\omega_{ng} + \omega)} \right) + \\
&\left(r_{gn'}^j r_{n'n}^k r_{gn}^i + r_{gn'}^k r_{n'n}^j r_{gn}^i \right) \times \left(\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} + 2\omega)} \right) + \\
&+ 4\sum_{n \neq g} \left\{ \frac{\left[r_{gn}^j r_{gn}^k \Delta_m^i (\omega_{ng}^2 - 4\omega^2) + r_{gn}^i (r_{gn}^k \Delta r_n^j + r_{gn}^j \Delta r_n^k)(\omega_{gn}^2 + 2\omega^2) \right]}{\left((\omega_{ng}^2 - \omega^2)(\omega_{ng}^2 - 4\omega^2) \right)} \right\} \Bigg] \Bigg\}
\end{aligned}
\tag{2}
$$

where the summations are over the complete sets of eigenstates $|n\rangle$ and $|n'\rangle$ of the unperturbed molecular system. The quantities $r_{gn'}^i$ and $r_{nn'}^i$ are matrix elements of the ith components of the dipole operator between the unperturbed ground and excited states and between two excited states, respectively; $\Delta r_n^i = r_{nn}^i - r_{gg}^i$ is the difference between the excited-state and ground state dipole moments. Although all 27 components of the β tensor can be computed, only the vector component in the dipolar direction (β_μ) is sampled by electric-field-induced second harmonic generation (EFISH) experiments. In order to compare with the experimental results, we followed the formula below to calculate β_μ:

$$
\beta_\mu = (\mu_x\beta_x + \mu_y\beta_y + \mu_z\beta_z)/(\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}
\tag{3}
$$

where

$$
\beta_i = \beta_{iii} + 1/3\sum_{j \neq i}(\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad i,j \in (x,y,z)
\tag{4}
$$

In the computation, CI calculation includes 13 highest occupied and 13 lowest unoccupied orbitals in the singlet configuration and 3 highest occupied and 3 lowest unoccupied orbitals in the double configuration. All together, we get 215 configurations, which is sufficient for effective convergence of the SOS procedure.

Results and discussion

Investigated molecules

As shown in Fig. 1, when n is equal to 1 with the phenylenevinylene branches, the molecules are numbered as **1**, while n is equal to 2, correspondingly, the molecules are numbered as **2**; when the benzene rings is substituted by thiophene rings in the branches, the molecules are signed as **3**. Furthermore, when the end groups are CH_3, $N(CH_3)_2$, CN and NO_2, the molecules are denoted as **a**, **b**, **c** and **d** respectively. Thus we have **1a**, **1b**, **1c**, **1d**, **2a**, **2b**, **2c**, **2d**, **3a**, **3b**, **3c** and **3d**

molecules to investigate.

Absorption spectra

On the basis of optimized geometry by means of AM1 method, the absorption spectrum was calculated with INDO/SDCI method. The calculated absorptions and the properties of the main absorptions for the investigated molecules are listed in Table 1, and the calculated values are in good agreement with the experimental values. All the molecules showed good transparency in a wide range of the visible region and an intense absorption in the near UV region whose position was dependent on both the nature of the peripheral groups and the length and properties of the bridge system. As expected, a red shift of the absorption band was observed with increasing bridge length, such as $\lambda_{max}(2a) > \lambda_{max}(1a)$, $\lambda_{max}(2b) > \lambda_{max}(1b)$, $\lambda_{max}(2c) > \lambda_{max}(1c)$ and $\lambda_{max}(2d) > \lambda_{max}(1d)$ (shown in Table 1). Obviously, the oscillator strength is strongly correlated with the molecular length: the longer the molecule, the stronger the oscillator strength. For example, the oscillator strengths of 2 series molecules are generally larger than that of 1 series and 3 series. This point has ever been pro-

duced by Yi et al.[25] Furthermore, when the benzene rings is substituted by thiophene rings in the branches, the absorption peak position is also red shifted. For example, the absorption positions are 389, 394, 399 and 439 nm for 3a, 3b, 3c and 3d, respectively, whereas those of 1a, 1b, 1c and 1d are positioned at 361, 366, 366 and 384 nm, respectively. This phenomina can also be explained from the frontier orbital energh gap ΔE ($E_{LUMO} - E_{HOMO}$). Taking molecules 1a, 1d and 3a, 3d as examples, ΔE is 6.52 and 5.51 eV for 1a and 1d repectively, while they are 6.17 and 6.02 eV for molecules 3a and 3d respectively. The calculated results indicate that different substituted groups have different effect on the absorption properties, and when benzene is replaced by thiophene ring, the energy gap is reduced, comparing between 1a and 3a and between 1d and 3d, respevtively.

NLO properties

On the basis of equilibrium geometries and correct spectroscopy, using INDO/SDCI-SOS method, the second-order susceptibilities (β) of the investigated molecules were computed. The results are listed in Table 1.

Table 1 Absorption wavelength (λ_{max}) and oscillator strength (f), molecular second-order optical susceptibilities (β) and dipole moments ($\Delta\mu_{eg}$) of the investigated molecule

Molecule	$|g> \rightarrow |e>$	$\lambda_{max}(nm)$	f	$\Delta\mu_{eg}$	β (10^{-30}esu)
1a	$1 \rightarrow 3$	360.8	1.73	11.5	32.28
	$1 \rightarrow 4$	359.8	2.01	12.3	
1b	$1 \rightarrow 2$	366.3	1.84	11.9	52.17
	$1 \rightarrow 3$	365.0	1.97	12.3	
1c	$1 \rightarrow 2$	366.4	1.84	11.9	4.93
	$1 \rightarrow 3$	365.9	2.26	13.2	
1d	$1 \rightarrow 2$	384.1 (385)[a]	1.59	11.4	7.27
	$1 \rightarrow 3$	381.1	2.18	13.3	
2a	$1 \rightarrow 2$	390.1	2.21	13.5	40.77
	$1 \rightarrow 3$	389.4	3.16	16.2	
2b	$1 \rightarrow 2$	393.0	2.43	14.3	74.12
	$1 \rightarrow 3$	392.6	3.04	16.0	
2c	$1 \rightarrow 2$	394.8	2.69	15.1	8.42
	$1 \rightarrow 3$	394.4	2.98	15.8	
2d	$1 \rightarrow 2$	400.4	2.06	13.3	12.41
	$1 \rightarrow 3$	399.7	3.32	16.8	
3a	$1 \rightarrow 2$	388.9	1.76	12.1	45.83
	$1 \rightarrow 3$	386.1	1.53	11.2	
3b	$1 \rightarrow 2$	394.3	1.60	11.6	79.28
	$1 \rightarrow 3$	391.6	1.74	10.3	
3c	$1 \rightarrow 2$	399.1	1.74	12.2	19.97
	$1 \rightarrow 3$	397.5	1.83	12.4	
3d	$1 \rightarrow 2$	438.7	1.32	11.1	29.51
	$1 \rightarrow 3$	437.4	1.83	13.0	

[a] The experimental value.[23]

For all the molecules, the value of β is enhanced with the substituent strength increasing, such as β (**1b**) $> \beta$ (**1a**), β (**1d**) $> \beta$ (**1c**), β (**2b**) $> \beta$ (**2a**), β (**2d**) $>$ β(**2c**), and β(**3b**) $> \beta$(**3a**), β(**3d**) $> \beta$(**3c**) (Shown in Table 1). Futhermore, when the benzene rings are replaced by thiophene rings in the molecular branches, the β is enhanced (the values of series **3** are larger than those of series **1**), proving that the thiophene rings strongly influence the nonlinear response for the investigated molecules. This strategy is particularly successful: molecules **3c** and **3d** were found to exhibit a β value three or four times larger than those of molecules **1c** and **1d** with the same length, whereas molecules **3a** and **3b** exhibit larger β values than molecules **2a** and **2b** and maintain suitable transparency in the visible region, indicative of good NLO properties for these thiophene-substituted molecules.

According to the two-level formula,[26,27] the β value can be described as:

$$\beta \propto \Delta\mu_{eg} f / W^3 \tag{5}$$

where $\Delta\mu_{eg} = \mu_e - \mu_g$ is the difference of dipole moments between ground state and the most important excited state, W the transition energy, and f the oscillator strength.

As $\Delta\mu_{eg}$ is correlated with the charge transfer (Δq), the influence of substitution effects on β can be analyzed from the calculation of the charge transfer between the ground state and the most important excited state.

In order to explain the phenomena above, we calculated the net charge and the charge changes between the ground and the main excited state for all investigated molecules (Table 2). For both electron-withdrawing (acceptor) and electron-releasing (donor) abilities, the stronger the group has, the more charge changes are: Δq(**1b**) $> \Delta q$ (**1a**), Δq (**1d**) $> \Delta q$ (**1c**), Δq (**2b**) $>$ Δq(**2a**), Δq(**2d**) $> \Delta q$(**2c**), Δq(**3b**) $> \Delta q$(**3a**), and Δq(**3d**) $> \Delta q$(**3c**). So according to expression (5), the larger charge changes lead to the larger $\Delta\mu_{eg}$ and then result in comparatively larger β values. But this is not followed by series **2** and **3** as shown in Table 1. Series **2** should show larger β values than series **3** since series **2** have comparatively larger f, $\Delta\mu_{eg}$ and similar W. In order to elucidate this phenomina, taking molecules **2b** and **3b**

as examples, we plot the picture of the second-order polarizabilites versus the excited states N (Fig. 2). We should notice from Fig. 2 that molecules **3b** and **2b** show different situations: the second-order polarizability of molecule **2b** mainly comes from the contribution of excited states **2** and **3**, while for molecule **3b**, besides the second and third excited states, there are other excited states that have some contributions to β. So when we inculde enough excited states in the SOS formula, series **3** show larger β values than series **2**. The characteristic of series **3** is the substitution of thiophene ring for benzene ring in the bridge, so the nonlinear second-order polarizabilities of series **3** are larger than that of series **1**, indicating that thiophene ring is benefit to the enhancement of the NLO response. While for series **2**, compared with series **3**, the bridges are lenghened, so series **2** and **3** show the different situation above.

We now consider the effect of thiophene ring on β. Heterocyclic five- or six-membered ring systems have generally been divided into two classes to reflect the electron density on the ring skeletal carbon atoms. In five-membered aromatic heterocyclic molecules, there are excessive electrons, so they are called electron-excessive or electron-rich systems. On the contrary, six-membered aromatic heterocyclic systems are considered electron-deficient. Compared with benzene ring, thiophene ring is an electron-excessive system. To understand how it influencs the nonlinear response when benzene bridge is replaced by thiophene bridge, we should compare the charge changes between **3** and **1**. So, we calculated the net charge of the triphenylbenzene for both ground and the main excited states as well as the charge changes between them. As shown in Table 2, the charge changes for molecules **3a**, **3b**, **3c** and **3d** are -0.0335, -0.0399, 0.0605 and 0.1131 respectively, and those for molecules **1a**, **1b**, **1c** and **1d** are -0.0186, -0.0246, 0.0485 and 0.1537, which are smaller than that of the corresponding **3** series molecules. Furthermore, the absorption peak of **3** series molecules is red shifted compared with that of **1** series molecules (that have smaller W^3). According to expression (5), these combinations lead to the large nonlinear susceptibilities for **3** molecules, indicating that thiophene is benefit to the charge transfer between the periphery and the triphenyl-benzene crux.

Table 2 Net charge of ground ($q_{(g)}$) and the main excited state ($q_{(e)}$) (having the larger oscillator strength) and the charge change (Δq) between them for the triphenylbenzene crux part

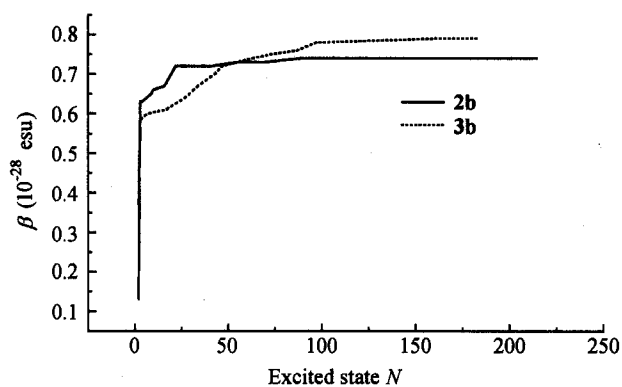| Mol.	1a	1b	1c	1d	2a	2b	2c	2d	3a	3b	3c	3d
$q_{(g)}$	-0.0287	-0.0340	0.0866	0.1350	-0.0041	-0.0083	-0.0268	0.0365	-0.0075	-0.0186	0.1594	0.2483
$q_{(e)}$	-0.0473	-0.0587	0.1359	0.2174	-0.0113	-0.0189	-0.0575	0.0855	-0.0410	-0.0585	0.2199	0.3614
Δq^a	-0.0186	-0.0246	0.0485	0.1537	-0.0072	-0.0106	0.0307	0.0510	-0.0335	-0.0399	0.0605	0.1131

^{a} $\Delta q = q_{(e)} - q_{(g)}$

Fig. 2 Relationship between the excited states N and second-order polarizabilities β.

The frontier orbitals were plot to show charge transfer, taking molecules **1d** and **3a** as examples. For **1d**, its main excited states are 2nd and 3rd, they are mixed up with the transitions of HOMO to LUMO, LUMO + 1 and LUMO + 2, HOMO − 1 to LUMO and LUMO + 2, and HOMO − 2 to LUMO and LUMO + 1. We depict the orbitals of HOMO − 1, HOMO, LUMO + 1 and LUMO + 2 in Fig. 3. It shows that charge transfer of HOMO to LUMO, LUMO + 1 and LUMO + 2 was equal to the charge

transfer from the center to the three branch periphery and the other transitions of HOMO − 1 to LUMO and LUMO + 2, and HOMO − 2 to LUMO and LUMO + 1 could be seen that the charge transfer from center to the end group, NO_2, in all the charge transfer could be considered from the center to the periphery till the substituted group for molecule **1d**. As to molecule **3a**, the 2nd and 3rd excited states are also mainly made up of the charge transfer from HOMO, HOMO − 1 to LUMO, LUMO + 1 and LUMO + 2. Similarly, we plot the orbitals of HOMO − 1, HOMO, LUMO, LUMO + 1 and LUMO + 2 in Fig. 4. It is shown that the charge transfer from HOMO − 1 to LUMO, LUMO + 1 and LUMO + 2 can be qualitatively considered as the charge transfer from the two thiophene rings to the center, and the transition from HOMO to LUMO, LUMO + 1 and LUMO + 2 are also equal to the charge transfer from the two thiophene rings to the center. For the whole molecule of **3a**, the charge transfers from peripheries to the center. The analysis above indicate that for the multi-branched molecules with tripheylbenzene as π center, when the acceptor is grafted at the peripheriy, the intermolecular charge transfer is from center to the periphery, while donor is connected, the charge flows from periphery to center.
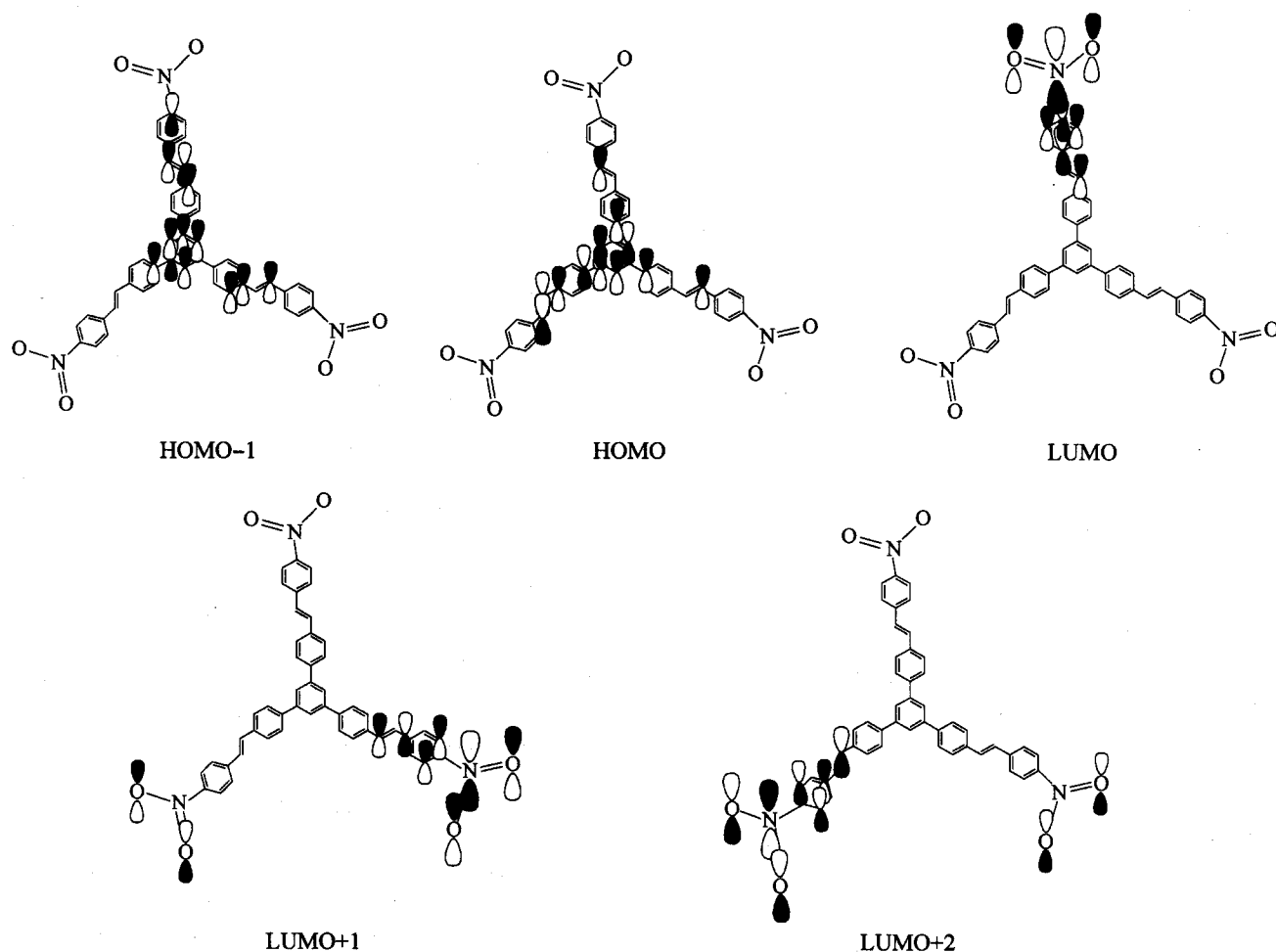

HOMO−1   HOMO   LUMO

LUMO+1   LUMO+2

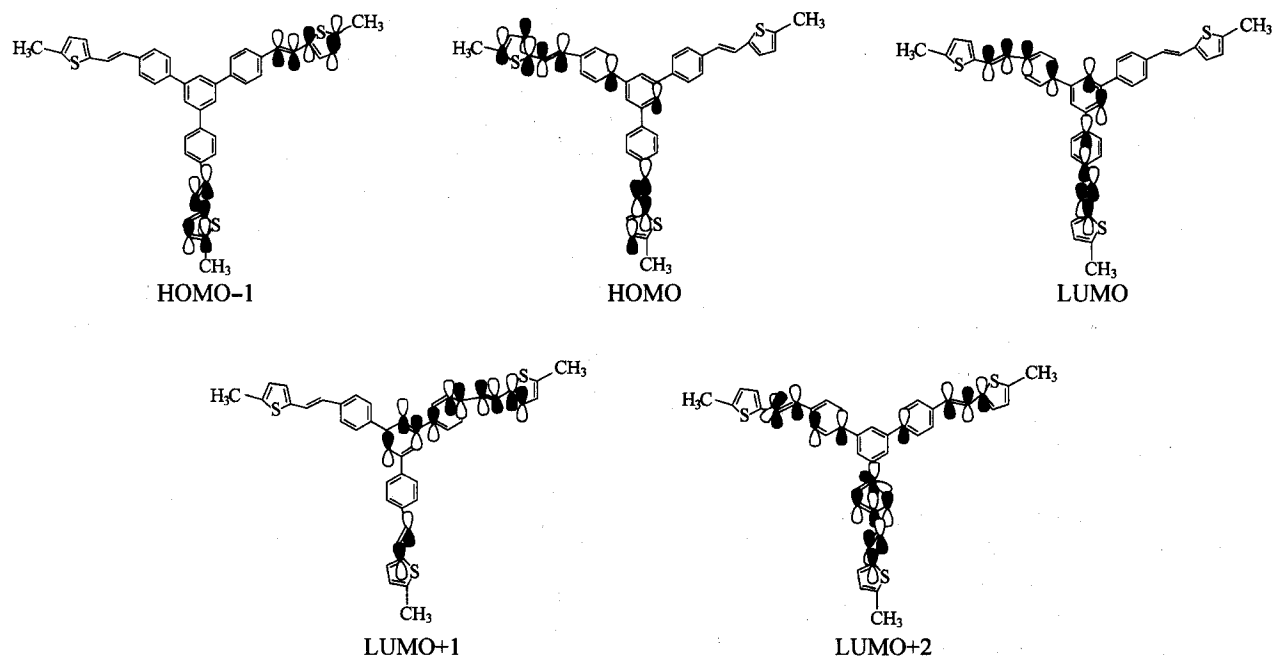**Fig. 3** Frontier orbitals of molecule **1d**.

Fig. 4 Frontier orbitals of molecule **3a**.

In addition, it is obvious from Table 1 that increasing the length of the branch can enhance the NLO responsibility. For these investigated molecules, when n changed from 1 to 2 for the corresponding molecules, the β values increase almost twice.

In conclusion, for the propeller-shaped molecules with triphenylbenzene as center, stronger substituent will be benefit to the enhancement of susceptibility of β. Especially, when the benzene rings is replaced by thiophene rings, the β is significantly enhanced due to electron-excessive properties of thiophene rings; in addition, lengthening the branches will also enlarge the NLO responsibilities for the investigated molecules. Moreover their transparency is kept in the visible range, being important for practical applications.

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