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Theoretical Study on the Second-Order Nonlinear Optical Properties of Asymmetric Spirosilabifluorene Derivatives

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The equilibrium geometries of four asymmetric spirosilabifluorene derivatives are optimized by means of the DFT/B3LYP method with the 6-31G* basis sets in this paper. On the basis of the optimized structures, the electronic structure and second-order nonlinear optical properties are calculated by using time-dependent density-functional theory (TDDFT) based on the 6-31G* level combined with the sum-over-states (SOS) method. The results show that these compounds possess remarkably larger molecular second-order polarizabilities than typical organometallic and organic compounds, and replacement of a carbon atom with nitrogen within the conjugated substituent has a great influence on the second-order nonlinear optical properties. Analysis of the main contributions to the second-order polarizability suggests that charge transfer from the *z*-axis directions plays a key role in the nonlinear optical response. These compounds have a possibility to be excellent second-order nonlinear optical (NLO) materials from the standpoint of large β values, small dipole moment, high transparency, and small dispersion behaviors.

1. Introduction

The development of organic molecular and polymeric compounds has brought forth a number of remarkable discoveries in electronic, optoelectronic, and electrooptic devices.[1] The continued emergence of these new technologies will mainly depend on performance enhancement in such matters as luminescence quantum efficiency, charge injection and transport efficiency, and temporal and thermal stability. Silicon-containing π-conjugated compounds have recently been paid much attention owing to their intense solid-state fluorescence and/or good electron transport properties in organic light-emitting diodes.[2] The siloles in particular have a relatively low-lying lowest unoccupied molecular orbital (LUMO) level due to the $\sigma^*-\pi^*$ conjugation between the σ^* orbital of the exocyclic Si−C bond and the π^* orbital of the butadiene fragment. These unique electronic properties have led to very high electron affinity and, in some cases, nondispersive and air-stable electron transport.[2g,h]

Materials with large hyperpolarizabilities are good candidates for use in optoelectronics and a variety of optical devices.[3] However, second-order NLO properties, which are of the most immediate interest for practical applications, derive at the molecular level from second-order polarizability. Nonlinear optical properties of a variety of linear push−pull polyenes have been extensively studied over last two decades.[4] It was shown that the NLO properties of these materials are sensitive to many factors such as conjugation length, donor and acceptor substitutions, and symmetric effects.[5] Enhancing the electron-donor and electron-acceptor ability or extending the π-conjugation length are proven to be effective methods to enhance the NLO properties.[6] Despite the large NLO properties exhibited at the molecular level by such compounds, their inherently large permanent dipole moments responsible for undesirable dipole−dipole interactions between neighboring entities have hampered the subsequent manifestation at the macroscopic level of a significant macroscopic second-order susceptibility, $\chi(2)$, be it in single-crystal or guest−host polymer format.[7] When the π-conjugation length is extended in such compounds, it causes the bathochromatic shift of the absorption band, which shortens the usable wavelength range and does not satisfy the optical transparency. Therefore, more practical nonlinear optical materials need to possess not only large nonlinear optical susceptibility at the macroscopic level but also high optical transparency.

The bonding concept of spiroconjugation was introduced some years ago by Hoffmann[8] and simultaneously by Simons and Fukunaga.[9] When four p orbitals are perpendicular in pairs to the intersecting planes, the overlap between p orbitals on atoms bound directly to the spiroatom is considerable, and consequently, exchange interactions may be become significant. Hoffmann et al. suggested that the overlap across the spiroatom may be sufficient to produce a noticeable increase in the gap between the bonding and antibonding orbitals but would be insufficient to significiently reduce the excitation energy.[10] That is, significant exchange interaction can be obtained without being accompanied by the reduction of the excitation energy. Many groups have examined the nonlinear optical properties of spiroconjugated compounds, where the spiroatom is a carbon, by experimental[11] and theoretical[12] techniques, showing that they have excellent NLO properties. Recently, Lee et al. synthesized asymmetric spirosilabifluorene derivatives, which possess a variety of merits, such as high thermal and morphological stabilities, high luminescence quantum efficiencies, excellent transparency, and favorable charge-transfer ability (asymmetric).[13] We anticipate that these compounds offer some interesting new opportunities to second-order nonlinear optical materials. In this paper, our goal is to shed light on the nature and origin of second-order nonlinear optical properties of spirosilabifluorene derivatives, using the TDDFT-SOS method.

2. Computational Procedures

Geometrical optimization of the asymmetric spirosilabifluorene derivatives under a C_2 symmetry constraint was carried

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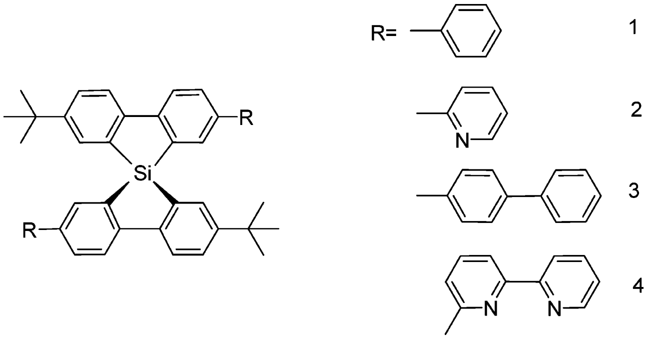

Figure 1. Molecular structures of the studied compounds.

out with the B3LYP[14] combinations of density functional theory and the 6-31G* basis set, as implemented in the *Gaussian 03* computational chemistry program.[15] The B3LYP functional is a combination of Becke's three-parameter hybrid exchange functional[14] and the Lee−Yang−Parr[16] correlation functional. Figure 1 presents the optimized geometrical structures of these compounds.

To elucidate the second-order nonlinear optical properties of these asymmetric spirosilabifluorene derivatives, we used the time-dependent density functional theory (TDDFT) model[17] with the B3LYP method at the 6-31G* basis set to calculate the transition energies, transition moment, and oscillator strengths, respectively. The static and frequency-dependent second-order polarizabilities were then calculated using the sum-over-states (SOS) method.[18] The expression of the second-order polarizability component of β_{ijk} was derived using the perturbation theory and assuming electric dipole coupling between the radiation field and the molecule. The zeroth-order Born−Oppenheimer approximation was also employed to separate the electronic and atomic components of β. The expression for β_{ijk} is[18]

$$\beta_{ijk} = \frac{1}{4\hbar^2} P(i, j, k; -\omega_\sigma, \omega_1, \omega_2) \sum_{m \neq g} \sum_{n \neq g} \left[\frac{\langle g|\mu_i|m\rangle \langle m|\mu_j^*|n\rangle \langle n|\mu_k|g\rangle}{(\omega_{mg} - \omega_\sigma - i\Gamma_{mg})(\omega_{ng} - \omega_1 - i\Gamma_{ng})} \right] \quad (1)$$

Here, $\langle g|\mu_i|m\rangle$ is an electronic transition moment along the *i*-axis of the Cartesian component, between the ground state $\langle g|$ and the excited state$|m\rangle$; $\langle m|\mu_j^*|n\rangle$ denotes the dipole difference operator equal to $[\langle m|\mu_j|n\rangle - \langle g|\mu_j|g\rangle\delta_{mn}]$; ω_{mg} is the transition energy; ω_1 and ω_2 are the frequencies of the perturbation radiation fields, and $\omega_\sigma = \omega_1 + \omega_2$ is the polarization response frequency; $P(i, j, k; -\omega_\sigma, \omega_1, \omega_2)$ indicates all permutations of ω_1, ω_2, and ω_σ along with associated indices *i, j, k*; Γ_{mg} is the damping factor. The transition energy, transition moments, and dipole moments can be obtained from the calculated results on the basis of the TDB3LYP model. First, 100 excited states were calculated using the TDB3LYP model for all compounds. Those physical values were then taken as input of the sum-over-states (SOS) formula to calculate the second-order polarizabilities. One hundred excited states are enough, according to the convergence curves of the sum-over-states (SOS) method (Figure 3). Furthermore, the accuracy of the TDDFT-SOS method was proven by Cheng et al.[19] and our group.[20] It should be noted that we only concern ourselves with the contributions from electric dipole transitions because they are the most intense as compared with vibrational and rotational transitions.[21]

TABLE 1: Calculated Static Second-Order Polarizability (10^{-30} esu) of the Studied Compounds

polarizability	1	2	3	4
β_{xyz}	0.21	1.38	0.44	1.85
β_{zxx}	2.39	1.47	0.96	1.58
β_{zyy}	1.40	7.13	3.17	6.91
β_{zzz}	7.05	12.8	9.48	16.65
β_{vec}	10.84	21.42	13.61	25.14

3. Results and Discussions

A measurement of the second-order polarizability $\beta(-2\omega; \omega, \omega)$ is related to second-harmonic generation (SHG). For those compounds with their dipole moment along the *z*-axis, the β_{vec} is defined as

$$\beta_{\mathrm{vec}} = \frac{1}{3} \sum_{i=x,y,z} (\beta_{zii} + \beta_{izi} + \beta_{iiz}) \quad (2)$$

To validate the adopted methods, the second-order polarizability of the spirolinked push−pull polyenes ($n = 0$) has been calculated; these compounds have a similar structure ($C_{11}H_{12}N_4O_4$) to the compounds examined here. For the simplified systems, the predicted β_{vec} value is 12.7×10^{-30} esu, using the methods described in section 2. This compares well with the literature value of 14.4×10^{-30} esu, at the same geometry, suggesting that the currently employed methods will be reliable for the compounds shown in Figure 1. Owing to the C_2 symmetry of our studied compounds, there are 13 nonzero components of second-order polarizability among the 27 components. However, only 4 tensor components are independent, because $\beta_{xyz} = \beta_{xzy} = \beta_{yxz} = \beta_{yzx} = \beta_{zxy} = \beta_{zyx}$, $\beta_{xxz} = \beta_{zxx} = \beta_{xzx}$, and $\beta_{yyz} = \beta_{zyy} = \beta_{yzy}$. Out of the 4 independent components, the main contribution to β_{vec} is β_{zzz}, which is the direction of the C_2 axis (*z*-direction). This indicates that the main charge transfer is along the C_2 axis (*z*-axis) direction.

The static second-order polarizability is termed the zero-frequency hyperpolarizability and is an estimate of the intrinsic molecular hyperpolarizability in the absence of any resonance effect. The calculated static second-order polarizability is several times larger than those of typical compounds with extensive π-electron conjugation. For example, the calculated β_{vec} value of compound **4** is about 200 times larger than the average second-order polarizability of the organic urea molecule[3g] and 6 times larger than that measured for highly π-delocalized phenyliminomethyl ferrocene complex.[22] Furthermore, the β_{vec} values of compounds **1** and **3** are nearly equivalent to that of literature ($n = 0$),[12a] which has a carbon atom as the spiro-center and strong electron acceptor groups (NO_2). To determine the better spiro-center, carbon or silicon, we replaced the silicon atom with carbon within compound **1**. The resulting compound has a predicted β_{vec} value of 10.17×10^{-30} esu, indicating that silicon is slightly superior to carbon for enhancing NLO characteristics. Continuing our comparison, the β_{vec} values of compounds **2** and **4** are slightly larger than that of a literature compound ($n = 6$)[12a] which has a longer conjugation length. Consequently, all indications lead us to believe that the compounds examined here have excellent second-order nonlinear optical response (Table 1).

The large molecular second-order polarizability can be understood in terms of a structure−property relationship. In Table 2, we list the calculated dipole moments, absorption $\lambda_{\max}$ values, oscillator strengths, and major contribution obtained using the TDB3LYP with the B3LYP geometries. All the compounds studied here have small dipole moments. This merit

TABLE 2: Computed Dipole Moment (μ in debye), Absorption Wavelengths (λ_{max} in nm), Oscillator Strengths (*f*), and Transition Nature of the Studied Compounds

	state	m	λ_{max}	exp[13]	f	major contribution
1	3^1B	0.77	294	307	0.33	HOMO → LUMO + 2 (51%)
2	5^1A	0.78	309	317	0.57	HOMO − 1 → LUMO + 1 (63%)
3	3^1B	0.84	303	315	0.43	HOMO → LUMO + 3 (55%)
4	11^1B	0.87	319		0.75	HOMO − 2 → LUMO (67%)

may guarantee that dipole−dipole interactions between the neighboring molecules are very small and the material has large macroscopic second-order susceptibility. Experimentally, the electronic absorption spectra have been measured in chloroform, which as a polar solvent would cause a bathochromic shift in the electronic transition energies relative to the gas phase. For this reason, our calculated absorbance wavelengths are slightly smaller than the experimental values. Although compound **3** increases the conjugation length compared to compound **1**, the change of absorption λ_{max} values is rather small (9 nm). Compounds **2** and **4** also have the same properties (10 nm). To determine whether this behavior is due to the presence of the spiro-center, we calculated the absorption spectra of free ligands corresponding to compounds **1**−**4**. The absorption spectra values of these free ligands are 328, 332, 355, and 361 nm, respectively. Those values are all larger than those of compounds **1**−**4**. Furthermore, the absorption λ_{max} value of the free ligands corresponding to compounds **1** and **3** is increased by 27 nm, and of those corresponding to compounds **2** and **4** by another 29 nm. The results imply that the spiro-center plays a key role in reducing bathochromic shift, and exchange interactions occur through the spiroconjugation path. This indicates that the absorption spectra of these compounds are little influenced in comparison to linear push−pull polyenes. That is, a bathochromic shift with the increase of the conjugation length is very small, and it is suggested that high transparency will be maintained. This transparency is worthy of remarks in considering practical application.

Why does replacement of a carbon atom with nitrogen within the conjugated substituent for compound **2** and compound **4** have a great influence on the second-order nonlinear optical properties? From the complex SOS expression, the two-level model that linked between β_{vec} and a low-lying charge-transfer transition has been established. For the static case, the following expression is employed to estimate β_{CT}:

$$\beta_{CT} \propto \frac{\Delta\mu f_{gm}}{{E_{gm}}^3} \tag{3}$$

where $\Delta\mu$ is the change of dipole moment between the ground and mth excited states, f_{gm} is the oscillator strength of the transition from the ground state (g) to the mth excited state (m), and E_{gm} is transition energy. Thus, the second-order polarizability caused by charge transfer, β_{CT}, is proportional to the optical intensity and inversely proportional to the cube of transition energy. As a result, a larger f_{gm} with a lower E_{gm} will lead to a larger the second-order polarizability. Since our studied compounds have a large energy gap, the model is valid for analysis. Within the systems studied, we observe that the oscillator strengths relative to the maximal absorption wavelength are enhanced by about 1× from compound **1** (0.33) to compound **2** (0.57). Upon examining the MOs, we see that the substituent containing nitrogen has a larger amount of electron density than its carbon counterpart (especially within the unoccupied MOs, Figure 2). We attribute this feature to a larger amount of electronegativity in nitrogen than in carbon. This indicates that compound **2** may have a larger amount of charge transfer within the transition than the analogous transition in compound **1**. Clearly, such a large oscillator strength is a decisive factor and leads to a considerably large second-order polarizability of compound **2**. Compounds **3** and **4** also have the same trend. It is concluded that the carbon atom replaced by nitrogen has great influence on the second-order nonlinear optical properties. Furthermore, a crucial feature is that the Si atom of all studied compounds participates in the light absorption processes (Figure 2). Thus, the direct role of the Si atom can be claimed in the second-order nonlinear optical response. Moreover, the electron density difference of the ground state

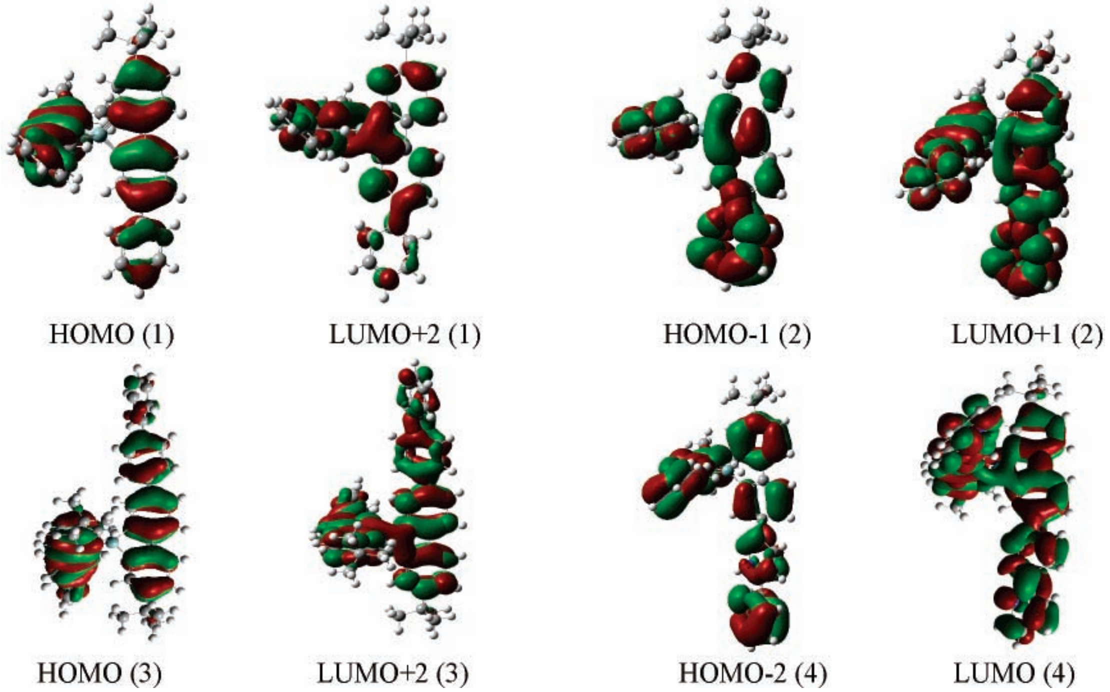

Figure 2. The frontier molecular orbitals constitute maximal absorption to our studied compound.

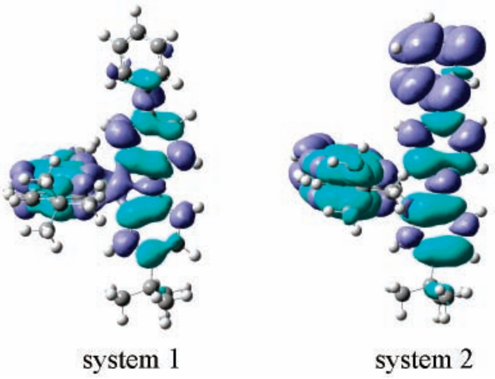

Figure 3. Electron density difference maps of the ground state and the excited state of interest.

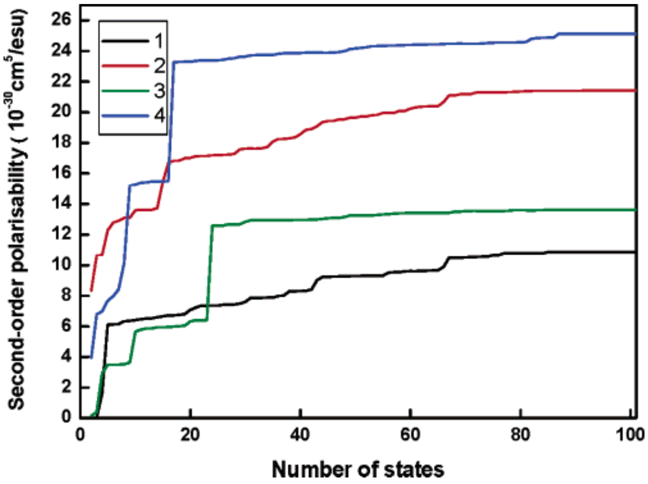

Figure 4. Plot of the β_{vec} values vs the number of states for the studied compounds.

and the excited state of interest has been done with the cubgen and cubeman utilities of *Gaussian 03* for compounds **1** and **2**. The maps are shown in Figure 3. The purple-colored regions indicate the regions in which electron density increases upon transition to the excited state, and the blue-colored regions indicate the regions in which electron density decreases upon the transition. The maps also show that there is more charge-transfer character in compound **2** relative to compound **1**. Compounds **3** and **4** also have the same trend. Those are in accordance with the conclusions based on the makeup of maximal absorption (Figure 2).

The accuracy of the some-over-states (SOS) methods mainly depends on the convergence of calculation results. In principle, the more excited states participate in the calculation, the more accuracy in the result obtained. When the excited state number is gradually increased, the denominator of eq 1 become larger and larger, and the numerator variation is very small. Hence, the second-order polarizability converges rapidly with the number of excited states included. Figure 4 presents the plot of the β_{vec} values versus the number of states for the studied compounds. It can be seen that the convergences are stable after summation over about 70 states for all the compounds. Accordingly, it is a reasonable approximation in the calculation of β_{vec} by employing 100 states in the SOS method in this work.

Now, we investigate the dispersion behavior of the second-order polarizabilities. The plot of calculated values of β_{vec} versus the input photon energy from 0.0 to 3.0 eV is shown in Figure 4. We find that the curves below 1.1 eV appear relatively flat for all compounds. These results indicate that the compounds exhibit a small dispersion in a width frequent zone and are available to be used for frequency conversion optical materials. The optical gap energies based on the results of the DFT/B3LYP calculations are about 3.5 eV for all compounds. In second harmonic generation (SHG) processes, there are one-photon (ω) and two-photon (2ω) processes; thus, there are ω and 2ω resonant enhancement. Figure 5 shows that the first enhancement oscillating band appears at 2ω ($\hbar\omega \approx 1.8$ eV) for the SHG. Accordingly, we can choose an input wavelength among the measuring techniques of SHG processes to obtain the nonresonant second-order polarizabilities from a known transition energy or absorption spectrum of the studied compounds.

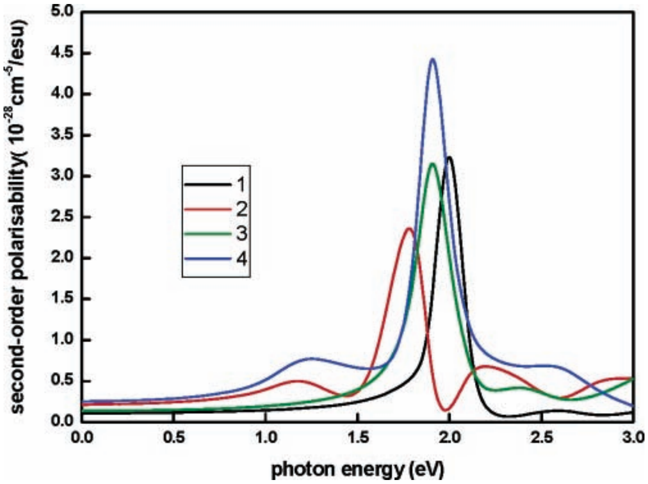

Figure 5. Calculated dispersion behavior of β_{vec} for the studied compounds.

4. Conclusion

We have investigated the electronic structure and the second-order nonlinear optics properties of the asymmetric spirosilabifluorene derivatives and elucidated structure−property relationships from the micromechanism. The results show that these compounds possess many favorable features for application in the second-order nonlinear optical field. First, these compounds have remarkably larger molecular second-order polarizability compared with the typical organic compounds. Second, all the compounds generate large nonresonant optical nonlinearities over a wide frequency zone; therefore, they can be used for a frequency conversion optical material. Third, a small dipole moment can guarantee manifestation of the large macroscopic second-order susceptibility. Fourth, they have high transparency in the visible light area. Thus, it can be concluded that asymmetric spirosilabifluorene derivatives will be a hopeful kind of second-order nonlinear optical material.

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