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Probing the linear and nonlinear optical properties of nitrogen-substituted carbon nanotube

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Abstract In view of their intriguing structural and electrical properties, the linear and nonlinear optical (NLO) responses of six carbon nanotube (CNT) molecules substituted by nitrogen atoms at one end have been explored by using the CAM-B3LYP method. Molecules **1**, **2** and **3** were obtained by increasing the lengths of the CNTs, and **1-Li**, **2-Li** and **3-Li** were constructed by doping one Li atom into the N-substituted end of **1**, **2** and **3** (mentioned above), respectively. Two effective approaches have been proposed to increase nonlinear optical properties(NLO): increasing the length of the CNT as well as doping one Li atom into the N-substituted end. The results show that both the linear polarizabilities (α_0) and nonlinear first hyperpolarizabilities (β_{tot}) values increase with increasing the lengths of the CNTs: 188 of **1** < 307 of **2** < 453 of **3** for α_0 and 477 of **1** < 2654 of **2** < 3906 au of **3** for β_{tot}. Significantly, compared with the non-doped CNTs, the β_{tot} values are remarkably enhanced by doping one Li atom into the N-substituted end: 477 of **1** < 23258 of **1-Li**, 2654 of **2** < 37244 of **2-Li**, and 3906 of **3** < 72004 au of **3-Li**. Moreover, the β_{vec} values show a similar trend to the β_{tot} values. Our results may be beneficial to experimentalists in exploring high-performance nonlinear optical materials based on CNT.

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Introduction

Driven by a series of important technological applications (e.g., telecommunication, information storage, optical switching, and signal processing) which can be realized if suitable materials are available [1–9], the research of nonlinear optical (NLO) materials has always been in the spotlight of scientific interest. In order to get considerable NLO response, not only various mechanisms and phenomena have been investigated, but also the prediction and design of molecules with large (hyper)polarizabilities have received much attention [10–14]. Generally speaking, inorganic and organic materials [15–19] are the two main types of nonlinear optical (NLO) materials. Traditionally, inorganic NLO crystals such as lithium niobate ($LiNbO_3$) and potassium dihydrogen phosphate (KH_2PO_4) are known to exhibit second harmonic generation (SHG) effect. In comparison with inorganic materials, it is relatively easy to modify the structures of organic molecules, which makes it possible to synthesize tailor-made molecules and to fine-tune the properties for desired application [20–23]. However, the organic NLO molecules suffer from chemical and thermal instability, which greatly restricts their applications in reality.

Surprisingly, carbon is the chemical genius and it can create structures (such as graphite, diamond, fullerene, nanotube, and so forth) with entirely different properties by bonding in different ways. Owing to their unique mechanical and electrical properties, especially their unparallel thermal stability, carbon nanotubes (CNTs) have always been promising candidates in a wide variety of applications

since Iijima first described them in 1991 [24–27]. CNTs can be considered as rolled-up graphene sheets and their properties vary with different structures. The main two types of CNTs include multiwalled nanotubes (MWNTs) and single-walled nanotubes (SWNTs). Both experimental and theoretical studies have suggested that the single-walled nanotubes (SWNTs) are probably more important in nanotechnology. The geometry of each CNT is uniquely identified by the chiral vector (n, m) that describes which two points on graphene's hexagonal lattice are brought together to form the CNT [28, 29]. In addition, the length, diameter, and the number of caps are also important in determining the properties of CNT. In some reports, it has been suggested that 4 Å, e.g., the (5, 0)-CNT, is the smallest stable diameter for a CNT [30]. On the other hand, the nitrogen substituted effect could enhance the first hyperpolarizability of CNT effectively [31, 32]. Furthermore, in the field of developing high-performance organic NLO materials, a large number of research works have been directed toward doping alkalimetal atoms into organic compounds [33–38]. Li and his co-workers have performed much fascinating research on these kinds of NLO materials, in which the alkalimetal-doped compounds have shown significantly large NLO responses [39–41].

Therefore, in the present work, six CNT molecules with one end fully substituted by nitrogen atoms have been designed to explore the strategies to improve the linear polarizability and the nonlinear first hyperpolarizability of (5, 0)-CNT. Then, extending the length of the CNT and doping one Li atom into the N-substituted end are proposed to improve the NLO properties.

Computational details

Since the hybrid Becke-style three-parameter exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) is known to yield similar geometries for medium-sized molecules as Møller-Plesset perturbation theory (MP2) calculations do with same basis sets, it has been widely used to optimize the geometries of medium-sized molecules [42–47]. Thus, in the present work, the optimized structures of the six N-substituted CNT molecules were obtained at the B3LYP/6-31 g(d) theory level.

Choosing a proper method to calculate the (hyper)polarizability of a system is crucial. As everyone knows, the MP2 method is more reliable, but the large resource and time consumption make it costly for large systems. The DFT method has been widely used to predict the optoelectronic properties of molecules because of its modest computational cost, but it has been found unsuccessful in calculating (i) the polarizability of long chains, (ii) excitations for Rydberg states and especially (iii) charge-transfer excitations. The

problems have been attributed to the incorrect long-range form of the exchange potential. Fortunately, based on the coulomb-attenuating method (CAM), Yanai et al. [48] introduced a new hybrid exchange-correlation energy functional (CAM-B3LYP) to overcome such problems. Briefly, CAM-B3LYP combines the features of hybrid functionals such as B3LYP with the long-range corrected functionals [49–53]. It has been demonstrated that due to the improved description of the long-range exchange interaction, CAM-B3LYP provides significant improvements for the limitations mentioned above. There, it has been widely adopted to predict the molecular properties of charge-transfer processes [54–56]. In order to testify that CAM-B3LYP is reliable to calculate the first hyperpolarizability of the systems studied in this work, the first hyperpolarizability of 1 were calculated by B3LYP, BhandhLYP, CAM-B3LYP and M062X, respectively. The results are listed in Table 1, which indicate that these methods have similar β_i (i = x, y and z) and β_{tot} values. Then, CAM-B3LYP was selected to calculate the NLO properties of the systems studied in this work with the consideration of computational cost and accuracy. At the same time, the basis-set-dependent [57–62] was tested. β_i (i = x, y and z) and β_{tot} values of 1-Li were calculated by CAM-B3LYP with different basis sets(one is the 6-31 + g(d) basis set for C, N and H atoms, and the 6-311++g(3df) basis set for Li atoms; the other is 6-31++g(d) basis set for C, N and H atoms, and the 6-311++g(3df) basis set for Li atoms). The two basis sets obtained similar β_i (i = x, y and z) and β_{tot} values (seen in Table 1). Thus, the 6-31 + g(d) basis set for C, N and H atoms, and the 6-311++g(3df) basis set for Li atoms may obtain the accurate data for the systems studied in this work. The crucial transition energies and the transition natures were obtained by using the configuration interaction with single excitations (CIS) method.

The polarizability (α_0) is defined as follows:

$$\alpha_0 = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right). \tag{1}$$

The static first hyperpolarizability is noted as [63]:

$$\beta_{tot} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{\frac{1}{2}}, \tag{2}$$

where $\beta_i = \left(\beta_{iii} + \beta_{ijj} + \beta_{ikk}\right), i, j, k, = x, y, z.$

$$\beta_{vec} = \frac{\beta_x u_x + \beta_y u_y + \beta_z u_z}{\sqrt{u_x^2 + u_y^2 + u_z^2}}. \tag{3}$$

All of the calculations were performed with the Gaussian 03 [64] and Gaussian 09 [65] program package.

Table 1 β_i (i = x, y and z) and β_{tot} of 1 calculated by B3LYP, BhandhLYP, CAM-B3LYP and M062X; β_i (i = x, y and z) and β_{tot} of 1-Li calculated by CAM-B3LYP with two different basis sets

		B3LYP	BhandhLYP	CAM-B3LYP	M062X
1	β_x(au)	2	2	2	2
	β_y(au)	-7	-4	-4	-4
	β_z(au)	580	594	477	440
	β_{tot}(au)	580	594	477	440
				CAM-B3LYP 6-31 + g(d) for C, N 6-311++g(3df) for Li	CAM-B3LYP 6-31++g(d) for C, N 6-311++g(3df) for Li
1-Li	β_x(au)			-19082	-19671
	β_y(au)			-13281	-13702
	β_z(au)			-662	-681
	β_{tot}(au)			23258	23982

Results and discussion

Equilibrium geometries and natural bond orbital analysis

The optimized structures of the six N-substituted CNT molecules are given in Fig. 1. From Fig. 1, molecules **1**, **2** and **3** were obtained by increasing the lengths of the nitrogen-substituted CNTs, while **1-Li**, **2-Li** and **3-Li** were built up by doping one Li atom into the N-substituted end of **1**, **2** and **3** (mentioned above), respectively. The important geometrical parameters and NBO charges are collected in Table 2.

From Table 2, due to the substitution of the nitrogen atoms, the diameter of the N-substituted end (the upper end D_u) becomes smaller than that of the non-substituted end (the lower end D_l). For each additional layer, the length
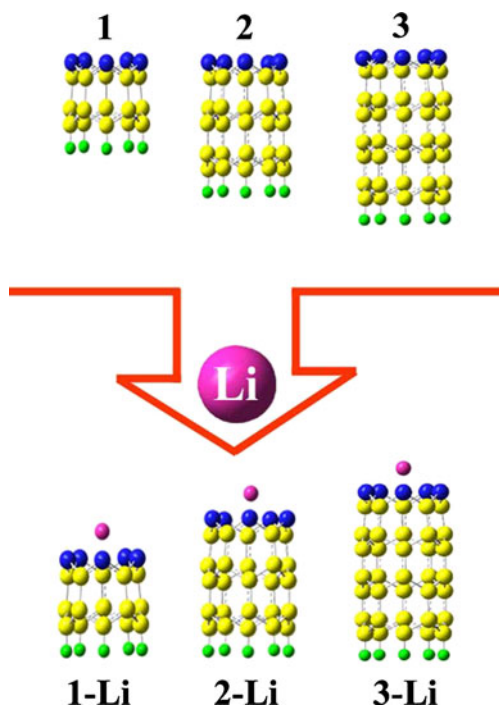

Fig. 1 Optimized geometries of the studied systems

of the N-substituted CNT is increased by about 2.10 Å. On the other hand, the geometrical structure is slightly changed by doping one Li atom into the N-substituted end of the corresponding molecule: by doping one Li atom into the corresponding molecule, (1) the length of the N-substituted CNT becomes slightly shorter (3.93 of **1** > 3.92 of **1-Li**, 6.08 of **2** > 6.05 of **2-Li**, and 8.18 of **3** > 8.16 Å of **3-Li**). (2) The C-N average distance becomes slightly larger (1.36 of **1** < 1.37 of **1-Li**, 1.37 of **2** < 1.38 of **2-Li**, and 1.37 of **3** < 1.38 Å of **3-Li**). (3) The value of D_u becomes slightly larger (3.84 of **1** < 3.87 of **1-Li**, 3.86 of **2** < 3.89 of **2-Li**, and 3.87 of **3** < 3.89 Å of **3-Li**).

To interpret the interaction between the Li atom and the N-substituted CNT molecule, natural bond orbital (NBO) analysis has been performed (See Table 2). The charges of the nitrogen atoms of **1**, **2** and **3** range from -0.41 to -0.44, while that of **1-Li**, **2-Li** and **3-Li** range from -0.55 to -0.59. It is obvious that the charges of the N atoms become more negative by doping one Li atoms into the N-substituted CNT

Table 2 Selected geometrical parameters and NBO charges of the non-doped and the Li-doped studied systems

	1	2	3
C-N[a]	1.36	1.37	1.37
Length	3.93	6.08	8.18
D_u	3.84	3.86	3.87
D_l	4.41	4.46	4.48
q(N)	-0.44	-0.41	-0.41
	1-Li	2-Li	3-Li
N-Li	2.26	2.27	2.26
C-N	1.37	1.38	1.38
Length	3.92	6.05	8.16
D_u	3.87	3.89	3.89
D_l	4.48	4.48	4.47
q(N)	-0.59	-0.56	-0.55
q(Li)	0.88	0.88	0.88

[a] Bond lengths are given in angstroms

molecules. At the same time, the charge of the Li atom of each molecule is 0.88 (close to 1), which indicates that the valence electron of the Li atom becomes more diffuse due to the interaction between the Li atom and the N-substituted CNT molecule. Based on the analysis above, the Li-doped CNT molecules may be expected to show some special properties compared with the non-doped molecules.

The linear and nonlinear optical properties

The linear and nonlinear optical properties of the non-doped CNTs

The polarizabilities and the first hyperpolarizabilities of the three non-doped N-substituted CNT molecules at the CAM-B3LYP level are given in Table 3, Figs. 2 and 3. From the data, it can be found that the polarizabilities (α_0) of the three non-doped N-substituted CNT molecules improve with increasing the lengths of the N-substituted CNTs: 188 of **1** < 307 of **2** < 453 au of **3**. Similarly, the nonlinear first hyperpolarizabilities (β_{tot}) of these three non-doped N-substituted CNT molecules enhance with increasing the lengths of the CNTs: 477 of **1** < 2654 of **2** < 3906 au of **3**. According to the analysis above, it can be concluded that increasing the length of the CNT is an effective way to enhance both linear and nonlinear optical properties of the N-substituted CNT. Furthermore, the β_{vec} values of 1, 2 and 3 are listed in Table 3. The data indicate that the β_{vec} and β_{tot} show the same trend.

In order to explain the improvement of the optical properties of the non-doped N-substituted CNT by increasing the length of the CNT, we must get a comprehensive understanding of the origin of the β_{tot} values by using "sum-over-states" (SOS) expression [66], a simple link between β_{tot} and the low-
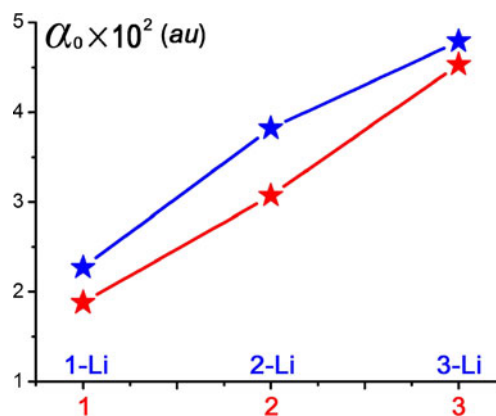

Fig. 2 The polarizabilities of the studied systems

lying charge-transfer transition established by Oudar and Chemla [67, 68]. For static case ($\omega=0.0$), the expression of SOS in literature is employed as follows:

$$\beta_{tot} \propto \frac{f_0 \cdot \Delta\mu}{\Delta E^3} \qquad (3)$$

In the above expression, β_{tot} is proportional to the difference of the dipole moment between the ground state and the excited state ($\Delta\mu$) and the oscillator strength (f_0), but inversely proportional to the third power of the transition energy (ΔE). Hence, the transition energy (ΔE) is the decisive factor for the first hyperpolarizability. The ΔE values of the three non-doped N-substituted CNT molecules are listed in Table 3. As shown in Table 3, the ΔE values decrease with increasing the lengths of the N-substituted CNTs: 7.57 of **1** >6.22 of **2** > 5.20 eV of **3**. Therefore, the β_{tot} values are increased by increasing the lengths of the N-substituted CNTs. Furthermore, for **1**, **2** and **3**, the transition natures

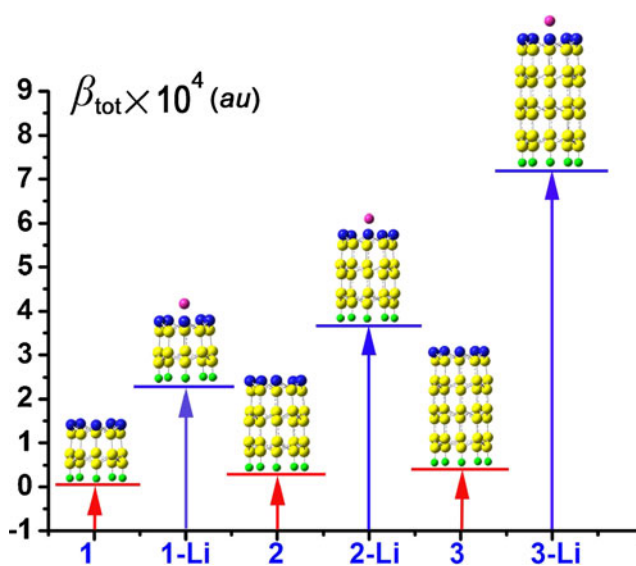**Table 3** Calculated polarizabilities (α_0), first hyperpolarizabilities (β_{tot} and β_{vec}), transition energies (ΔE) and transition natures of the non-doped studied and the Li-doped studied systems

	1	2	3
α_0 (au)	188	307	453
β_{tot} (au)	477	2654	3906
β_{vec} (au)	475	3676	3844
ΔE (eV)	7.57	6.22	5.20
Transition nature	H-7→L+2[a]	H-9→L+1	H-5→L+4
	1-Li	2-Li	3-Li
α_0 (au)	227	382	479
β_{tot} (au)	23258	37244	72004
β_{vec} (au)	4364	-15892	29711
ΔE (eV)	3.17	3.01	2.43
$\frac{\Delta\mu \cdot f_0}{\Delta E^3}$ (au)	17.04	82.40	114.69
Transition nature	H-1→L+1	H-1→L+2	H-2→L

[a] *H* HOMO and *L* LUMO

Fig. 3 The first hyperpolarizabilities of the studied systems

corresponding to the ΔE values are HOMO-7→LUMO + 2 transition, HOMO-9→LUMO + 1 transition and HOMO-5→LUMO + 4 transition, respectively.

The linear and nonlinear optical properties of the Li-doped N-substituted CNTs

The polarizabilities and the first hyperpolarizabilities of the three Li-doped N-substituted CNT molecules at the CAM-B3LYP level are also given in Table 3, Figs. 2 and 3. It can be found that the polarizabilities (α_0) of the three Li-doped N-substituted CNT molecules are also improved by increasing the lengths of the CNTs: 227 of **1-Li** < 382 of **2-Li** < 479 au of **3-Li**. Similarly, the nonlinear first hyperpolarizabilities (β_{tot}) of the three Li-doped CNT molecules are also enhanced by increasing the lengths of the CNTs: 23258 of **1-Li** < 37244 of **2-Li** < 72004 au of **3-Li**. At the same time, β_{vec} of 1-Li, 2-Li and 3-Li were calculated and shown in Table 3. The trend of β_{vec} is the same as that of β_{tot}.

Significantly, compared with the non-doped N-substituted CNT molecules, the nonlinear first hyperpolarizabilities (β_{tot}) of the N-substituted CNT molecules have a remarkable improvement by doping one Li atom into the N-substituted: 477 of **1** < 23258 of **1-Li**, 2654 of **2** < 37244 of **2-Li** and 3906 of **3** < 72004 au of **3-Li**. Therefore, it can be concluded that the Li-doped effect is a more effective way to enhance the nonlinear first hyperpolarizabilities of the CNT.

Similarly, the ΔE values have also been considered to explain the origin of the β_{tot} values, and the data are also listed in Table 3. From Table 3, the ΔE values also decrease with increasing the lengths of the Li-doped CNTs: 3.17 of **1-Li** > 3.01 of **2-Li** > 2.43 of **3-Li**. On the other hand, the ΔE values of the Li-doped molecules are all smaller than that of the corresponding non-doped molecules when the layers of two CNT molecules are equal (3.17 of **1-Li** < 7.57 of **1**, 3.01 of **2-Li** < 6.22 of **2**, 2.43 of **3-Li** < 5.20 eV of **3**), which leads to a remarkable improvement of the β_{tot} values of the Li-doped N-substituted CNT molecules compared with the non-doped molecules. Furthermore, for **1-Li**, **2-Li** and **3-Li**, the transition natures corresponding to the ΔE values are HOMO-1→LUMO + 1 transition, HOMO-1→HOMO + 2 transition and HOMO-2→LUMO transition, respectively.

Furthermore, the Li-doped N-substituted CNT molecules taken as examples to calculate their $\frac{\Delta\mu \cdot f_0}{\Delta E^3}$ values were performed by CIS method and shown in Table 3, which improves with increasing the lengths of the Li-doped CNTs: 17.04 of **1-Li** < 82.40 of **2-Li** < 114.69 au of **3-Li**. The trend is in good agreement with the trend of β_{vec} of 1-Li, 2-Li and 3-Li.

In addition, the electron clouds of the crucial transitions of the studied systems are illustrated in Fig. 4. From Fig. 4, it can be observed that for **1**, **2** and **3**, the electron clouds of
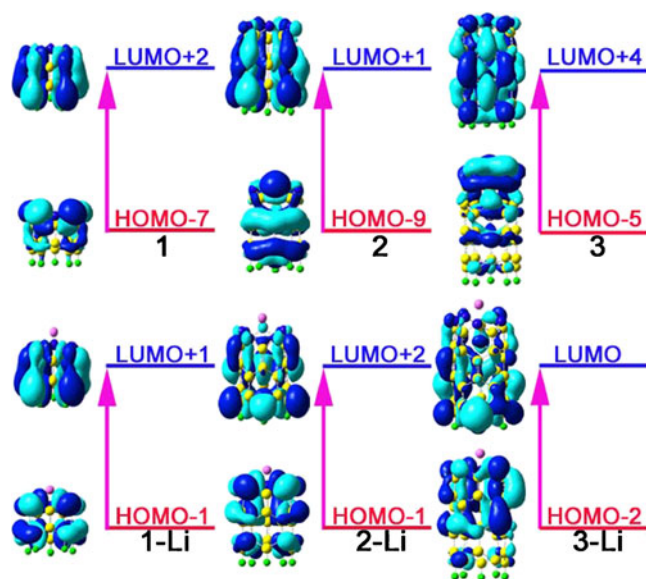

Fig. 4 Frontier molecular orbitals of the studied systems

the ground state mainly locate at the N-substituted end (the upper end), while that of the excited state mainly locate at the non-substituted end (the lower end). That is, the direction of the electron clouds transition is from the upper end to the lower end, and the electron clouds transitions become obvious from **1** to **3**. Similar electron cloud transitions can also be observed in the case of the Li-doped CNTs. Therefore, compared with the non-doped CNT molecules, the dipole moment between the ground state and the excited state ($\Delta\mu$) of the Li-doped molecules change little, it is the Li-doped effect that seriously decreases the ΔE values, leading to the larger β_{tot} values of the Li-doped CNTs.

Conclusions

In the present paper, six carbon nanotube (CNT) molecules with one end fully substituted by nitrogen atoms have been designed for the first time. Their linear and nonlinear optical properties have been improved from two aspects: increasing the length of the N-substituted CNT as well as doping one Li atom into the N-substituted end. The results show that the two approaches mentioned above are available to enhance the polarizability (α_0) and the first hyperpolarizability (β_{tot}) of the N-substituted CNT. Interestingly, in comparison with increasing the length of the N-substituted CNT, doping one Li atom is a more effective way to improve significantly the nonlinear optical properties of the N-substituted CNTs. Moreover, the transition energy analysis shows that the ΔE values become smaller as increasing the lengths of the N-substituted CNTs for both Li-doped molecules and non-doped molecules. In particular, for two N-substituted CNT molecules with the same layers, the transition energy drops significantly by

doping one Li atom into the N-substituted end, leading to a remarkable improvement in the β_{tot} value. Moreover, the β_{vec} values show similar trend to the β_{tot} values.

A new designing idea is proposed to enhance the linear and nonlinear optical properties of N-substituted CNT by increasing the length of N-substituted CNT or doping one Li to N-substituted CNT. It is our expectation that a new type of NLO material based on N-substituted CNT will be synthesized in experiment soon.

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