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How the Number and Location of Lithium Atoms Affect the First Hyperpolarizability of Graphene

Yang-Yang Hu, Shi-Ling Sun, Shabbir Muhammad, Hong-Liang Xu,* and Zhong-Min Su*

Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, Jilin, People's Republic of China

How do the number and location of lithium atoms affect the first hyperpolarizability (β_{tot}) of graphene? In this paper, based on pentacene, a series of graphene (multi)lithium salts Li_n@pentacene ($n = 1, 2, 3, 4, 5,$ and 6) have been designed to answer this question. β_{tot} obviously increases stepwise with an increase in the number of lithium atoms: 1369−1843 for Li@pentacene < 3510−4081 for Li_2@pentacene < 6933−7934 for Li_3@pentacene < 11 188−12 145 for Li_4@pentacene < 14 904 au for Li_5@pentacene, which are much larger than pentacence. This pattern suggests that the lithium salt effect on the first hyperpolarizability is very large. Unexpectedly, when an additional lithium atom is doped into the graphene multilithium salt Li_5@pentacence, which leads to Li_6@pentacence, the β_{tot} value dramatically increases to a value of 4 501 764 au with a remarkable increase of 302-fold in contrast to Li_5@pentacence. On the other hand, when the number of lithium atoms is equal, the location of lithium atoms also affects the β_{tot} value: the closer the lithium atoms are clustered, the larger the β_{tot} value: for Li_3@pentacence, 6933 au of system 10 < 7401 au of system 9 < 7934 au of system 8. Furthermore, their transition energies (ΔE) are also obtained. The results show that ΔE decreases stepwise with an increase in the number of the lithium atoms, and ΔE of Li_6@pentacence sharply decreases to 0.299 eV, which may explain the huge β_{tot} value. This study may stimulate the search for new types of graphene NLO materials based on alkali metals for NLO application.

Introduction

Nonlinear optical (NLO) materials research has developed at a truly relentless pace over the last four decades.[1] Because of the critical role they play in contemporary optical communications,[2] novel NLO materials are still in great demand. Considerable efforts have been made toward finding high-performance NLO materials.[3] So far, there are mainly two conventional classes of NLO materials: inorganic materials[4] and organic materials.[5] Of the two classes of NLO materials, the organic materials are of major interest because of their low dielectric constants, high laser damage thresholds, fast time responses, and off-resonance nonlinear optical susceptibilities comparable to or exceeding those of ferroelectric inorganic crystals.[6] Some useful strategies based on organic NLO compounds are as follows: the planar donor−π-conjugated bridge−acceptor (D-π-A) model, extended π-electron systems, twisted π-electron systems, enhanced push−pull effects, incorporation of alkali metal into the organic complexants, etc.[7] As a result, many types of new nonlinear optical materials molecules can be obtained.
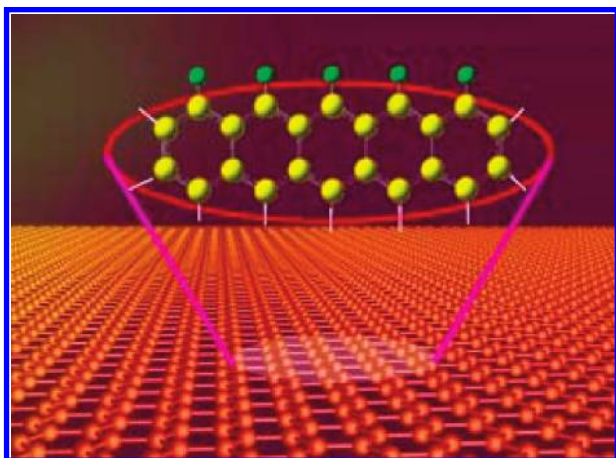
The discovery of graphene has ushered in a new era of materials research.[8] Owing to its unique structure and properties, such as high electronic and thermal conductivities (the charge carriers of graphene can travel for micrometers without scattering at room temperature, and graphene can sustain current densities 6 orders of magnitude higher than that of copper, which shows record thermal conductivity and stiffness[9]), great mechanical strength (it is the thinnest known material in the universe and the strongest ever measured), large surface areas (∼2600 m²/g), and high chemical stability, graphene could be utilized for potential applications including graphene field effect transistors, graphene sheet supercapacitors, lithium secondary batteries, etc.[10] Best of all, since the development of various effective techniques involving micromechanical exfoliation, epitaxial growth, and chemical vapor deposition, graphene can now be produced in higher quality for fundamental studies and potential applications in nanoelectronics.[11] Nevertheless, because the basic building block of graphene has a symmetric center, its second hyperpolarizability is quite small. Fortunately, chemical doping is an important approach to adjust the electrical properties of graphene.[12] Formulation of different doping methods for this two-dimensional material will be key to its future applications and requires drastically different approaches from conventional methods for bulk materials. Some records show that one can considerably enhance the dipole polarizability and the second hyperpolarizability of unsaturated organic molecules by replacing hydrogen atoms with lithium. Another article has also confirmed that the lithiation effect can lead to an enormous increase in the second hyperpolarizability of the smaller π-conjugated benzene.[13] This molecule was synthesized[14] in 1978 by Shimp et al. and was isolated in 1992 by Baran et al.[15] The semiempirical results and the ab initio studies of other lithium-unsaturated molecules have also showed that the lithium atom bears responsibility for the particularly large values of the studied properties. In consequence, the lithiation effect may make graphene a new member of the large family of NLO materials.

Pentacenes and pentacene derivatives have been used as key components in nanoelectronics because of their inherent electronic properties, excellent film-forming characteristics, and the ability to adjust the electronic behavior required by a particular device.[16] Furthermore, in a recent science article, pentacene has

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* Corresponding author. E-mail: zmsu@nenu.edu.cn.

First Hyperpolarizability of Graphene

J. Phys. Chem. C, Vol. 114, No. 46, 2010 **19793**

SCHEME 1

been imaged by AFM.[17] The tuning of the electronic properties of pentacene, such as charge injection barriers, HOMO−LUMO gaps, charge transfer rates, and molecular ordering of pentacenes, is accomplished by substituting pentacene with different functional groups.[18] Therefore, in the present paper, we chose linear pentacene as the model of the graphene edge (see Scheme 1) to investigate the effect of the number and location of Li atoms on graphene's first hyperpolarizability (β_{tot}). We have only reported research on the exterior of a graphene sheet, but we think this is adequate, because it could represent the essential
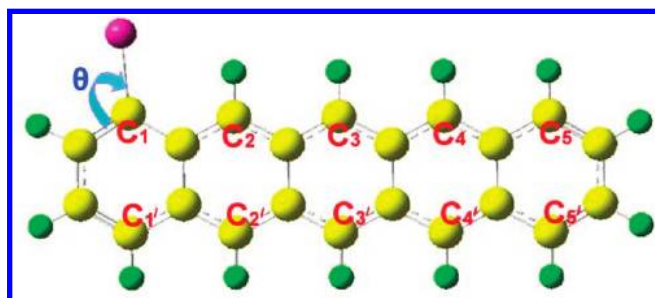
structural element of graphene, i.e., the zigzag edge which could be systematically extended by increasing the length of the polycyclic chain or adding an extra honeycomb lattice inward. Additionally, we hope that this model will heighten the chemists' structural sensitivity and promote the study of lithiated graphenes on a large scale.

Computational Details

The optimized geometrical structures of Li_n@pentacene (n = 1, 2, 3, 4, 5, and 6) are obtained by using the B3LYP method. The 6-31+G(d) basis set is employed for C and H atoms, and the 6-311G(3df) basis set is employed for Li atoms. These basis sets are demonstrated to be suitable for our present complexes as explained in Supporting Information.

Choosing a proper method to calculate the (hyper)polarizability of a system is crucial. The MP2 method is more reliable in calculating (hyper)polarizability, but it is quite costly for large systems. The B3LYP method has been reported to overestimate the (hyper)polarizabilities for some large systems.[19] Fortunately, Champagne et al. have proposed the BHANDHLYP method, which includes a higher percentage of HF exchange than that of the B3LYP method and successfully reduces the overestimation of the (hyper)polarizability.[20] Furthermore, Nakano and his co-workers pointed out that, for a medium-size system, *p*-quinodimethane, the BHANDHLYP method can also reproduce the (hyper)polarizability values from the more sophisticated CCSD(T) method.[21] The first hyperpolarizabilities of Li@benzene calculated by the four methods (HF, B3LYP, BHANDHLYP, and MP2) are 1176, 2986, 1793, and 2187 au, respectively. The data suggest that the B3LYP greatly overestimates the first hyperpolarizability of Li@benzene, while the BHANDHLYP value is close to the MP2 value. Obviously, the BHANDHLYP method is a good compromise between the quality and efficiency of hyperpolarizability calculations. So in this work, the BHANDHLYP method is used to explore the dependence of the first hyperpolarizability (β_{tot}) of graphene on the number and location of Li atoms. The method and basis set effect on the values of the studied systems are compared by testing Li@benzene (see Supporting Information), but considering that it could be regarded as a fraction of the studied systems, the results are trusted.
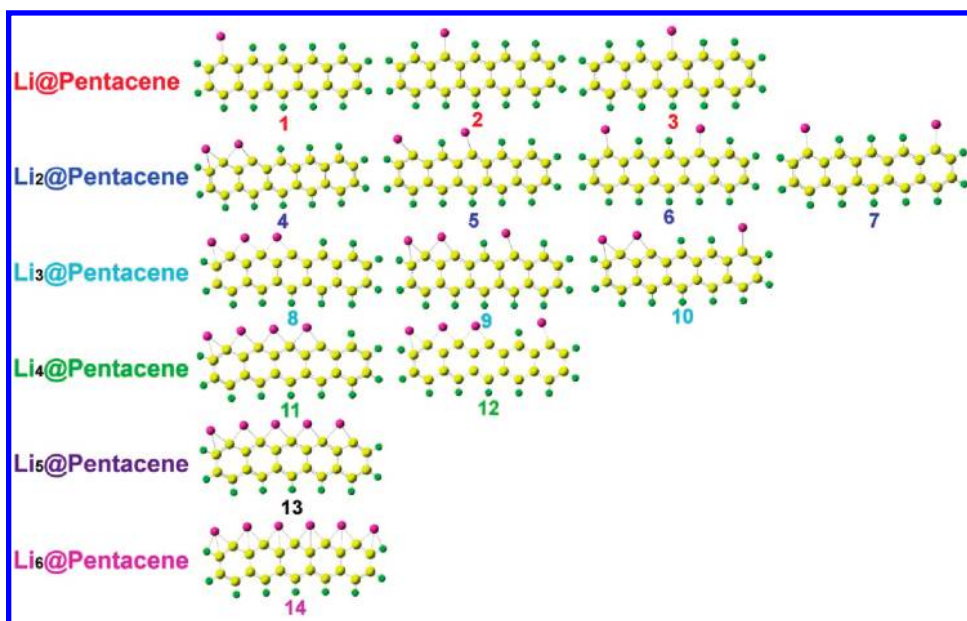

Figure 1. Labeled geometry of Li_n@pentacene (n = 1, 2, 3, 4, 5, and 6).

Figure 2. Optimized geometries of Li_n@pentacene (n = 1, 2, 3, 4, 5, and 6).

TABLE 1:   Geometrical Parameters of Li$_n$@pentacene (n = 0, 1, 2, 3, 4, 5, and 6)

	pentacene	Li@pentacene			Li$_2$@pentacene				Li$_3$@pentacene			Li$_4$@pentacene		Li$_5$@pentacene	Li$_6$@pentacene
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
C$_1$–Li$_1$		1.96			1.90	1.87	1.95	1.96	1.91	1.90	1.90	1.91	1.91	1.91	1.93
C$_2$–Li$_2$			1.97		1.90				1.93	1.90	1.90	1.94	1.93	1.94	1.99
C$_3$–Li$_3$				1.97		1.95			1.89			1.92	1.89	1.92	1.97
C$_4$–Li$_4$							1.96			1.94		1.89		1.92	1.96
C$_5$–Li$_5$								1.96			1.96		1.94	1.89	1.97
C$_5$–Li$_6$															1.93
C$_1$–C$_5$	9.892[a]	9.91	9.90	9.91	9.90	9.89	9.92	9.92	9.96	9.91	9.91	10.04	9.99	10.13	10.06
C$_{1'}$–C$_{5'}$	9.892	9.89	9.88	9.89	9.88	9.89	9.88	9.89	9.85	9.88	9.88	9.81	9.85	9.78	9.80
θ		119[b]	121	122	74	81	117	120	74	74	74	74	74	74	76

[a] Bond lengths are given in angstroms. [b] Bond angles are given in degrees.

TABLE 2:   NBO Charges of Li$_n$@pentacene (n = 1, 2, 3, 4, 5, and 6)

	Li@pentacene			Li$_2$@pentacene				Li$_3$@pentacene			Li$_4$@pentacene		Li$_5$@pentacene	Li$_6$@pentacene
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Li$_1$	0.90			0.89	0.91	0.89	0.89	0.90	0.89	0.89	0.90	0.90	0.90	0.73
Li$_2$		0.89		0.79				0.75	0.78	0.78	0.74	0.74	0.75	0.62
Li$_3$			0.89		0.88			0.79			0.72	0.76	0.74	0.67
Li$_4$						0.88			0.88		0.78		0.72	0.67
Li$_5$							0.89			0.89		0.87	0.77	0.62
Li$_6$														0.73

The static first hyperpolarizability is noted as

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

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

All of the calculations in this job are carried out by using the GAUSSIAN 03 program package.[22] The dimensional plots of the molecular orbitals are generated with the GaussView program.[23]

Results and Discussion

In the present paper, the five top C atoms are labeled as C$_1$, C$_2$, C$_3$, C$_4$, and C$_5$ in sequence, and the corresponding Li atoms connected to them are Li$_1$, Li$_2$, Li$_3$, Li$_4$, Li$_5$, and Li$_6$ (Li$_6$ is also connected to C$_5$), while the five bottom C atoms are labeled as C$_{1'}$, C$_{2'}$, C$_{3'}$, C$_{4'}$, and C$_{5'}$ in sequence (see Figure 1). The fourteen systems are classified into six groups by the number of the Li atoms: Li@pentacene, Li$_2$@pentacene, Li$_3$@pentacene, Li$_4$@pentacene, Li$_5$@pentacene, and Li$_6$@pentacene. We start the discussion with the simplest group (Li@pentacene), in which

only one Li atom is attached to pentacence. Clearly, Li@pentacene contains three isomers with a connecting Li atom to C$_1$, C$_2$, or C$_3$, respectively. We call them system 1, system 2, and system 3, respectively. By calculating the β_{tot} values of the three systems above, system 1 is found to own the largest β_{tot} value. Therefore, system 1 is selected as the parent complex to build Li$_2$@pentacene by adding the second Li atom to system 1. As a result, we get Li$_2$@pentacene which contains system 4, system 5, system 6, and system 7. Similarly, Li$_3$@pentacene is constructed by adding the third Li atom to system 4 which has the largest β_{tot} value in Li$_2$@pentacene, and then we get Li$_3$@pentacene which contains system 8, system 9, and system 10. Finally, all fourteen systems are obtained by the same approach in this work. Moreover, all fourteen systems are shown in Figure 2.

A. Equilibrium Geometries Analysis. The optimized structures of Li$_n$@pentacene (n = 1, 2, 3, 4, 5, and 6) at the B3LYP level are presented in Figure 2 and Table 1. According to the data in Table 1, three interesting relationships between the number and location of Li atoms and the structures of Li$_n$@pentacence (n = 1, 2, 3, 4, 5, and 6) are as follows: (1)
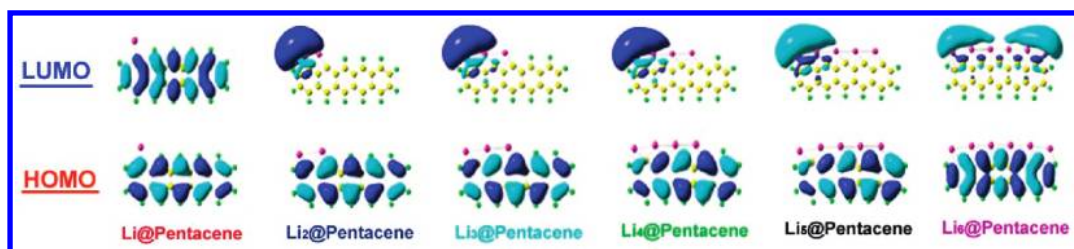
Figure 3. HOMO and LUMO orbitals of Li$_n$@pentacene (n = 1, 2, 3, 4, 5, and 6). Here, we have only listed the first system in each group.

TABLE 3:   The Energy Gap (E_{gap}) of the Highest Occupied Molecular Orbitals (HOMOs) and the Lowest Unoccupied Molecular Orbitals (LUMOs) of Li$_n$@pentacene (n = 1, 2, 3, 4, 5, and 6)

	Li@pentacene	Li$_2$@pentacene	Li$_3$@pentacene	Li$_4$@pentacene	Li$_5$@pentacene	Li$_6$@pentacene
	1	4	8	11	13	14
LUMO (au)	−0.052	−0.055	−0.065	−0.070	−0.073	−0.068
HOMO (au)	−0.187	−0.181	−0.169	−0.163	−0.161	−0.105
E_{gap} (au)	0.135	0.126	0.104	0.093	0.088	0.037

TABLE 4: Calculated Polarizability (α), First Hyperpolarizability (β_{tot}), Transition Energy (ΔE), Oscillator Strength (f_0), and Transition Nature of the Studied Systems[a]

	pentacene	Li@pentacene				Li$_2$@pentacene			Li$_3$@pentacene			Li$_4$@pentacene	Li$_5$@pentacene		Li$_6$@pentacene
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
α (au)	323	340	338	338	358	357	356	357	379	376	377	400	399	421	617
β_{tot} (au)	0	1843	1660	1369	4081	3705	3510	3664	7934	7401	6933	12145	11188	14904	4501764
f_0		2.411	2.473	2.900	0.988	2.473	2.247	2.443	1.121	0.329	0.447	0.215	0.107	0.095	0.119
ΔE		4.131	4.134	4.147	4.180	4.140	4.112	4.144	3.919	3.693	3.799	3.413	2.978	2.955	0.299
transition nature		H-3→L[b] H→L+5			H-4→L+1 H-2→L+3				H-4→L+2 H-3→L+1			H-4→L+1 H-6→L		H-3→L+1 H-5→L	H→L

[a] We have only listed the first system in each group, and the others have been given in Supporting Information. [b] H = HOMO and L = LUMO.
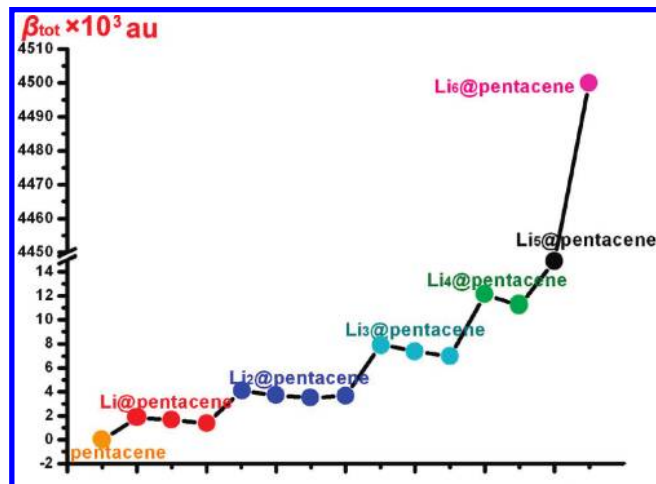

Figure 4. The first hyperpolarizabilities of Li$_n$@pentacene ($n = 0, 1, 2, 3, 4, 5,$ and 6).

When adding Li atoms to pentacene, the upside distance of pentacene (C_1-C_5) increased and the downside distance ($C_{1'}-C_{5'}$) decreased. For example, for Li$_5$@pentacene, the distance of C_1-C_5 is 10.13 and $C_{1'}-C_{5'}$ is 9.78. As a result, the systems tend to form a serious of fan-shaped complexes. (2) Li@pentacence has larger C_1-Li_1 distance than that of Li$_n$@pentacence ($n = 2, 3, 4, 5,$ and 6). For instance, the C_1-Li_1 is 1.96 in Li@pentacence, while the C_1-Li_1 is 1.91 in Li$_5$@pentacence. (3) When two neighboring Li atoms are separated by two or more H atoms, the distance of C–Li approaches the value of C_1-Li_1 in Li@pentacence where only one Li atom is connected to pentacence. For example, in Li$_2$@pentacence $C_2-Li_2(1.90) < C_3-Li_3(1.95) < C_4-Li_4(1.96) = C_5-Li_5(1.96)$.

We now discuss the bond angles of these systems. In this section, we only choose the first bond angle (θ) of each system to investigate the effect of the Li atoms on the bond angle (except the second bond angle in system 2 and the third bond angle in system 3, which are also labeled as θ). The position of the first bond angle is significantly representative, so we limit our discussion to this angle. (1) Compared with Li@pentacence, θ becomes smaller in Li$_n$@pentacence ($n = 2, 3, 4, 5,$ and 6) after adding the second Li atom to C_2. For instance, in Li@pentacence, θ is 119, while in Li$_5$@pentacence, θ is 74. (2) In Li$_2$@pentacence, when the two neighboring Li atoms are separated by two or more H atoms, θ approaches the value in Li@pentacence where only one Li atom is connected to pentacence. For example, θ is 119 for system 1, while θ is 74 for system 4 < 81 for system 5 < 117 for system 6 < 120 for system 7. However, in Li$_n$@pentacence ($n = 3, 4, 5,$ and 6), we have not observed such a phenomenon. Therefore, the small first bond angle of Li$_n$@pentacence ($n = 2, 3, 4, 5,$ and 6) comes from the influence of the Li atom which is connected to C_2.

B. Natural Bond Orbital (NBO) and Electronic Structure Analysis. To interpret the bond character and the interaction between Li atoms and pentacene, natural bond orbital (NBO) analysis[24] has been performed, and the results are listed in Table 2. From Table 2, it is clear that the Li atoms show positive charge, which demonstrates the electron transfer from Li atom to pentacene. The charges of the Li atoms are close to +1, which suggests that the Li atoms substitute the H atoms of pentacene to form lithium salts. Moreover, three interesting laws are found: (1) The Li$_1$ atom which is connected to C_1 possesses more charge compared with the other Li atoms. For instance, in Li$_5$@pentacence, the charge value of Li$_1$ is 0.90, Li$_2$ is 0.75,
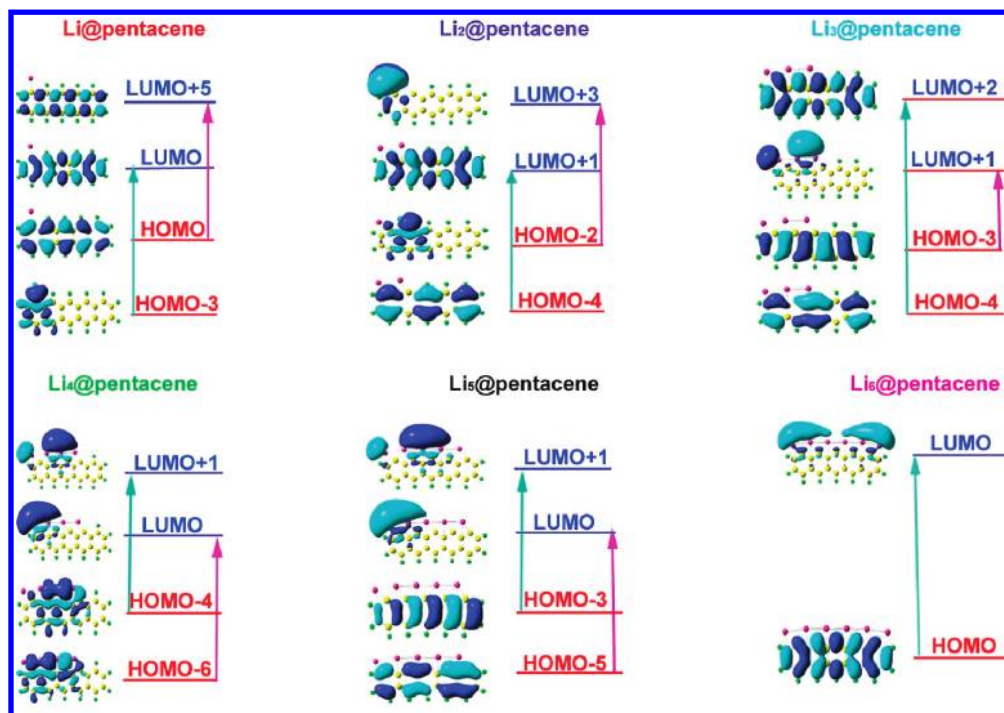
Figure 5. Frontier molecular orbitals of Li_n@pentacene (n = 1, 2, 3, 4, 5, and 6). (The azure arrow represents the first transition nature, and the pink arrow represents the second transition nature.) We have only listed the first system in each group, and the others are given in Supporting Information.

Li_3 is 0.74, Li_4 is 0.72, and Li_5 is 0.77. (2) When two neighboring Li atoms are separated by two or more H atoms, the charges of the Li atoms resemble the value of the Li atom in Li@pentacene. For example, in Li_2@pentacene, the charge value of Li_2(0.79) < Li_3(0.88) = Li_4(0.88) < Li_5(0.89). (3) Vividly, the charges of Li atoms in Li_6@pentacene appear to be a symmetric distribution (Li_1 = Li_6 = 0.73, Li_2 = Li_5 = 0.62, Li_3 = Li_4 = 0.67). The differences mentioned above may bring some special properties to Li_6@pentacene compared with the other groups.

In order to get a complete understanding of the structure of Li_n@pentacene (n = 1, 2, 3, 4, 5, and 6), The electronic structures of the first system in each group have been probed. The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are listed in Figure 3. From Figure 3, three interesting results are observed: (1) For Li@pentacene, the HOMO is localized at pentacene, while the LUMO is also localized at pentacene. Thus, the charge transfer between pentacene and the Li atom is not clear. (2) For Li_n@pentacene (n = 2, 3, 4 and 5), similar to that for Li@pentacene, the HOMOs are localized at pentacene, while the LUMOs are mainly located at the Li_1 end. Obvious charge transfer is observed. Further, as the number of Li atoms increases from 2 to 5, the electron density becomes increasingly large. (3) For Li_6@pentacene, the HOMO is also localized at pentacene. Significantly, the LUMO distributes symmetrically at the Li_1 and Li_6 ends, so Li_6@pentacene has the largest charge transfer. Further, we have listed the energy gap (E_{gap}) of HOMO and LUMO in Table 3. From Table 3, the E_{gap} shows a decreasing trend from Li@pentacene to Li_6@pentacene, which may lead to gradually increased first hyperpolarizabilities of the studied systems.

C. First Hyperpolarizabilities. The electric properties of Li_n@pentacene (n = 1, 2, 3, 4, 5, and 6) at the Bhandhlyp level are given in Table 4 and Figure 4. It can be found that there is a trend of increasing polarizabilities (α) from Li@pentacene

to Li_6@pentacene, 338–340 for Li@pentacene < 356–358 for Li_2@pentacene < 376–379 for Li_3@pentacene < 399–400 for Li_4@pentacene < 421 for Li_5@pentacene < 617 au for Li_6@pentacene. Particularly, the change in the first hyperpolarizabilities is interesting and has become the focus of our attention. Due to the addition of the Li atoms, there is a stepwise escalation of β_{tot} for (multi)lithium salts Li_n@pentacene (n = 1, 2, 3, 4, 5, and 6): 1369–1843 for Li@pentacene < 3510–4081 for Li_2@pentacene < 6933–7934 for Li_3@pentacene < 11188–12145 for Li_4@pentacene < 14904 for Li_5@pentacene < 4501764 au for Li_6@pentacene. On the other hand, when the number of lithium atoms is equal, the closer the lithium atoms are clustered, the larger the β_{tot} value (for Li_3@pentacene, 6933 of system 10 < 7401 of system 9 < 7934 of system 8). Especially, owing to the addition of the sixth Li atom to form Li_6@pentacene, the β_{tot} value dramatically increases to a value of 4 501 764 with a remarkable increase of 302-fold in contrast to Li_5@pentacene. Further, compared with the known NLO materials that have been reported, such as Li@$B_{10}H_{14}$[25] (the β_{tot} value is 23 075 au), the large donor–acceptor polyene systems[26] (the range of the β_0 values is 8818–152 502 au), and the electron-rich cis-{$Ru^{II}(NH_3)_4$}$^{2+}$ center complexes[27] (the range of the β_0 values is 4283–34 957 au), the β_{tot} (4 501 764) of Li_6@pentacene is considerable.

As we know, pentacene is a centrosymmetric molecule, so the β_{tot} value of pentacene is naught. Why are the β_{tot} values of Li_n@pentacene (n = 1, 2, 3, 4, 5, and 6) much larger than that of pentacene? To gain an understanding of the origin of the β_{tot} values, we consider the widely used two-level model:[28]

$$\beta_{tot} \propto \frac{f_0 \Delta\mu}{\Delta E^3}$$

where ΔE, f_0, and $\Delta\mu$ are the transition energy, oscillator strength, and difference in the dipole moments between the

ground state and the crucial excited state. In the two-level expression, the third power of the transition energy is inversely proportional to the β_{tot} value so the transition energy is the decisive factor in the first hyperpolarizability. The crucial transition energies of the fourteen systems are obtained by the TDDFT method. The ΔE and f_0 values are illustrated in Table 4. From Table 4, the ΔE values show a descending trend from Li@pentacene to Li$_5$@pentacene (4.131−4.147 for Li@pentacene > 4.112−4.180 for Li$_2$@pentacene > 3.693−3.919 for Li$_3$@pentacene > 2.978−3.413 for Li$_4$@pentacene > 2.955 for Li$_5$@pentacene), which is consistent with the order of β_{tot}. In addition to this, Li$_n$@pentacene ($n = 1, 2, 3, 4,$ and 5) have smaller ΔE values, while Li$_6$@pentacene has the smallest ΔE value, which is 0.299 (almost one tenth the value of Li$_5$@pentacene). Furthermore, an increase of ΔE values is observed in every group, which explains why β_{tot} values gradually decrease as the location of the last Li atom changes.

To gain a comprehensive understanding of the relative magnitude of the ΔE values, the electron clouds in the crucial transitions of those changes have been considered (see Figure 5). From Figure 5, it is obvious that there is a significant charge transfer between Li and pentacene, causing a large change in the dipole moment and leading to a remarkable decrease in the ΔE value. Moreover, for Li$_6$@pentacene, there is not only large change in the dipole moment, but because of the addition of a sixth Li atom, the entire pentacene and the six Li atoms have the fullest interaction and form a large conjugated system in which the charge distribution is more uniform. Naturally, the transition energy of the system is strikingly lowered, which results in an extremely large β_{tot} value. This is also in accordance with the analysis of the geometries of stationary points, natural bond orbital (NBO), and electronic structure above.

Conclusion

We have investigated the influence of the number and location of Li atoms on the first hyperpolarizability of graphene. The interaction between the Li atoms and the pentacene part plays an important role in the large first hyperpolarizabilities of the studied systems. The results show that β_{tot} obviously increases stepwise as the number of the Li atoms increases, while among the systems in the same group, the closer the lithium atoms are clustered, the larger the β_{tot} value. In particular, for Li$_6$@pentacene, the β_{tot} value dramatically increases to a value of 4 501 764 esu with a remarkable increase of 302-fold in contrast to Li$_5$@pentacene. The NBO and transition energy analysis shows that because of the doping of the Li atoms, there is a significant charge transfer between Li and pentacene, causing a large change in the dipole moments and leading to a remarkable decrease in the ΔE value. Especially, for Li$_6$@pentacene, there is not only a large change in the dipole moments but the Li atoms and the pentacene form a very large conjugated system that strikingly lowers the transition energy of the system and results in an extremely large β_{tot} value. So, by adding Li atoms to pentacene, we obtained an excellent NLO response. Similarly, by adding Li atoms to graphene, we should expect to get high performance NLO materials.

This study proposes a new design wherein the first hyperpolarizability can be greatly increased by doping alkali atoms into graphene. It is our expectation that new types of NLO materials based on graphene will be developed in the near future.

Supporting Information Available: Basis set effects on the molecular geometries, calculated polarizabilities and hyperpolarizabilities of Li@benzene with different methods. Computed transition energies, oscillator strengths, and transition nature of the studied systems. This information is available free of charge via the Internet at http://pubs.acs.org.

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