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A Dependence on the Petal Number of the Static and Dynamic First Hyperpolarizability for Electride Molecules: Many-Petal-Shaped Li-Doped Cyclic Polyamines

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Doping Li atom into higher flexible cyclic polyamines with many amine unit petals (ethyleneimine) forms the *n*-petal-shaped Li-doped cyclic polyamines ($n = 3-5$). Three structures, referred to as three-petal-shaped Li-[9]aneN_3, four-petal-shaped Li-[12]aneN_4, and five-petal-shaped Li-[15]aneN_5, with all-real frequencies are obtained at the MP2/6-31+G(d) level. Because the chemical doping with Li and the deformation of the complexant produce more diffuse excess electron, the three molecules with the excess electrons exhibit considerably large static first hyperpolarizabilities (β_0) at the MP2 level. Additionally, the β_0 value increases with increasing the petal number (n) as follows: 52282 ($n = 3$) < 65505 ($n = 4$) < 127617 au ($n = 5$). This shows a new complexant effect on β_0, that is, a dependence on the petal number (n) of β_0 owing to the flexibility of the complexants increasing with the petal number.
The MP2 frequency-dependent β values are estimated by using the multiplicative approximation. The frequency dispersion is found to be strong. For the MP2 frequency-dependent β values, the more pronounced dependence on the petal number (n) of β (-2ω; ω, ω) and β ($-\omega$; ω, 0) are shown.

Introduction

So far, a great deal of work has been carried out to study the nonlinear optical (NLO) properties for many different types of NLO materials.[1]

In our previous work, we found that model systems with excess electrons have considerably large first hyperpolarizabilities (β_0) up to 10^7 au.[2] It has been demonstrated that the loosely bound excess electron plays a crucial role in the large first hyperpolarizability.

Recently, novel compounds with loosely bound excess electrons, electrides, and alkalides, which were synthesized by Wagner et al., have attracted much attention because of their broad or potential applications in chemical synthesis, catalysis, nanodevices, and functional materials.[3] Electrides are ionic salts in which anionic sites are occupied by excess electrons, while alkalides are other ionic salts containing alkali-metal anions. Very recently, our group focused on the investigation of the first hyperpolarizability (β_0) of electride and alkalide molecules because they exhibited large first hyperpolarizabilities.[4,5] Doping alkali metals into proper organic complexants forms electride and alkalide molecules with excess electrons, which is an effective way to enhance β_0. For example, the electride molecule Li@calix[4]pyrrole[4a] and the alkalide molecule Li^+(calix[4]pyrrole)Na^- [5a] have large β_0 values according to our calculation. Using a more flexible complexant to form electride and alkalide molecules is another way in enhancing β_0 because such a complexant easily yields excess electron.[5b] In our previous work on alkalide molecules, comparing with Li^+(calix[4]pyrrole)Na^-,[5a] the β_0 value of 77921 au for model system $Li(NH_3)_4Na$[5b] with a flexible complexant is about 5 times larger than that of 14772 au for Li^+(calix[4]pyrrole)Na^- with an inflexible complexant. The theoretical study reveals that the β_0 value strongly relates to the flexibility of complexant. However, for electride molecules, the flexibility effect of complexant on β_0 and the relationship between the cycle size and the flexibility of complexant have not been reported yet.

The cyclic polyamines are well-known and are widely employed as excellent complexants for the metal complexes.[6] To investigate the size effect of cyclic complexants on the first hyperpolarizability for the electride molecule, three cyclic polyamines containing 3−5 amine units (ethyleneimine), that is, 1,4,7-triazacyclononane ([9]aneN_3), 1,4,7,10-tetraazacyclododecane ([12]aneN_4), and 1,4,7,10,13-pentaazacyclopentadecane ([15]aneN_5), are chosen as complexants to form electride molecules as the cyclic polyamines are more flexible than calix[4]pyrrole.

This paper aims at investigating the effect of alkali-metal doping on the nonlinear optical (NLO) property by characterizing cyclic polyamines with and without an explicit alkali atom (Li) as dopant, by observing the flexibility effect of complexant on the enhancement of β_0 for the Li-doped cyclic polyamines with electride characteristic, and by revealing the size effect of cyclic complexants on β_0, that is, the dependence on the petal number (n) of the hyperpolarizability. These results may be beneficial to design high-performance NLO materials.

Computation Details

Three structures of the Li-doped cyclic polyamines with all-real frequencies were obtained using the second-order Møller−Plesset perturbation theory (MP2) with the 6-31+G (d) basis set (see Table S1 in the Supporting Information). The static first hyperpolarizabilities were evaluated by a finite-field (FF) approach at the MP2 level. In our previous papers,[4c,5] the MP2 method has been chosen to calculate the first hyperpolarizabilities for the open-shell system with excess electron. This is because, with reasonable computation costs, the MP2 results

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are also very close to those obtained from the more sophisticated correlation methods (e.g., the QCISD[7]). In this work, the 6-311++G basis set is employed for the C, N, and H atoms, and the 6-311++G (3df) basis set is employed for the Li atom. Although the size of basis set 6-311++G is less than half of that of 6-311++G (2d, 2p), the β_0 value of 52 282 au obtained from 6-311++G basis set is only 3.8% different from that of 50 295 au obtained from 6-311++G (2d, 2p) for Li-[9]aneN$_3$ (see Table S2 in the Supporting Information). In calculations, the $<S^2>$ values in MP2 wave functions are 0.75 for the three structures.

To choose a suitable applied electric field (AEF), the first hyperpolarizabilities of the three-petal-shaped Li-[9]aneN$_3$ were calculated at the MP2 level in a series of fields (see Table S3 in the Supporting Information). The data of Table S3 shows that the change of the first hyperpolarizability is not large (near 10%) when the AEF varies from 0.0001 to 0.0010 au. A plateau for the first hyperpolarizabilities in an AEF range from 0.0001 to 0.0010 au is shown (see Figure S2 in the Supporting Information). Hereby, the AEF of 0.0010 au is used in the calculation of the first hyperpolarizabilities.

The dipole moment (μ_0) and polarizability (α_0) are defined as follows:

$$\mu_o = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \tag{1}$$

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2}$$

The static first hyperpolarizability is noted as

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \tag{3}$$

where

$$\beta_i = \frac{3}{5}(\beta_{iii} + \beta_{ijj} + \beta_{ikk}) \quad i, j, k = x, y, z$$

The frequency-dependent first hyperpolarizabilities of the three Li-doped compounds were obtained by the coupled-perturbed Hartree−Fock (CPHF) method.[8] The basis set employed are the 6-311++G for the C, N, and H atoms and the 6-311++G (3df) for the Li atom.

The frequency-dependent β is noted as

$$\bar{\beta}(\omega) = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \tag{4}$$

where

$$\beta_i = \frac{1}{5}[2\beta_{jji}(-2\omega;\omega,\omega) + \beta_{ijj}(-2\omega;\omega,\omega)]$$

($i, j = x, y$, and z) for the second-harmonic generation (SHG) and

$$\beta_i = \frac{1}{5}[\beta_{jji}(-\omega;\omega,0) + 2\beta_{jij}(-\omega;\omega,0)]$$

($i, j = x, y$, and z) for the electro-optical Pokcets effect (EOPE).

The MP2 frequency-dependent β was estimated by using the multiplicative approximation: [9]

$$\beta(\omega)^{\mathrm{MP2}} \cong \beta(\omega)^{\mathrm{HF}}\beta(0)^{\mathrm{MP2}}/\beta(0)^{\mathrm{HF}} \tag{5}$$

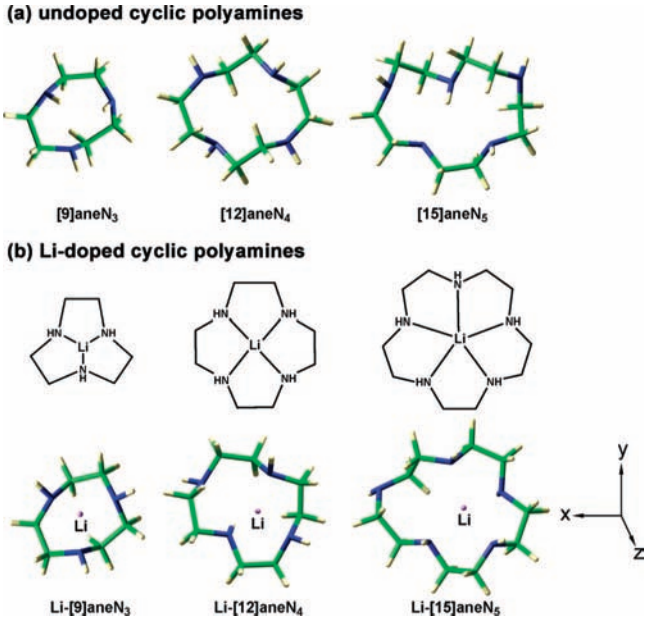

Figure 1. The geometric structures of the undoped and Li-doped cyclic polyamines.

TABLE 1: Selected Geometrical Parameter (Å), Vertical Ionization Energy (VIE, eV), and LUMO−HOMO Energy Gap ($\Delta\epsilon_{\mathrm{gap}}$, eV)

	Li-[9]aneN$_3$	Li-[12]aneN$_4$	Li-[15]aneN$_5$
N−N[a]	2.734 (2.807)	2.936 (3.109)	2.835 (3.167)
	2.819 (3.048)	**2.692 (3.098)**	2.830 (3.059)
	2.834 (2.889)	**2.737 (3.109)**	2.863 (2.998)
		3.183 (3.098)	**3.412 (3.128)**
			3.642 (3.258)
$\sum\lvert\Delta(\mathrm{N-N})\rvert$	0.357	1.036	1.363
Li−N	2.071	2.048	2.145
	2.093	2.118	2.078
	2.156	2.095	2.156
		3.498	2.078
			4.036
VIE	2.882	2.746	2.322
$\Delta\epsilon_{\mathrm{gap}}$	3.001	2.892	2.160

[a] Numbers in parentheses are the N−N distances in the undoped cyclic polyamines.

All calculations in this work were carried out using the GAUSSIAN 03 package.[10] The dimensional plots of molecular orbital were generated with the Gauss View program (Gaussian, Inc., Pittsburgh, PA).[11]

Results and Discussions

A. Equilibrium Geometries and Electride Characteristic. The geometrical structures of the Li-doped cyclic polyamines are shown in Figure 1b, and the important geometrical parameters are collected in Table 1. When an amine unit (ethyleneimine) is considered as a petal, these molecules exhibit many-petal cyclic structures.

The N−N distances are elongated or shortened in Li-doped cyclic polyamines in comparison with those in the undoped cyclic polyamines (see Figure 1a). For Li-[9]aneN$_3$, the N−N distances are appreciably shortened as compared to that of [9]aneN$_3$. For Li-[12]aneN$_4$ and Li-[15]aneN$_5$, some distances are strongly shortened and others are elongated (see Table 1). This shows that doping Li atom strongly affects the structures of cyclic polyamines. The Δ(N−N) denotes the difference of N−N distance between the Li-doped and undoped cyclic

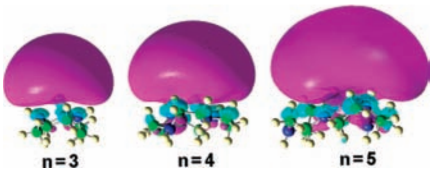

Figure 2. The 0.01 isosurface of HOMOs in the Li-doped cyclic polyamines. The excess electron cloud becomes more diffuse with increasing the petal number.

polyamine. The $\sum|\Delta(N-N)|$ may represent molecular flexibility and increases with increasing the petal number (n). This indicates that the flexibility of complexant increases with the increase of cycle size (or the petal number).

The Li−N distances in Li-doped compounds are Li−N coordination distances, which relate to the structural characteristic and properties of the Li-doped many-petal cyclic polyamines. In the Li-[9]aneN$_3$, all the three short Li−N distances (2.071∼2.156 Å) are almost identical. In the Li-[12]aneN$_4$, among four Li−N distances, three Li−N distances (2.048∼2.118 Å) are short, while one distance is very long (3.498 Å). In the Li-[15]aneN$_5$, four Li−N distances (2.078∼2.156 Å) are short, while one distance is very long (4.036 Å). Obviously, the complexants, [12]aneN$_4$ and, especially, [15]aneN$_5$, are strongly deformed by the chemical doping with Li. This shows that both the interaction between Li and cyclic polyamine and the flexibility for the cyclic polyamines increase with the increase of cycle size (or the petal number), which determines the changes of the physical properties of Li-doped cyclic polyamine compounds.

Figure 2 displays the highest occupied molecular orbitals (HOMOs). The excess electron clouds from Li atoms are pushed away by lone pairs of N atoms in the Li-doped cyclic polyamines. The greater the petal number is, the more diffuse the excess electron cloud becomes. This is because the repulsion effect of complexant to 2s electron of Li atom becomes larger when the petal number increases. Because of the formation of the excess electrons, the Li-doped cyclic polyamines have electride characteristic and small vertical ionization energies (VIE).

The VIE values of the Li-doped cyclic polyamines at the MP2 level with 6-311++G basis set for the C, N, and H atoms and the 6-311++G (3df) basis set for the Li atom are given in Table 1. These VIE values of 2.322∼2.882 eV are smaller than that of 4.16 eV for Li@calix[4]pyrrole with electride characteristic[4a] as the cyclic polyamine complexants are more flexible than the calix[4]pyrrole complexant. The VIE value decreases with increasing the petal number (n) in the order of 2.882 ($n = 3$) < 2.746 ($n = 4$) < 2.322 eV ($n = 5$). The decrease of the VIE values indicates that the excess electrons in the Li-doped cyclic polyamines become more diffuse with increasing the petal number. In addition, the order of LUMO−HOMO energy gaps ($\Delta\epsilon_{gap}$) is consistent with the orders of VIE and the excess electron dispersions.

B. Static First Hyperpolarizabilities. The static electric properties of three Li-doped cyclic polyamines are given in Table 2. Doping Li atom into cyclic polyamines greatly enhances the β_0 values by more than 470 times from 0∼272 au of the undoped cyclic polyamines to 5.2×10^4∼1.3×10^5 au of the Li-doped cyclic polyamines. This implies that the cyclic polyamines are good complexants. When doping alkali-metal Li into these complexants with higher flexibility to form electride molecules with more diffuse excess electrons, the β_0 value is greatly enhanced.

TABLE 2: The Dipole Moment (μ_0, au), Polarizability (α_0, au), First Hyperpolarizability (β_0, au), Transition Moment (μ_{n0}, au), Transition Energy (E_{n0}, eV), Difference in the Dipole Moment between the Ground State and the Crucial Excited State ($\Delta\mu_{n0}$, au), Transition Nature, and Electronic Spatial Extent ($<R^2>$, au)

	Li-[9]aneN$_3$	Li-[12]aneN$_4$	Li-[15]aneN$_5$
μ_0	3.823	3.932	4.756
α_0	603.55	678.54	1066.23
β_x	10 341	28 779	54 669
β_y	−6570	−10 340	−4194
β_z	50 826	51 298	139 261
β_{zzz}[a]	68 837 (77 688)	74 078 (94 269)	149 665 (196 203)
β_0[b]	52 282 (150)	65 505 (0)	127 617 (272)
μ_{n0}	3.085	2.469	2.581
E_{n0}	0.899	0.718	0.560
$\Delta\mu_{n0}$	1.484	1.796	2.079
transition	HOMO→LUMO	HOMO→LUMO	HOMO→LUMO
$<R^2>$	1332	2484	4045

[a] Numbers in parentheses are the β_{zzz} values obtained from eq 6. [b] Numbers in parentheses are the β_0 values of the undoped cyclic polyamines.

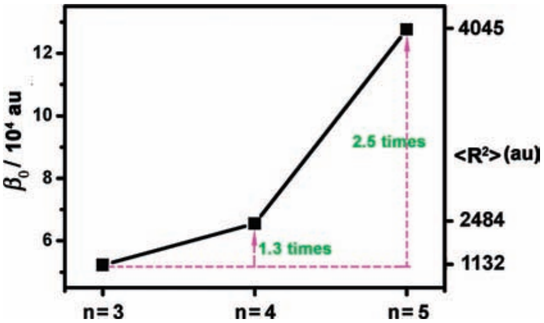

Figure 3. The monotonous dependence on the petal number (n) of the static first hyperpolarizability (β_0), and the β_0 values versus $<R^2>$ for the Li-doped cyclic polyamines.

Table 2 shows that these Li-doped cyclic polyamine compounds present considerably large β_0 values up to 1.3×10^5 au of Li-[15]aneN$_5$, which is a new record for electride molecules. The β_0 values (52 282∼127 617 au) of the Li-doped cyclic polyamines are larger than those of the known electride molecules with large β_0 values.[4] Especially, with the same coordination number (four N atoms), the β_0 value of 6.5×10^4 au for Li-[12]aneN$_4$ is about 9 times larger than that of 7.3×10^3 au for the corresponding Li@calix[4]pyrrole. The complexant [12]aneN$_4$ is strongly deformed by the chemical doping with Li and exhibits more flexible feature than the complexant calix[4]pyrrole. This indicates that the β_0 value is strongly related to the flexibility of the complexant. Furthermore, the β_0 value of 1.3×10^5 au for Li-[15]aneN$_5$ is about 6 times as large as that of 2.1×10^4 au for the organometallic complex *trans*-[Ru(4-C=CHC$_6$H$_4$NO$_2$)Cl(dppe)$_2$]PF$_6$[12] and is close to that of 1.7×10^5 au for a long dipolar donor−acceptor conjugated organic molecule.[13]

Interestingly, a petal number dependence of the β_0 value is found in the Li-doped many-petal cyclic polyamines. The β_0 value increases with increasing the petal number (n) in the order of 52 282 ($n = 3$) < 65 505 ($n = 4$) < 12 7617 au ($n = 5$) (see Table 2). From Figure 3, there is a substantial increase in β_0 because of replacing [9]aneN$_3$ by [12]aneN$_4$ and, particularly, by [15]aneN$_5$ since the interaction between Li and cyclic polyamine and the deformation of the cyclic polyamines increase with the increase of the petal number (or cycle size).

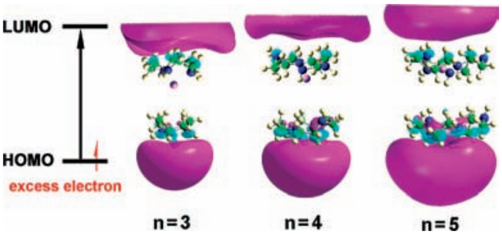

Figure 4. The crucial transitions of the Li-doped cyclic polyamines (0.010 isosurface).

TABLE 3: The Estimated Frequency-Dependent β (-2ω; ω, ω) and β ($-\omega$; ω, 0) Values (au)

		MP2 (CPHF)	
	ω (au)	β (-2ω; ω, ω)	β ($-\omega$; ω, 0)
Li-[9]aneN_3	0.0	52 282 (14 354)	
	0.005	69 987 (19 215)	55 978 (15 369)
	0.01	134 329 (36 880)	69 032 (18 953)
Li-[12]aneN_4	0.0	65 505 (22 587)	
	0.005	75 404 (26 001)	68 497 (23 619)
	0.01	140 043 (48 290)	79 103 (27 276)
Li-[15]aneN_5	0.0	127 617 (39 880)	
	0.005	243 160 (75 987)	145 238 (45 386)
	0.01	477 202 (148 125)	231 807 (72 439)

The electronic spatial extent $<R^2>$ is a physical property which characterizes the electron density volume around the molecule.[14] In the Li-doped cyclic polyamines, the electronic spatial extent $<R^2>$ increases with increasing the petal number, and its order is 1132 ($n = 3$) < 2484 ($n = 4$) < 4045 au ($n = 5$), which is identical with the order of β_0. This indicates that the β_0 depends on $<R^2>$. The dependence of the electronic spatial extent $<R^2>$ for β_0 is depicted in Figure 3.

From Table 2, the tensor component β_{zzz} values are close to β_z and β_0 values. To further understand the petal number dependence of β_0, the following two-level expression is employed.[15]

$$\beta_{zzz} = \frac{6\mu_{n0}^2\Delta\mu_{n0}}{E_{n0}^2} \tag{6}$$

E_{n0}, μ_{n0}, and $\Delta\mu_{n0}$ are the transition energy, transition moment, and the difference of dipole moment between the ground state and the crucial excited state, respectively. From Table 2, the β_{zzz} values obtained from eq 6 are in good agreement with those from the finite-field (FF) approach. Thus, eq 6 can be used to interpret the first hyperpolarizability.

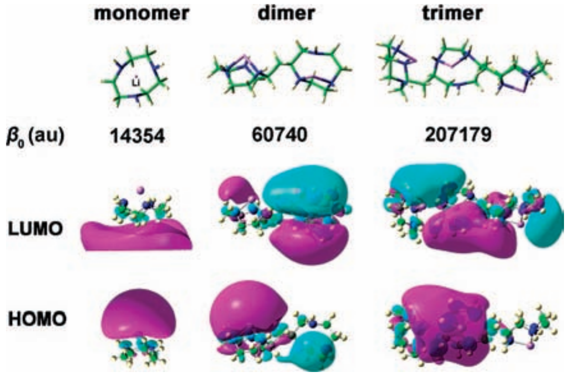

Figure 6. The geometrical structures and frontier molecular orbitals (0.010 isosurface) of the monomer, dimer, and trimer of Li-[9]aneN_3.

The E_{n0}, μ_{n0}, and $\Delta\mu_{n0}$ are estimated by the configuration interaction with single excitations (CIS) method and are listed in Table 2. The E_{n0} values are pretty small because of the diffuse excess electron transitions, and their order is 0.899 ($n = 3$) > 0.718 ($n = 4$) > 0.560 eV ($n = 5$). The order of E_{n0} is consistent with that of β_{zzz}, which shows that transition energy is one controlling factor for β_0. The $\Delta\mu_{n0}$ value is another controlling factor for β_0, and its order is 1.484 ($n = 3$) < 1.796 ($n = 4$) < 2.079 au ($n = 5$), which is also consistent with the order of β_{zzz}. Obviously, as E_{n0} decreases and $\Delta\mu_{n0}$ increases with increasing the petal number, it is expected from eq 6 that the β_{zzz} and the corresponding β_0 increase with increasing the petal number (see Table 2). In fact, among the three compounds, the five-petal-shaped Li-[15]aneN_5 possesses the largest β_0 value of 127 617 au because it has the smallest transition energy and the largest difference of dipole moment between the ground state and the crucial excited state.

The CIS approximate results show that the crucial transitions of the Li-doped cyclic polyamines consist of many components in which the main component is the HOMO→LUMO transition. The HOMO→LUMO transitions are plotted in Figure 4. As shown in Figure 4, one can see that the HOMO electron cloud is mainly located on the 4s orbital of the Li atom below the cyclic complexant, while the LUMO electron cloud is mainly located on the 4s orbitals of the C and N atoms above the complexant. In the crucial transition, a long-range charge transfer occurs from the Li atom to the opposite side of the Li atom through the complexant, which leads to a large $\Delta\mu_{n0}$ value. Furthermore, the distance between the centers of the HOMO and LUMO electron clouds increases with increasing the petal number (see Figure 4). Consequently, the $\Delta\mu_{n0}$ value increases with increasing the petal number.

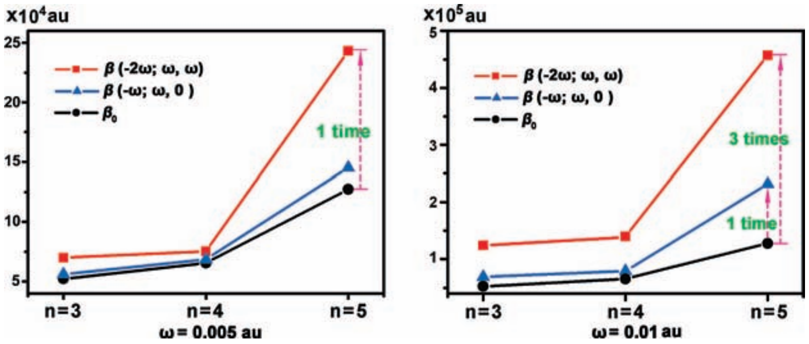

Figure 5. The dispersion effect at $\omega = 0.005$ and 0.01 au and monotonous dependence on the petal number of β_0, β (-2ω; ω, ω), and β ($-\omega$; ω, 0).

C. Frequency-Dependent First Hyperpolarizabilities. To understand the dispersion effect on the β value, the frequency-dependent β of the Li-doped cyclic polyamines were calculated using the CPHF method. Moreover, the MP2 frequency-dependent β values have also been estimated by using the multiplicative approximation (eq 5). Table 3 lists the CPHF and estimated MP2 frequency-dependent values: second-harmonic generation (SHG) β $(-2\omega;\ \omega,\ \omega)$ and electro-optical Pokcets effect (EOPE) β $(-\omega;\ \omega,\ 0)$.

As shown in Table 3 and Figure 5, for the three electride molecules, the computed frequency-dependent β $(-2\omega;\ \omega,\ \omega)$ and β $(-\omega;\ \omega,\ 0)$ at $\omega = 0.005$ and 0.01 au are larger than the corresponding static β_0 at $\omega = 0.0$ au. For example, for Li-[15]aneN_5, the β $(-2\omega;\ \omega,\ \omega)$ at $\omega = 0.01$ is about 3 times larger than its static β_0. This indicates that the dispersion effect on the β value is strong for the Li-doped many-petal cyclic polyamines. For the same electride molecule, each frequency-dependent value increases with the increment of the corresponding external frequency $\omega = 0.0-0.01$ au. For example, for Li-[15]aneN_5, the β $(-2\omega;\ \omega,\ \omega)$ at $\omega = 0.010$ is about 2 times larger than that at $\omega = 0.005$ au. It is also shown that the β $(-2\omega;\ \omega,\ \omega)$ is larger than the β $(-\omega;\ \omega,\ 0)$ for each electride molecule. Taking Li-[15]aneN_5 as an example, the β $(-2\omega;\ \omega,\ \omega)$ is about 1 time larger than the β $(-\omega;\ \omega,\ 0)$ at $\omega = 0.010$.

Significantly, the MP2 frequency-dependent β $(-2\omega;\ \omega,\ \omega)$ and β $(-\omega;\ \omega,\ 0)$ at $\omega = 0.005$ and 0.01 au also show the dependence on the petal number (see red and blue lines in Figure 5). Specially, the β $(-2\omega;\ \omega,\ \omega)$ value at $\omega = 0.01$ strongly increases with increasing the petal number in the order of 134 329 ($n = 3$) < 140 043 ($n = 4$) < 477 202 au ($n = 5$). This shows that the dispersion effect enhances the dependence on the petal number of the β value.

A possibility from molecule to material is simply considered. Doping Li atoms into the polymer of [9]aneN_3 forms Li-doped polymer with electride characteristic. The geometrical structures and frontier molecular orbitals for the Li-doped polymers (the dimer and trimer of Li-[9]aneN_3) are obtained at the density functional theory (DFT) B3LYP/6-31G level and are shown in Figure 6. Their static first hyperpolarizabilities (β_0) are evaluated by the finite-field (FF) approach at the Hartree−Fock level with 6-311++G basis set for the C, N, and H atoms and with the 6-311++G (3df) basis set for the Li atom and are illustrated in Figure 6. The order of the β_0 values is 14354 (monomer) < 60740 (dimer) < 207179 au (trimer), and their ratio is 1:4:14. This shows that the β_0 value increases with increasing polymerization degree. The Li-doped cyclic polyamine polymers may have large β_0 values and can be considered as candidates for potential high-performance NLO materials.

Conclusion

In this work, the three electride molecules with more diffuse excess electron are produced by the chemical doping with Li and the deformation of the complexant, and they exhibit considerably large first hyperpolarizabilities. Specially, a new complexant effect on β, that is, the dependence on the petal number (n) of β, is found for the first time because the flexibility of the cyclic polyamine complexants increases with increasing the petal number (n). Thus, using a more flexible complexant with a larger petal number to form electride molecule is an important approach to enhance β. This work is beneficial for designing potential NLO materials.

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Supporting Information Available: The basis set effect on the molecular geometry and the static first hyperpolarizability. The choice of the applied electric field. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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