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Lithium Salt Electride with an Excess Electron Pair—A Class of Nonlinear Optical Molecules for Extraordinary First Hyperpolarizability

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A new lithium salt electride with an excess electron pair is designed, for the first time, by means of doping two sodium atoms into the lithium salt of pyridazine. For this series of electride molecules, the structures with all real frequencies and the static first hyperpolarizability (β_0) are obtained at the second-order Møller−Plesset theory (MP2). Pyridazine $H_4C_4N_2$ becomes the lithium salt of pyridazine $Li-H_3C_4N_2$ as one H atom is substituted by Li. The lithium salt effect on hyperpolarizability is observed as the β_0 value is increased by about 170 times from 5 to 859 au. For the electride effect, an electride $H_4C_4N_2\cdots Na_2$ formed by doping two Na atoms into pyridazine, the β_0 value is increased by about 3000 times from 5 to 1.5×10^4 au. Furthermore, combining these two effects, that is, lithium salt effect and electride effect, more significant increase in β_0 is expected. A new lithium salt electride $Li-H_3C_4N_2\cdots Na_2$ is thus designed by doping two Na atoms into $Li-H_3C_4N_2$. It is found that the new lithium salt electride, $Li-H_3C_4N_2\cdots Na_2$, has a very large β_0 value (1.412×10^6 au). The β_0 value is 2.8×10^5 times larger than that of $H_4C_4N_2$, 1644 times larger than that of $Li-H_3C_4N_2$, and still 93 times larger than that of the electride $H_4C_4N_2\cdots Na_2$. This extraordinary β_0 value is a new record and comes from its small transition energy and large difference in the dipole moments between the ground state and the excited state. The frequency-dependent β is also obtained, and it shows almost the same trends as $H_4C_4N_2 \ll Li-H_3C_4N_2 \ll H_4C_4N_2\cdots Na_2 \ll Li-H_3C_4N_2\cdots Na_2$. This work proposes a new idea to design potential candidate molecules with high-performance NLO properties.

Introduction

During the past twenty years, a lot of valuable work was carried out on designing various different types of nonlinear optical (NLO) materials[1] because of their potential use in optic device applications.

It has been reported that the molecular clusters with excess electrons have exhibited considerably large first hyperpolarizability.[2] There are two kinds of molecule systems with excess electrons. One is electride,[3] in which the valence electron of an alkali atom is polarized by a ligand to form an excess electron. Recently, our group has theoretically designed several novel electrides with the large first hyperpolarizability, for example Li@calix[4]pyrrole, and $Li_n-H-(CF_2-CH_2)_3-H$ ($n = 1, 2$).[4] The other one is alkalide, a molecule doped with two alkali atoms (one near the ligand and the other far away from the ligand). Only the alkali atom near the ligand is polarized to form an excess electron; then, the excess electron cloud wraps around the other alkali atom to form an alkali anion. These alkalides, such as Li^+(calyx[4]pyrrole)M^- (M = alkali atoms) and (M^+@n^{6}adz)M′− (M, M′ = Li, Na, K; $n = 2, 3$), also exhibit considerable large first hyperpolarizabilities.[5]

Currently, the lithium salt effect (lithiation effect) on the second hyperpolarizability has been investigated. The lithiation of the benzene molecule[6] may lead to an enormous increase of the second hyperpolarizability.[7] However, the lithium salt effect on the first hyperpolarizability has not been investigated yet.

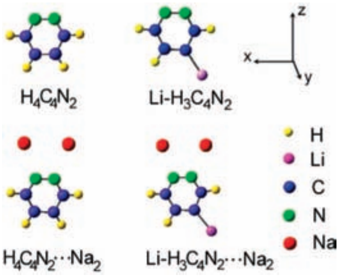

Figure 1. Structures of the lithium salt electride ($Li-H_3C_4N_2\cdots Na_2$) and its correlative molecules: the pyridazine $H_4C_4N_2$, the lithium salt $Li-H_3C_4N_2$, and the electride $H_4C_4N_2.\cdots Na_2$ by MP2/6-311+G(d, p) method.

In order to design NLO molecules with large first hyperpolarizability, not only the lithium salt $Li-H_3C_4N_2$ but also more important lithium salt electride $Li-H_3C_4N_2\cdots Na_2$ with an excess electron pair by doping two Na atoms into the lithium salt of pyridazine are considered. In $Li-H_3C_4N_2\cdots Na_2$, the line of two Na atoms runs almost parallel to the edge between two N atoms (see Figure 1). These two N atoms with lone pair are able to polarize the two Na atoms to form an excess electron pair. The new electride with an excess electron pair is different from the previously studied NLO electrides with a single excess electron; it is also different from the reported alkalides with only one excess electron. It is a new species with the form of a molecule doped with two alkali metal atoms.

In this paper, a new designing idea is given for the first time to combine lithium salt and electride effects to enhance the first

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hyperpolarizability. The effect of the combination is very dramatic. This work opens a new way to design high-performance NLO materials.

Computation Details

A. Static NLO Properties. The four closed-shell structures with all real frequencies are obtained by MP2/6-311+G (d, p). For lithium salt electride $Li-H_3C_4N_2\cdots Na_2$, the MP2 structure is checked and very close to the more precise single- and double-excitation quadratic configuration (QCISD) structure (see Table S1 in the Supporting Information). And for the two structures at MP2 and QCISD level, the difference of static first hyperpolarizabilities is only 3%. Therefore, in this work, the MP2 structures are used in the calculations of the first hyperpolarizabilities. The static first hyperpolarizabilities are evaluated by a finite field (FF) approach at the MP2 level. This is because, with reasonable computation costs, the MP2 results are also very close to those obtained from the more sophisticated correlation methods (for example, the QCISD).[8] In the calculations of first hyperpolarizabilities and the natural bond orbital (NBO)[9] charges, the basis set employed are 6-311++G (d, p) for the C, N, and H atoms and the 6-311++G (3df, 3pd) for alkali atoms.

To find a proper applied electric field (AEF), the first hyperpolarizabilities of lithium salt electride $Li-H_3C_4N_2\cdots Na_2$ are calculated at the MP2 level in a series of fields (see Table S2 in the Supporting Information). The data of Table S2 show that the β_0 value slowly decreases with the increase of the field. The slow trend is shown by the gradual decrease of β_0 to be only 9% from 1.555×10^6 to 1.412×10^6 au, as the AEF increases from 0.0005 to 0.0010. The suitable AEF in the calculation of static electric properties is chosen as 0.0010 au.

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

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \tag{1}$$

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

The static first hyperpolarizability is noted as

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

where

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

B. Frequency-dependent NLO Properties. The frequency-dependent NLO properties of the four molecules are evaluated by the coupled-perturbed Hartree–Fock (CPHF) method.[10] The basis set employed are 6-311++G (3df, 3pd) for alkali atoms and 6-311++G (d, p) for the C, N, and H atoms.

The frequency-dependent β is noted as

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

where, $\beta_i = 1/5\ [2\beta_{jji}(-2\omega;\omega,\omega) + \beta_{ijj}(-2\omega;\omega,\omega)]$ ($i, j = x, y,$ and z) for the second harmonic generation (SHG) and $\beta_i = 1/5\ [\beta_{jji}(-\omega;\omega,0) + 2\beta_{jij}(-\omega;\omega,0)]$ ($i, j = x, y,$ and z) for the electro-optical Pokcets effect (EOPE).

In addition, the MP2 frequency-dependent β is estimated by using the multiplicative approximation:[11]

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

All of the calculations were carried out by using the GAUSSIAN 03 program package.[12] The dimensional plots of molecular orbitals were generated with the Gauss View program (Gaussian, Inc. Pittsburgh, PA).[12b]

TABLE 1: Selected Geometrical Parameters (Å) and NBO Charges at MP2 Level

	$H_4C_4N_2$	$Li-H_3C_4N_2$	$H_4C_4N_2\cdots Na_2$	$Li-H_3C_4N_2\cdots Na_2$
N−N	1.342[a]	1.342	1.339	1.340
C−Li		1.999		2.017
N···Na			2.723, 2.742	2.529, 2.586
Na···Na			3.169	3.205
q_{2N}	−0.452	−0.515	−0.550	−0.656
q_{Li}		0.904		0.875
q_{2Na}			−0.005	0.046

[a] 1.350 Å by MP2/ aug-CC-Pvdz method from ref 9.

Results and Discussions

A. Optimized Structures. For pyridazine $H_4C_4N_2$ and other three related molecules (lithium salt $Li-H_3C_4N_2$, electride $H_4C_4N_2\cdots Na_2$ and lithium salt electride $Li-H_3C_4N_2\cdots Na_2$), the optimized structures with all real frequencies are obtained at the MP2/6-311+G (d, p) level (see Figure 1). The geometrical parameters are collected in Table 1. To understand the stability of molecules, for $Li-H_3C_4N_2\cdots Na_2 \rightarrow Li-H_3C_4N_2 + 2\ Na\ (s)$, its reaction enthalpy is calculated at MP2 level; the obtained enthalpy of 8.8 kcal/mol shows that the lithium salt electride $Li-H_3C_4N_2\cdots Na_2$ has some stability.

When comparing these four molecules, the N−N bond length does not change evidently (about 1.340 Å), when doping two Na atoms into the pyridazine or substituting H atom by Li atom of pyridazine. The N−N bond length of 1.340 Å is consistent with 1.350 Å at MP2/ aug-CC-pVDZ level in the pyridazine.[13] Comparing the lithium salt to the lithium salt electride, the change of C−Li bond lengths is also small: 1.999 ($Li-H_3C_4N_2$) and 2.017 Å ($Li-H_3C_4N_2\cdots Na_2$). It shows that doping Na atoms does not obviously change the C−Li bond length. However, for the N···Na distance, lithium salt effect is obvious comparing the two electrides, $H_4C_4N_2\cdots Na_2$ and $Li-H_3C_4N_2\cdots Na_2$. The two N···Na distances 2.723 and 2.742 of $H_4C_4N_2\cdots Na_2$ are larger than 2.529 and 2.586 Å of $Li-H_3C_4N_2\cdots Na_2$, whereas the Na···Na distance 3.169 for $H_4C_4N_2\cdots Na_2$ is shorter than 3.205 Å for $Li-H_3C_4N_2\cdots Na_2$. It indicates that lithium salt effect on molecular structure decreases the distance of N···Na but increases the distance of Na···Na. The N···Na distance and Na···Na distance somehow show the structure−property relationship. The ability to form excess electron pair is different as the N···Na and the Na···Na distances vary; these factors are related to the enhancement of the first hyperpolarizability.

B. NBO Charges. From Table 1, the charges of Li atoms are close to +1, which indicates that the H of pyridazine substituted by Li forms a lithium salt. Because the excess electron pair in the doubly occupied orbital is very diffuse (5s and 6s) and the excess electron cloud wraps around the Na atoms, the charges of Na atoms are small in the two electrides ($H_4C_4N_2\cdots Na_2$ and $Li-H_3C_4N_2\cdots Na_2$).

In the two electrides, the two N atoms polarize the two Na atoms to form the excess electron pair, which is of great importance for large first hyperpolarizability. The atomic charge of two N atoms is related to the ability of polarizing alkali metal Na atoms. For these four molecules, the charge order of two N atoms is $-0.452(H_4C_4N_2) < -0.515(Li-H_3C_4N_2) < -0.550(H_4C_4N_2\cdots Na_2) < -0.656\ (Li-H_3C_4N_2\cdots Na_2)$ at MP2 level as listed in Table 1. This exhibits that the two effects of lithium salt effect and electride increase the negative charge of two N atoms. Figure 2 exhibits a monotonic dependence of first

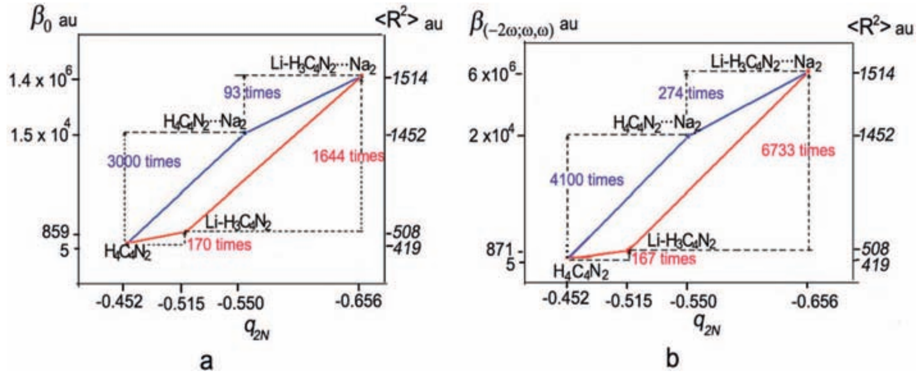

Figure 2. Relationships between β and electronic spatial extent $<R^2>$ and the total charge of two N atoms: β_0 (a) and β $(-2\omega; \omega, \omega)$ (b).

TABLE 2: Transition Energy ΔE, Electronic Spatial Extent $<R^2>$, Oscillator Strength f_0, Polarizability α_0, Difference in the Dipole Moments between the Ground State and the Excited State $\Delta\mu$, First Hyperpolarizability β_0, and Crucial Transitions[a]

	$H_4C_4N_2$	$Li-H_3C_4N_2$	$H_4C_4N_2\cdots Na_2$	$Li-H_3C_4N_2\cdots Na_2$
ΔE (eV)	8.512	4.819	1.556	1.318
$\Delta\mu$ (au)	0.039	2.126	1.457	5.197
$\Delta\mu/\Delta E^3$(au)	1.27	383	7867	46992
$<R^2>$(au)	419	508	1425	1514
f_0	0.8590	0.0807	0.7677	0.4032
α_0 (au)	56	70	474	1193
β_x (au)	−2	−61	7145	954452
β_y (au)	0	0	18	−720
β_z (au)	4	857	1.3×10^4	1.023×10^6
β_{zzz} (au)	−12	979	1.4×10^4	8.73×10^5
	−25	1075	1.0×10^4	1.077×10^6
β_0 (au)	5	859	1.5×10^4	1.412×10^6
crucial transition	0.53(HOMO-1→LUMO+4) 0.33(HOMO→LUMO+1)	0.58(HOMO-1→LUMO) 0.24(HOMO-1→LUMO+3)	0.65(HOMO→LOMO) 0.22(HOMO→LOMO+6)	0.57(HOMO→LUMO+1) 0.29(HOMO→LUMO+5)

[a] The values of β_{zzz} in the second line are at QCISD level.

hyperpolarizability on the atomic charge of two N atoms. The lithium salt electride $Li-H_3C_4N_2\cdots Na_2$ has the largest negative charge on the two N atoms (−0.656) under the actions of the two effects; therefore, it is expected that it has the largest value of first hyperpolarizability.

C. Static Polarizability and First Hyperpolarizability. The static polarizabilities and first hyperpolarizabilities of the four molecules are obtained at MP2 level and are listed in Table 2. From Table 2, the MP2 value of β_{zzz} is close to the corresponding QCISD value of β_{zzz} for four molecules. It shows that MP2 results are reliable. From Table 2, the order of the α_0 values is 56 ($H_4C_4N_2$) < 70 ($Li-H_3C_4N_2$) < 474 ($H_4C_4N_2\cdots Na_2$) < 1193 au ($Li-H_3C_4N_2\cdots Na_2$). When comparing $H_4C_4N_2$ with both $Li-H_3C_4N_2$ and $H_4C_4N_2\cdots Na_2$, the lithium salt effect slightly increases the polarizability, and the electride effect increases the α_0 by about 7 times compared to that of $H_4C_4N_2$. When comparing two electrides ($H_4C_4N_2\cdots Na_2$ and $Li-H_3C_4N_2\cdots Na_2$), the lithium salt effect increases the α_0 by about 1.5 times compared to that of $H_4C_4N_2\cdots Na_2$. This shows that both lithium salt effect and electride effect increase the polarizability.

For the first hyperpolarizability, from Table 2, the order of the β_0 values is 5 ($H_4C_4N_2$) $\ll$ 859 ($Li-H_3C_4N_2$) $\ll$ 1.5×10^4 ($H_4C_4N_2\cdots Na_2$) $\ll$ 1.412×10^6 au ($Li-H_3C_4N_2\cdots Na_2$). Comparing different values of β_0 exhibits very interesting changes. The pyridazine ($H_4C_4N_2$ without symmetric center) becomes the lithium salt of pyridazine $Li-H_3C_4N_2$ by substituting H with Li atom, and the β_0 value increases by about 170 times from 5 to 859 au, which exhibits the large lithium salt effect on β_0. Although the electride $H_4C_4N_2\cdots Na_2$ is formed by doping two Na atoms into $H_4C_4N_2$, the β_0 value remarkably increases by about 3000 times from 5 to 1.5×10^4au, which shows that the electride effect on β_0 is remarkable. Surprisingly, the β_0 value of $Li-H_3C_4N_2\cdots Na_2$ is dramatically increased when combining the two effects of lithium salt and electride. The new lithium salt electride $Li-H_3C_4N_2\cdots Na_2$ exhibits extraordinary static first hyperpolarizability, the β_0 value being 1.412×10^6 au, which is extremely larger, by about 2.8×10^5 times, than that of the $H_4C_4N_2$. When comparing the electride $H_4C_4N_2\cdots Na_2$ without lithium salt effect and the lithium salt electride $Li-H_3C_4N_2\cdots Na_2$ with lithium salt effect, β_0 value enhances 93 times from 1.5×10^4 to 1.412×10^6au, which exhibits the large lithium salt effect in the electirdes.

In addition, because the diffuse extent of the orbitals in crucial transition (see Figure 3) and $<R^2>$ increase with increasing q_{2N}, the dependences of β_0 on electronic spatial extent $<R^2>$ and the total charge of the two N atoms q_{2N} are also depicted in Figure 2a.

The extremely large static first hyperpolarizability (1.412×10^6 au) of $Li-H_3C_4N_2\cdots Na_2$ is a new record of β_0 value. When comparing with the large β_0 values of reported electrides, the β_0 value of $Li-H_3C_4N_2\cdots Na_2$ is about 200 times larger than that of the electride Li@calyx[4]pyrrole (7326 au)[4a] and near 20 times larger than that of the electride $Li_n-H-(CF_2-CH_2)_3-H$ (n = 1, 2) (3694−76978 au).[4b] The alkalide is another kind of compounds containing excess eclectron; its β_0 value is larger than that of the corresponding electride. However, the β_0 value of $Li-H_3C_4N_2\cdots Na_2$ is still much larger than that of the previously designed cup-like alkalide Li^+(calyx[4]-pyrrole)M'^-(3.6×10^4 au)[5a] and cage-like alkalides (M^+@n^6adz)M'^- (M = Li, Na, and K; $1.6 \times 10^5 \sim 3.2 \times 10^5$au).[5b]

When comparing to the other two well-known NLO molecules, a donor−acceptor polyene compound (1.7×10^5 au)[14a] and an organometallic system Ru(trans-4,4′-dieutylaminostyryl-

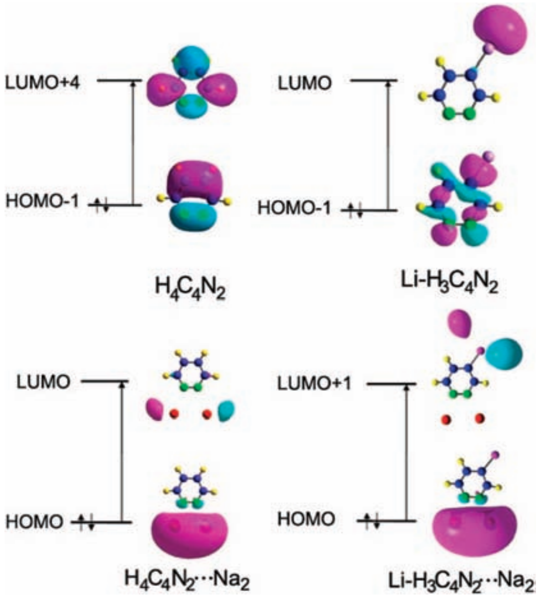

Figure 3. Crucial transitions: lithium salt electride (Li−$H_3C_4N_2\cdots Na_2$) with large long-range charge transfer and its correlative molecules, the pyridazine $H_4C_4N_2$, lithium salt Li−$H_3C_4N_2$, and electride $H_4C_4N_2\cdots Na_2$.

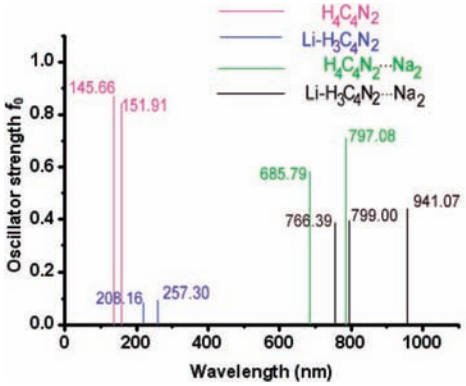

Figure 4. Linear absorption spectral of the lithium salt electride(Li−$H_3C_4N_2\cdots Na_2$) and its correlative molecules, pyridazine $H_4C_4N_2$, lithium salt Li−$H_3C_4N_2$, and electride $H_4C_4N_2\cdots Na_2$.

2,2′-bipyridine)$_3^{2+}$ (8.6×10^4 au),[14b,c] the β_0 value of the lithium salt electride is still 8−16 times larger than that of the two molecules. Recently, Champagne's and other groups have studied the zwitterionic systems and charged species which usually exhibit exceptional hyperpolarizabilities;[15] for example, the β_0 value of 4-[8-(4-[Dimethylamino]phenyl)-octa-1,3,5,7-tetraenyl]-1-methyl-pyridinium Hexafluorophosphate[15c] is 3.35×10^5 au, and the β value of TMC[15f] is as high as 1.116×10^6 au at 1907 nm. The two exceptional hyperpolarizabilities are close to that of Li−$H_3C_4N_2\cdots Na_2$.

The molecular hyperpolarizability relates to its electronic spectrum. To show the change in trend of the absorption spectra for lithium salt electride (Li−$H_3C_4N_2\cdots Na_2$) and its correlative molecules, the calculated linear absorption spectra of four molecules are shown in Figure 4. There exist dramatic differences in those four spectra. When the pyridazine ($H_4C_4N_2$) becomes the lithium salt of pyridazine Li−$H_3C_4N_2$, the strongest peak shifts from 151.91 to 257.30 nm, but the absorption strength decreases. While the pyridazine ($H_4C_4N_2$) becomes the electride $H_4C_4N_2$...Na_2, the strongest peak shifts from 151.91 to 797.08 nm (the strongest peak shift from the UV to the infrared region), and the absorption strength decreases slightly. For the new lithium salt electride Li−$H_3C_4N_2\cdots Na_2$, the strongest peak is at 941.07 nm in the infrared region. When the electride $H_4C_4N_2\cdots Na_2$ becomes the lithium salt electride Li−$H_3C_4N_2\cdots Na_2$, the strongest peak increases by about 150 nm from 797.08 to 941.07nm, and the absorption strength decreases slightly. These results exhibit that both lithium salt and electride effects have red-shift effects.

From Table 2, the tensor component β_{zzz} value is close to β_z and β_0 values. To understand the controlling factors of static first hyperpolarizability for lithium salt electride and its relative molecules, the following two-level expression is employed.[16]

$$\beta_0 \propto \frac{\Delta\mu f_0}{\Delta E^3} \tag{6}$$

where ΔE, f_0, and $\Delta\mu$ are the transition energy, oscillator strength, and the difference of the dipole moment between the ground state and the crucial excited state, respectively.

The crucial transitions are illustrated in Figure 3, and the ΔE values are roughly calculated by CIS/6-311+G (d, p) method and are also listed in Table 2. The order of ΔE is 8.512 ($H_4C_4N_2$) > 4.819 (Li−$H_3C_4N_2$) > 1.556 ($H_4C_4N_2\cdots Na_2$) > 1.318 eV (Li−$H_3C_4N_2\cdots Na_2$). For these four molecules, the order of ΔE is consistent with the order of β_0, which shows that transition energy is one controlling factor for β_0. Obviously, the two electrides with excess electrons have smaller ΔE values, and 1.556 for $H_4C_4N_2\cdots Na_2$ without lithium salt effect > 1.318 eV for Li−$H_3C_4N_2\cdots Na_2$ with the lithium salt effect, which indicates that the lithium salt effect decreases the ΔE value in the electrides. From eq 6, for the lithium salt electride, the smallest ΔE value relates to the largest β_0 value.

The $\Delta\mu$ value is another controlling factor for β_0. The $\Delta\mu$ values are 0.039 ($H_4C_4N_2$), 2.126 (Li−$H_3C_4N_2$), 1.457 ($H_4C_4N_2\cdots Na_2$) and 5.197 au (Li−$H_3C_4N_2\cdots Na_2$). As listed in Table 2, one can see that the order of $\Delta\mu/\Delta E^3$ is consistent with the order of β_0.

To understand the relative magnitude of those $\Delta\mu$ values, we consider those changes of electron clouds in the crucial transitions. As shown in Figure 3, for $H_4C_4N_2$, the electron transition associates with the very small charge transfer in the pyridazine ring, and its $\Delta\mu$ value is very small. Interestingly, for the lithium salt Li−$H_3C_4N_2$, although it does not have an excess electron, it has unoccupied orbitals for excess electrons. Because its crucial transition is from doubly occupied Π-orbital of pyridazine ring to the unoccupied s-type orbital of excess electron from Li atom, the transition associates with the large charge transfer with a long distance from the pyridazine ring to Li atom; therefore, its $\Delta\mu$ value is large (2.126 au). For the electride $H_4C_4N_2\cdots Na_2$ with excess electron pair, the crucial transition is from the excess electron orbital of ground state to diffuse that of the excited state in the two Na areas; it associates with the obvious charge transfer, thus it has a moderate $\Delta\mu$ value (1.457 au).

The lithium salt electride Li−$H_3C_4N_2\cdots Na_2$ has the two characters of both electride and lithium salt. In the lithium salt electride, the HOMO is a doubly occupied excess electron orbital in the area of two Na atoms, and the LUMO+1 is a diffuse orbital of excess electron in the Li atom area. Its crucial transition is from HOMO, the s-type orbital of the ground-state excess electron from the two Na, to the p-type orbital of excited-state excess electron from Li atom. In the transition, the charge transfer is large from two Na to Li atom area and is a long-range transfer (about 6.9 Å); therefore, the $\Delta\mu$ value is considerably large (5.197 au).

For the lithium salt electride, it has not only the smallest ΔE value but also the largest $\Delta\mu$ value; therefore, the first

TABLE 3: Estimated MP2 and CPHF Values of Frequency-Dependent Hyperpolarizabilities (au)[a]

frequency (au)	$\beta(-2\omega;\ \omega,\ \omega)$	$\beta(-\omega;\ \omega,\ 0)$
	$H_4C_4N_2$	
0.0000	5 (23)	
0.0050	5.2 (24)	5.2 (24)
0.0100	5.2 (24)	5.2 (24)
0.0239	5.4 (25)	5.2 (24)
0.0000	859 (489)	
	$Li{-}H_3C_4N_2$	
0.0050	862 (491)	859 (489)
0.0100	871 (496)	862 (491)
0.0239	939 (535)	885 (504)
0.0000	1.5×10^4 (7×10^3)	
	$H_4C_4N_2\cdots Na_2$	
0.0050	1.6×10^4 (7×10^3)	1.6×10^4 (7×10^3)
0.0100	2.1×10^4 (1.0×10^4)	1.7×10^4 (8×10^3)
0.0239	2.13×10^5 (9.6×10^4)	2.9×10^4 (1.3×10^4)
0.0000	1.412×10^6 (4.99×10^5)	
	$Li{-}H_3C_4N_2\cdots Na_2$	
0.0050	2.331×10^6 (8.24×10^5)	1.62×10^6 (5.76×10^5)
0.0100	5.865×10^6 (2.075×10^6)	2.295×10^6 (8.12×10^5)
0.0239	9.49×10^5 (3.3×10^5)	3.35×10^5 (1.18×10^5)

[a] The CPHF Values are in Parenthesis.

hyperpolarizability of the lithium salt electride is the largest (extraordinary).

D. Frequency-Dependent NLO Properties. Table 3 lists the CPHF and estimated MP2 frequency-dependent values: $\beta(-2\omega;\ \omega,\ \omega)$ and $\beta(-\omega;\ \omega,\ 0)$ at $\omega = 0.005$, 0.01, and 0.0239 au.

For the $H_4C_4N_2$, the estimated MP2 frequency-dependent values, $\beta\ (-2\omega;\ \omega,\ \omega)$ and $\beta\ (-\omega;\ \omega,\ 0)$ from $\omega = 0.000$ to 0.0239 au are very close to the MP2 static β_0 value of 5 au. And for the lithium salt $Li{-}H_3C_4N_2$, by comparing with its β_0, the large $\beta\ (-2\omega;\ \omega,\ \omega)$ or $\beta\ (-\omega;\ \omega,\ 0)$ at $\omega = 0.0239$ au only increases by about 9 or 3%. It shows that the frequency-dependent effect is weak for $H_4C_4N_2$ and $Li{-}H_3C_4N_2$.

But for the electride $H_4C_4N_2\cdots Na_2$, comparing with the large β_0, the MP2 estimated $\beta\ (-2\omega;\ \omega,\ \omega)$ values are 1.6×10^4, increasing by about 8% at $\omega = 0.0050$, 2.1×10^4, by about 39% at $\omega = 0.0100$, and 2.13×10^5 au increasing by about 13 times at $\omega = 0.0239$ au. The $\beta\ (-\omega;\ \omega,\ 0)$ values are 1.6×10^4 increasing by about 3% at $\omega = 0.0050$, 1.7×10^4, increasing by about 12% at $\omega = 0.0100$, and 2.9×10^4 au increasing by 89% at $\omega = 0.0239$ au. It indicates that the dispersion of the electride $H_4C_4N_2\cdots Na_2$ is much stronger than that for $H_4C_4N_2$ and $Li{-}H_3C_4N_2$.

The dispersion effect on the lithium salt electride $Li{-}H_3C_4N_2\cdots Na_2$ is very strong. Comparing with extraordinary static β_0, the second harmonic generation (SHG) $\beta\ (-2\omega;\ \omega,\ \omega)$ values are 2.331×10^6 increasing by about 64% at $\omega = 0.0050$, 5.865×10^6, increasing by about 3 times at $\omega = 0.0100$, but 9.49×10^5 au, decreasing by 32% at $\omega = 0.0239$ au, whereas the electro-optical Pokcets effect (EOPE) $\beta\ (-\omega;\ \omega,\ 0)$ values are 1.629×10^6, increasing by about 13% at $\omega = 0.0050$, 2.295×10^6 increasing by about by about 62% at $\omega = 0.0100$, but 3.35×10^5 au decreasing by 76% at $\omega = 0.0239$ au. For lithium salt electride $Li{-}H_3C_4N_2\cdots Na_2$, obviously, the $\beta\ (-2\omega;\ \omega,\ \omega)$ and $\beta\ (-\omega;\ \omega,\ 0)$ at $\omega = 0.0100$ au are the largest values.

When comparing $\beta\ (\omega)$ values at $\omega = 0.0100$ au for the four molecules (see Table 3), the order of the $\beta\ (-2\omega;\ \omega,\ \omega)$ is 5.2 ($H_4C_4N_2$) ≪ 871 ($Li{-}H_3C_4N_2$) ≪ 2.1×10^4($H_4C_4N_2\cdots Na_2$) ≪ 5.865×10^6au ($Li{-}H_3C_4N_2\cdots Na_2$). It is found that from $H_4C_4N_2$ to $Li{-}H_3C_4N_2$, the $\beta\ (-2\omega;\ \omega,\ \omega)$ value increases by 167 times from 5.2 to 871 au. This indicates a large lithium salt effect on $\beta\ (-2\omega;\ \omega,\ \omega)$ which is almost similar to that on β_0 (170 times).

From the $H_4C_4N_2$ to the electride $H_4C_4N_2\cdots Na_2$, the $\beta\ (-2\omega;\ \omega,\ \omega)$ value increases by about 4100 times (from 5.2 to 2.1×10^4au), which is much larger than the 3000 times of β_0. It shows that the electride effect on $\beta\ (-2\omega;\ \omega,\ \omega)$ at $\omega = 0.0100$ au is much stronger than that on β_0.

For the lithium salt electride $Li{-}H_3C_4N_2\cdots Na_2$, the frequency-dependent $\beta\ (-2\omega;\ \omega,\ \omega)$ value is also extraordinary, 5.865×10^6au, which comes from the combination of lithium salt and electride effects. As above-mentioned for the static case (see Figure 2a), the lithium salt effect is 167 times, and the large electride effect is 4100 times (Figure 2b). For the frequency-dependent case, it is similar to the static case; $\beta\ (-2\omega;\ \omega,\ \omega)$ and $\beta\ (-\omega;\ \omega,\ 0)$ values are about 10^6 times larger than those of the $H_4C_4N_2$. It is noted that for $Li{-}H_3C_4N_2\cdots Na_2$, the frequency-dependent $\beta\ (\omega)$ value at $\omega = 0.0239$ au is close to the resonance frequency, and the $\beta\ (\omega)$ value diminishes.

In this paper, a novel designing idea is presented for the first time. The idea comes from the combination of lithium salt and electride effects to enhance the first hyperpolarizability. This work may contribute to the development of potential high-performance NLO materials.

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Supporting Information Available: Choice of calculation level and applied electric field. This material is available free of charge via the Internet at http://pubs.acs.org.

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