

One lithium atom binding with *P*-nitroaniline: lithium salts or lithium electrides?

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Abstract Recently, both lithium (Li) salts and Li electrides formed by one Li atom interacting with ligand complexes, have been widely investigated. An interesting question emerges: is the configuration of one Li atom interacting with ligand complexes a Li salt or electride? In the present work, four configurations *n*-Li-PNA (*n*=1–4) were obtained by binding one Li atom with the *p*-nitroaniline (PNA) at different positions to explore this question. The results show that 1-Li-PNA and 2-Li-PNA are typical Li salts, and 4-Li-PNA is a typical Li electride. Significantly, 3-Li-PNA possesses both characteristics of Li salt and electride. At the same time, 3-Li-PNA has the largest first hyperpolarizability (2.9×10^6 au) by ROMP2 method compared with the other three configurations. Furthermore, the first hyperpolarizability of 3-Li-PNA is about 2600 times larger than that of PNA. Further, the vertical ionization potential (VIP) and interaction energy (E_{int}) indicate that 3-Li-PNA is less stable than 1-Li-PNA and 2-Li-PNA (Li salts), but is more stable than 4-Li-PNA (Li electrides).

Keywords Electride · Li salt · NLO · PNA

Introduction

Both lithium (Li) salts and Li electrides are formed by interacting one Li atom with ligand (L) complexes. Among them, the Li salt is an ionic compound in which Li is the cation

(the charge of Li is close to +1), and the Li electride is also an ionic compound with an excess electron (the electron is an anion and the charge of Li is much smaller than +1). Thus, the Li salt can be expressed as Li^+L^- and the Li electride can be considered as $(\text{LiL})^+\text{e}^-$. During the past decade, many Li salts and electrides were designed to investigate the structure–property relationship by theoretical chemists [1–14]. For example, on the basis of electrides studied by the Dye's group [15–17], Li's group theoretically designed a new electride: Li@calix [4] pyrrole in which the 2s electron of the Li atom was pushed out by the action of four N atoms to become an excess electron [1].

Over the past two decades, high-performance nonlinear optical (NLO) materials have continued to be in the limelight because of their potential applications in advanced telecommunications, electronic-optical devices, and optical data processing technologies etc. [18–26]. Since large macroscopic optical nonlinearity depends on high microscopic molecular nonlinearity, much effort has been devoted to search for important influencing factors to enhance molecular nonlinearity [1–3, 27–37].

Both Li salts and Li electrides show large first hyperpolarizability, which indicates that they are potential NLO materials. However, there are noticeable differences between Li salts and Li electrides. The natural bond orbital (NBO) charge of Li in Li salts is very close to +1, while the NBO charge of Li in Li electrides is significantly smaller than that in Li salts. For example, the NBO charge of Li in $\text{Li}_5\text{-[5]}$ cyclacene is 0.8. The paper shows that $\text{Li}_5\text{-[5]}$ cyclacene is a new Li salt. When doping a Li atom into $\text{Li}_5\text{-[5]}$ cyclacene, a new tubiform electride $\text{Li-Li}_5\text{-[5]}$ cyclacene is formed. As expected, the NBO charge of Li is 0.3 which is much smaller than 0.8 [8]. On the other hand, there are obvious diffuse electron clouds in the singly-occupied molecular orbitals (SOMOs) for Li electrides [1, 2, 5, 8, 10]. However, the Li salts have obvious diffuse electron clouds in the lowest unoccupied molecular orbitals (LUMOs) [3, 4, 6, 7, 9].

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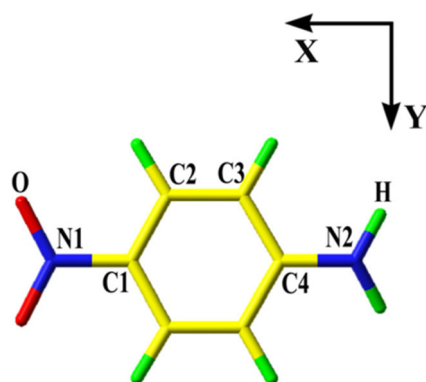
Here is an interesting question: is the configuration of Li interacting with ligand complexes a Li salt or electride? This question has not been solved yet, although many papers on the NLO properties of Li doped molecules have been published [1–14].

The donor- π -conjugated bridge-acceptor (D- π -A) model is a successful strategy for the design of NLO molecular materials [23, 27, 30, 32]. The *p*-nitroaniline (PNA) (Scheme 1) which contains the electron-drawing group ($-\text{NO}_2$), electron-donating group ($-\text{NH}_2$), and π -conjugated bridge ($-\text{C}_6\text{H}_4-$) has been deeply investigated by scientists [38–41]. Due to high second harmonic generation (SHG) efficiency, PNA is a prototypical second-order NLO molecule.

In the present work, four configurations (1-Li-PNA, 2-Li-PNA, 3-Li-PNA, and 4-Li-PNA) were obtained by binding one Li atom with the *p*-nitroaniline (PNA) at different positions. To get a better understanding of *n*-Li-PNA ($n=1, 2, 3, 4$), the $\text{Li-NO}_2\text{H}$ and Li-NH_3 were also designed in theory. The frontier molecular orbitals (FMOs), natural bond orbital (NBO) charges, and the vertical ionization potential (VIP) values of $\text{Li-NO}_2\text{H}$ and Li-NH_3 are shown in Fig. 1. It is obvious that the $\text{Li-NO}_2\text{H}$ has Li salt characteristic with larger NBO charges of Li (0.859) and diffuse electron cloud in LUMO. Meanwhile, the Li-NH_3 is a typical Li electride with smaller NBO charge of Li (0.015), and the 2s valence electron of the Li atom was pushed out to become an excess electron by the action of the N atom in Li-NH_3 . Compared with $\text{Li-NO}_2\text{H}$, Li-NH_3 has larger first hyperpolarizability and smaller VIP value.

Computational details

According to previously reported investigations, the hybrid meta exchange correlation functional (M06-2X) performs well in calculation of main-group thermochemistry, noncovalent interactions, and electronic excitation energies to Rydberg states [42, 43]. The optimized structures of PNA, 1-Li-PNA, 2-Li-PNA, 3-Li-PNA, and 4-Li-PNA with all real



Scheme 1 The framework shape of PNA

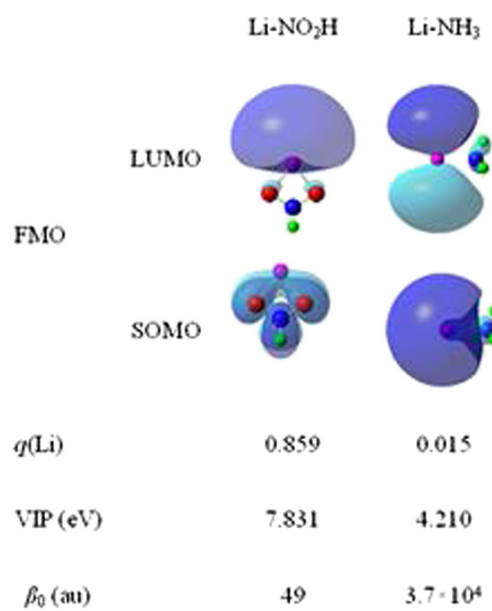


Fig. 1 The β_0 (au), VIP (eV), $q(\text{Li})$, and FMOs of $\text{Li-NO}_2\text{H}$ and Li-NH_3

frequencies were obtained by the M06-2X/6-31G(d). The bond length alternation (BLA) parameter is defined as the following formula (Scheme 1):

$$\text{BLA} = (R_{\text{C1-C2}} + R_{\text{C3-C4}}) / 2 - R_{\text{C2-C3}}. \quad (1)$$

The nucleus independent chemical shifts NICS was calculated at the B3LYP/6-311++G(2d) with gauge-independent atomic orbital (GIAO) method. NICS(0) was calculated at the center of benzene ring, and the NICS(1) was calculated at 1 Å below the center of benzene ring. The corresponding data are listed in Table S1. The results show that NICS(0) values are similar to NICS(1) values. The natural bond orbital (NBO) [44] charges were also evaluated at the B3LYP/6-311++G(2d) level.

The static first hyperpolarizabilities were calculated by the MP2 method with numerical derivatives. Taking into account the computation costs, the MP2 results are very close to those obtained from the more sophisticated correlation methods (for example, the QCISD). It is worth mentioning that the reliability of the computed hyperpolarizability of open shell system [45] may be affected by the spin contamination ($\langle S^2 \rangle$). As one can see from supporting information Table S2, the largest $\langle S^2 \rangle$ value is 1.313 which is far larger than the standard value 0.750 for the pure doublet state. Therefore, the ROMP2 method [46] was used to calculate the hyperpolarizabilities of *n*-Li-PNA ($n=1, 2, 3, 4$). The magnitude of the applied electric field was chosen as 0.001 au for the calculation of the hyperpolarizabilities, which is proven to be the most adequate value for the numerical differentiation. The 6-311++G basis set was employed for the C, N, O and H atoms, and the 6-311++G(3df,3pd) basis set was for the Li atom. The 6-311++

G basis set employed here is sufficient in reproducing hyperpolarizabilities as already investigated by Maroulis et al. [47] on the predictive capability of small sized basis sets.

The first hyperpolarizability is noted as:

$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2 \right)^{1/2}, \quad (2)$$

where:

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

In our previous work, the interaction energy (E_{int}) calculated by the M06-2X is almost equal to that calculated by the MRMP2/CASSCF(2,2). Therefore, the E_{int} in the present work was calculated by the M06-2X. The counterpoise (CP) procedure was applied to calculate the interaction qualitatively for correcting the basis set superposition (BSSE). The E_{int} is the difference between the energy of the Li-PNA and the sum of the energies of the Li and PNA according to the equation:

$$E_{\text{int}} = E_{ab}(X_{ab}) - [E_a(X_{ab}) + E_b(X_{ab})]. \quad (3)$$

All of the calculations were performed with Gaussian 09 program package [48].

Results and discussion

Geometric structures and nucleus independent chemical shift (NICS) values

When the Li atom moves over the plane of the benzene ring of PNA, four configurations n -Li-PNA ($n=1, 2, 3, 4$) were obtained and shown in Fig. 2. The important geometric parameters are listed in Table S3. As shown in Table S3, the bond lengths of PNA obtained at the M06-2X/6-31G(d) are very similar to experimental data [49]. For a molecule with single and double bonds, the bond length alternation (BLA) is a critical geometric parameter. As shown in Table 1, the BLA values increase from 0.016 (PNA) to 0.036 (2-Li-PNA) and slightly decrease to 0.034 Å (3-Li-PNA). Then, the BLA values sharply decrease from 0.034 (3-Li-PNA) to 0.007 Å (4-Li-PNA). Thus, the position of Li atom affects the bond lengths of PNA, which leads to the variation of BLA values.

To the best of our knowledge, aromaticity is a very important property for conjugated molecules. However, aromaticity cannot be measured directly by experiment. Luckily, some valuable papers have demonstrated that the nucleus

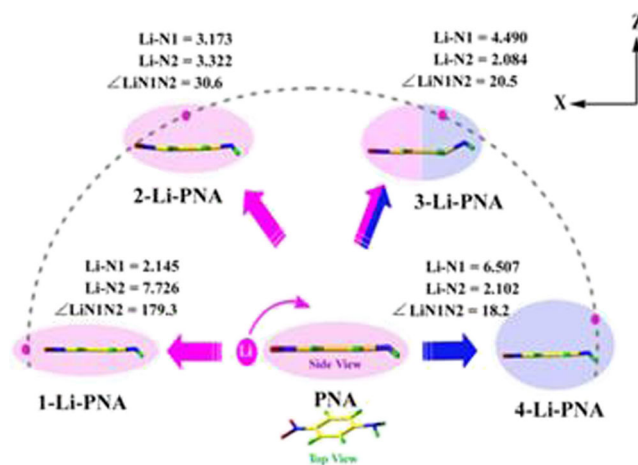


Fig. 2 The geometric structures of five configurations with all real frequencies were obtained by the M06-2X/6-31G(d). The important bond length (Å) and bond angle ($^{\circ}$)

independent chemical shift (NICS) has a strong correlation with aromaticity, which can be calculated by theoretical methods [50–53]. A negative NICS value generally accounts for aromaticity, whereas positive NICS value represents antiaromaticity. From Table 2, it is clear that PNA (−7.6), 1-Li-PNA (−6.4), and 4-Li-PNA (−7.4 ppm) are aromatic, whereas 2-Li-PNA (3.9) and 3-Li-PNA (3.4 ppm) are antiaromatic. The NICS(0) values indicate that the aromaticities of four configurations are the following changes: aromaticity (1-Li-PNA) → antiaromaticity (2-Li-PNA) → antiaromaticity (3-Li-PNA) → aromaticity (4-Li-PNA). Interestingly, the variation of NICS(0) values is consistent with BLA values as shown in Fig. 3. Significantly, for antiaromatic configurations, 2-Li-PNA has the largest BLA value (0.036 Å), and 3-Li-PNA has the second largest BLA value (0.034 Å) and the smallest Li-C4 (2.021) and Li-N2 (2.084 Å) bond lengths. While aromatic 4-Li-PNA has the smallest BLA value (0.007 Å).

Natural bond orbital (NBO) charges and frontier molecule orbitals (FMOs) analysis

Further, we focus on the NBO charges $q(\text{Li})$ and the FMOs of n -Li-PNA ($n=1, 2, 3, 4$). As listed in Table 2, the NBO charges $q(\text{Li})$ of 1-Li-PNA (0.867) and 2-Li-PNA (0.868) are close to +1. As shown in Fig. 4, it is noticeable that the electron clouds in the LUMOs of 1-Li-PNA and 2-Li-PNA

Table 1 Geometric parameters of five configurations were calculated at the M06-2X/6-31G(d). The NICS values were calculated at the B3LYP/6-311++G(2d)

	PNA	1-Li-PNA	2-Li-PNA	3-Li-PNA	4-Li-PNA
BLA (Å)	0.016	0.019	0.036	0.034	0.007
NICS (ppm)	−7.60	−6.43	3.90	3.39	−7.43

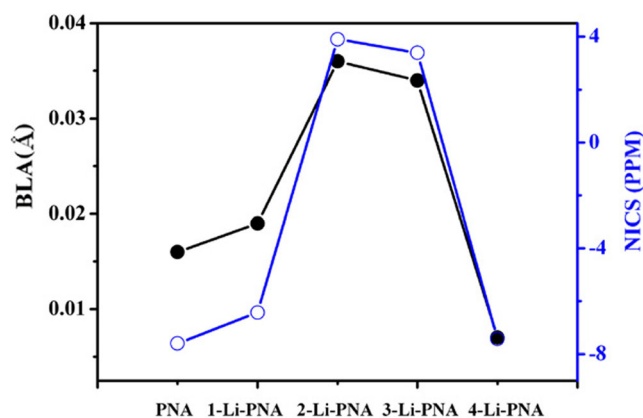
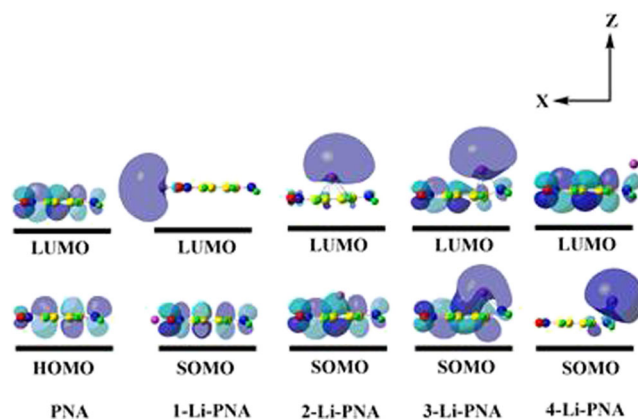
Table 2 The NBO charges (au) of PNA, 1-Li-PNA, 2-Li-PNA, 3-Li-PNA, and 4-Li-PNA

	PNA	1-Li-PNA	2-Li-PNA	3-Li-PNA	4-Li-PNA
$q(\text{Li})$		0.867	0.868	0.709	0.160
$q(\text{C4})$	0.194	0.150	0.039	-0.033	0.126
-NO ₂	-0.307	-1.044	-0.660	-0.528	-0.347
-NH ₂	-0.008	-0.051	-0.063	-0.099	-0.099
-C ₆ H ₄ -	0.313	0.227	-0.144	-0.082	0.285

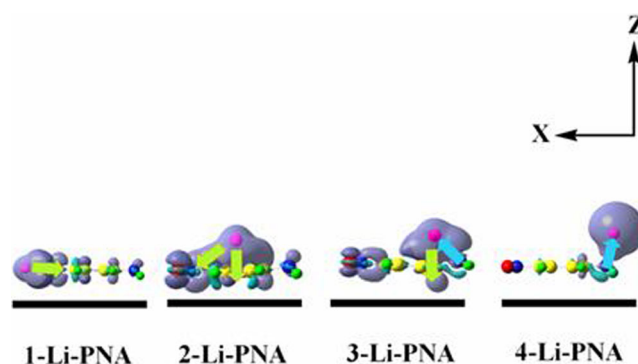
have obvious diffuse. Thus, 1-Li-PNA and 2-Li-PNA are typical Li salts. However, compared with 1-Li-PNA, 4-Li-PNA has smaller NBO charge $q(\text{Li})$ (0.160). Meanwhile, the valence electron of the Li atom of 4-Li-PNA is ejected out as the excess electron in the SOMO under the action of lone pair of N atom in PNA, which is similar to Li-NH₃ and reported cup-like electride Li@calix [4]-pyrrole [1]. Thus, 4-Li-PNA is predicted to be a typical Li electride.

From the above discussion, it can be concluded that the n -Li-PNA ($n=1, 2, 4$) configurations change from Li salts to Li electrides when the Li atom moves over the plane of the benzene ring of PNA from -NO₂ to -NH₂. What kinds of characteristics does 3-Li-PNA possess, a Li salt or a Li electride?

To answer this question, we first focus on the NBO charge $q(\text{Li})$ of 3-Li-PNA. From Table 2, it is clear that the NBO charge $q(\text{Li})$ of 3-Li-PNA (0.709) is slightly smaller than those of 1-Li-PNA and 2-Li-PNA, but is obviously larger than that of 4-Li-PNA. Further, as shown in Fig. 4, there are obvious diffuse electron clouds in the LUMO of 3-Li-PNA. Therefore, 3-Li-PNA possesses Li salts characteristic. On the other hand, 3-Li-PNA also has obvious diffuse electron clouds in the SOMO, indicating that 3-Li-PNA possesses Li electride characteristics. From Fig. 4, it is obvious that the diffuse electron cloud in the SOMO of 3-Li-PNA is pulled down by a mysterious force compared with that of 4-Li-PNA.

**Fig. 3** The BLA values and the NICS(0) values of PNA and n -Li-PNA ($n=1, 2, 3, 4$)**Fig. 4** The frontier molecular orbitals (FMOs) of PNA and n -Li-PNA ($n=1, 2, 3, 4$) (isovalue = 0.02 au)

To find the mysterious force, the electron density difference between the PNA and Li-PNA is analyzed by Multiwfn program [54]. As shown in Fig. 5, the electron density of C4 atom in 3-Li-PNA increases obviously. As a result, the NBO charge (in Table 2) of C4 atom in 3-Li-PNA is a negative value which is quite different from that of PNA. It may be the reason that the valence electron of the Li atom is ejected out under the action of lone pair of N atom in PNA. Simultaneously, the valence electron of the Li in 3-Li-PNA is partly pulled down by C4 atom. Furthermore, Fig. 5 shows that the valence electron of the Li atom in 2-Li-PNA is bound by a π -conjugated bridge (-C₆H₄-) and an electron-drawing group (-NO₂). As a result, the NBO charges of -C₆H₄- (-0.144) and -NO₂ (-0.660) in 2-Li-PNA are smaller than those in PNA. On the other hand, the electron density of -NO₂ in 1-Li-PNA obviously increases and the NBO charge of -NO₂ (-1.044) is more negative than those in PNA, which indicates that the electron cloud of the Li atom is mainly bound by -NO₂ in 1-Li-PNA. Therefore, as vividly shown in Fig. 5, the -NO₂, -NH₂, and -C₆H₄- of PNA have a diverse effect on Li atom due to the different positions of Li atom. For example, in the case of 1-Li-PNA and 2-Li-PNA, the electron of Li atom is pulled by -NO₂, and that of 4-Li-PNA is pushed by -NH₃.

**Fig. 5** The electron-density differences between the PNA and n -Li-PNA ($n=1, 2, 3, 4$) (light blue indicates a decrease of electron density while dark blue indicates an increase of electron density)

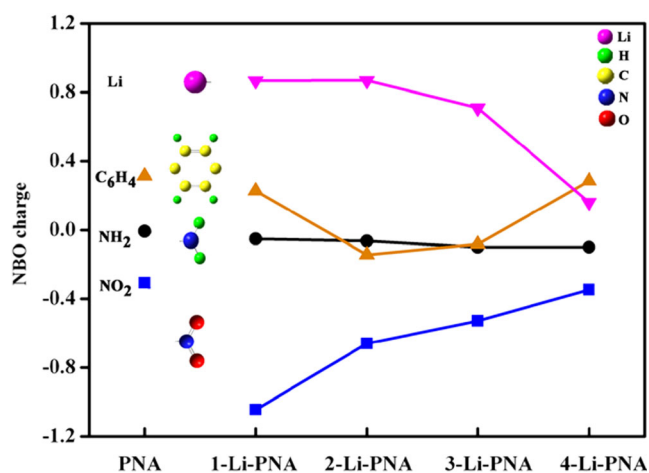


Fig. 6 The NBO charges of $-\text{NO}_2$, $-\text{NH}_2$, $-\text{C}_6\text{H}_4$, and Li

However, that of 3-Li-PNA is both pulled and pushed by $-\text{C}_6\text{H}_4$ - and $-\text{NH}_2$.

From Fig. 6, we can find that the NBO charge of $-\text{NO}_2$ becomes more positive when the Li atom moves along the arc-shaped position of PNA from $-\text{NO}_2$ to $-\text{NH}_2$. The NBO charges of $-\text{NH}_2$ are essentially the same, indicating that the Li atom has little effect on the NBO charge of $-\text{NH}_2$. It is worth mentioning that the NBO charge of $-\text{C}_6\text{H}_4$ shows interesting variation. When the Li atom moves along the arc-shaped position of PNA from $-\text{NO}_2$ to $-\text{NH}_2$, the NBO charges of $-\text{C}_6\text{H}_4$ are in the order: 1-Li-PNA (0.227) \rightarrow 2-Li-PNA (-0.144) \rightarrow 3-Li-PNA (-0.082) \rightarrow 4-Li-PNA (0.285). As mentioned earlier, the electron density difference is in accordance with NBO charge of $-\text{C}_6\text{H}_4$ for n-Li-PNA ($n=1, 2, 3, 4$).

The above discussions indicate that 3-Li-PNA possesses both Li salts and Li electrides characteristics, and Li-NH₃ (Li electride) has smaller vertical ionization potential value and larger first hyperpolarizability value than that of Li-NO₂H (Li salt). Thus, we further investigate the variations of the vertical ionization potential values and the hyperpolarizabilities of n-Li-PNA ($n=1, 2, 3, 4$).

Vertical ionization potential (VIP), interaction energy (E_{int}), and the static first hyperpolarizability (β_0)

As suggested by previous investigations [1, 2], the vertical ionization potential (VIP) value is an important criterion to judge the redox ability of a molecule. The higher VIP value indicates that the molecule is more stable. From Table 3, the VIP values of Li salts (5.845 for 1-Li-PNA and 5.233 for 2-Li-PNA) are larger than Li electrides (4.455 eV for 4-Li-PNA). In particular, the VIP value of 4-Li-PNA is higher than the designed Li@calix [4] pyrrol (4.12) [1] and Li-doped fluorocarbon chain (3.79 eV) [2]. The VIP value (5.018 eV) of 3-Li-PNA with both Li salts and electrides characteristics is larger than that of 4-Li-PNA, but is smaller than those of 1-Li-PNA and 2-Li-PNA. Thus, 3-Li-PNA is less stable than Li salts (1-Li-PNA and 2-Li-PNA), but it is more stable than Li electride (4-Li-PNA).

The interaction energy (E_{int}) values evaluated in Table 3 change in the order: 1-Li-PNA (-74.84) $>$ 2-Li-PNA (-27.53) $>$ 3-Li-PNA (-25.43) $>$ 4-Li-PNA (-7.85 kcal mol⁻¹), which indicates that the E_{int} values are in a decreased trend when the Li atom moves from $-\text{NO}_2$ to $-\text{NH}_2$. Our previous papers show that the E_{int} value evaluates the stability of compounds. The more negative E_{int} value indicates that the compounds are more stable. Thus, the E_{int} values indicate that the 3-Li-PNA with both Li salt and electride characteristics is less stable than Li salts (1-Li-PNA and 2-Li-PNA), but is more stable than Li electride (4-Li-PNA). Furthermore, the variation of E_{int} values is in accordance with that of VIP values.

The first hyperpolarizability (β_0) values of n-Li-PNA ($n=1, 2, 3, 4$) were calculated by ROMP2 and listed in Table 3. The β_0 value (6.6×10^2) of 1-Li-PNA is very similar to that (1.1×10^3 au) of PNA. The β_0 value of 2-Li-PNA (7.2×10^3 au) with Li salt characteristic is larger than that (1.6×10^4 au) of 4-Li-PNA with Li electride characteristic, which indicates that the compound with Li electride characteristic has larger β_0 value. Interestingly, the β_0 value of 3-Li-PNA (2.9×10^6 au) is far larger than those of 1-Li-PNA and 2-Li-PNA (Li salts) and 4-

Table 3 The first hyperpolarizability β_0 (au) values of PNA and n-Li-PNA ($n=1, 2, 3, 4$) were calculated by ROMP2 method. Transition energy ΔE (eV) and oscillator strength f_0 at CIS/6-311++G (2d), and the ΔE and f_0 values in the second line were calculated at TD-B3LYP/6-311++G (2d) level. The vertical ionization potential VIP (eV) and transition energy E_{int} (kcal mol⁻¹)

	PNA	1-Li-PNA	2-Li-PNA	3-Li-PNA	4-Li-PNA
VIP	8.617	5.845	5.233	5.018	4.455
E_{int}		-74.84	-27.53	-25.43	-7.85
β_x	1.1×10^3	6.6×10^2	-7.1×10^3	2.7×10^6	-1.0×10^3
β_y	0	6	-6	-3.9×10^1	2.7×10^1
β_z	-2.7×10^1	-3.0×10^1	1.2×10^3	1.0×10^6	-1.6×10^4
β_0	1.1×10^3	6.6×10^2	7.2×10^3	2.9×10^6	1.6×10^4
f_0	0.335	0.400	0.197	0.241	0.196
ΔE	0.323	0.311	0.109	0.117	0.172
	5.120	6.200	3.105	1.417	1.424
	3.974	4.006	2.531	1.113	1.769

Li-PNA (Li electride) and is about 2600 times than that of PNA because 3-Li-PNA possesses both Li salt and electride characteristics.

In previous papers [1, 2], it is demonstrated that the larger β_0 value is associated with the smaller transition energy (ΔE). To understand the difference of β_0 values, we focus on the variation of ΔE values. The ΔE values were obtained by the TD-DFT and CIS method and listed in Table 3. Both TD-DFT and CIS results show the same trend. The 3-Li-PNA with Li salt and electride characteristics has the smallest ΔE values which are 1.113 eV (TD-DFT) and 1.417 eV (CIS). Thus, the ΔE values are opposite to the trend of β_0 values. Obviously, the transition energy is the important factor on determining the first hyperpolarizability of n-Li-PNA ($n=1, 2, 3, 4$), which is in accordance with the two-level expression proposed by Oudar and co-workers [55, 56].

Conclusions

In the present work, four configurations (1-Li-PNA, 2-Li-PNA, 3-Li-PNA, and 4-Li-PNA) were designed theoretically by one Li atom binding with the *p*-nitroaniline (PNA) at different positions. The result of nucleus independent chemical shift values indicates that the aromaticities of four configurations are the following changes: aromaticity (1-Li-PNA) \rightarrow antiaromaticity (2-Li-PNA) \rightarrow antiaromaticity (3-Li-PNA) \rightarrow aromaticity (4-Li-PNA). From the analysis of natural bond orbital charge and frontier molecular orbital, it can be concluded that 1-Li-PNA and 2-Li-PNA are typical Li salts in which the electron clouds in the LUMOs of 1-Li-PNA and 2-Li-PNA have obvious diffuse. 4-Li-PNA is a typical Li electride with smaller NBO charge $q(\text{Li})$ (0.160), meanwhile, the valence electron of the Li atom is ejected out as the excess electron in the SOMO under the action of lone pair of N atom in PNA. Significantly, 3-Li-PNA possesses both Li salt and electride characteristics. In addition, 3-Li-PNA has the largest first hyperpolarizability (2.9×10^6 au) by the ROMP2 method, which is much larger (about 2600 times) than that of PNA. Moreover, the vertical ionization potential (VIP) and interaction energy (E_{int}) indicate that the 3-Li-PNA is less stable than Li salt (1-Li-PNA and 2-Li-PNA), but is more stable than the Li electride (4-Li-PNA). We hope that the present work can inspire experimentalists for designing and synthesizing high-performance nonlinear optical materials.

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