Theor Chem Acc (2011) 128:241–248
DOI 10.1007/s00214-010-0837-0

REGULAR ARTICLE

# Three-propeller-blade-shaped electride: remarkable alkali-metal-doped effect on the first hyperpolarizability

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Received: 9 July 2010 / Accepted: 9 October 2010 / Published online: 12 December 2010

**Abstract** Significant alkali-metal-doped effects on the structure and the first hyperpolarizability ($\beta_0$) of effective multi-nitrogen complexant tris[(2-imidazolyl)methyl]amine (TIMA) are investigated. Three imidazoles of TIMA like three blades of propeller connect with methyls by the C–C single bonds. Because of the three C–C single-bond cooperative rotations, the TIMA behaves with great flexibility, and it is a high-performance multi-nitrogen complexant for the alkali metal doping. Thus, the new complexes $A_m$-TIMA ($A_m$ = Li, Na, and K) with electride characteristic have diffuse excess electron than the reported electride-type system due to the strong interaction between the complexant TIMA and alkali metal. For the first hyperpolarizability, three engaging electrides $A_m$-TIMA with the diffuse excess electrons exhibit considerably large $\beta_0$ values using the MP2 (full) method and the $\beta_0$ values of new electrides are greatly larger (3,464–29,705 times) than that (338 au) of TIMA. Surprisingly, the K-TIMA sets a new record $\beta_0$ value to be $1.00 \times 10^7$ au which far exceeds than that (3,694–76,978 au) of the reported electride-type system Li@calix[4]pyrrole (J Am Chem Soc 127:10977–10981, 2005) and $Li_n-H-(CF_2-CH_2)_3-H$ ($n = 1, 2$) (J Am Chem Soc 129:2967–2970, 2007) and 31,123 au of the organometallic system (J Am Chem Soc 121:4047–4053, 1999) Ru(trans-4,4′-diethylaminostyryl-2,2′-bipyridine)$_3^{2+}$, as well as $1.23 \times 10^6$ au of the large donor-CNT systems (Nano Lett 8:2814–2818, 2008). Clearly, the alkali-metal-doped effect on the first hyperpolarizability is very dramatic for the high-performance multi-nitrogen complexant TIMA. Considering simple possibility from molecule to material, the $\beta_0$ values of optimized Li-TIMA-dimer and Li-TIMA-tetramer are investigated by BHandHLYP method. Interestingly, results show that the order of $\beta_0$ value is Li-TIMA-monomer < Li-TIMA-dimer < Li-TIMA-tetramer. So the new three-propeller-blade-shaped electrides can be considered as candidates for high-performance nonlinear optical materials.

**Keywords** First hyperpolarizability · Electride · Three-propeller-blade-shaped

## 1 Introduction

Nonlinear optics [1, 2] (NLO) as rapidly growing field have attracted much attention due to the wider application of NLO materials [3–10] in optical computation, telecommunications, electro-optic (EO) modulation, second harmonic generation, and high-speed signal processing [11–13]. So research on the high-performance nonlinear optical materials is a key to the development of nonlinear optics, in which theoretical investigations [6, 8, 14–23] play an eminent role.

Recently, several new kinds of NLO systems with excess electron have been investigated [24–33]. For electrides [34–36] and alkalides [37], the excess electron is formed by chemical doping (alkali atoms as dopant). Champagne [8] investigated the effect of charging on the second and first hyperpolarizabilities of polyacetylene chains by explicitly doped alkali metal atoms. These investigations demonstrated that charging dramatically enhances the static electronic and vibrational hyperpolarizabilities.

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**Electronic supplementary material** The online version of this article (doi:10.1007/s00214-010-0837-0) contains supplementary material, which is available to authorized users.

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Furthermore, Dye et al. [34–36] indicated that the stable electrides are resistant to thermal decomposition at room temperature due to the absence of oxygen–carbon bond. And Li and co-workers found that the complexants with nitrogen-carbon bond are beneficial to design the stable high-performance nonlinear optical molecules with excess electron.

On the other hand, Li' s group investigated that the $\beta_0$ value of alkalides $Li^+(NH_3)_4M^-$ [30] with large flexibility $(NH_3)_4$ is about six times larger than that of the corresponding $Li^+$(calix[4]pyrrole)$M^-$ [29] with small flexibility calix[4]-pyrrole. It means that the complexant flexibility is another important factor in enhancing the hyperpolarizability.

The imidazoles of TIMA are like three blades of propeller connect with methyls by the C–C single bonds. Because of the three C–C single bond cooperative rotations, the TIMA behaves with great flexibility and also includes nitrogen–carbon bonds. So the deformation of flexible TIMA can enhance the alkali-metal-doping effect. Thus, in the present paper, the enhanced alkali-metal-doped effects on the structure and the first hyperpolarizability ($\beta_0$) for the effective tris[(2-imidazolyl)methyl]amine (TIMA) are studied for the first time. Obviously, under the action of the TIMA, the alkali metal atoms ionize and resemble $A_m^+$ with a Rydberg-like excess electron, [38] as shown in Fig. 3b (the HOMO plots). It shows that two classes of clusters have more electride-like characteristics. Surprisingly, because the enhanced chemical doping with alkali metal and the three C–C single bond cooperative rotations of TIMA, the K-TIMA sets a new record $\beta_0$ value to be 10,040,301 au which far exceeds (130–2718 times) that of reported high-performance NLO molecule [28, 31].

Further, considering simple possibility from molecule to material, the $\beta_0$ values of optimized Li-TIMA-dimer and Li-TIMA-tetramer are investigated. Results show that the ratio of $\beta_0$ value is about 1:2:4 for Li-TIMA-monomer, Li-TIMA-dimer, and Li-TIMA-tetramer. So the new three-propeller-blade-shaped electrides can be considered as candidates for potential high-performance nonlinear optical materials.

## 2 Computational details

The calculations have been performed by using the following procedure.

### 2.1 Structures and static NLO properties

The optimized structures of TIMA, $A_m$-TIMA ($A_m$ = Li, Na and K) with all real frequencies are obtained using the B3LYP/6-31G(d) level. The first hyperpolarizabilities are evaluated by a finite-field approach according to the Hartree–Fock theory (HF), performing hybrid DFT (BHandHLYP) and Møller Plesset perturbation [MP2(full)] methods. In our previous papers [24–33], the MP2 method has been chosen for calculating the first hyperpolarizability. Because the MP2(full) method is full-core electron correlation in MP2, which reproduces QCISD predictions of the first hyperpolarizability very closely [26], the MP2(full) $\beta_0$ values are used to discuss the structure–property relationships for single molecule.

Further, considering simple possibility from molecule to material, Li-TIMA-dimer and Li-TIMA-tetramer are optimized by B3LYP/6-31G(d) level, and their first hyperpolarizabilities are obtained by BHandHLYP method. Champagne and Nakano pointed out that for a medium-size system, p-quinodimethane, the BHandHLYP method can also reproduce the (hyper)polarizability values from the more sophisticated single, double, and perturbative triple excitation coupled-cluster [CCSD(T)] [19] method. In order to further test BHandHLYP result, the HF, CAM-B3LYP, and M05-2× are used to calculate the $\beta_0$ values of the Li-TIMA-monomer and Li-TIMA-dimer.

Unless otherwise indicated, all calculations made use of the Gaussian 03 suite of programs and the 6–31 + G (d) basis set is employed for the N, C and H atoms, and the 6–311 + G (3df) basis set for the Li, Na, and K atoms was used throughout.

For more details of the basis set effects on the first hyperpolarizability, readers are referred to Table S1 of the Supporting Information. The magnitude of the applied electric field is chosen as 0.001 au for the calculation of the hyperpolarizability, which is proven to be the most adequate value for the numerical differentiation. Additionally, the natural bond orbital (NBO) [39] charges are calculated at the MP2 level.

The dipole moment ($\mu_0$) and polarizability ($\alpha_0$) are defined as follows:

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

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

The static first hyperpolarizability is defined as:

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

where

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

### 2.2 Frequency-dependent NLO properties

The frequency-dependent NLO properties of the nitrogen edge-doped supershort single-walled carbon nanotubes were evaluated at the Coupled Perturbed Hartree-Fock (CPHF) level.

The frequency-dependent $\beta$ is defined as:

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

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

Except the M05-2× and CAM-B3LYP methods were used GAUSSIAN 09 program package [40]. All of the calculations were performed with the GAUSSIAN 03 program package [41]. The dimensional plots of molecular orbitals were generated with the GaussView program [42] (Gaussian, Inc. Pittsburgh, PA).

## 3 Results and discussions

### 3.1 Equilibrium geometries

The geometrical structures for TIMA and $A_m$-TIMA ($A_m$ = Li, Na and K) are shown in Fig. 1, and the important geometrical parameters are collected in Table 1. The alkali metal like diamond is inlaid into the center of three-propeller-blade-shaped TIMA like pendant of necklace. And the four N atoms near the doped alkali metal have two manners: N atom in the center of TIMA is denoted as $N_1$ and three $N$ atoms in the three bladed of TIMA are denoted as $N_{i\ (i\ =\ 2,\ 3,\ \text{and}\ 4)}$ (see Fig. 1).

How does the alkali-metal-doped effect influence the structure for the three-propeller-blade-shaped molecule TIMA?

The three imidazoles of TIMA like three blades of propeller can be rotated as three C–C single bond cooperative rotations; thus, the TIMA behaves great flexibility. From Fig. 1; Table 1, the $N_1$–$N_{i\ (i\ =\ 2,\ 3\ \text{and}\ 4)}$ bonds and $N_i$–$N_{j\ (i,\ j\ =\ 2,\ 3\ \text{and}\ 4;\ i\ \neq\ j)}$ bonds are decreased from 3.339 and 5.329 for TIMA to 2.877–2.994 and 3.582–4.256 for $A_m$-TIMA, respectively, due to the three C–C single bond cooperative rotations. The dihedral angles between the bladed planes (for example, the imidazole N2–C4–N5–C5–C6) and the plane $C_1$–$C_2$–$C_3$ are increased over 30° from acute angle 62° for TIMA to near right angle 93°–100° for $A_m$-TIMA ($A_m$ = Li, Na and K). Due to the alkali-metal-doped effect, three bladed planes (imidazoles) of TIMA are almost perpendicular to the plane $C_1$–$C_2$–$C_3$ (see Fig. 2). The changes of dihedral angles and N–N bonds lead to that the lone pair electron of N atom of imidazole closely surrounded the alkali metal atom.

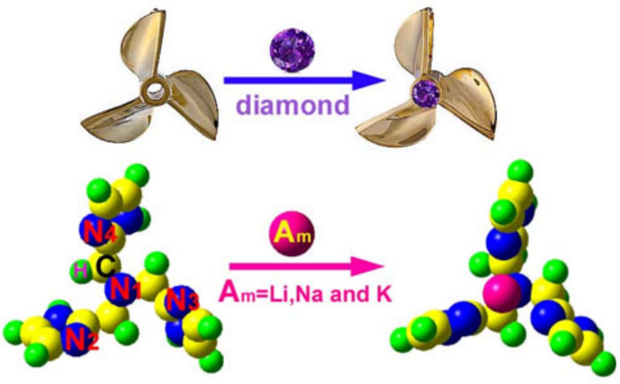

**Fig. 1** Geometrical structures for three propeller-blade-shaped molecules TIMA and $A_m$-TIMA ($A_m$ = Li, Na, and K) and their analogues

**Table 1** Selected geometrical parameters for three-propeller-blade-shaped complexant TIMA and electrides $A_m$-TIMA ($A_m$ = Li, Na, and K) at the B3LYP/6-31G (d) level

| | TIMA | $A_m$-TIMA | | |
|---|---|---|---|---|
| | | $A_m$ = Li | $A_m$ = Na | $A_m$ = K |
| $A_{mi}$–$N_1$(Å) | | 2.190 | 2.427 | 3.253 |
| $A_m$–$N_{2\ (3\ \text{and}\ 4)}$(Å) | | 2.077 | 2.393 | 2.915 |
| $N_1$–$N_{2\ (3\ \text{and}\ 4)}$(Å) | 3.339 | 2.877 | 2.994 | 2.980 |
| $N_i$–$N_{j\ (i,\ j=2,\ 3\ \text{and}\ 4;\ i\ \neq\ j)}$(Å) | 5.329 | 3.582 | 4.035 | 4.256 |
| $N_{2(3\ \text{and}\ 4)} - A_m - N_1$ | | 84.7 | 76.8 | 57.5 |
| Dihedral angle[a] | 62° | 96° | 100° | 93° |
| $v_1$ | 19.407 | 36.047 | 45.431 | 35.088 |

[a] Dihedral angle between the bladed plane (imidazole) $N_2$–$C_4$–$N_5$–$C_5$–$C_6$ and the plane $C_1$–$C_2$–$C_3$. (see Fig. 2)

Further, the calculated vibrational frequencies of the TIMA and $A_m$-TIMA ($A_m$ = Li, Na and K) are all positive; no imaginary frequencies are obtained, suggesting that they are located in the minimal point of each molecule potential energy surface (PES). The lowest vibrational frequency $v_1$ is also listed in Table 1. The results show that the $v_1$ of TIMA is assigned as the vertical rotation vibration mode of three-propeller blades, which show an increasing trend of the above-mentioned dihedral angle. For $A_m$-TIMA ($A_m$ = Li, Na and K), all of the $v_1$ are assigned as the stretching vibration mode of two-propeller blades. It can be concluded that $A_m$-TIMA ($A_m$ = Li, Na and K) should be stable molecules.

### 3.2 The NBO charges of $A_m^+$

An interesting relationship between the atomic number of doped alkali metal and the NBO charges of $A_m^+$ and $N^-$ is found: the order of NBO charges $A_m$: 0.2325 for $A_m$ = Li < 0.2483 for $A_m$ = Na > 0.1302 for $A_m$ = K. It is obvious that the TIMA cannot completely eject the

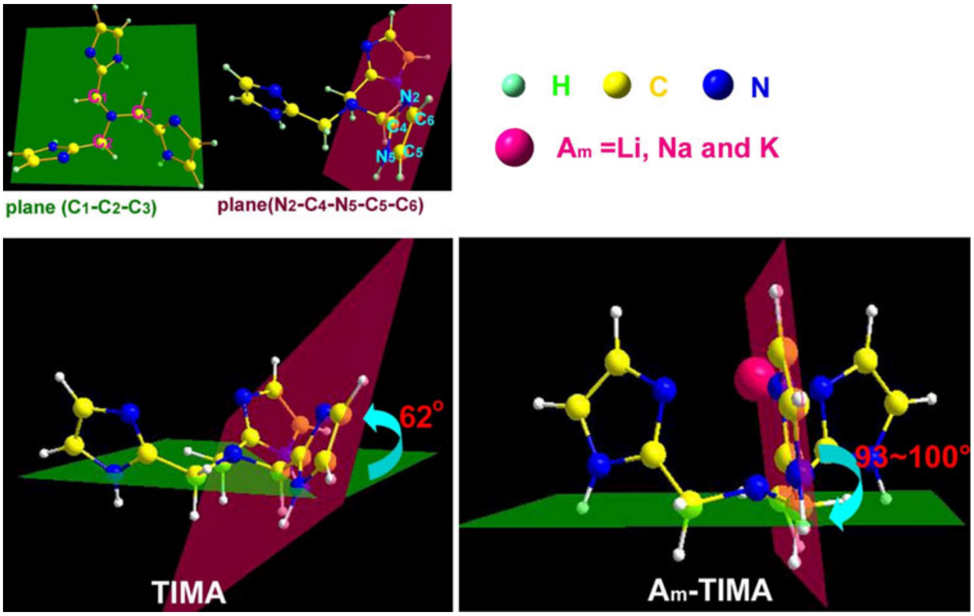

**Fig. 2** The dihedral angle between the bladed plane N2–C4–N5–C5–C6 and the plane C1–C2–C3 for TIMA and $A_m$-TIMA

electron from the Li atom because of the small electron affinity (0.60, 0.54, and 0.49 eV for the Li, Na, and K atoms, respectively) [43].

As shown in Fig. 3 (the HOMO plots), the alkali metal atoms (Li, Na and K) have big diffuse orbit and its valence electron is loosely bound in complexes. These complexes have the electride characteristics. So naturally, $A_m$-TIMA ($A_m$ = Li, Na and K) should have large first hyperpolarizability.

### 3.3 The static first hyperpolarizability

The electric properties of $A_m$-TIMA ($A_m$ = Li, Na and K) are calculated by the MP2(full) method are given in Table 2. From Table 2, the order of the $\beta_0$ values is 338 (for TIMA) $\ll$1,170,710 (for Li-TIMA) < 1,312,493 (for Na-TIMA) < 10,040,301 au (for K-TIMA). The alkali metal atom doping into the highly flexible TIMA greatly enhances the $\beta_0$ value by 3464–29705 times (see Fig. 4). Surprisingly, the K-TIMA sets a new record of $\beta_0$ value to be 10,040,301 au. It is significant to compare the $\beta_0$ values of $A_m$-TIMA ($A_m$ = Li, Na and K) to large $\beta_0$ value of the reported high-performance NLO systems. The $\beta_0$ value $1.00 \times 10^7$ au of K-TIMA ($A_m$ = Li, Na and K) is greatly larger than that (the range of the $\beta_0$ values is 3,385–76,978 au) of the known electrides Li@calix[4]pyrrole [28] and $Li_n$–H–$(CF_2$–$CH_2)_3$–H ($n$ = 1, 2) [31], and 1,234,171 au of large donor-CNT systems NT(6,0)–$(NH_2)_2$ [16], as well as 31,123 au of organometallic system Ru(trans-4,4′-diethylaminostyryl-2,2′-bipyridine)$_3^{2+}$ [44]. Clearly, the alkali-metal-doped effect on the first hyperpolarizability is very dramatic for the high-performance multi-nitrogen complexant TIMA.

Further, we have designed a simple model m-TIMA to explore the effect of structure on the $\beta_0$ value, where the geometry of m-TIMA is taken from the equilibrium geometry of Li-TIMA with the Li atom removed. Result shows that the $\beta_0$ value (351 au) of m-TIMA is very close to that (338 au) of TIMA. This means that the change of structure has only a small effect on the static first hyperpolarizability for the pure complexant. The deformation of TIMA leads to that the lone pair electron of N atom of imidazole closely surrounds the doping alkali metal atom. Due to the strong interaction between the complexant TIMA and alkali metal, the new electride $A_m$-TIMA has diffuse excess electron than the known electrides. It further testifies that the chemical doping with alkali metal and the great flexibility of complexant TIMA play dominantly roles for improving the static first hyperpolarizability.

Further, in order to find the controlling factors of huge first hyperpolarizability for the new three-propeller-blade-shaped electrides, the following two-level expression [45–48] is employed.

$$\beta_0 \propto \frac{\Delta\mu \cdot f_0}{\Delta E^3} \tag{5}$$

In the above expression, $\beta_0$ is proportional to the difference of dipole moment between the ground state and the crucial excited state ($\Delta\mu$) and the oscillator strength ($f_0$), but inversely proportional to the third power of the transition energy ($\Delta E$).

The $\Delta\mu$, $f_0$ and $\Delta E$ values for TIMA and $A_m$-TIMA ($A_m$ = Li, Na and K) are estimated by the CIS method with the 6–31 + G (d) basis set and are listed in Table 2. The CIS results show that crucial excited states are the HOMŌLUMO for Li-TIMA and HOMŌLUMO + 1 for

**Fig. 3** The crucial transitions (**a**) and the mechanism causing the excess electron of HOMO (**b**) for $A_m$-TIMA ($A_m$ = Li, Na, and K)

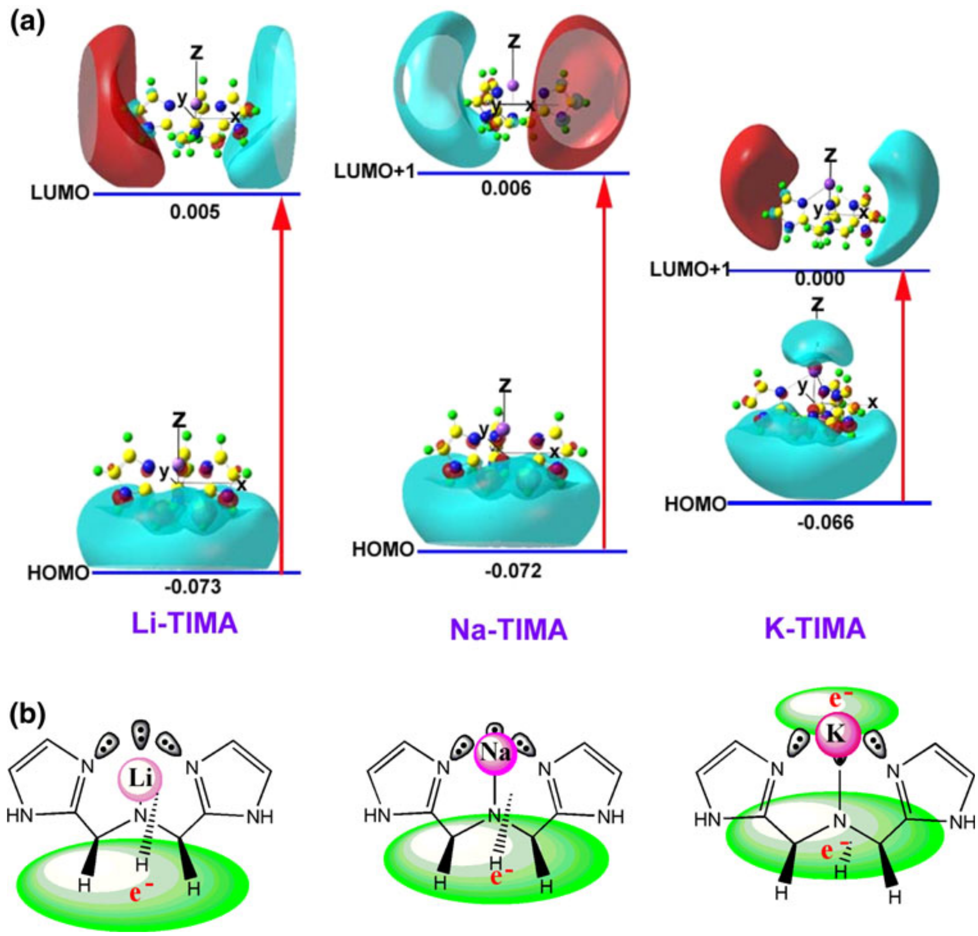

**Table 2** The first hyperpolarizability $\beta_0$ (au), the NBO charge of alkali atom ($A_m$), the transition energy $\Delta E$, the oscillator strength $f_0$ and the difference of dipole moment $\Delta\mu$ for three-propeller-blade-shaped complexant TIMA, electrides $A_m$-TIMA ($A_m$ = Li, Na and K) and model m-TIMA

| | TIMA | $A_m$-TIMA | | | m-TIMA |
|---|---|---|---|---|---|
| | | $A_m = $ Li | $A_m = $ Na | $A_m = $ K | |
| $\alpha_0$ | 184 | 2,284 | 2,170 | 3,761 | 149 |
| HF $\beta_0$ | 169 | 1,420,644 | 1,474,370 | 13,779,768 | 140 |
| BHandHLYP $\beta_0$ | 315 | 435,521 | 486,675 | 985,006 | 329 |
| MP2(full) $\beta_0$ | 338 | 1,170,710 | 1,312,493 | 10,040,301 | 351 |
| Enhancement factor | 1 | 3,464 | 3,883 | 2,9705 | 1 |
| $f_0$ | 0.225 | 0.316 | 0.315 | 0.443 | 0.215 |
| $\Delta E$ (eV) | 6.658 | 0.517(0.581)[a] | 0.556 | 0.506 | 6.325 |
| $\Delta\mu$ (Debye) | 0.819 | 1.174 | 1.604 | 10.381 | 0.130 |
| $\frac{\Delta\mu \cdot f_0}{\Delta E^3}$ | 0.0006 | 2.694 | 2.934 | 35.432 | 0.0001 |
| $A_m^+$ | | 0.232 | 0.248 | 0.130 | |

[a] At the CASSCF(3, 5)/6–31 + g(d) level

Na-TIMA and K-TIMA. These HOMO and the related unoccupied molecule orbitals are shown in Fig. 3a. Clearly, the electron invoked in the crucial excited state is in the HOMO, which is the diffuse s electron of the alkali metal atom. Under the action of the lone pairs of three N atoms in the three imidazoles, the 2s and 3s electrons of the Li and Na atoms are ejected out as the excess electrons for the Li-TIMA and Na-TIMA, respectively. In these cases, the excess electrons locate down the TIMA. Interestingly, the excess electron of K-TIMA is composed by two sections, one locate up K atom and other one down the TIMA. The Fig. 3b depicts this mechanism clearly. So these interactions between excess electron and the alkali metal core are more weakened.

To confirm the CIS results, the complete-active-space self-consistent-field (CASSCF) method is employed to

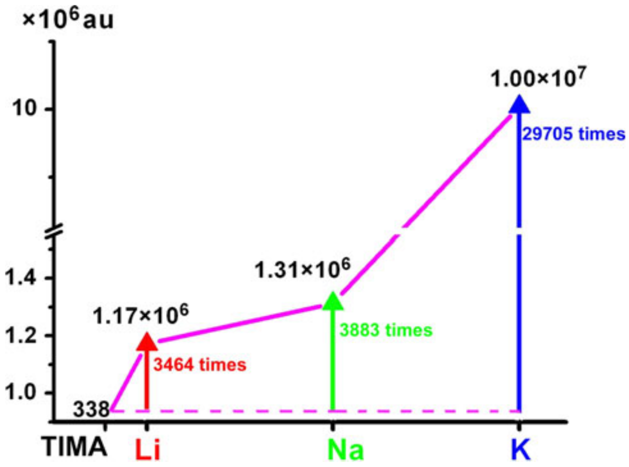

**Fig. 4** The static first hyperpolarizabilities ($\beta_0$) for TIMA and $A_m$-TIMA ($A_m$ = Li, Na, and K)

calculate the excited states of Li-TIMA. Data are given in Table 2. In Table 2, the transition energy of Li-TIMA is 0.581, which is very close to that of the CIS result (0.517 eV).

Interestingly, owing to the enhanced alkali-metal-doped effect, the $\Delta E$ is greatly decreased from 6.6578 (TIMA) to 0.5061–0.5562 eV ($A_m$-TIMA), which are smaller than that (1.295–1.982 eV) of the known electrides Li@calix[4]pyrrole [28], $(HCN)_nLi$ [26], and $Li_n$–H–$(CF_2$–$CH_2)_3$–H ($n = 1, 2$) [31]. Among the three electrides, the K-TIMA has the smallest $\Delta E$ and the largest $\Delta\mu$ in its crucial transition, which helps explain why the K-TIMA has a new record $\beta_0$ value to be 10,040,301 au.

From Table 2, the order of the $\frac{\Delta\mu \cdot f_0}{\Delta E^3}$ value is 0.0006 for TIMA ≪ 2.694 for Li-TIMA < 2.934 for Na-TIMA ≪ 35.432 for K-TIMA. Significantly, two relationships between the structure and $\frac{\Delta\mu \cdot f_0}{\Delta E^3}$value are shown: 1. The alkali metal atom doping into the three-propeller-blade-shaped molecule TIMA with higher flexibility greatly enhances the $\frac{\Delta\mu \cdot f_0}{\Delta E^3}$ value. 2. The $\frac{\Delta\mu \cdot f_0}{\Delta E^3}$ values increases with the increase in the atomic number of the doped alkali metal ($A_m$) for three-propeller-blade-shaped electrides $A_m$-TIMA ($A_m$ = Li, Na, and K). Naturally, the interesting relationships between the structure and $\beta_0$ value are explained by Eq. 5.

**Table 3** The first hyperpolarizability $\beta_0$ (au) for three-propeller-blade shaped electrides: Li-TIMA, Li-TIMA-dimer, and Li-TIMA-tetramer

| Method | Li-TIMA | Li-TIMA-dimer | Li-TIMA-tetramer |
|---|---|---|---|
| HF | 1,420,644 | 2,885,998 | |
| M05-2× | 487,529 | 1,729,096 | |
| camb3lyp | 159,801 | 1,190,545 | |
| BHandHLYP | 435,521 | 1,182,699 | 2,552,366 |

**Table 4** The estimated CPHF frequency-dependent $\beta$ ($-\omega$; $\omega$, 0), $\beta$ ($-2\omega$; $\omega$, $\omega$) values for Li-TIMA and Li-TIMA-dimer

| | $\omega$ (au) | Li-TIMA | Li-TIMA-dimer |
|---|---|---|---|
| $\beta$ ($-\omega$; $\omega$, 0) | 0.0 | 1,479,320 | 2,726,842 |
| | 0.005 | 1,615,576 | 3,632,968 |
| | 0.01 | 2,216,507 | 12,942,012 |
| | 0.0239 | 1,767,355 | 189,352,829 |
| $\beta$ ($-2\omega$; $\omega$, $\omega$) | 0.0 | 1,479,320 | 2,726,842 |
| | 0.005 | 1,726,586 | 6,642,600 |
| | 0.01 | 3,276,533 | 56,354,783 |
| | 0.0239 | 819,187 | 18,710,165 |

Further, considering simple possibility from molecule to material, the $\beta_0$ values of optimized Li-TIMA-dimer and Li-TIMA-tetramer (see Fig. 5) are investigated by BHandHLYP, HF, CAM-B3LYP, and M05-2× methods. All of the methods give some conclusion: the order of $\beta_0$ value is Li-TIMA-monomer < Li-TIMA-dimer < Li-TIMA-tetramer (Table 3).

On the other hand, the frequency-dependent $\beta$ values of the Li-TIMA and Li-TIMA-dimer were estimated using CPHF method. Moreover, the frequency-dependent $\beta$ values are provided in Table 4.

Note that the dispersion effect on the Li-TIMA is very strong. Compared with the large $\beta_0$ values of 1,479,320 au, the estimated frequency-dependent values $\beta$ ($-2\omega$; $\omega$, $\omega$) and $\beta$ ($-\omega$; $\omega$, 0) are 3,276,533 and 2,216,507 au, increasing by about 121 and 50% at $\omega = 0.01$ au, respectively. When $\omega$ is increased to 0.0239 au, the $\beta$

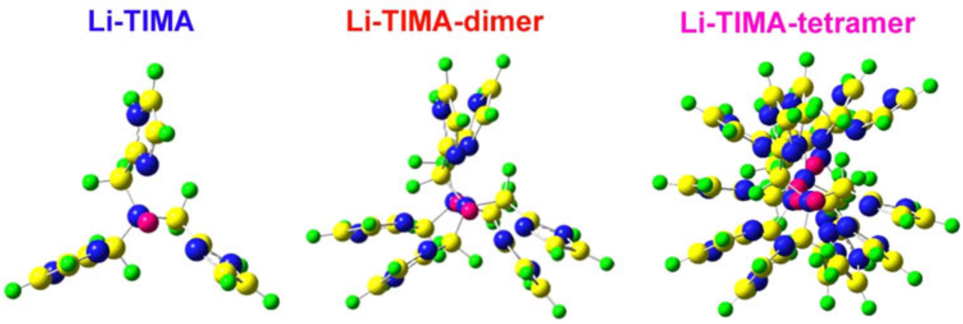

**Fig. 5** The structures for Li-TIMA, Li-TIMA-dimer, and Li-TIMA-tetramer

$(-2\omega; \omega, \omega)$ and $\beta$ $(-\omega; \omega, 0)$ are decreased to be 819,187 and 1,767,355, respectively.

Interestingly, the Li-TIMA-dimer also have larger $\beta$ $(-2\omega; \omega, \omega)$ of 56,354,783 and $\beta$ $(-\omega; \omega, 0)$ of 12,942,012 at $\omega = 0.01$ au. However, when $\omega$ is increased to 0.0239 au, the $\beta$ $(-2\omega; \omega, \omega)$ is decreased to be 18,710,165, and the $\beta$ $(-\omega; \omega, 0)$ is increased to be 189,352,829 au. Obviously, comparing the Li-TIMA, the frequency-dependent effect is the most obvious for Li-TIMA-dimer.

## 4 Conclusion

In the present work, we have obtained a valuable description of the first hyperpolarizabilities of $A_m$-TIMA ($A_m$ = Li, Na, and K). It indicates that the alkali metal $A_m$ doped into higher flexible TIMA to form engaging three-propeller-blade-shaped electrides with diffuse excess electron, which have very low-lying excited states to bring such huge $\beta_0$ value. The $\beta_0$ values of new three-propeller-blade-shaped electrides $A_m$-TIMA are greatly larger (3,464−29,705 times) than those of TIMA. Specially, the K-TIMA sets a new record $\beta_0$ value to be 10,040,301 au which exceeds than that of the reported NLO molecule. Further, considering simple possibility from molecule to material, results show that the order of $\beta_0$ value is Li-TIMA-monomer < Li-TIMA-dimer < Li-TIMA-tetramer.

As a result, our investigation may evoke one's attention to design new three-propeller-blade-shaped electrides as candidates for high-performance nonlinear optical materials.

**Acknowledgments** This work was supported by the National Natural Science Foundation of China (No. 20773046, 20703008, and 21003019), and Chang Jiang Scholars Program (2006), Program for Changjiang Scholars and Innovative Research Team in University (IRT0714), Science Foundation of Young Teachers of Northeast Normal University (20090402 and 09QNJJ008) and project supported by the Foundation for Young Scholars of Jilin Province, China (Grant No. 20100178 and 20100114).

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