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N-methylbenzoaza-18-crown-6-ether Derivatives as Efficient Alkali Metal Cations Sensors: the Dipole Moment and First Hyperpolarizability

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Abstract

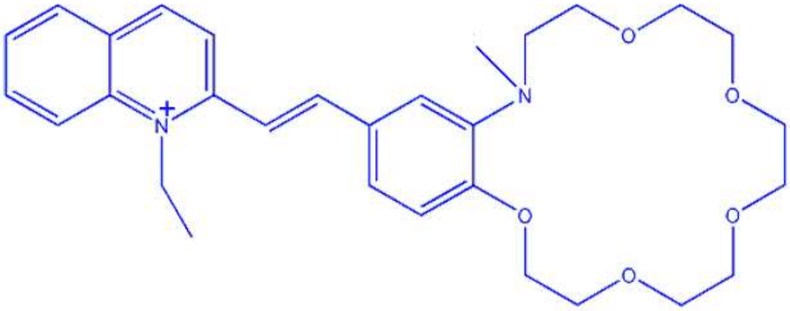
In this work, the **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ complexes formed by the N-methylbenzoaza-18-crown-6-ether derivatives (**1**) complexation with one alkali metal cation (**Li**$^+$, **Na**$^+$ and **K**$^+$**)** were investigated. Significantly, the dipole moments of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ enhance with increasing the atomic number. However, their first hyperpolarizabilities (β_0) decrease with increasing the atomic number. Further results show that the interaction energies increase in the order of **1-Li**$^+$> **1-Na**$^+$> **1-K**$^+$. Moreover, the transition energies of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ are inversely proportional to the β_0 values. Therefore, the interaction energy and transition energy are the major factor determining the β_0 values of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$. The combing large variations of the dipole moment and the first hyperpolarizability can be used as a detection sensor for alkali metal cations. It is our hope that this work will provide valuable knowledge for designing alkali metal cations sensors by electro-optical properties.

Introduction

The topical problem, regarding detecting cations, has attracted the attentions of chemists, clinical biochemists, toxicologists, and environmentalists.[1] Generally, the numerous analytical methods for cations recognition not only require samples with large size, but also do not allow continuous monitoring. However, the methods based on fluorescent sensors[2, 3] possess distinct advantages in terms of sensitivity, selectivity, response time and so on. Therefore, many efforts are being devoted to develop selective fluorescent sensors for detecting cations.[1, 4-8]

Crown ethers possess many remarkable attributes, but their most significant property is capable of selective binding of metal ions and neutral molecules, which has made them become a standard among supra-molecular host molecules.[9] After extensive studies on searching for different types of crown compounds for cation binding, the interest is gradually focused on crown ethers derivatives with a combination of O and N atoms as a part of the macrocycle.[10] Meanwhile the influence of the crown ethers sizes and constitution on the binding constant has been studied, showing that the binding constant is mainly dependent on the ratio of the crown ether ring size and the diameter of the cation. Later works discover that the K^+, Ca^{2+}, Na^+ and NH_4^+ are all bound more strongly by 18-crown-6 than by any other macrocycles.[11]

In terms of the application of azacrown ether fragments in photosensitive ligands, those compounds with the nitrogen atom conjugated with the chromophore are intriguing. Specially, derivatives of *N*-phenylazacrown ethers and 1-aza-2, 3-benzocrown ethers are of importance.[2,12-15] However, compared with benzocrown-ether-based analogues, the complexes of N-phenylaza-crown ethers with alkali and alkaline-earth metal cations have lower thermodynamic stability.[9,16] Many efforts have been done to resolve the dilemma.[13,17-22] Luckily, it was found that N-alkyl derivatives of benzoaza-crown ethers, with nitrogen directly connecting to the benzene ring, are favourable for the formation of complexes with the metal and ammonium cations.[22-23] Recently, a series of novel 2-benzothiazole-, 4-pyridine-, and 2- and 4-quinoline-based styryl dyes containing an N-methylbenzoaza-15(18)-crown-5(6)-ether moiety were synthesized, which have high performance as optical molecular sensors for alkali and alkaline-earth metal cations.[24] On the other hand, previous works have demonstrated that the cations recognition can be performed by probing the variation of the nonlinear optical (NLO) properties,[25-31] such as the theoretical investigation on NLO molecular switches of spiropyran/merocyanine systems as selective cations sensors for alkali, alkaline earth, and transition metals. Different cations produce the contrasts of β_0 values because of the first hyperpolarizability (β_0) depending strongly on the nature of the binding metal cations, which is the key for detecting cations.[32]



Scheme 1 Structure of N-methylbenzoaza-18-crown-6-ether derivatives.

In this work, the parent N-methylbenzoaza-18-crown-6-ether derivatives (**1**) is shown in **Scheme 1**, and the electro-optical properties of **1** complexation with alkali metal cations (**Li**$^+$, **Na**$^+$ and **K**$^+$) have been investigated. Significantly, the large contrasts of the dipole moment and the first hyperpolarizability appear when **1** was complexation with alkali metal cations **Li**$^+$, **Na**$^+$ and **K**$^+$, which can therefore be used as detection sensor for alkali metal cations.

Computational methods

The geometric structures (**1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$) of the N-methylbenzoaza-18-crown-6-ether derivatives complexation with alkali metal cations were obtained from the experimental data (J. Org. Chem. 2013, 78, 9834-9847). On the basis of optimized geometric structures, the natural bond orbital (NBO) charge was performed with BHandHLYP/6-31+G*. Furthermore, the counterpoise (CP) procedure was used to calculate the interaction energy (E_{int}) qualitatively, which is calculated as the difference between the energies of the fragments and the sum of the energies of the monomers according to Equation (1).

$$E_{\mathrm{int}}(1\text{-M}) = E_{1\text{-M}}(X_{AB}) - [E_{1}(X_{AB}) + E_{\mathrm{M}}(X_{AB})] \quad (\mathrm{M}= \mathbf{Li^{+}}, \mathbf{Na^{+}} \text{ and } \mathbf{K^{+}}) \qquad (1)$$

The same basis set X_{AB} was used for the monomer and **1-Li**$^{+}$, **1-Na**$^{+}$ and **1-K**$^{+}$ complexes calculations. Choosing approximate theoretical methods of evaluating the NLO properties is important, because the hyperpolarizability depends on the choice of density functional (DFT) method employed. Because of the lack of experimental data of the first hyperpolarizability for our studied complexes, the theoretical results obtained with different DFT methods may ensure the reliability of present calculations. Therefore, the dipole moment, polarizability and first hyperpolarizability were performed using four DFT methods (BHandHLYP, CAM-B3LYP, LC-BLYP and M06-2X). At the same time, the transition properties including oscillator strength, transition energy and crucial transition were calculated with BHandHLYP method to explore the original reason of difference of the first hyperpolarizability. Further, based on the geometrical structure, the UV-Vis absorption spectra of 1-Li^{+}, 1-Na^{+} and 1-K^{+} were investigated by the time dependent (TD) BHandHLYP functional, and was processed by SWizard and OriginPro software.

The average dipole moment (μ_0) and polarizability (α_0) are noted as:

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

$$\alpha_0 = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \qquad (3)$$

The static first hyperpolarizability (β_0) is defined as follows:

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}} \qquad (4)$$

Where

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

All of the calculations were performed with Gaussian 09W program package.[33]

Results and discussion

1. Geometric structures

The geometric structures of **1-Li$^+$**, **1-Na$^+$** and **1-K$^+$** are shown in Figure 1, and important geometric parameters are listed in Table 1. From Figure 1, we can see that the alkali metal cations directly interact with the O and N atoms. For each alkali metal cation, the closest neighbors are four O atoms for **1-Li$^+$**, five O atoms for **1-Na$^+$** and six atoms (five O atoms and one N atom) for **1-K$^+$**, respectively. Demonstrated by the data shown in Table 1, the four O_n-Li^+ (n=2-5) distances of **1-Li$^+$** range between 1.992 to 2.139 Å, which are smaller than the distances of N_6-Li^+ (5.126 Å) and O_1-Li^+ (4.242 Å). For **1-Na$^+$**, the five O_n-Na^+ (n=1-5) distances are about 2.500 Å, which are smaller than the distance of N_6-Na^+ (3.083 Å). However, the five O_n-K^+ (n=1-5) distances and one N_6-K^+ of 1-K^+ are in a small range from 2.645 to 2.925 Å. Moreover, the average distance between the metal and the oxygen atom increases in the order of $Li^+ < Na^+ < K^+$, with enhancing the closest neighbors in combination, resulting in the deformation of geometric structures shown in Figure 1. Therefore we could speculate that the interesting geometric structures are induced by the crown ether cavity size and alkali metal cation diameter. The Li^+ has the smallest diameter, which enable to attract just four O atoms. While, the diameter of K^+ is appropriate for the cavity size of N-methylbenzoaza-18-crown-6-ether, and K^+ locates in the center of the N-methylbenzoaza-18-crown-6-ether.

Further, the interaction energies (E_{int}) between the alkali metal cations and the parent molecule were calculated and shown in Table 1. From Table 1, it can be seen that the E_{int} values are in the order of 1-Li$^+$ (79.45) >1-Na$^+$ (54.80) > 1-K$^+$ (35.61 kcal/mol), indicating the interaction between the alkali metal cations and the parent molecule weakens with the enhancement in the atomic number. The variation of E_{int} values could be mainly ascribed to the increasing average distance between the metal and the oxygen atom in the order of Li$^+$ < Na$^+$ < K$^+$. Additionally, the natural bond orbital (NBO) charges of **1-Li$^+$**, **1-Na$^+$** and **1-K$^+$** were calculated, and listed in Table 1. The NBO charge of Li in **1-Li$^+$** is 0.791 au, which is smaller than 0.831 au of Na in **1-Na$^+$** and 0.838 au of K in **1-K$^+$**. In other word, the alkali metal NBO charges of **1-Li$^+$**, **1-Na$^+$** and **1-K$^+$** enhance with increasing the average distances between the metal cations and the oxygen atom, as well closest neighbors.

2. Electro-optical properties.

The dipole moment (μ_0), polarizability (α_0) and first hyperpolarizability (β_0) were calculated with four DFT methods (BHandHLYP, CAM-B3LYP, LC-BLYP and M06-2X), given in Table 2 and Figure 2. From Figure 2, it can be seen that the μ_0 values obtained with LC-BLYP method are the smallest, while the μ_0 values obtained with BHandHLYP, CAM-B3LYP and M06-2X methods are almost same. Similar to the μ_0 values, the α_0 and β_0 values obtained with four DFT methods follow the same pattern (see Table 2). Significantly, followed by increasing the atomic number of the alkali metal, the μ_0, α_0 and β_0 values present three different trends. For example, the μ_0 values at BHandHLYP follow the order of **1-Li$^+$** (1.892) < **1-Na$^+$** (2.012) < **1-K$^+$** (3.188 Debye), indicating that μ_0 values enhance with increasing the atomic number of the alkali metal, which are caused by the variation of geometric structure when complexation with **Li$^+$**, **Na$^+$** and **K$^+$**. From Figure 2, one can see that the α_0 value of **1-Na$^+$** is slightly larger than those of 1-**Li$^+$** and 1-**K$^+$**. However, the effect on first hyperpolarizability becomes more striking with increasing the atomic number of the alkali metal. Moreover, the change of β_0 values is different from our previous works, with a conclusion that the β_0 values increase with increasing the atomic number of the alkali metal.[34-39] Figure 2 illustrates the relationship between β_0 values and different complexes, it is clear that the β_0 values of **1-Li$^+$**, **1-Na$^+$** and **1-K$^+$** decrease with increasing the atomic number of the alkali metal. For example, the order of β_0 values (BHandHLYP) is **1-Li$^+$** (11839) > **1-Na$^+$** (8734) > **1-K$^+$** (7829 au). On the other hand, it can be observed from the data in Table 2 that the β_x values of **1-Li$^+$** are small (changing from -66 to -119 au with four DFT methods), and the β_0 values are mainly decided by the β_y and β_z values. However, for 1-**Na$^+$** and **1-K$^+$**, the three directions (β_x, β_y and β_z) have the equal contributions to the β_0 values. It can be seen that the contrasts of μ_0 and β_0 values are larger than that of α_0 values. Moreover, there are great contrasts among the μ_0 and β_0 values of **1-Li$^+$**, **1-Na$^+$** and **1-K$^+$**. Therefore, the combining variations of the first hyperpolarizability and dipole moment can be used as the detecting sensor for alkali metal cations.

It has been suggested that the alkali metal cations can enhance the first hyperpolarizability by decreasing the transition energy of the crucial excited state. To further explain the difference of first hyperpolarizability, the well-known two-level model is utilized. In the expression, the β_0 is proportional to the oscillator strength (f_0) and the difference of dipole moment between the ground state and the crucial excited state (Δu), and is inversely proportional to the transition energy (ΔE). The transition properties were estimated with BHandHLYP method, displayed in Table 3. The UV-Vis spectra are shown in Figure 3 and the absorption maxima (λ_{max}) of **1-Li$^+$**, **1-Na$^+$** and **1-K$^+$** are summarized in Table 3. From Figure 3, it can be seen that the absorption maxima of **1-Li$^+$**, **1-Na$^+$** and **1-K$^+$** produce blue-shift with increasing the atomic number of the alkali metal, which are 391nm for**1-Li$^+$**, 382nm for **1-Na$^+$** and 375nm for **1-K$^+$**, respectively. At the same time, as shown in Table 3 and Figure 4, the corresponding Δ*E* values of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ enhance with increasing the atomic number of the alkali metal, and the order is **1-Li**$^+$ (3.172) < **1-Na**$^+$ (3.246) < **1-K**$^+$ (3.308ev). Based on the two-level model, the larger first hyperpolarizability is associated to systems with smaller excitation energy. Therefore, the Δ*E* is the major factor in producing the difference of first hyperpolarizability. Table 3 also reveals that the main transition is from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) for all complexes. Corresponding plots of HOMO and LUMO are illustrated in Figure S1, displaying the charge-transfer between HOMO and LUMO character from styryl to quinoline.

Conclusions

In summary, the geometric structure, natural bond orbital charge and electro-optical properties of the N-methylbenzoaza-18-crown-6-ether derivatives complexation with alkali metal cations (**1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$) were studied. Such conclusions are obtained.

(1) The results of geometric structure indicate: for each alkali metal cation, the closest neighbors are four O atoms for **1-Li**$^+$, five O atoms for **1-Na**$^+$ and six atoms (five O atoms and one N atom) for **1-K**$^+$, respectively. The average distance between the metal and the oxygen atom increases in the order of $Li^+ < Na^+ < K^+$, and the interaction energies are in the order of 1-Li$^+$ (79.45) >1-Na$^+$ (54.80) > 1-K$^+$ (35.61 kcal/mol),

(2) Interestingly, the electro-optical properties calculated with four different DFT methods show that the dipole moment (μ_0), polarizability (α_0) and first hyperpolarizability (β_0) present three different trends with increasing the atomic number of the alkali metal. The μ_0 values of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ enhance with increasing the atomic number of the alkali metal, and the α_0 value of **1-Na**$^+$ is slightly larger than those of **1-Li**$^+$ and **1-K**$^+$. However, the β_0 values of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$

decrease with increasing the atomic number of the alkali metal.

(3) Further, the UV-Vis spectra and crucial transition energy (Δ*E*) were calculated with BHandHLYP method. The results show that the absorption maxima of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ produce blue-shift with increasing the atomic number of the alkali metal, which are in the sequence of **1-Li**$^+$ (391) > **1-Na**$^+$ (382) > **1-K**$^+$ (375nm). Correspondingly, the Δ*E* values of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ are in the order of **1-Li**$^+$ (3.172) < **1-Na**$^+$ (3.246) < **1-K**$^+$ (3.308ev). Therefore, the crucial transition energy is the major factor in producing the difference of first hyperpolarizability.

Our work theoretically predicts the electric-optical properties of the N-methylbenzoaza-18-crown-6-ether derivatives complexation with alkali metal cations (**1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$), indicating the alkali metal cations recognition can be performed by the combining variation of the dipole moment and the first hyperpolarizability.

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Supporting Information

The equilibrium geometries and HOMO and LUMO plots of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ are given in supporting information.

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Table 1 Geometric parameters (Å) of **1-Li$^+$**, **1-Na$^+$** and **1-K$^+$**, the interaction energy E_{int} (kcal/mol) and the NBO charge (au) of alkali metal M, N_6 and N_7 of **1-Li$^+$**, **1-Na$^+$** and **1-K$^+$**.

	1-Li$^+$	1-Na$^+$	1-K$^+$
O_1-M[a]	4.242	2.600	2.891
O_2-M	2.114	2.505	2.645
O_3-M	2.012	2.598	2.827
O_4-M	2.139	2.522	2.813
O_5-M	1.992	2.409	2.832
N_6-M	5.126	3.083	2.925
E_{int}	79.45	54.80	35.61
q(M)	0.791	0.831	0.838

[a] See Figure 1

Table 2 Dipole moment (μ_0, Debye), polarizability (α_0, au) and the first hyperpolarizability (β_0, au) of **1-Li$^+$**, **1-Na$^+$** and **1-K$^+$** calculated with four density functional methods.

		1-Li$^+$	**1-Na$^+$**	**1-K$^+$**
BHandHLYP	μ_0	1.892	2.012	3.188
	α_0	409	414	409
	β_x	-88	4219	-3102
	β_y	-4611	1640	-2427
	β_z	10904	7469	-6766
	β_0	11839	8734	7829
CAM-B3LYP	μ_0	1.910	2.045	3.198
	α_0	416	420	416
	β_x	-103	4705	-3481
	β_y	-4893	1760	-2634
	β_z	11749	8321	-7560
	β_0	12727	9720	8730
M06-2X	μ_0	1.924	2.041	3.193
	α_0	417	421	416
	β_x	-119	4926	-3634
	β_y	-5125	1780	-2685
	β_z	12423	8676	-7824
	β_0	13439	10134	9035
LC-BLYP	μ_0	2.023	2.251	3.419
	α_0	390	397	393
	β_x	-66	3739	-2610
	β_y	-3513	1347	-1946
	β_z	8517	6600	-5630
	β_0	9214	7704	6503

Table 3 Oscillator strength (f_0), and transition energy (ΔE) and crucial transition. λ_{max} refers to the absorption maxima of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ in UV-Vis spectra.

	1-Li$^+$	**1-Na**$^+$	**1-K**$^+$
f_0	1.253	1.422	1.330
ΔE (eV)	3.172	3.246	3.308
Crucial transition	HOMO→LUMO	HOMO→LUMO	HOMO→LUMO
λ_{max}(nm)	391	382	375

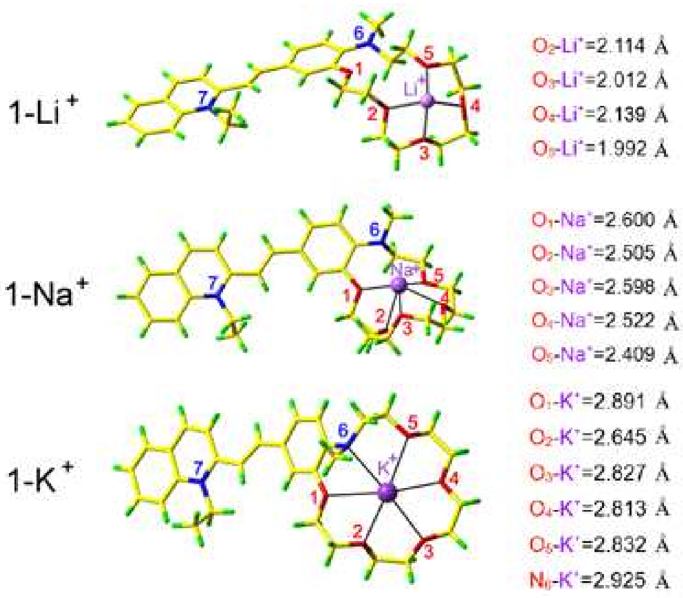

Figure 1 The geometric structures of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ from the experimental data. Color code: carbon (yellow), hydrogen (green), oxygen (red), nitrogen (blue), and the alkali metal cation (purple).

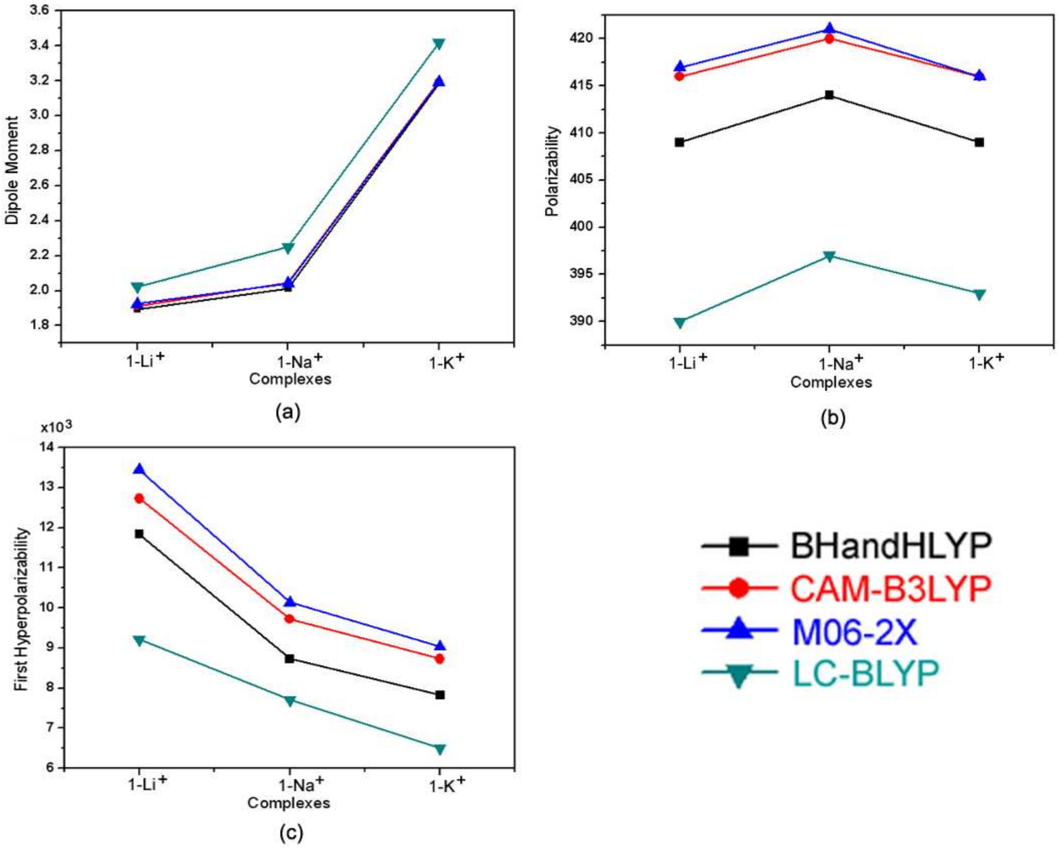

Figure 2 (a) Relationship between the dipole moment ($\mu_{0,}$ Debye) and **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ with four density functional methods. (b) Relationship between the polarizability ($\alpha_{0,}$ au) and **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ with four density functional methods. (c) Relationship between the first hyperpolarizability ($\beta_{0,}$ au) and **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ with four density functional methods.

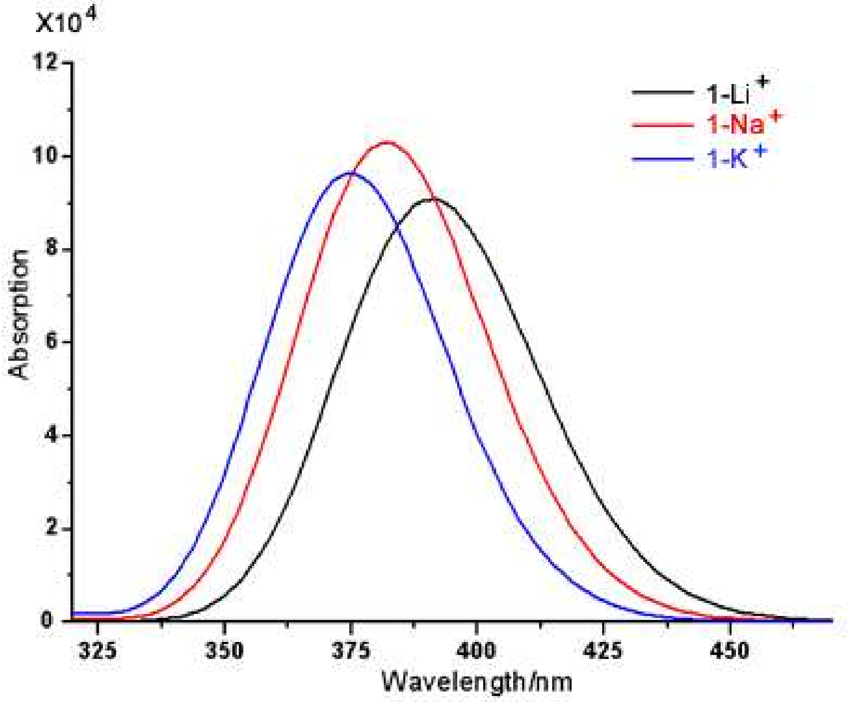

Figure 3 UV-Vis spectra of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ with BHandHLYP method.

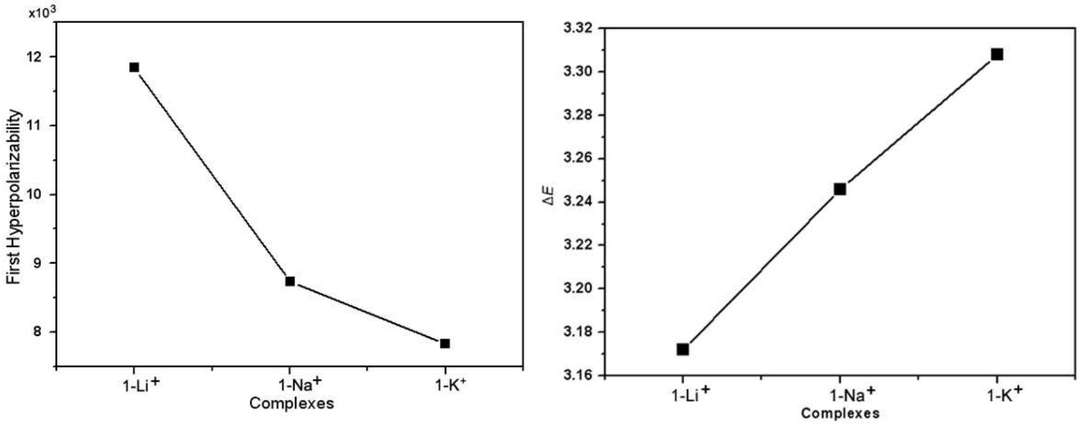

Figure 4 First hyperpolarizability ($\beta_{0,}$ au) and transition energy (ΔE, eV) of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ with BHandHLYP method.

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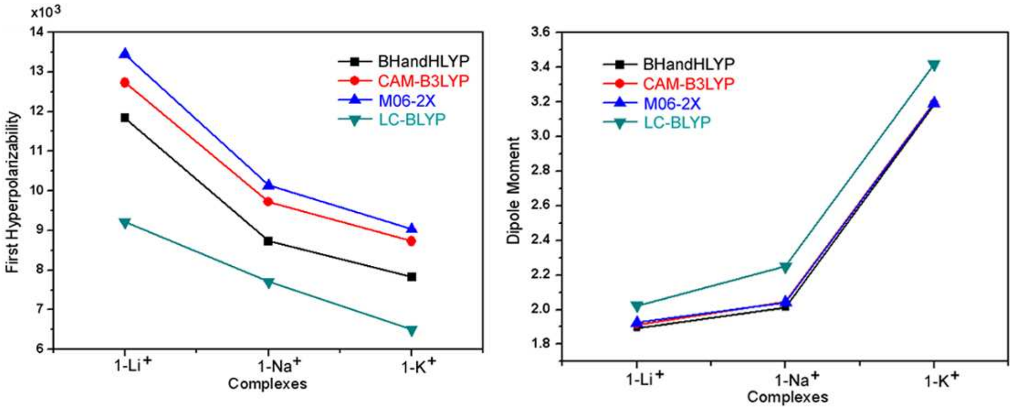

The **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ complexes formed by the N-methylbenzoaza-18-crown-6-ether derivatives (**1**) complexation with one alkali metal cation (**Li**$^+$, **Na**$^+$ and **K**$^+$**)** were investigated. The results show that the dipole moments (μ_0) of **1-Li**$^+$, **1-Na**$^+$ and **1-K**$^+$ enhance with increasing the atomic number. However, their first hyperpolarizabilities (β_0) decrease with increasing the atomic number. The combing variations of the dipole moment and the first hyperpolarizability can be used as a detection tool for alkali metal cations.