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Nonlinear Optical Properties of Alkalides Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K): Alkali Anion Atomic Number Dependence

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Since the past two decades, a great deal of work has been carried out to study the nonlinear optical properties (NLO) for many different types of NLO materials.[1] In our previous works,[2] we have proposed a method for designing high-performance NLO materials. We found that the systems with excess electrons have large NLO responses. The excess electron plays a crucial role to enhance the first hyperpolarizability (β) in the new type of NLO materials.

At present, "alkalides" and "electrides" are typical compounds with the excess electrons that have been synthesized in experiment. Electrides are a novel kind of ionic salt in which anionic sites are occupied solely by electrons.[3] In contrast to electrides, alkalides are another ionic salt where anionic sites are occupied by alkali anions (e.g., Na^-, K^-, Rb^-, or Cs^-).[4] As a result, the excess electron in the alkali anion ought to be loosely bound in space because of the small electron affinity of alkali atoms. Undoubtedly, these two types of compounds should assess the large NLO response because of the excess electrons.

It has been found that both the sole electron anion and the alkali anion can increase β due to lower transition energy of the crucial excited states.[2] However, there exists a significant difference between the sole electron anion and the alkali anion. The difference is that, besides the small transition energy, the alkali anions can have large oscillator strengths for the crucial excited states. For example, the calculated systems with the electride characteristic, including $(HCN)_nLi$, $Li(HCN)_n$[2c] and Li^+(calix[4]pyrrole)e^-,[2e] have an oscillator strength of about 0.2, while the oscillator strength of $AdzH^+Na^-$ [2d] is over 0.6. Clearly, these two crucial factors can significantly increase the NLO responses of the alkalides. Therefore, it can be expected that alkalides should have larger β values than those of electrides with the same cation.

In this work, we design a new type of alkalide compounds, Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K), which may be stable at room temperature. We exhibit the effect of the alkali anion on the enhancement of β compared to that of electride Li^+(calix[4]pyrrole)e^-, which has already been shown to have a considerably large β value.[2e] This work explores a new approach to enhance β in alkalide compounds by choosing alkali anions with larger atomic numbers.

It is well-known that the traditional organic alkalides are thermally unstable at room temperature because of the reductive cleavage of the C−O bond in conventional complexants. Therefore, the Dye group proposed a way to avoid the cleavage of the C−O bond for synthesizing the thermally stable alkalide compounds at room temperature.[5] At present, the compounds with the C−N bond are considered as promising complexants to form the room-temperature stable alkalide compounds. It should be mentioned that the room-temperature stable alkalides, K^+(aza222)Na^- and K^+(aza222)K^-, have been reported, in which "aza" is a nitrogen analogue of a cryptand.[6] Based on this fact, Li^+(calix[4]pyrrole)M^- may be stable at room temperature because calix[4]pyrrole containing the C−N bonds acts as the complexant.

The geometric structures with all real frequencies of Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K) are calculated using the density functional theory (DFT/B3LYP) with the 6-31G basis set. Their polarizability (α) and β are also obtained by the B3LYP method, in which the 6-311++G basis set is employed for the calix[4]pyrrole framework and the 6-311++G(3df) basis set is employed for the alkali atoms. Because the systems in this work are too large to allow a complete investigation of basis set effects, the 6-311++G basis set employed here is sufficient in reproducing hyperpolarizabilities as already investigated by Maroulis et al.[7] on the predictive capability of small sized basis sets. All the calculations in this work were carried out using the GAUSSIAN 03 program package.[8] In Li^+(calix[4]pyrrole)M^- with C_{4v} symmetry, the cation (Li^+) is located inside while the anion (M^-) is outside of the cuplike cryptand calix[4]pyrrole, as shown in Figure 1.

The α and β of Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K) are evaluated by numerical differentiation with an electric field magnitude of 0.001 au. The results of B3LYP, HF, and MP2 method are all summarized in Table 1. Comparing the β values from the different methods, it shows that the B3LYP method is valid in this work. As shown in Table 1 (the B3LYP results), the Li^+(calix[4]pyrrole)M^- molecules have considerably large (hyper)polarizabilities, which are $\alpha = 425$ au, $\beta = 8.9 \times 10^3$ au for M = Li; $\alpha = 451$ au, $\beta = 1.0 \times 10^4$ au for M = Na; and $\alpha = 588$ au, $\beta = 2.4 \times 10^4$ au for M = K. In our previous work,[2e] α and β of calix[4]pyrrole are determined only as 251 and 390 au, respectively. Obviously, doping the alkali atoms into the calix[4]pyrrole can greatly enhance the α and β of the system. Especially, the β values are enhanced by 20−60 times.

How are the β values of Li^+(calix[4]pyrrole)M^- enhanced when the alkali atoms are doped in the calix[4]pyrrole molecule? The simplest model to estimate the β value is the two-level model.[9] For the static case, the two-level expression is employed to estimate the value of β:

$$\beta \cong \frac{3\Delta\mu \cdot f_0}{2\Delta E^3} \qquad (1)$$

where ΔE, f_0, and $\Delta\mu$ are the transition energy, oscillator strength, and the difference in dipole moment between the ground state and the crucial excited state, respectively. In the two-level expression, the third power of the transition energy is inversely proportional to the β value. Therefore, for any noncentrosymmetric molecule, the low transition energy (<1 au) is the decisive factor for the large β.

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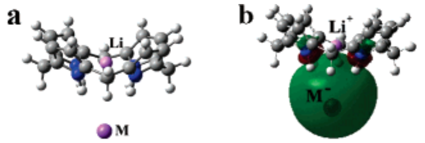

Figure 1. Structure (a) and HOMO (b) of the Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K) molecule. In (b), the M^- is formed as the excess electron cloud enwrapping the M atom.

Table 1. Distance between Li^+ and M^-, Polarizability (α), the First Hyperpolarizability (β), the Charge (q), and Other Quantities of the Crucial Transition of Li^+(calix[4]pyrrole)M^-

		Li^+(calix[4]pyrrole)M–		
properties		M = Li	M = Na	M = K
$R_{Li+ \cdots M-}$ (Å)		3.659	3.948	4.632
α (au)	DFT	425	451	588
	HF[a]	409	452	633
	MP2[a]	398	437	585
β (au)	DFT	8944	10 061	24 455
	HF[a]	14 233	19 358	52 540
	MP2[a]	10 969	14 772	35 934
q (Li^+)		0.7903	0.7939	0.7623
q (M^-)		−0.3303	−0.3614	−0.2533
$\Delta\mu$ (au)[b]		7.4	8.0	8.2
ΔE (eV)		2.293	2.235	1.757
λ (nm)		540.66	554.65	705.64
f_0		0.4798	0.4639	0.5405

[a] 6-31G for C, H atoms, 6-31+G for N atoms, and 6-311++G(3df) for the alkali atoms. [b] Estimated from the two-level expression.

The TD-DFT calculations are carried out to get the crucial excited states of Li^+(calix[4]pyrrole)M^-. The orbitals invoked in the crucial excited state are depicted in the Supporting Information. The ΔE and f_0 of the crucial excited states for three molecules are also listed in Table 1. From Table 1, one can see that the ΔE values of Li^+(calix[4]pyrrole)M^- are pretty small to be 2.293, 2.235, and 1.757 eV for M = Li, Na, and K, respectively. They are much smaller than that of calix[4]pyrrole (6.016 eV[2e]). Obviously, from eq 1, the smaller ΔE, the larger β of Li^+(calix[4]pyrrole)M^-.

Then, why do the Li^+(calix[4]pyrrole)M^- compounds have such small transition energies? As presented in Figure 1b, we find that, from the TD-DFT calculations, the electron invoked in the crucial excited state is in the HOMO, which is the diffuse s electron of the Li atom inside the calix [4]pyrrole. The lone pairs of four N atoms push out the 2s electron of the Li atom inside calix[4]pyrrole to form the excess electron and thus the electron is located in the diffuse s orbital. Its electron cloud enwraps the whole M atom and thus creates an M^-. The NBO calculations (see Table 1) show that the charges of the M atom are −0.33 for the Li atom, −0.36 for the Na atom, and −0.25 for the K atom. It is obvious that the alkali atom M cannot completely seize the 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).[10] As a result, this excess electron is diffuse and easily excited, so the transition energies of the crucial excited state for Li^+(calix[4]pyrrole)M^- are quite small. The ΔE of alkalides can be decreased by increasing the atomic number of the alkali anion. Among these three molecules, the ΔE of Li^+(calix[4]pyrrole)K^- is the smallest, and consequently, the β of Li^+(calix[4]pyrrole)K^- is the largest.

Next, we compare β values between electrides and alkalides. Comparing with the calculated Li^+(calix[4]pyrrole)e^- value at the same level, we find that the β values of Li^+(calix[4]pyrrole)M^- are much larger than that of Li^+(calix[4]pyrrole)e^- (β = 7326 au). Therefore, the sole electron of an electride replaced by the alkali anion M^- of an alkalides can effectively enhance β. According to the two-level model, we analyze each influencing factor that can increase β, including ΔE, $\times a6_0$, and $\Delta\mu$. We find that, besides the lower ΔE, the alkali anions cause the large $\times a6_0$ in each system. We find that all the f_0 values of the Li^+(calix[4]pyrrole)M^- molecules are over two times larger than that of Li^+(calix[4]pyrrole)e^-.

The β value (211×10^{-30} esu) of Li^+(calix[4]pyrrole)K^- is comparable to that (-240×10^{-30} esu) of the dicyanoquinodial system.[11] This will give hints to experimentalists in designing high performance NLO materials from alkalide systems.

In addition, we roughly estimate the $\Delta\mu$ values of four systems by a two-level expression (eq 1) and other known quantities. The $\Delta\mu$ values of these four systems are $\Delta\mu(e^-) = 9.2$, $\Delta\mu(Li^-) = 7.4$, $\Delta\mu(Na^-) = 8.0$, and $\Delta\mu(K^-) = 8.1$ au. It can be seen that there is no big difference in the $\Delta\mu$ values of these four systems. Therefore, in these systems, the ΔE and $\times a6_0$ are two principle factors for increasing β.

In summary, we designed a new type of alkalide compound with the cuplike complexant, Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K), which may be stable at room temperature. We find that this kind of compound with the alkali anion possesses the considerably larger first hyperpolarizability. The alkali anion plays a crucial role in the large β. And β increases as the atomic number of the alkali anion increases. Therefore, using the larger alkali anion in alkalide compounds is a new approach to obtaining a large β.

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Supporting Information Available: Complete ref 8 and the orbitals invoked in the crucial excited state for Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K). This material is available free of charge via the Internet at http://pubs.acs.org.

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