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On the Potential Application of Superalkali Clusters in Designing Novel Alkalides with Large Nonlinear Optical Properties

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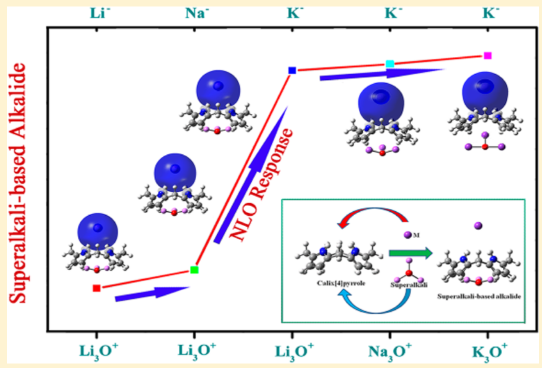
Supporting Information

ABSTRACT: A new series of superalkali-based alkalides, i.e., Li_3^+(calix[4]pyrrole)M^-, Li_3O^+(calix[4]pyrrole)M^-, and M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K), have been theoretically designed and investigated by means of density functional theory computations. These species have diverse structural isomers, in which the embedded superalkali units maintain their identities and prefer the horizontal orientation over the vertical one. All the proposed alkalides exhibit considerable first hyperpolarizabilities (β_0) up to 34 718 au. Especially, a prominent M^- atomic number dependence of (hyper)polarizabilities is observed for the Li_3^+(calix[4]pyrrole)M^- and Li_3O^+(calix[4]pyrrole)M^- compounds. Besides, the dependence of the nonlinear optical response of such alkalides on the species of involved superalkalis is also investigated. We hope that this work will promote further application of superalkalis and, on the other hand, attract more research interest and efforts in exploring new, unconventional alkalides.



1. INTRODUCTION

Superalkalis[1] are a dominant subset of superatoms[2,3] exhibiting behaviors reminiscent of alkali metal atoms. Such species are characterized by lower ionization potentials (IPs) than those (5.4−3.9 eV)[4] of alkali metal atoms and thereby can donate one electron to the other molecules and exist in the form of cations. Especially, they can be used in the synthesis of unusual charge-transfer salts with the counterpart possessing relatively low electron affinity.[5,6] Superalkalis have been found to preserve their identities like an atom when assembled into compounds;[7−10] hence, they offer the exciting prospect of serving as building blocks for new materials with tunable properties. Because of these features, superalkalis have been of great interest and a large number of new superalkali species have been reported in recent years.[11−14]

Alkalides are crystalline salts that contain complexed cations, with charge balance provided by alkali metal anions.[15] Because of their unusual electronic features, alkalides have been widely studied since the first synthesis and structure determination of Na^+(cryptand-[2.2.2])Na^-.[16,17] In 1999, two room-temperature stable alkalides were successfully synthesized by Dye and coworkers,[18] which indicated the application prospect of these unique compounds. It has been demonstrated that the systems containing diffuse electrons usually have large nonlinear optical (NLO) responses.[19−25] As alkalides are typical compounds with loosely bound electrons, they have attracted our great attention.[26−32] In 2006, Chen et al.[26] have theoretically designed a kind of alkalides, i.e., Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K), which are found to possess considerable first hyperpolarizabilities (β_0) of 8944−24 455 au at the B3LYP level. Later, the NLO properties of the Li^+(calix[4]pyrrole)Li^- dimer, trimer, and polymer have been theoretically studied, and it is demonstrated that introducing more alkali metal anions into the alkalides will be an important strategy for improving their NLO responses.[27] More recently, the substituent effect on the NLO properties of Li^+(calix[4]pyrrole)Li^- has been systemically investigated.[28] The authors demonstrate that electron-donating substituents help to enhance the first hyperpolarizability of Li^+(calix[4]pyrrole)Li^-, whereas electron-withdrawing substituents have the opposite effect. In addition, endeavors have also been devoted to studying the NLO properties of various alkalides with other complexants, such as flexible ammonia complexants,[29,30] adamanzane[31] and H_5Azacryptand[2.2.2][32] cage complexants, etc.

It can be noticed that almost all the previously investigated alkalides are alkali-metal-based; that is, the excess electrons of the anions are derived from the encapsulated alkali metal atoms in complexants. In 2002, Redko et al.[33] synthesized a sodide in which an encapsulated proton serves as the cation. Later, they reported another successful attempt to synthesize a barium-based sodide with the stoichiometry Ba^{2+}(H_5Azacryptand-[2.2.2]$^-$)$Na^-\cdot 2MeNH_2$.[34] These works further broadened the research field of alkalides. The interesting electronic features of alkalides and superalkali clusters as well as the extensive studies on them prompt us to consider the following questions: As the superalkalis have similar chemical characteristics to alkali metal atoms, can superalkali clusters be encapsulated into certain

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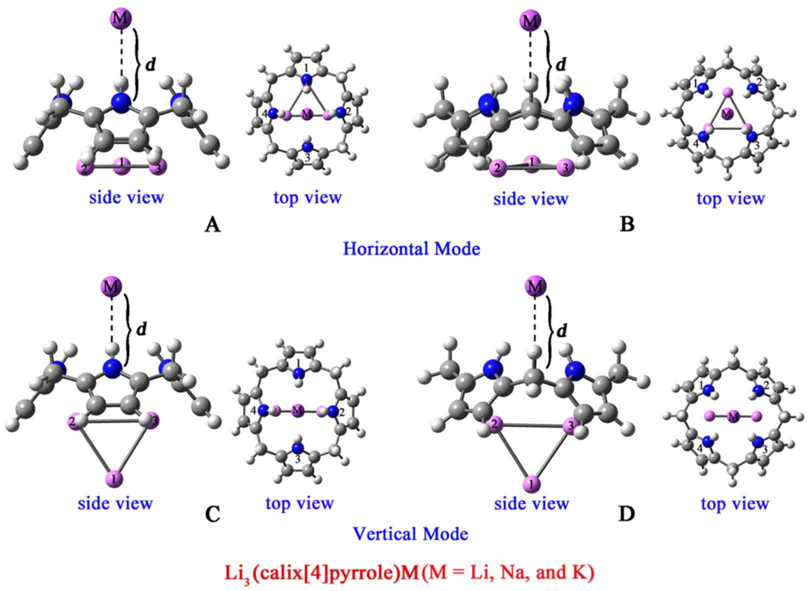

Figure 1. Geometric structures of the Li_3(calix[4]pyrrole)M (M = Li, Na, and K) compounds. The capital letters **A**–**D** represent the four isomers whose energies increase in the order **A** < **B** < **C** < **D**.

complexants to construct novel alkalides? If this way is workable, do these superalkali-based alkalides have various structures and considerable NLO responses? Does the NLO response of such systems depend on the species of involved superalkalis? Lately, we have attempted to design a series of alkalides involving superalkali Li_3,[35] namely, $Li_3(NH_3)_nNa$ (n = 1−4).[36] However, the ammonia complexants are too small to completely enwrap the Li_3 cluster, so the resulting Li_3^+ cation and Na^- anion tend to bind each other and form a Li_3Na cluster in almost all the structures of $Li_3(NH_3)_nNa$. As a result, the NLO responses of these Li_3-based alkalides are much smaller than those of traditional alkalides $Li(NH_3)_nNa$ (n = 1−4).[29]

In the present work, we designed and studied a new class of superalkali-based alkalides, namely, Li_3^+(calix[4]pyrrole)M^-, Li_3O^+(calix[4]pyrrole)M^-, and M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K). Herein, two kinds of superalkalis, i.e., Li_3 and M_3O (M = Li, Na, and K),[35,37−41], were inserted into the larger calix[4]pyrrole complexant, respectively. More conformations were obtained for the investigated species compared with the traditional Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K)[26] alkalides. In these systems, both Li_3 and M_3O exhibit the electronic characteristics resembling a single alkali metal atom. All the proposed species possess the typical alkalide characteristics and exhibit considerable NLO properties. Especially, the first hyperpolarizability (β_0) of the most stable K_3O^+(calix[4]pyrrole)K^- is as large as 34 718 au, which is much larger than that of alkali-metal-based Li^+(calix[4]pyrrole)K^-. In addition, these nonconventional alkalides possess larger complexation energies compared with the corresponding Li^+(calix[4]pyrrole)M^- alkalides. These results reveal that the superalkalis may be superior candidates for designing alkalides with large NLO responses. Besides, the diversity of superalkalis contributes to expanding the research field of alkalides. Therefore, it is highly desired to obtain more superalkali-based alkalides containing various superalkalis and complexants.

2. COMPUTATIONAL DETAILS

A new density functional, Coulomb-attenuated hybrid exchange−correlation functional (CAM-B3LYP) has recently been developed for long-range interaction and charge-transfer systems.[42,43] It has been previously reported that CAM-B3LYP can provide not only molecular geometries close to experimentally observed structures but also the (hyper)polarizabilities close to those of coupled cluster calculations.[44] Besides, CAM-B3LYP has been proven to be efficient for calculating the (hyper)polarizabilities of Li^+(calix[4]pyrrole)Li^-.[28] Hence, the CAM-B3LYP method, with satisfactory performance in both quality and efficiency, is a good choice to explore the static (hyper)-polarizabilities of currently studied systems. In the present work, the optimized geometric structures of the Li_3(calix[4]pyrrole)M, Li_3O-(calix[4]pyrrole)M, and M_3O(calix[4]pyrrole)K (M = Li, Na, and K) compounds with real frequencies were obtained under the CAM-B3LYP level with the 6-31+G(d) basis set. As for the calculation of the static electric properties, the CAM-B3LYP/6-311++G(d, p) method was employed.

The static mean polarizability (α_0) and mean first hyperpolarizability (β_0) are defined as follows

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

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

where $\beta_i = {}^3/_5(\beta_{iii} + \beta_{ijj} + \beta_{ikk})$, $i, j, k = x, y, z$.

The mean dipole moment (μ_0) is expressed as

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (3)$$

The natural bond orbital (NBO) analysis[45] and vertical ionization energies (VIEs) calculation were also performed at the CAM-B3LYP/6-311++G(d, p) level. The time-dependent density functional theory (TD-DFT) calculations were performed to get the transition energies (ΔE) of the crucial excited states (the excited state with the largest oscillator strength) for these proposed compounds at the TD-CAM-B3LYP/6-311++G(d, p) level. Besides, the complexation energies (E_c) of superalkali(calix[4]pyrrole)M, defined as $E_c = E$[superalkali(calix-[4]pyrrole)M] − E(superalkali) − E(M) − E(calix[4]pyrrole), were calculated at the CAM-B3LYP/6-311++G(d, p) level. We used the counterpoise procedure[46] to eliminate the basis set superposition error (BSSE) effect given as follows[47]

Table 1. Relative Energies (E_{rel}, in kcal/mol), Symmetry Groups, Li1−Li2(3) and Li2−Li3 Bond Lengths (in Å), Li2−Li1−Li3 Angles and N1−N2−N3−N4 Dihedral Angles (in deg), the Approximate Distances between M and the N1−N2−N3−N4 Plane (d, in Å), and Complexation Energies (E_c, in kcal/mol) of the Li_3(calix[4]pyrrole)M (M = Li, Na, and K) Compounds

compounds	isomers	E_{rel}	symmetry	$L_{Li1-Li2(3)}$	$L_{Li2-Li3}$	∠Li2Li1Li3	$D_{N1-N2-N3-N4}$	d	E_c
Li_3(calix[4]pyrrole)Li	**A**	0.00	C_s	2.807	2.987	64.3	0.1	3.256	−62.20
	B	0.28	C_s	2.915	2.781	57.0	0.0	3.263	−62.30
	C	4.74	C_{2v}	2.904	3.143	65.5	1.4	3.241	−57.78
	D	9.33	C_{2v}	2.934	3.225	66.7	0.0	3.314	−53.39
Li_3(calix[4]pyrrole)Na	**A**	0.00	C_s	2.806	2.978	64.1	0.2	3.469	−59.06
	B	0.18	C_s	2.913	2.778	57.0	0.0	3.465	−59.30
	C	4.74	C_{2v}	2.906	3.136	65.3	1.5	3.505	−54.61
	D	9.05	C_{2v}	2.934	3.223	66.6	0.0	3.499	−50.72
Li_3(calix[4]pyrrole)K	**A**	0.00	C_s	2.804	2.975	64.1	0.1	4.142	−50.91
	B	0.24	C_s	2.909	2.772	56.9	0.0	4.135	−51.13
	C	4.72	C_{2v}	2.908	3.142	65.4	1.4	4.128	−46.57
	D	9.03	C_{2v}	2.937	3.236	66.9	0.0	4.181	−42.86

Table 2. NBO Charges on M (Q_M), Li1 (Q_{Li1}), Li2 (Q_{Li2}), and Li3 (Q_{Li3}) Atoms and the Sum of Charges on Li_3 (Q_{sum}) as Well as VIE Values (in eV) of the Li_3^+(calix[4]pyrrole)M^- (M = Li, Na, and K) Compounds

compounds	isomers	Q_M	Q_{Li1}	Q_{Li2}	Q_{Li3}	Q_{sum}	VIE
Li_3^+(calix[4]pyrrole)Li^-	**A**	−0.302	0.093	0.279	0.279	0.651	4.252
	B	−0.330	0.310	0.157	0.157	0.624	4.229
	C	−0.312	0.293	0.171	0.171	0.635	4.226
	D	−0.413	0.256	0.181	0.181	0.618	4.153
Li_3^+(calix[4]pyrrole)Na^-	**A**	−0.344	0.101	0.276	0.276	0.653	4.163
	B	−0.368	0.303	0.160	0.160	0.623	4.150
	C	−0.355	0.298	0.166	0.166	0.630	4.131
	D	−0.454	0.257	0.181	0.181	0.619	4.067
Li_3^+(calix[4]pyrrole)K^-	**A**	−0.260	0.098	0.274	0.274	0.646	3.628
	B	−0.286	0.298	0.158	0.158	0.614	3.626
	C	−0.268	0.295	0.163	0.163	0.621	3.590
	D	−0.387	0.251	0.181	0.181	0.613	3.539

$$E_c = E_{ABC}(X_{ABC}) - E_A(X_{ABC}) - E_B(X_{ABC}) - E_C(X_{ABC}) \quad (4)$$

where the whole basis set, X_{ABC}, was used for the subunit energy (E_A, E_B, and E_C) calculations.

All the calculations were performed by using the Gaussian 09 program package.[48] Dimensional plots of molecular configurations and orbitals were generated with the GaussView program (Gaussian, Inc. Pittsburgh, PA).

3. RESULTS AND DISCUSSION

3.1. Li_3^+(calix[4]pyrrole)M^- (M = Li, Na, and K).

3.1.1. Geometrical Characteristics. To get the equilibrium structures of Li_3(calix[4]pyrrole)M (M = Li, Na, and K), a lot of initial structures were considered. Finally, four types of resulting conformations have been obtained and are shown in Figure 1. The relative energies, selected geometrical parameters, and complexation energies of these Li_3(calix[4]pyrrole)M species are listed in Table 1.

As shown in Figure 1, the framework of calix[4]pyrrole (CP) is hardly changed upon introducing M and Li_3. From Table 1, it can be seen that the four N atoms of CP in these Li_3(calix[4]pyrrole)M compounds are nearly coplanar as the N1−N2−N3−N4 dihedral angles are only 0.0−1.5°. As shown in Figure 1, each Li_3(calix[4]pyrrole)M (M = Li, Na, and K) possesses four conformations whose energies increase in the order **A** < **B** < **C** < **D**. On the basis of the side view of these structures, the Li_3 ring has two kinds of orientations, which are designated as horizontal (**A**, **B**) and vertical (**C**, **D**) modes, respectively. Thus, the former mode is superior to the latter one for constituting a stable Li_3(calix[4]pyrrole)M compound. It is also noted that the Li_3 cluster in each Li_3(calix[4]pyrrole)M isomer is obviously far from the N1−N2−N3−N4 plane compared with the position of Li^+ in Li^+(calix[4]pyrrole)M^-.[26]

As shown in Table 1, structures **A** and **B** have C_s symmetries while **C** and **D** possess C_{2v} symmetry groups. In all the Li_3(calix[4]pyrrole)M (M = Li, Na, and K) compounds, the Li_3 units preserve their isosceles triangle structures. For comparison, the optimized structure of the isolated Li_3 cluster was also obtained at the CAM-B3LYP/6-31+G(d) level and is shown in Figure S1 in the Supporting Information. It is found that the bond lengths of 2.804−2.937 Å for Li1−Li2 and Li1−Li3 bonds in Li_3(calix[4]pyrrole)M are a little longer than those of 2.766 Å for isolated Li_3, whereas the Li2−Li3 bond lengths in Li_3(calix[4]pyrrole)M are shortened by 0.141−0.605 Å compared with that of 3.377 Å for isolated Li_3. Therefore, the Li_3 cluster shows a tendency to transform itself into an equilateral triangle in the Li_3(calix[4]pyrrole)M compounds, especially in isomers **A** and **B**. This is also reflected by the apex angles ∠Li2Li1Li3 of 56.9−66.9° in these Li_3(calix[4]pyrrole)-M species, which are much smaller than that of 75.2° for isolated Li_3 and close to that of 60° for a regular triangle.

It is also discerned that the structures of Li_3 units in the CP cryptands are hardly affected by the upper M atom. From Table 1, it is worth noting that the Li_3 units in the similar structures possess nearly the same geometrical parameters. For instance, the Li1−Li2 and Li2−Li3 bond lengths of the most stable Li_3(calix[4]pyrrole)M (M = Li, Na, and K) series are 2.804−

2.807 and 2.975−2.987 Å, respectively, and the ∠Li2Li1Li3 angles of them are 64.1−64.3°. On the other hand, the orientation of Li_3 has little effect on the position of the upper M atom. From Table 1, the distance between M and the N1−N2−N3−N4 plane (*d*) hardly varies among the four structural isomers. Instead, it is found that the *d* distances strongly correlate with the atomic number of M. As shown in Table 1, the *d* distances gradually increase in the order 3.241−3.314 Å (M = Li) < 3.465−3.505 Å (M = Na) < 4.128−4.181 Å (M = K). This increasing tendency can be attributed to the gradually increasing atomic radii of M.[49]

We also evaluated the complexation energies (E_c) of the Li_3(calix[4]pyrrole)M complexes (see Table 1). It is shown that Li_3(calix[4]pyrrole)K have larger E_c values (−42.86 to −51.13 kcal/mol) than that of −38.81 kcal/mol for the corresponding Li-based Li^+(calix[4]pyrrole)K^-, indicating that the three segments of Li_3(calix[4]pyrrole)K are more tightly bound. The case is the same for M = Li and Na; that is, the E_c values of Li_3(calix[4]pyrrole)Li (−53.39 to −62.30 kcal/mol) and Li_3(calix[4]pyrrole)Na (−50.72 to −59.30 kcal/mol) are also larger than those of −47.64 and −45.78 kcal/mol for the corresponding Li^+(calix[4]pyrrole)Li^- and Li^+(calix[4]pyrrole)Na^-, respectively. Thus, the introduction of superalkali Li_3 into the alkalide design not only brings forward more structural isomers but also produces more stable species.

3.1.2. Alkalide Characteristics and VIE. To explore the electronic characteristics of Li_3(calix[4]pyrrole)M (M = Li, Na, and K), the NBO calculations[41] were performed at the CAM-B3LYP/6-311++G(d, p) level, and the related results are shown in Table 2. From the table, all the NBO charges on the upper M atoms are negative (−0.260 to −0.454|e|), demonstrating the alkalide characteristics of these compounds. Meanwhile, the total charges on the Li_3 units (Q_{sum}) are 0.613−0.653|e|, indicating an electron transfer from Li_3 to the (calix[4]pyrrole)M subunit. Thus, the studied species can be written as Li_3^+(calix[4]pyrrole)M^-. The alkalide identities of Li_3^+(calix[4]pyrrole)M^- can also be confirmed by their highest occupied molecular orbitals (HOMOs). Just as shown in Figure 2, the diffuse electron cloud enwraps the M atom and creates an M^- anion in each isomer.

From Table 2, it is noted that Na^- possesses the largest negative charges in the Li_3^+(calix[4]pyrrole)M^- (M = Li, Na, and K) series. For instance, the Q_M values of the lowest-energy Li_3^+(calix[4]pyrrole)M^- vary in the order −0.344|e| (M = Na) > −0.302|e| (M = Li) > −0.260|e| (M = K). This case has also been reported for alkali-metal-based Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K).[26] As for the structural isomers, the negative charges on the upper alkali anions increase in the order **A** < **C** < **B** < **D**, such as −0.302|e| (**A**) < −0.312|e| (**C**) < −0.330|e| (**B**) < −0.413|e| (**D**), for Li_3^+(calix[4]pyrrole)Li^-. This indicates that the location of Li_3 has some effect on the M^- charge, though it almost has no influence on the position of M^-, as pointed out above.

The data in Table 2 reveal that the Li_3^+(calix[4]pyrrole)M^- (M = Li, Na, and K) series have approximately equal Q_{sum} values, such as 0.651|e| (Li_3^+(calix[4]pyrrole)Li^-) ≈ 0.653|e| (Li_3^+(calix[4]pyrrole)Na^-) ≈ 0.646 |e| (Li_3^+(calix[4]pyrrole)K^-), for the most stable isomer **A**. This means that the charge transfer from Li_3 to (calix[4]pyrrole)M hardly depends on the M atomic number. In contrast, the Q_{sum} values for the structural isomers increase in the sequence of **D** < **B** < **C** < **A**, reflecting the dependence of such a charge transfer on the location of superalkali Li_3.

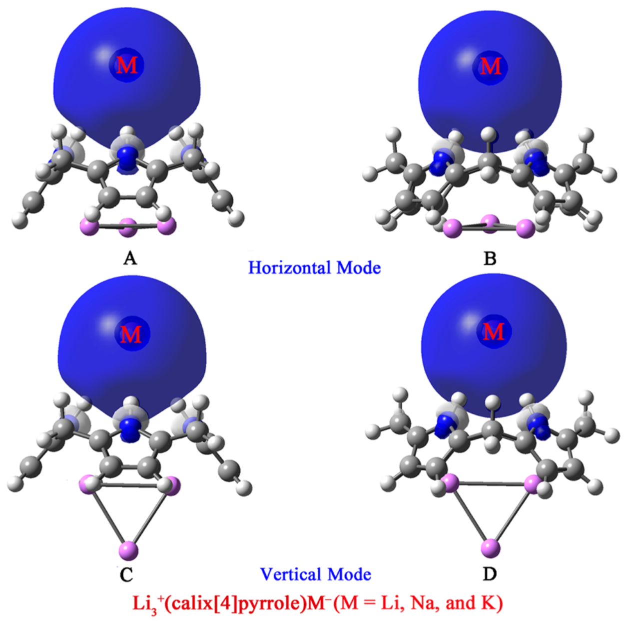

Figure 2. Highest occupied molecular orbitals (HOMOs) of the Li_3^+(calix[4]pyrrole)M^- (M = Li, Na, and K) compounds.

The vertical ionization energies (VIEs) of Li_3^+(calix[4]pyrrole)M^- (M = Li, Na, and K) are in the range of 3.539−4.252 eV (Table 2), which are smaller than the ionization energy (4.34 eV)[4] of the K atom. These low VIE values further confirm that the investigated systems contain diffuse electrons. From Table 2, the VIE values generally decrease with the increase of M atomic number, implying that the smaller the electron affinity of M is, the more diffuse the electron cloud is.

3.1.3. Nonlinear Optical Properties. As pointed out above, these Li_3^+(calix[4]pyrrole)M^- (M = Li, Na, and K) complexes possess typical alkalide characteristics with loosely bound excess electrons around M^-. Hence, they could be expected to have large NLO responses. In the present work, the static electric properties of the Li_3^+(calix[4]pyrrole)M^- species were calculated and are listed in Table 3. To better visualize the results, the dependences of the polarizability (α_0) and the first hyperpolarizability (β_0) values on the geometric structures and the atomic number of M are exhibited in Figure 3.

Table 3. Mean Dipole Moments (μ_0, in au), Mean Polarizabilities (α_0, in au), and Mean First Hyperpolarizabilities (β_0, in au), as Well as the Transition Energies (ΔE, in eV) of the Crucial Excited States of the Li_3^+(calix[4]pyrrole)M^- (M = Li, Na, and K) Compounds

compounds	isomers	μ_0	α_0	β_0	ΔE
Li_3^+(calix[4]pyrrole)Li^-	A	1.233	514	7169	2.232
	B	1.100	515	7074	2.223
	C	1.870	536	5725	2.211
	D	2.173	547	6007	2.247
Li_3^+(calix[4]pyrrole)Na^-	A	1.511	536	9153	2.292
	B	1.391	537	9006	2.372
	C	2.202	559	7557	2.307
	D	2.484	570	7984	2.318
Li_3^+(calix[4]pyrrole)K^-	A	1.254	678	30 158	1.816
	B	1.147	680	29 857	1.821
	C	1.918	702	28 422	1.826
	D	2.311	722	29 079	1.820

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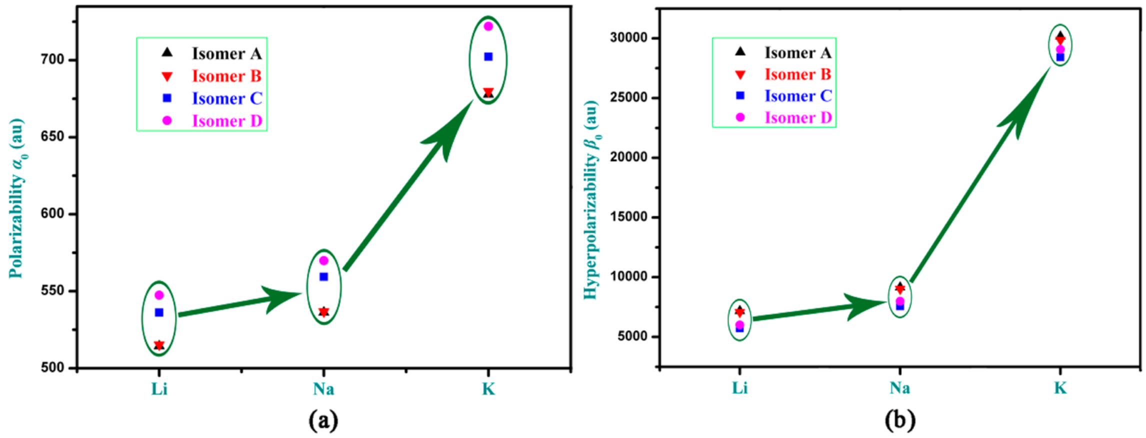

Figure 3. Dependences of (a) polarizability α_0 and (b) the first hyperpolarizability β_0 values on the geometrical structure and M^- atomic number of the Li_3^+(calix[4]pyrrole)M^- (M = Li, Na, and K) compounds.

From Figure 3, an obvious dependence of (hyper)-polarizabilities on the anion atomic number is observed for the Li_3^+(calix[4]pyrrole)M^- species. Thus, the (hyper)-polarizabilities of these compounds can be regulated by changing the M atom. Take the most stable structures **A** as examples. Their α_0 values increase in the order 514 au (M = Li) < 536 au (M = Na) < 678 au (M = K), and β_0 values show the same sequence of 7169 au (M = Li) < 9153 au (M = Na) < 30 158 au (M = K), which are in accordance with the increasing M^- atomic number. This is the same case for the alkali-metal-based alkalides Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K).[26] Besides, it can be seen from Figure 3 and Table 3 that the α_0 and β_0 values of potassides are much larger than those of lithides and sodides. To be specific, the α_0 values are in the range of 514−570 au for M = Li and Na, while of 678−722 au for M = K; the β_0 values are 5725−9153 au for M = Li and Na, but as large as 28 422−30 158 au for M = K.

From Table 3, it can be seen that the isomers with the vertical mode possess evidently larger μ_0 and α_0 values than those with the horizontal mode. By contrast, the structural dependence of the β_0 values of the Li_3^+(calix[4]pyrrole)M^- alkalides is less pronounced (see Figure 3). Still, it could be discerned from Table 3 that, for each Li_3^+(calix[4]pyrrole)M^- system, the order of β_0 is **C** < **D** < **B** < **A**. Take the Li_3^+(calix[4]pyrrole)K^- species as examples. The β_0 values increase in the order 28 422 au (**C**) < 29 079 au (**D**) < 29 857 au (**B**) < 30 158 au (**A**). The varying trend of β_0 reveals that the Li_3 unit adopting the horizontal mode is beneficial for a larger β_0. Thus, the most stable isomer **A** possesses the largest β_0 value but the smallest α_0 value among the structural isomers.

In the previous studies of alkali-metal-based alkalides,[26,29,30] it has been demonstrated that the small transition energy (ΔE) of the crucial transition state is the decisive factor for their large β_0 values. Likewise, the superalkali-based Li_3^+(calix[4]pyrrole)-M^- alkalides show small ΔE values of 1.816−2.372 eV, as is shown in Table 3. Furthermore, the potassides possess much smaller ΔE values of 1.816−1.826 eV than those of 2.211−2.372 eV for lithides and sodides, which justifies the dramatically larger β_0 values of the former species. Meanwhile, the ΔE values show small differences among the four structural isomers, so the structural dependence of β_0 for the Li_3^+(calix-[4]pyrrole)M^- alkalides is weak, as shown in Figure 3.

3.2. Li_3O^+(calix[4]pyrrole)M^- and M_3O^+(calix[4]-pyrrole)K^- (M = Li, Na, and K). *3.2.1. Geometrical Characteristics.* Superalkalis M_3O (M = Li, Na, and K)[37−41] have been extensively studied by theoretical and experimental researchers in the past several decades. Especially, the Li_3O^+ and Na_3O^+ cations have been detected in crystal salts $Li_3O^+NO_2^-$ and $Na_3O^+NO_2^-$,[5,6,50−52] and the Na_3O and K_3O molecules have been used to design unusual superatom-assembled compounds.[8] Hence, we also considered the potential of these well-known superalkalis to serve as building blocks for superalkali-based alkalides. By optimizing a mass of initial structures, the minimum structures of Li_3O(calix[4]-pyrrole)M and M_3O(calix[4]pyrrole)K (M = Li, Na, and K) have been obtained and are illustrated in Figure 4 and Figure S2 (Supporting Information), and their key geometric parameters are summarized in Table 4.

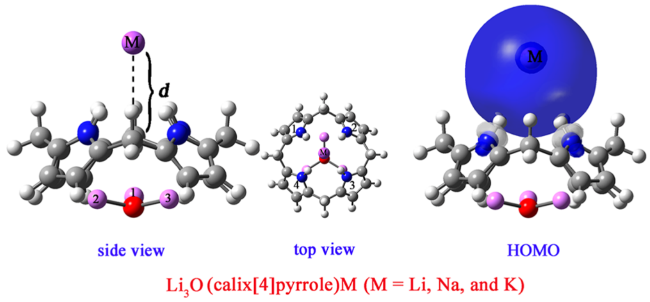

Figure 4. Geometric structures and highest occupied molecular orbitals (HOMOs) of the Li_3O(calix[4]pyrrole)M (M = Li, Na, and K) compounds.

As shown in Figure 4, only one kind of C_s-symmetrical structures are obtained for the Li_3O(calix[4]pyrrole)M (M = Li, Na, and K) series, in which the Li_3O units also prefer the horizontal mode. From Table 4, it is found that the geometric parameters of Li_3O units hardly change with the upper M atoms. The Li−O bond lengths are ca. 1.68 Å, which are very close to those of the isolated Li_3O (see Figure S1, Supporting Information). Hence, the Li_3O molecule preserves its structural integrity after being inserted into the calix[4]pyrrole complexant but shows a tendency from a planar structure toward a triangular pyramid.

The distance between M and the N1−N2−N3−N4 plane of Li_3O(calix[4]pyrrole)M also elongates as the atomic number of M increases from Li to K. From Table 4, the d distance increases in the order 3.271 Å (M = Li) < 3.468 Å (M = Na) <

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Table 4. Symmetry Groups, O−M1 and O−M2(3) Bond Lengths (in Å), M2−O−M3 Angles and N1−N2−N3−N4 Dihedral Angles (in deg), the Approximate Distances between M and the N1−N2−N3−N4 Plane (d, in Å), and Complexation Energies (E_c, in kcal/mol) of the Li_3O(calix[4]pyrrole)M and M_3O(calix[4]pyrrole)K (M = Li, Na, and K) Compounds

compounds	isomers	symmetry	L_{O-M1}	$L_{O-M2(3)}$	∠M2OM3	$D_{N1-N2-N3-N4}$	d	E_c
Li_3O(calix[4]pyrrole)Li		C_s	1.683	1.679	112.0	0.0	3.271	−70.19
Li_3O(calix[4]pyrrole)Na		C_s	1.682	1.679	111.9	0.0	3.468	−67.30
Li_3O(calix[4]pyrrole)K		C_s	1.682	1.679	111.7	0.0	4.148	−59.13
Na_3O(calix[4]pyrrole)K	**A**	C_s	2.051	2.038	113.1	0.0	4.128	−45.94
	B	C_{2v}	1.997	2.075	104.3	0.0	4.188	−37.23
	C	C_s	2.076	2.021	156.5	1.4	4.181	−35.58
K_3O(calix[4]pyrrole)K	**A**	C_{2v}	2.334	2.436	95.0	0.0	4.147	−41.54
	B	C_s	2.429	2.361	127.2	0.7	4.093	−41.91
	C	C_1	2.364	2.392	108.8	2.6	4.189	−37.77

Table 5. NBO Charges on Upper M Atom (Q_M) and M1 (Q_{M1}), M2 (Q_{M2}), M3 (Q_{M3}), and O (Q_O) Atoms of M_3O, and the Sum of Charges on M_3O (Q_{sum}) as Well as VIE Values (in eV) of the Li_3O^+(calix[4]pyrrole)M^- and M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K) Compounds

compounds	isomers	Q_M	Q_{M1}	Q_{M2}	Q_{M3}	Q_O	Q_{sum}	VIE
Li_3O^+(calix[4]pyrrole)Li^-		−0.405	0.777	0.769	0.769	−1.611	0.704	4.198
Li_3O^+(calix[4]pyrrole)Na^-		−0.440	0.777	0.759	0.769	−1.611	0.694	4.115
Li_3O^+(calix[4]pyrrole)K^-		−0.371	0.778	0.768	0.768	−1.609	0.705	3.580
Na_3O^+(calix[4]pyrrole)K^-	**A**	−0.321	0.844	0.870	0.870	−1.788	0.796	3.523
	B	−0.428	0.957	0.828	0.828	−1.816	0.797	3.312
	C	−0.263	0.468	0.915	0.915	−1.784	0.514	3.540
K_3O^+(calix[4]pyrrole)K^-	**A**	−0.352	0.799	0.915	0.915	−1.787	0.842	3.335
	B	−0.341	0.914	0.885	0.898	−1.797	0.900	3.328
	C	−0.485	0.940	0.857	0.857	−1.798	0.856	3.163

4.148 Å (M = K). In contrast, it is found that the d distance hardly changes when Li_3 is replaced by Li_3O. For example, the d distance (3.271 Å) of Li_3O(calix[4]pyrrole)Li is very close to those of 3.241−3.314 Å for Li_3^+(calix[4]pyrrole)Li^-. This implies that the d distance mainly depends on the atomic number of M^- instead of the species of superalkalis.

From Table 4, the complexation energies of Li_3O(calix[4]-pyrrole)M are −70.19, −67.30, and −59.13 kcal/mol for M = Li, Na, and K, respectively, which are comparable to those of Li_3(calix[4]pyrrole)M, and much larger than those (−47.64 to −38.81 kcal/mol) of the Li^+(calix[4]pyrrole)M^- (M = Li, Na, and K) compounds, indicating that the segments of the Li_3O-based alkalides are bound more tightly compared with the Li-based alkalides.

In order to investigate the effect of superalkali units on the structures and NLO properties of M_3O(calix[4]pyrrole)K, the structures of Na_3O(calix[4]pyrrole)K and K_3O(calix[4]-pyrrole)K have been also obtained at the CAM-B3LYP/6-31+G(d) level and are depicted in Figure S2 (Supporting Information). Interestingly, more structures are gained for Na_3O- and K_3O-based potassides. From Figure S2, the structure with horizontally embedded Na_3O is found to be the most stable one (**A**) of Na_3O(calix[4]pyrrole)K, whereas the other two structures (**B** and **C**) containing vertical Na_3O units are higher in energy by 7.08 and 11.23 kcal/mol, respectively. Especially, isomer **C** possesses a unique structure, in which one vertex Na atom of Na_3O points upward. For K_3O(calix[4]pyrrole)K, the isomers **B** and **C** are similar to structures **A** and **B** of Na_3O(calix[4]pyrrole)K, respectively. As to the most stable structure **A** of K_3O(calix[4]pyrrole)K, the K_3O unit leans at a ca. 27° angle with respect to the horizontal.

From Figure S2 (Supporting Information) and Table 4, though the Na_3O and K_3O units still keep their structural integrity, their geometries are distorted to some degree. For instance, the ∠M2OM3 angles are 156.5° for isomer **C** of Na_3O(calix[4]pyrrole)K and 95.0° for isomer **A** of K_3O(calix-[4]pyrrole)K, which are deviated from that in isolated M_3O by 36.5° and 25.0°, respectively. It is also noted from Table 4 that the d distances of Na_3O(calix[4]pyrrole)K and K_3O(calix[4]-pyrrole)K are 4.093−4.189 Å, respectively, which are close to that of Li_3O(calix[4]pyrrole)K. This confirms the above-mentioned conclusion that the d distances hardly change with the embedded superalkali species.

3.2.2. Alkalide Characteristics and VIE. For Li_3O(calix[4]-pyrrole)M and M_3O(calix[4]pyrrole)K (M = Li, Na, and K), their NBO charges and VIE values were calculated and are listed in Table 5. The NBO analyses reveal that these designed M_3O-based compounds can also be written as Li_3O^+(calix[4]-pyrrole)M^- and M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K). From Table 5, the charges on the upper alkali metal anions vary from −0.263 to −0.485|e|, indicating the alkalide characteristics of these species. This is also supported by their HOMOs shown in Figure 4 and Figure S3 (Supporting Information), in which the upper M atoms are surrounded by loosely bound excess electrons.

Similar to the case of Li_3^+(calix[4]pyrrole)M^-, the Q_M values of Li_3O^+(calix[4]pyrrole)M^- (M = Li, Na, and K) vary in the order Q_{Na} (−0.440|e|) > Q_{Li} (−0.405|e|) > Q_K (−0.371|e|). For the lowest-energy M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K) series, the order of Q_K is −0.371|e| (M = Li) > −0.352|e| (M = K) > −0.321|e| (M = Na), indicating that the charges on the upper anion can be affected by the inserted superalkali species. The charges on the Li_3O units (Q_{sum}) in Li_3O^+(calix[4]-pyrrole)M^- (M = Li, Na, and K) are in the range of 0.694−0.705|e|, implying that the Li_3O cluster behaves like an alkali metal atom and donates an electron in these compounds.

Table 6. Mean Dipole Moments (μ_0, in au), Mean Polarizabilities (α_0, in au), and Mean First Hyperpolarizabilities (β_0, in au), as Well as the Transition Energies (ΔE, in eV) of the Crucial Excited States of the Li_3O^+(calix[4]pyrrole)M^- and M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K) Compounds

compounds	isomers	μ_0	α_0	β_0	ΔE
Li_3O^+(calix[4]pyrrole)Li^-		1.742	447	11 764	2.256
Li_3O^+(calix[4]pyrrole)Na^-		2.026	468	13 555	2.363
Li_3O^+(calix[4]pyrrole)K^-		1.820	614	33 252	1.829
Na_3O^+(calix[4]pyrrole)K^-	**A**	1.931	632	33 890	1.789
	B	5.124	662	29 330	1.770
	C	2.638	631	32 959	1.825
K_3O^+(calix[4]pyrrole)K^-	**A**	3.922	672	34 718	1.771
	B	3.464	669	34 688	1.769
	C	6.271	706	32 875	1.720

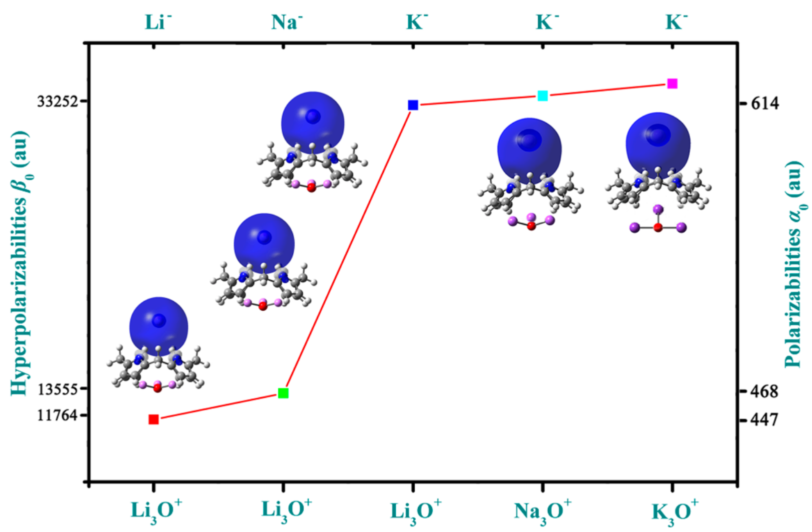

Figure 5. Dependences of polarizability (α_0) and first hyperpolarizability (β_0) values on the M atomic number of the Li_3O^+(calix[4]pyrrole)M^- and M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K) compounds.

Besides, the charge transfer from the Li_3O unit to the (calix[4]pyrrole)M part hardly depends on the upper M^-. By contrast, the Q_{sum} shows an increasing tendency of 0.705|e| (M = Li) < 0.796|e| (M = Na) < 0.842|e| (M = K) for the most stable M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K) series, which is reasonable considering the VIE order of 3.707 eV (Li_3O) > 3.526 eV (Na_3O) > 2.879 eV (K_3O) at the CAM-B3LYP/6-311++G(d, p) level.

From Table 5, it is found that the VIE values of Li_3O^+(calix[4]pyrrole)M^- reduce in the order 4.198 eV (M = Li) > 4.155 eV (M = Na) > 3.580 eV (M = K). Similarly, the VIE values of M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K) also decrease in the order 3.580 eV (M = Li) > 3.523 eV (M = Na) > 3.335 eV (M = K). The former decreasing trend of VIE is related to the reduced electron affinities of the upper M atoms, whereas the latter is in line with the decreasing VIE order of M_3O.

3.2.3. Nonlinear Optical Properties. The static electric properties of Li_3O^+(calix[4]pyrrole)M^- and M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K) are given in Table 6. The results also show obvious dependences of α_0 and β_0 on the atomic number of M^- for Li_3O^+(calix[4]pyrrole)M^-. From Table 6, the order of α_0 is 447 au (M = Li) < 468 au (M = Na) < 614 au (M = K) and the same tendency of 11 764 au (M = Li) < 13 555 au (M = Na) < 33 252 au (M = K) is found for β_0. In addition, the M atomic number dependences of α_0 and β_0 of M_3O^+(calix[4]pyrrole)M^- are also exhibited in Figure 5. From the figure, the potassides exhibit particularly large β_0 values, no matter which superalkali cluster they contain.

Interestingly, the unique isomer **C** of Na_3O^+(calix[4]pyrrole)K^- possesses similar electric properties to those of isomer **A**, although it is of the vertical mode. From Table 6, the isomers with the vertical mode exhibit much larger μ_0 values compared with the others, except for isomer **C** of Na_3O^+(calix[4]pyrrole)K^-. In contrast, the structural dependences of the α_0 and β_0 values are relatively small. From Figure 5, the α_0 and β_0 values of the most stable M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K) species do not strongly depend on the involved superalkali, though they increase with the increasing atomic number of M in the M_3O units. Thus, the NLO response of such alkalides can be enhanced by increasing the atomic number of both M^- and M in the M_3O. As a result, the β_0 increases 3-fold from 11 764 au of Li_3O^+(calix[4]pyrrole)Li^- to 34 718 au of K_3O^+(calix[4]pyrrole)K^-. The β_0 of K_3O^+(calix[4]pyrrole)K^- is also much larger than that (29 340 au) of the corresponding alkali-metal-based Li^+(calix[4]pyrrole)K^- at the same computational level, indicating that the introduction of superalkali may be propitious to enhance the NLO response of traditional alkalides.

The ΔE values of the crucial excited states of Li_3O^+(calix[4]pyrrole)M^- and M_3O^+(calix[4]pyrrole)K^- were also computed and are shown in Table 6. According to the famous two-level model,[53−55] β_0 is inversely proportional to the third power of ΔE. From Table 6, the ΔE values of lithide and sodide

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are 2.256 and 2.363 eV, respectively, whereas the ΔE of potassides are much smaller (1.720−1.829 eV), which is similar to the case of Li_3^+(calix[4]pyrrole)M^-. This is why the β_0 values of M_3O^+(calix[4]pyrrole)K^- are much larger than those of the Li_3O-based lithide and sodide. In addition, the ΔE values of the most stable M_3O^+(calix[4]pyrrole)K^- decrease in the order 1.829 eV (M = Li) > 1.789 eV (M = Na) > 1.771 eV (M = K), which is just inverse to the order of their β_0 values. Thus, the ΔE is also the decisive factor in determining the β_0 values of these superalkali-based alkalides.

4. CONCLUSIONS

A series of superalkali-based compounds, namely, Li_3^+(calix[4]pyrrole)M^-, Li_3O^+(calix[4]pyrrole)M^-, and M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K), have been designed and systemically studied by the density functional theory method. The alkalide characteristics of these compounds are demonstrated by the analyses of NBO charges, VIE values, and their HOMOs. Compared with the alkali-metal-based alkalides, these novel alkalides exhibit the structural diversity as well as larger complexation energies. Interestingly, in all the resulting alkalides, the superalkali clusters preserve their identities and behave just like alkali metal atoms. The position of the upper M^- anion is closely related to its atomic number but seems almost unaffected by the species of inserted superalkali. Likewise, the change of M^- has little bearing on the geometrical structure of the superalkali subunit.

The superalkali-based alkalides show large NLO responses with considerable hyperpolarizabilities (β_0), especially for the potassides. Besides, the insertion of lower IP superalkalis also has a positive effect on enhancing the β_0 values of the investigated alkalides. Hence, the superalkali clusters may be potential candidates for designing nontraditional alkalides with remarkable and tunable NLO responses.

■ ASSOCIATED CONTENT

Supporting Information

Geometric structures of Li_3, Li_3O, Na_3O, K_3O, Na_3O(calix[4]pyrrole)K, and K_3O(calix[4]pyrrole)K; highest occupied molecular orbitals (HOMOs) of Na_3O^+(calix[4]pyrrole)K^- and K_3O^+(calix[4]pyrrole)K^-; and crucial transition states of the most stable Li_3^+(calix[4]pyrrole)M^-, Li_3O^+(calix[4]pyrrole)M^-, and M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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