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Article

Compounds of Superatom Clusters: Preferred Structures and Significant Nonlinear Optical Properties of the BLi$_6$-X (X = F, LiF$_2$, BeF$_3$, BF$_4$) Motifs

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A new type of superalkali-(super)halogen compound, BLi$_6$-X (X = F, LiF$_2$, BeF$_3$, BF$_4$), is theoretically predicted. The interaction between superalkali BLi$_6$ and different shaped superhalogen X is found to be strong and ionic in nature. Bond energies of these BLi$_6$-X species are in the range of 151.3−220.6 kcal/mol at the CCSD(T)/aug-cc-pVDZ level, which are much larger than the traditional ionic bond energy of 130.1 kcal/mol for LiF. Furthermore, because of their delocalized electron character, these superalkali-(super)halogen species exhibit extraordinarily large first hyperpolarizabilities with β_0 ranging from 5166.5 to 17791.0 au. Besides, the examination of the variation of nonlinear optical (NLO) properties with the size of (BLi$_6$-BeF$_3$)$_n$ assemblies shows the dependence of NLO properties on the chain length of (BLi$_6$−BeF$_3$)$_n$. The present investigation gives hints to scientists in extending the research in atomic dimension to direct the interaction between superatoms, and using superatoms as building blocks to synthesize novel meaningful materials with unusual properties such as nonlinear optical properties.

Introduction

In the last decades, enormous progress has been made in the synthesis, characterization, and fundamental understanding of materials using atoms as building blocks of matter. Nevertheless, in a precursory theoretical work, Khanna and Jena[1] proposed that atomic clusters with suitable size and composition could be designed to mimic the chemistry of atoms in the Periodic Table and that such clusters could be described as superatoms. Ever since Al$_{13}$K was predicted to form an ionically bound superatom complex that would resemble a familiar halogen salt,[2] superatoms have become basic units in chemistry and attracted more and more attention. Most recently, the Castleman group demonstrated the superatom characteristics of Al$_{13}$ and Al$_{14}$ clusters in two classes of gas-phase aluminum−iodine clusters and indicated that superatoms indeed had synthetic utility and would represent potential building blocks for the assembly of novel nanostructured materials.[3,4] Therefore, research on superatoms will provide compounds with novel structures, special

bonding nature and properties, and thus promote the development of chemistry (including nanoscale chemistry and supramolecular chemistry) and materials' science.

Two famous subsets of superatoms of interest are superhalogens[5−16] and superalkalies[17−22] that have been theoretically and experimentally studied for more than 20 years.

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Superhalogens with high electron affinities (EAs) are of a great importance in chemistry since they can be used for the oxidation of counterpart systems with relatively high ionization potentials (such as O_2, Xe) and allow the synthesis of unusual chemical compounds. Although superhalogens have been known and have been of interest since the early 1960s, they were first given the moniker "superhalogens" in 1981, when a simple formula for a class of high EA species MX_{k+1} (M is a main group or transition metal atom, X is a halogen atom or a monovalent group with high EA such as CN, and k is the maximum formal valence of M) was proposed.[5] Such superhalogen anions as BF_4^-, $AlCl_4^-$, and AsF_6^- are commonly found as fragments in gas-phase molecules and in crystalline solids.

As for superalkalies characterized by low ionization potentials (IPs), they are also well-known for the ability of being used in the synthesis of a new class of charge−transfer salts in which the corresponding anions are formed by the species with low electron affinity. Gutsev and Boldyrev also proposed a class of superalkalies characterized by the formula ML_{k+1} where L is an alkali metal atom.[17] For example, the BLi_6 cluster that accords with this formula was reported to possess the superalkali characteristics with the first IP = 3.75 eV (at the CCSD(T)/aug-cc-pVDZ level) in our previous work.[23]

Considering the high EA and low IP features of superhalogens and superalkalies, respectively, it is reasonable to expect that they serve as components of novel nontraditional superalkali-superhalogen solid salts to mimic the well-known alkali halide salts. Lately, Khanna and co-workers[24] theoretically demonstrated a kind of superatom compound formed by combining superhalogens Al_{13} and superalkalies (K_3O and Na_3O). It is found that the same chemical principles, working for the atomic cluster, can be extended to a cluster with superatom motifs. Thus, the characterization of the superatom interaction and prediction of the unusual properties of superatom compounds should be a meaningful project.

In the present work, we have focused on this idea and chosen polyhedral superalkali BLi_6 as the building block to interact with F atom and different shaped superhalogens X (X = LiF_2, BeF_3, BF_4). First, BLi_6 and these superhalogens X satisfy the ML_{k+1} and MX_{k+1} formulas, respectively, so they stand for the most basic and widely seen superatoms; we consider that the principles obtained from this study will help to provide a useful guidance for superatom researches. Second, BLi_6 is a regular octahedron with high symmetry (O_h); it provides an ideal prototype for studying superalkali-superhalogen interactions in a variety of assemblies. Third, LiF_2, BeF_3, and BF_4 represent linear, planar, polyhedral superhalogens, respectively, because their anions are linear (LiF_2^-), regular triangular (BeF_3^-), and regular tetrahedral

(BF_4^-), respectively. By studying the superalkali-(super)halogen compounds BLi_6-X (X = F, LiF_2, BeF_3, BF_4), we explore the preferred orientations between superalkali and different shaped superhalogens, reveal their bonding properties, exhibit the considerable stabilities with large bond energies as well as highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) gaps, and especially predict extraordinarily large nonlinear optical (NLO) responses of such compounds. To show how these compounds assemble to form extended structures, we also present results on $(BLi_6-BeF_3)_n$ assemblies containing up to four units. The variation of the NLO properties with the size of $(BLi_6-BeF_3)_n$ assemblies is also analyzed.

Methods

The computations were performed using Dunning's augmented correlation-consistent polarized valence basis sets of contracted Gaussian functions,[25] aug-cc-pVDZ.

The optimum configurations and vibrational frequencies for the BLi_6-X (X = F, LiF_2, BeF_3, BF_4) compounds were obtained by the second-order MP2(FC) method.[26] The NLO properties and natural bond orbital (NBO)[27] charges of these compounds are also calculated at the MP2/aug-cc-pVDZ level. The calculations of the first hyperpolarizability (β_0) and related properties (μ, and α_0) relied on the finite-field approach.[28] The total energy of a molecular system in the presence of a homogeneous electric field can be expressed as[29,30]

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \ldots \quad (1)$$

where E^0 is the molecular total energy without the electric field, and F_α is the electric field component along the α direction; μ_α, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ are the dipole moment, the polarizability, and the first hyperpolarizability, respectively. The total static dipole moment μ, the mean polarizability α_0, and the mean first hyperpolarizability β_0 are defined as

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$
$$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (2)$$
$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

where

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

The intramolecular interaction energies (E_{int}) between BLi_6 and X subunits of BLi_6-X compounds were calculated at the

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CCSD(T)/aug-cc-pVDZ level. We used the counterpoise (CP) procedure[31] to eliminate the basis set superposition error (BSSE) effect given by eq 3:[32]
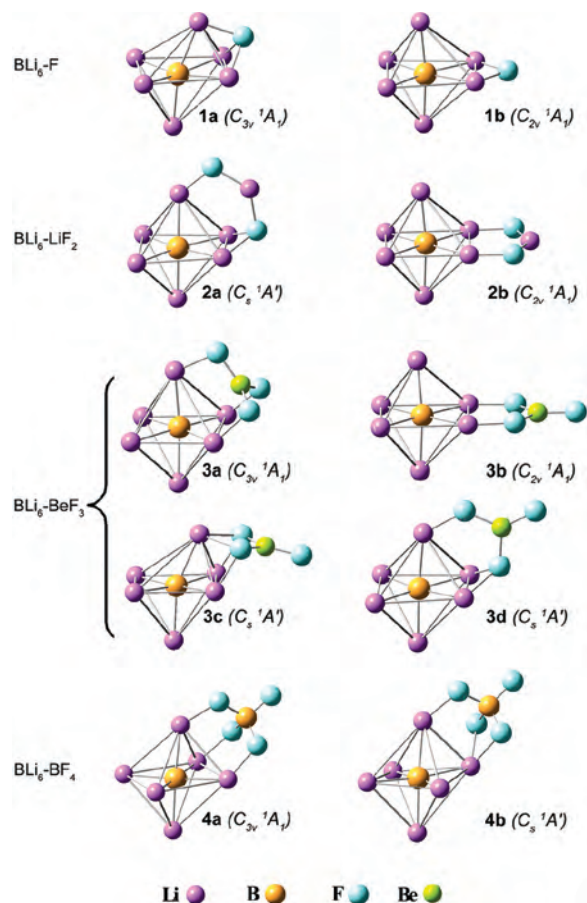
$$E_{int} = E_{AB}(X_{AB}) - E_A(X_{AB}) - E_B(X_{AB}) \qquad (3)$$

where the same basis set, X_{AB}, was used for the subunit energy (E_A and E_B) calculations as for the complex energy (E_{AB}) calculation.

All the calculations in this work are carried out by using the GAUSSIAN 03 program package.[33] The dimensional plots of molecular configurations and orbitals were generated with the GaussView program[34] (Gaussian, Inc., Pittsburgh, PA).

Results and Discussions

A. Geometrical Features and Bond Energies. The optimized geometries of the superalkali-(super)halogen compounds BLi_6-X (X = F, LiF_2, BeF_3, BF_4) at the MP2/aug-cc-pVDZ level are displayed in Figure 1. The interaction orientations between BLi_6 and X are listed in Table 1. The reactive site of a cluster may be apex, side, and face, so there are many possible orientations for the cluster−cluster interaction; as a result, the 2, 2, 4, 2 isomers for the BLi_6-X compounds, respectively, were obtained. All the structures presented in Figure 1 are minima on the potential energy surface, and their corresponding harmonic vibrational frequencies are collected in the Supporting Information, Table S1. The MP2 Infrared and Raman spectra are presented in Supporting Information, Figure S1. From Table 1, the BLi_6-X compounds show large HOMO−LUMO gaps ranging from 4.56 to 5.12 eV, which are significantly large compared with the HOMO−LUMO gaps of 1.24 eV in $Al_{13}K_3O^{24}$ and of about 1.9 eV in C_{60}.[35] It suggests that all the BLi_6-X compounds may be thermodynamically stable.

The bond energies E_b of the BLi_6-X compounds are defined as the negative of the intramolecular interaction energies. It is found that the isomer corresponding to the lowest relative energy simultaneously exhibits the largest bond energy (see Table 1). Thus, according to the bond

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Figure 1. Optimized structures of the BLi_6-X compounds at the MP2/aug-cc-pVDZ level, showing a variety of interaction orientations between BLi_6 and different shaped (super)halogens.

energy order, we can get the stability order among the isomers for each BLi_6-X compound, and consequently find the preferential orientations between BLi_6 and different shaped superhalogens.

For BLi_6-F, the F atom can occupy the hollow (**1a**) or the bridge site (**1b**) of the BLi_6 octahedron, but **1a** exhibits larger bond energy of 153.7 kcal/mol than **1b** does (151.3 kcal/mol), so the preferred interaction between BLi_6 and F atom is the face-point orientation. For the interaction between BLi_6 and linear LiF_2, the face-side orientation (**2a**) is superior to side-side orientation (**2b**), which is reflected by the larger bond energy of **2a** (204.2 kcal/mol) than that of **2b** (198.7 kcal/mol). Among the four isomers of BLi_6−BeF_3, the bond energy order is 220.6 kcal/mol (**3a**) > 205.7 kcal/mol (**3b**) > 205.6 kcal/mol (**3c**) > 205.2 kcal/mol (**3d**), so the preferential orientation order is, face-face (**3a**) > side-side (**3b**) > face-side (**3c**, **3d**). As to BLi_6−BF_4, face-face orientation (**4a**) is more beneficial than side-face orientation (**4b**) because the former shows larger bond energy (218.4 kcal/mol) than that of the latter (211.2 kcal/mol).

Because of the ionic bond character between superalkali BLi_6 and superhalogens X (see next section), the BLi_6-X compounds can be written as $(BLi_6)^+X^-$ (X = F, LiF_2, BeF_3, BF_4). For comparisons, the structures of BLi_6^+, LiF_2^-, BeF_3^-, and BF_4^- are displayed in the Supporting Information, Figure S2. On the whole, the structural deformations of BLi_6^+ and X^- (X = LiF_2, BeF_3, BF_4) moieties in $(BLi_6)^+X^-$ are small

Table 1. Relative Energies E_{rel} (kcal/mol), HOMO-LUMO Gap (eV), Bond Energies E_b (kcal/mol), NBO Charges on the BLi_6 subunit, and the Total Static Dipole Moment μ, Mean Polarizabilities α_0, and the Mean First Hyperpolarizabilities β_0 (in au.) of the BLi_6-X Compounds

		orientation	E_{rel}	gap	E_b	charge[a]	μ	α_0	β_0
BLi_6-F	**1a**	face-point	0.00	4.56	153.7	0.957	0.4219	400.25	11459.3
	1b	side-point	1.26	4.67	151.3	0.964	1.0215	355.23	14254.9
BLi_6-LiF_2	**2a**	face-side	0.00	4.58	204.2	0.948	0.8663	356.11	17791.0
	2b	side-side	2.11	4.90	198.7	0.957	1.1920	327.01	13052.7
BLi_6-BeF_3	**3a**	face-face	0.00	5.12	220.6	0.969	1.6811	303.04	9801.4
	3b	side-side	13.99	5.07	205.7	0.971	3.6745	327.22	5166.5
	3c	face-side	15.88	4.76	205.6	0.957	1.4510	345.84	7806.3
	3d	face-side	16.10	4.87	205.2	0.965	1.9825	345.79	5902.3
BLi_6-BF_4	**4a**	face-face	0.00	5.03	218.4	0.968	1.8546	328.49	5329.6
	4b	side-face	10.65	5.02	211.2	0.968	2.4580	325.04	7400.4
LiF		point-point		12.45	130.1		2.5709	9.17	90.2

[a] NBO charge on the BLi_6 subunit.

compared with their isolated BLi_6^+ and X^- structures. It indicates that the structural and electronic integrities of BLi_6^+ and X^- are maintained inside the $(BLi_6)^+X^-$ compound because of its ionic bonding nature. So, it is expected that some of the unique properties of individual BLi_6^+ and X^- will be retained when they interact with each other in the superalkali-superhalogen superstructures. This is meaningful for experimentalists to detect the X^- subunits from the BLi_6-X compounds since many superhalogen anions have been investigated by experimental techniques such as photoelectron spectroscopy for years.

B. Bonding Properties of the BLi_6-X Compounds. As is shown in Table 1, the BLi_6-X compounds possess large bond energies in the range of 151.3−220.6 kcal/mol, which are much larger than the traditional ionic bond energy of 130.1 kcal/mol for LiF. It indicates that there is a strong interaction between superalkali BLi_6 and (super)halogens X. To explore the bonding nature between BLi_6 and X, the NBO analyses were performed. From Table 1, the NBO charge (0.948−0.971) on the BLi_6 moiety in each BLi_6-X system is close to +1. Thus, for these BLi_6-X species the superatom valences are +1 for BLi_6 and −1 for X. It means that BLi_6 loses an electron to become BLi_6^+ and the (super)halogen gets the electron to become X^-. Hence, the superalkali BLi_6 and (super)halogens X exhibit the characteristics of single alkali atom and halogen atom, respectively, when they are interacting with each other in cluster assemblies. This should lead to an ionic character of bonding between BLi_6 and X. According to the atom-in-molecule (AIM) theory, the Laplacian of the electron density at a bond critical point (BCP), $\nabla^2\rho(r)$, can be used to describe the chemical bonding nature of covalent, ionic, hydrogen bonds, and van der Waals interactions.[36] Thus, we calculated the $\nabla^2\rho(r)$ values for all the Li−F bonds that connect BLi_6 and X at the MP2/aug-cc-pVDZ level. The results range from 0.141 to 0.361 au., also suggesting that ionic bonds form between BLi_6 and X, which agrees with the NBO analyses mentioned above. Thus, the BLi_6-X compounds can be written as $(BLi_6)^+X^-$ (X = F, LiF_2, BeF_3, BF_4). Summarizing the above analyses, we can come to the conclusion that the NaCl-like compounds form between superalkali BLi_6 and (super)halogens X. However, it should be noted that a superatom consists of several atoms, so multiple ionic bonds can form between a

superalkali and a (super)halogen (see Figure 1). As a result, the superalkali-superhalogen compound will exhibit a larger bond energy than a traditional alkali-halide.

More interestingly, besides the bonding properties, the molecular orbitals of BLi_6-X are very similar to those of a traditional alkali-halide. We choose BLi_6−BF_4 as an example and compare its molecular orbitals (MOs) with those of NaCl (see Supporting Information, Figure S3). It is readily seen that both MOs show wonderful resemblances.

In view of the similar bonding properties and MOs between BLi_6-X and traditional alkali-halide, the superatom can mimic a single atom and can be regarded as an extension of the periodic table to a third dimension. Consequently, scientists can extend the research in the atomic dimension to direct the interaction between superatoms and to use superatoms as building blocks to synthesize novel meaningful materials with unusual properties.

C. Significant NLO Properties. Since the electrons are delocalized in superatoms (which can be seen from Supporting Information, Figure S3), we consider that the compound that consists of superatoms is easily polarizable and can be expected to have large polarizability α. Furthermore, according to the time-dependent density-functional theory (TD-DFT) calculations (see Supporting Information, Table S2), the transition energy ΔE values of the BLi_6-X compounds are pretty small, namely, 2.842−3.119 eV. They are much smaller than that of LiF molecule (37.719 eV). From the "sum-over-states" (SOS) expression, Oudar and Chemla established a simple link between the static first hyperpolarizability (β_0) and a low-lying charge-transfer transition by the two-level model.[37,38] For the static case (ω = 0.0), the following two-level expression is employed to estimate β_0 in the literature:[37,39]

$$\beta_0 \propto \frac{\Delta\mu \cdot f_0}{\Delta E^3} \quad (4)$$

In the above expression, β_0 is proportional to the difference of dipole moments 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 (ΔE). According to the two-level model (eq 4), for any noncen-

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trosymmetric molecule, the low transition energy is the decisive factor for a large β_0 value. As a result, the BLi_6-X compounds with small ΔE should exhibit large β_0 values.

The mean polarizabilities α_0 and the mean first hyperpolarizabilities β_0 of the BLi_6-X compounds are evaluated by numerical differentiation with an electric field magnitude of 0.001 au. As shown in Table 1, the BLi_6-X compounds have considerably large NLO responses, with α_0 ranging from 303.04 to 400.25 au and β_0 in the range from 5166.5 to 17791.0 au, while the α_0 and β_0 of LiF are determined as only 9.17 and 90.2 au, respectively. Obviously, the superalkali-superhalogen compounds show extraordinarily larger NLO properties compared to the traditional alkali halide. The β_0 values are enhanced by 57 to 197 times. Especially, the β_0 values of some BLi_6-X compounds are even comparable to those of some organic systems reported in our previous works, such as, electride Li^+(calix[4]pyrrole)e^- (7326 au)[40] and alkalides Li^+(calix[4]pyrrole)Li^- (10969 au), and Li^+(calix[4]pyrrole)Na^- (14772 au).[41] This will give hints to experimentalists in designing high performance NLO materials from superatom systems such as the superalkali-superhalogen compounds. Interestingly, by comparisons among the β_0 values of the BLi_6-X compounds with similar interaction orientation between BLi_6 and X, it is found that the β_0 values decreased with increasing electron affinities of X. For example, the β_0 are ordered as follows: **1a** (11459.3 au.) > **3a** (9801.4 au.) > **4a** (5329.6 au.), **1b** (14254.9 au.) > **2b** (13052.7 au.) > **3b** (5166.5 au.) and **2a** (17791.0 au.) > **3d** (5902.3 au.). The calculated UV−vis linear absorption spectra of these BLi_6-X compounds are presented in the Supporting Information, Figure S4, which are useful for comparison with experimental absorption spectra.

D. One-Dimensional Assemblies of BLi_6−BeF_3 (3a). Since the BLi_6-X compounds form NaCl-like ionic compounds, it is possible to use these superalkali-superhalogen compounds as building blocks for the growth to solid superalkali-superhalogen salts. We now discuss the periodic systems constructed with the selected BLi_6−BeF_3 (**3a**) compound with the largest bond energy as the structural units up to $(BLi_6−BeF_3)_4$. With the configuration of BLi_6−BeF_3 (**3a**), it could be possible to design a one-dimensional cluster array like a nano quantum wire. Experimentally, such one-dimensional (1D) superstructures could be realized by inserting the clusters into 1D nanoscale templates such as carbon nanotubes.

The ground-state geometries of the $(BLi_6−BeF_3)_n$ compounds were obtained at the B3LYP/6−31G(d) level. As shown in Figure 2, the $(BLi_6−BeF_3)_n$ compounds align like a linear chain as a consequence of the superalkali-superhalogen interaction. As is pointed by Khanna et. al,[24] maintaining the HOMO−LUMO gap is an important requirement to ensure that the basic building blocks maintain their identity. To this end, we examined the variation of the HOMO−LUMO gap as the BLi_6−BeF_3 compounds are
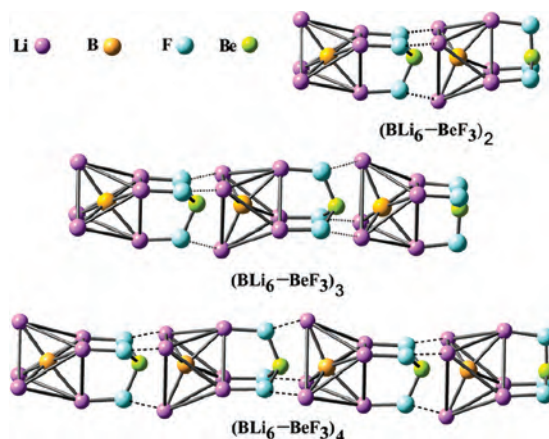

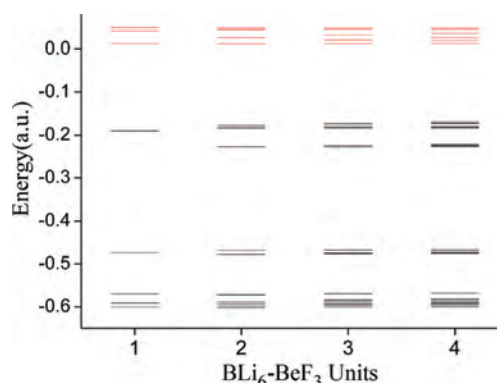**Figure 2.** Assemblies of the BLi_6−BeF_3 (**3a**) compound.

Figure 3. One-electron levels for $(BLi_6−BeF_3)_n$ assemblies. The black lines are the occupied states, while the red lines are the unoccupied states.

assembled at the MP2/6−31G(d) level. The results are shown in Figure 3. Note that while the assembly of BLi_6−BeF_3 compounds leads to additional levels, the electronic levels are bunched in individual bands maintaining a similar HOMO−LUMO gap. This shows that basic electronic features of BLi_6−BeF_3 are maintained upon assembly.

The NBO charges and $\nabla^2\rho(r)$ values of the $(BLi_6−BeF_3)_n$ compounds are obtained following the same analyses as in section B. From the results at the MP2/6−31G(d) level, the BLi_6 and BeF_3 subunits carry from 0.855 to 0.985 and from −0.840 to −0.991 NBO charges, respectively. The $\nabla^2\rho(r)$ values of all the Li−F bonds connected BLi_6 and BeF_3 subunits are in the range of 0.312−0.307 au. Both indicate that the BLi_6 and BeF_3 subunits are connected by ionic bonds in $(BLi_6−BeF_3)_n$ assemblies.

To predict the variation of the NLO properties with the size of the $(BLi_6−BeF_3)_n$ assemblies, the mean first hyperpolarizabilities β_0 and related properties (μ, α_0) of the $(BLi_6−BeF_3)_n$ compounds were examined at the MP2/6−31G(d)//B3LYP/6−31G(d) level, and plots of these properties as a function of the number of BLi_6−BeF_3 units are shown in Figure 4. As can be seen from Figure 4, α_0 increases sharply and linearly with increasing BLi_6−BeF_3 units, while μ shows relatively slower but linear increase when $n > 1$.

The β_0 value also increases with increasing n, and it may reach a maximum at a certain n value. According to theoretical calculations, a linear dependence between β and

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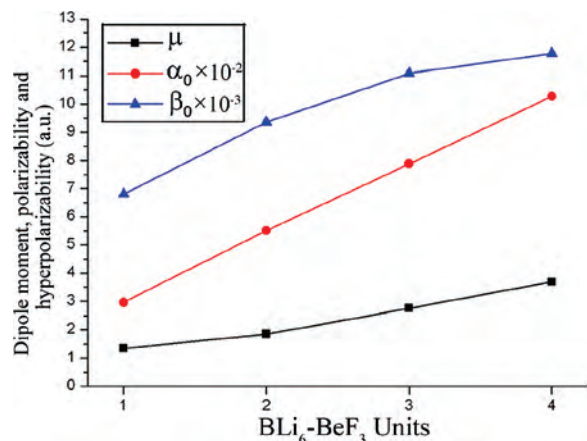
Figure 4. Mean first hyperpolarizabilities β_0, total static dipole moment μ, and mean polarizabilities α_0 of the $(BLi_6-BeF_3)_n$ assemblies.

the length of the conjugated chain must not be expected.[42,43] In extended conjugated systems, the number of excited states contributing to β increases upon chain lengthening.[44] In an effort to quantify the NLO dependence with the chain length, Jayaprakash et al. found that the equation $\beta = an^b$ (where a and b are constant values and n is the number of double bonds)[45] gives a good correlation for their compounds. Although limited data are available for our compounds, we also obtain the β_0 dependence with the chain length (L) using the same relationship. We found from the plot of log β_0

versus log L (see Supporting Information, Figure S5) that the exponent b is 0.2872 for the $(BLi_6-BeF_3)_n$ compounds. Though this value of the exponent is much lower than those obtained for the conjugated systems, the lessons learned from this investigation may, in the future, be useful in the design of new compounds with controllable optical properties.

Conlusions

In summary, we have presented the theoretical evidence for a new type of superalkali-(super)halogen compound, BLi_6-X. The preferred orientations between polyhedral BLi_6 and F atom, linear LiF_2, planar BeF_3, and polyhedral BF_4, are face-point, face-side, face-face, and face-face, respectively. Such compounds may represent a new kind of potential NLO materials because they exhibit large bond energies and extraordinarily large NLO responses. These predictions await experimental confirmation, which would open a new branch of chemistry of materials using superatoms as building blocks.

Supporting Information Available: The vibrational frequencies, Infrared and Raman spectra, molecular orbitals, transition properties referred to the crucial excited state, UV−vis linear absorption spectra for BLi_6-X (X = F, LiF_2, BeF_3, BF_4), plot of log β_0 values against logarithm of the chain length, L, of the $(BLi_6-BeF_3)_n$ compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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