

Structures and Large NLO Responses of New Electrides:
Li-Doped Fluorocarbon ChainHong-Liang Xu,[†] Zhi-Ru Li,^{*,†} Di Wu,[†] Bing-Qiang Wang,[†] Ying Li,[†]
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Abstract: An alkali-metal-doped effect on the nonlinear optical (NLO) property in new electrides is studied. The electrides are formed by doping alkali atom Li into a fluorocarbon chain $\text{H}-(\text{CF}_2-\text{CH}_2)_3-\text{H}$. Six stable structures of the $\text{Li}_n-\text{H}-(\text{CF}_2-\text{CH}_2)_3-\text{H}$ ($n = 1, 2$) complexes with all real frequencies are obtained at the MP2/6-31+G (d) level. Among these six structures, the largest first static hyperpolarizabilities (β_0) are found to be 76 978 au, which is much larger than the β_0 value of 112 au for $\text{H}-(\text{CF}_2-\text{CH}_2)_3-\text{H}$. Clearly, the Li-atom-doped effect on the first hyperpolarizability is dramatic. Three interesting relationships between the structure and β_0 value have been observed. (1) For the one-Li-atom-doped systems as well as for the structures with two opposite Li atoms, the shorter the distance between the Li atom and difluoromethyl group, the larger the β_0 value. (2) The β_0 values of the two-Li-atom-doped chains are much larger than those of the one-Li-atom-doped systems, except for the case of cis-AB where the Li–Li distance (2.847 Å) is close to the bond length of the Li_2 molecule (2.672 Å). (3) For the two-Li-atom-doped chains, the β_0 value increases as the Li–Li distance increases. These relationships between the structure and β_0 value may be beneficial to experimentalists for designing electrides with large NLO responses by using the alkali-metal-doped effect.

Introduction

In the investigation of high-performance nonlinear optical (NLO) materials, many valuable papers have been published on different types of NLO materials.¹

Recently, several kinds of new NLO systems with an excess electron have been investigated.² Those investigations demonstrated that the excess electron plays a crucial role in the large first hyperpolarizability. For electrides³ and alkalides,⁴ the excess electron is formed by chemical doping (alkali atoms as dopant).

The alkali-doped organic molecules, $\text{Li@calix}^4\text{pyrrole}^{2e}$ and $\text{Li}^+(\text{calix}^4\text{pyrrole})\text{M}^-$ ($\text{M} =$ alkali atoms),^{2f} have a large first hyperpolarizability (β_0) (ranging from 10 969 to 35 934 au), while the alkali-doped inorganic molecules, $\text{Li}^+(\text{NH}_3)_4 \text{M}^-$ ($\text{M} =$ alkali atoms),^{2g} have even larger β_0 values (ranging from 70 295 to 185 805 au). It thus demonstrates that the alkali metal doping observably enhances the first hyperpolarizability.

For conjugated polymer chains, people have great interest in the investigation of doping-enhanced NLO responses. Champagne et al.^{1h} investigated the effect of charging on the second hyperpolarizability of polyacetylene chains by explicit doping alkali metal atoms. It has been shown that charging dramatically enhances the static electronic and vibrational hyperpolarizabilities. Under suitable conditions, alkali metal atoms may replace hydrogen atoms of C–H bonds to form an alkali-metal-doped

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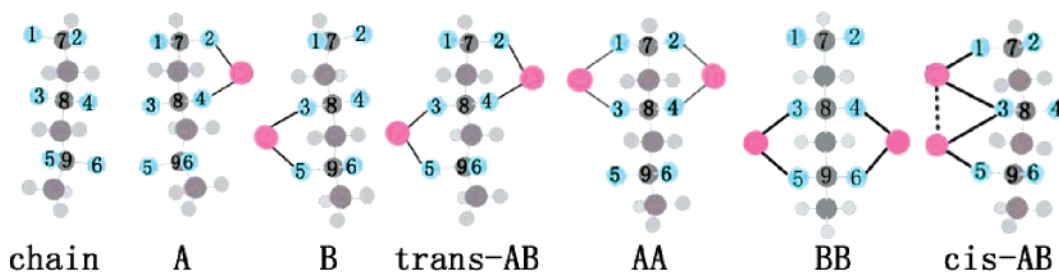


Figure 1. Geometrical structures of $\text{Li}_n\text{-H}-(\text{CF}_2-\text{CH}_2)_3\text{-H}$ ($n = 1, 2$) by MP2/6-31+G (d) method. Blue atoms are F, light gray atoms are H, dark gray atoms are C, and pink atoms are Li.

compound. It has been estimated that lithiation of the benzene molecule may lead to an enormous increase of the second hyperpolarizability.⁵

Poly(vinylidene fluoride) (PVDF or PVF_2) is a partially fluorinated polymer that possesses numerous desirable properties.⁶ In this paper, we study the alkali doping effect of a polar chain $\text{H}-(\text{CF}_2-\text{CH}_2)_3\text{-H}$. For $\text{Li}_n\text{-H}-(\text{CF}_2-\text{CH}_2)_3\text{-H}$ ($n = 1, 2$), under the action of the lone pairs of two F atoms, the 2s electron of the Li atom is ejected to become an excess electron and the transition energy of the crucial transition has a small value of 1.295–1.901 eV, which is close to 1.331–1.982 eV of the electrides $\text{Li@calix[4]pyrrole}^{2c}$ and $(\text{HCN})_n\text{Li}^{2c}$. Consequently, $\text{Li}_n\text{-H}-(\text{CF}_2-\text{CH}_2)_3\text{-H}$ ($n = 1, 2$) have the electride characteristics. And thus the β_0 values for electrides $\text{Li}_n\text{-H}-(\text{CF}_2-\text{CH}_2)_3\text{-H}$ ($n = 1, 2$) become larger and depend upon the number and situation of doped lithium atoms. In this work, a new design idea is proposed where the first hyperpolarizability can be greatly increased by the alkali atom doping into the polar chain by forming an electride system.

Computational Details

The stable structures of $\text{Li}_n\text{-H}-(\text{CF}_2-\text{CH}_2)_3\text{-H}$ ($n = 1, 2$) complexes with all real frequencies are obtained using the MP2/6-31+G(d) method (on basis set choice, see the Supporting Information). The first hyperpolarizabilities are evaluated by a finite-field approach at the MP2 level. In our previous papers,^{2a-c} the MP2 method has been chosen for calculating the first hyperpolarizability. This is because, with reasonable computation costs, the MP2 results are also very close to those obtained from the more sophisticated correlation methods (for example, the QCISD^{2c}). The 6-31+G (d) basis set is employed for the F, C, and H atoms, and the 6-311+G (3df) basis set, for the Li atom. We have shown that the basis sets chosen in this work for our purpose are adequate. As one can see from Table S2 of the Supporting Information, although the size of basis set 6-31+G(d) is less than half of that of 6-311++G (2d, 2p), the β_0 value (5995 au) obtained from the 6-31+G(d) basis set is only 6.2% different from the β_0 value (5624 au) obtained from 6-311++G(2d,2p) for structure A. For more details of the basis set effects on the first hyperpolarizability, readers are referred to Table S2 of the Supporting Information. The magnitude of the applied electric field is chosen as 0.001 au for the calculation of the hyperpolarizability, which is proven to be the most adequate value for the numerical differentiation.

The static first hyperpolarizability is noted as

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

where

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

Table 1. Selected Geometrical Parameters of $\text{Li}_n\text{-H}-(\text{CF}_2-\text{CH}_2)_3\text{-H}$ ($n = 1, 2$) Complexes at the MP2/6-31+G(d) Level

	chain	trans-AB	AA	BB	A	B	cis-AB
F–C (Å)	1.380		1.394				
	1.374	1.415	1.398		1.406		1.410
	1.380	1.402	1.405	1.405			
	1.378	1.405	1.407	1.405	1.413	1.411	
	1.383	1.431		1.412			
	1.389			1.412		1.420	1.426
F–Li (Å)		2.112	2.221	2.074	2.107	2.085	2.117
		2.018	2.057	2.099	2.070	2.054	3.250
		2.077	2.169	2.074			3.117
		2.081	2.054	2.101			2.026
		6.089	5.507	5.422			2.847

All of the calculations were performed with the GAUSSIAN 03 program package.⁷ The dimensional plots of molecular orbitals were generated with the GaussView program⁸ (Gaussian, Inc., Pittsburgh, PA).

Results and Discussions

A. Equilibrium Geometries. The optimized structures of $\text{Li}_n\text{-H}-(\text{CF}_2-\text{CH}_2)_3\text{-H}$ ($n = 0, 1, 2$) are shown in Figure 1. The important geometrical parameters are collected in Table 1.

When compared to F–C bonds in $\text{H}-(\text{CF}_2-\text{CH}_2)_3\text{-H}$, the F–C distances near the Li atom are slightly elongated by 0.014–0.048 Å in $\text{Li}_n\text{-H}-(\text{CF}_2-\text{CH}_2)_3\text{-H}$ ($n = 1, 2$). This shows that the doping Li atom can affect the nearby F–C distances. For one-Li-atom-doped systems, two different structures are obtained. Structure A is the Li atom close to the difluoromethyl group, whereas in structure B the Li atom is farther away from the difluoromethyl group. For two-Li-atom-doped systems, four different structures (AA, BB, cis-AB, and trans-AB) with three manners are obtained. In these manners, the two Li atoms, like two leaves, attach to the $\text{H}-(\text{CF}_2-\text{CH}_2)_3\text{-H}$ chain as a trunk. The structures AA and BB have two Li atoms attached on the two opposite sides of the chain. Two opposite Li atoms are close to the difluoromethyl group in structure AA but far from the difluoromethyl group in structure BB. In the structure trans-AB, two Li atoms sit on opposite sides of the chain; one is close to while the other one is far from the difluoromethyl group. However, in the structure cis-AB, the two Li atoms are located on the same side of the chain.

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Table 2. First Hyperpolarizability β_0 (au),^a the Transition Energy ΔE , and the Oscillator Strength f_0 for $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n = 1, 2$)

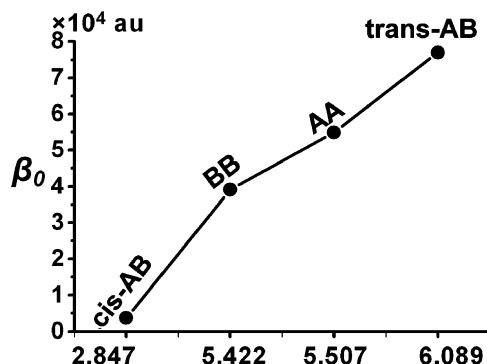
	chain	trans-AB	AA	BB	A	B	cis-AB
Li–Li (Å)		6.089	5.507	5.422			2.847
ΔE (eV)	12.497	1.295	1.359	1.367	1.814	1.817	1.901
f_0	0.3076	1.3180	1.6671	1.6083	0.2484	0.2510	0.4599
β_x (au)	30.6	–15 449	–19 265	–2133	4916	3499	–1028
β_y (au)	–48	–22381	–10151	374	–3067	–1770	2372
β_z (au)	–96	72 014	50 386	39 005	–1540	–3191	2639
β_0 (au)	112	76 978	54 890	39 065	5995	5056	3694

^a 1 au = $8.639\ 22 \times 10^{-33}$ esu.

For two Li-atom-doped systems, the Li–Li distance is the key point with great importance. The Li–Li distance (2.847 Å) of the structure cis-AB is the shortest. As this is very close to the Li–Li bond length (2.672 Å) of the Li_2 molecule,⁹ the two doped Li atoms may form a Li–Li bond in the structure cis-AB. In the two structures (BB and AA), the Li–Li distances (5.422 and 5.507 Å) are medium and similar. The Li–Li distance (6.089 Å) is the longest in the structure trans-AB. It will be shown in the following that the Li–Li distance is an important factor affecting the β_0 value in two-Li-atom-doped systems.

B. Static First Hyperpolarizabilities. The electric properties of $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n = 1, 2$) calculated at the MP2 level are given in Table 2. From Table 2, the Li atom(s) doping into the $\text{H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ chain greatly enhances the β_0 value by about 33–687 times. The order of the β_0 values is 76 978 (trans-AB) > 54 890 (AA) > 39 065 (BB) > 5995 (A) > 5056 (B) > 3694 au (cis-AB). It is also interesting to compare the β_0 values of $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n = 1, 2$) to the other systems with large β_0 values. The range of the β_0 values of $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n = 1, 2$) (3694–76 978 au) is much larger than that of the known electrides $(\text{HCN})_n\text{Li}^{2c}$ and $\text{Li@calix[4]pyrrole}^{2c}$ (the range of the β_0 values is 3385–15 682 au) and close to that of the large donor–acceptor polyenes systems^{10a} (the range of the β_0 values is 8818–152 502 au). Furthermore, the β_0 value of the trans-AB (76 978 au) is about 2.5 times larger than that of the organometallic system $\text{Ru}(trans\text{-}4,4'\text{-diethylaminostyryl-}2,2'\text{-bipyridine})_3^{2+}$ (31 123 au).^{10b}

From Table 2 and Figure 2, the β_0 value is related to the Li atom number and the Li atom position(s) for Li-atom-doped systems. Four interesting relationships between the structure and β_0 value have been observed. (1) For the one-Li-doped systems, the shorter the distance between the Li atom and difluoromethyl group, the larger the β_0 value (5995(A) > 5056 au (B)). (2) The β_0 values (39 065–76 978 au) of two-Li-doped systems are much larger than those (5056 and 5995 au) of one-Li-doped systems, except for the cis-AB where the Li–Li distance (2.847 Å) is close to the Li–Li bond length (2.672 Å) of the Li_2 molecule.⁹ (3) For two-Li-doped systems, the β_0 value increases with increasing Li–Li distance as shown in Figure 2. The system with a longer Li–Li distance has a more dispersive excess electron cloud, and the larger the dispersion of the excess electron cloud, the larger the β_0 value it has. The order of the β_0 values is 76 978 (trans-AB) > 54 890 (AA) > 39 065 (BB)

**Figure 2.** Relationship between first hyperpolarizabilities (β_0) and Li–Li distances for $\text{Li}_2\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$.

> 3694 au (cis-AB), which is consistent with the corresponding order of the Li–Li distance to be 6.089 (trans-AB) > 5.507 (AA) > 5.422 (BB) > 2.847 Å (cis-AB). Thus, the relationship between the β_0 value and relative positions of the two Li atoms is presented; that is, the β_0 value of the structures with two alternate Li atoms (trans-AB with larger Li–Li distance) is greater than those of the structures with two opposite Li atoms (smaller Li–Li distances for AA and BB). (4) Similar to the case of (1), for structures with opposite Li atoms (the Li–Li distances are almost the same in AA and BB), the β_0 value of structure AA with two Li atoms near the difluoromethyl group is also larger than that of structure BB with two Li atoms far from the difluoromethyl group.

From the “sum-over-states” (SOS) expression, Oudar and Chemla^{11,12} established a simple link between β_0 and a low-lying charge-transfer transition by the two-level model. For the static case ($\omega = 0.0$), the following two-level expression is employed to estimate β_0 in the literature:^{12,13}

$$\beta_0 \propto \frac{\Delta\mu \cdot f_0}{\Delta E^3} \quad (2)$$

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 is inversely proportional to the third power of the transition energy (ΔE). From the two-level expression (eq 2), it is obvious that the transition energy is the decisive factor in the first hyperpolarizability.

The transition energies (ΔE) of $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n = 1, 2$) are estimated by the CIS method with the 6-31+G (d) basis set and listed in Table 2. From Figure 1 and Table 2, The molecular structure dependences of transition energy are shown. (1) For the one-Li-atom-doped and opposite Li atom pair (AA and BB) systems, the shorter the distance between the Li atom and difluoromethyl group, the smaller the ΔE . (2) The ΔE values of the two-Li-atom-doped systems are much smaller than those of the one-Li-atom-doped systems, except for the case of cis-AB with the shortest Li–Li distance. (3) For the two-Li-atom-doped chains, the ΔE decreases as the Li–Li distance increases.

The order of ΔE values of $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n = 1, 2$) is 1.295 (trans-AB) < 1.359 (AA) < 1.367 (BB) < 1.814 (A) < 1.817 (B) < 1.901 eV (cis-AB). These transition energies

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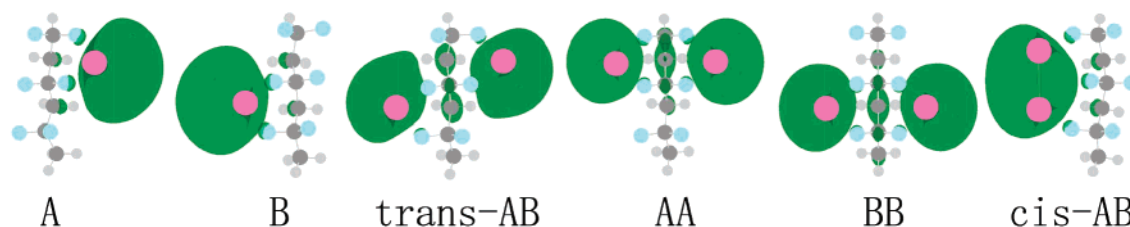


Figure 3. The 0.020 isosurfaces of HOMO in $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n = 1, 2$).

are much smaller than the value of 12.497 eV for $\text{H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$. Clearly, from eq 2, the order of the β_0 values for the different structures is $\text{trans-AB} > \text{AA} > \text{BB} > \text{A} > \text{B} > \text{cis-AB}$ in $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n = 1, 2$), inversely to the order of the ΔE values.

For $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n = 1, 2$), the magnitude of the ΔE values of crucial transition is quite small. It is around 1.295 to 1.901 eV, which is close to those of 1.331 to 1.982 eV of the electrides $\text{Li@calix[4]pyrrole}^{2e}$ and $(\text{HCN})_n\text{Li}$.^{2c} As shown in Figure 3 (the HOMO plots), the Li atom has a big diffuse orbit and its valence electron is loosely bound in complexes. These complexes have the electride characteristics. So naturally, $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n = 1, 2$) should have large first hyperpolarizabilities.

In the present work, we have obtained a valuable description of the first hyperpolarizabilities of $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n = 1, 2$). It indicates that the Li-atom-doped polar chain with

excess electron(s) may have very low-lying excited states to bring such a large β_0 value.

As a result, our investigation may evoke one's attention to the design of new electrides with large NLO responses by using the alkali-metal-doped effect.

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Supporting Information Available: Complete ref 7, the basis set effect of molecular geometries, and the basis set effects of the first hyperpolarizability. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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