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Quantum chemical study of structures, electronic spectrum, and nonlinear optical properties of polynuclear lithium compounds

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ABSTRACT

A theoretical study of polynuclear lithium compounds has shown that these species display large calculated nonlinear optical (NLO) responses. These compounds are based on aromatic subunits connected through polyhedral inorganic core (Li_7O_6 or Li_8O_6). These compounds show the calculated first hyperpolarizabilities (β) ranging from 262.55 to 16336.35×10^{-33} esu. The results show that subtle structural modification can substantially enhance the first hyperpolarizability. A basis for understanding the origin of these large NLO responses is proposed based on consideration of the molecular orbitals and electronic transition features of the compounds and the two-state model. Charge transfer from central core to the peripheral phenyl groups plays a key role in the nonlinear optical response. Moreover, the effects of different functionals and basis sets on first hyperpolarizability were systemically investigated.

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1. Introduction

The design of novel materials with large nonlinear optical (NLO) responses is currently of great interest due to their potential applications in optical and electro-optical devices. There are three generic classes of nonlinear optical (NLO) materials: inorganic salts, semiconductors, and organic compounds. Each class possesses its own complement of favorable and unfavorable attributes for NLO application [1]. Although inorganic salts have a large transparency range, are robust, are available as large single crystals, the purely electronic NLO effects are often accompanied by those arising from lattice distortions; response times are slow; and synchronization of the phase of the interacting optical fields is not easy to satisfy [2]. NLO response of semiconductors originates from saturable absorption. Their third-order NLO responses are among the largest known [3], but the NLO processes based on such resonant interactions may be relatively slow. The organic materials exhibit relatively low cost, ease of fabrication and integration into devices, tailorability, which allows one to fine-tune the chemical structure and properties for a given nonlinear optical process, high laser damage thresholds, low dielectric constants, fast nonlinear optical response times, and off-resonance nonlinear optical susceptibilities comparable to or exceeding those of ferroelectric inorganic crystals [4]. The main disadvantages of organic materials are low thermal stability, a facile relaxation to random orientation in poled guest–host systems, low optical transparency in the UV–vis region result from

low-energy transitions [5]. The limitations identified above spur investigations of novel NLO materials. Recent study shows that organometallic complexes offer greater scope for creation of multifunctional NLO materials by virtue of their greater design flexibility and low energy, yet sometimes intense electronic transitions [6–10].

Lithium has the lightest weight among metallic elements, and a very rich chemistry [11]. Organolithium compounds thus constitute an important and active field of studies with numerous applications [12,13]. Here, we mainly focused on their NLO properties. LiNbO_3 has exhibited excellent NLO response and is widely applied as inorganic NLO material [14,15]. Lithium 3,5-dinitrobenzoate ($\text{Li}(\text{dnb})$) was synthesized and characterized, which can form a 1D propeller chain structure and exhibits modest second-order nonlinear response [16]. Zhao et al. investigated the structural, electronic, and optical properties of medium-sized Li_n clusters ($n = 20, 30, 40, 50$) and found that the average polarizability of the Li clusters reduces rapidly with cluster size and can be approximately described by a classical metallic sphere model [17]. Li et al. theoretically designed and investigated NLO properties of series of Li-doped electrode/salt complexes. These alkali–metal-doped complexes have shown a remarkably large NLO response, and the Li valence electron played a crucial role in the large NLO value of these compounds [18–22]. Our group also investigated the NLO properties of the lithium decahydroborate (Li@B10H14) complex [23]. However, there are no NLO experimental reports on these Li-doped electrode/salt complexes, which might be due to the instability of these complexants and/or inadequate reactivity of the Li atom caused by the presence of some repulsive interaction between the Li electron and these organic compounds.

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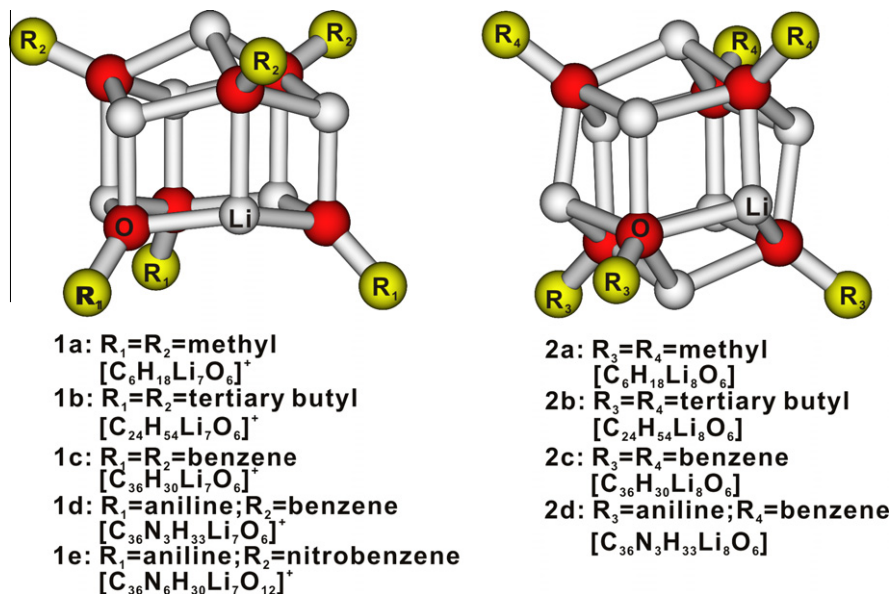


Fig. 1. Calculated equilibrium structures and their chemical formulas of the investigated compounds.

Although synthesis of pure lithium tert-butoxide is difficult, hexameric units $\text{Li}_6(\text{O}^t\text{Bu})_6$ at least in the gas phase were obtained [24]. Recently, $[\text{Li}_7(\text{O}^t\text{Bu})_6]^+$ cation was synthesized and characterized by X-ray diffraction analysis, in which all lithium atoms are three-coordinate, displaying no additional short contacts – i.e. agostic interactions – to methyl groups [25]. Moreover, Davies et al. synthesized a novel compound containing Li_8O_6 as core, in which Li_8O_6 is a rhombic dodecahedral cluster with 14 vertices, 12 faces, and 24 edges [26]. The inorganic nature of Li_8O_6 core might enhance the stability of the material and be helpful for experimentalists to handle it at room temperature and/or to use experimental conditions which are not possible to pure organic compounds. Based on the above structures, we design a series of compounds containing different conjugate bridges, donor and acceptor (Fig. 1). We hope that these compounds might possess the merits of both inorganic and organic material and offer some interesting new opportunities for nonlinear optical materials.

Recent studies show that density functional theory calculations are remarkably successful in predicting a wide range of problems in organometallic chemistry [27–33]. In this paper, with the help of quantum-chemical calculations, it is desirable to obtain the following information: (1) study the electron spectra character of these compounds; (2) determine the character of charge transfer; (3) predict the nonlinear optical properties and elucidate the structure–property relationships from the micromechanism.

2. Computational method

Geometrical optimization of the studied compounds without any symmetry constraint was carried out with the B3LYP [34] combinations of density functional theory (DFT) in the Gaussian 09 computational chemistry program [35]. The B3LYP functional is a combination of Becke's three-parameter hybrid exchange functional [18] and the Lee–Yang–Parr [36] correlation functional. Basis set of 6-311G* was applied to our studied compounds. B3LYP employing the 6-311G* basis set can well reproduce the experimental structures of lithium carbonate [37,38]. Time-dependent density functional (TD-DFT) calculations were carried out at the B3LYP/6-311G* level to determine the electronic transition energy, oscillator strength, and transition character. The polarizabilities and hyperpolarizability were calculated as performed in the Gaussian 09 program package. To evaluate electron correlation effects,

the static second-order polarizability was also calculated at the second-order Møller–Plesset (MP2) level. The effects of different DFT functionals and basis sets on polarizabilities and hyperpolarizability are also discussed.

The average polarizability value α_s can be obtained from the following formula:

$$\alpha_s = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (1)$$

In general, electric-field-induced second harmonic generation (EFISHG) and hyper-Rayleigh scattering (HRS) are the two main methods to determine the second-order NLO properties. Here, we focused on the HRS response of the studied compounds. In the case of plane-polarized incident light and observation made perpendicular to the propagation plane without polarization analysis of the scattered beam, the second-order NLO response that can be extracted from HRS data [39] can be described as:

$$\beta_{\text{HRS}}(-2\omega; \omega, \omega) = \sqrt{\langle \beta_{zzz}^2 \rangle + \langle \beta_{zzx}^2 \rangle} \quad (2)$$

$\langle \beta_{zzz}^2 \rangle$ and $\langle \beta_{zzx}^2 \rangle$ correspond to isotropic orientational averages of the β tensor components without assuming Kleinman's conditions [40] and are described as:

$$\begin{aligned} \langle \beta_{zzz}^2 \rangle = & \frac{1}{7} \sum_{\xi} \beta_{\xi\xi\xi}^2 + \frac{4}{35} \sum_{\xi} \beta_{\xi\xi\eta}^2 + \frac{2}{35} \sum_{\xi \neq \eta} \beta_{\xi\xi\xi} \beta_{\xi\eta\eta} \\ & + \frac{4}{35} \sum_{\xi \neq \eta} \beta_{\eta\xi\xi} \beta_{\xi\xi\eta} + \frac{4}{35} \sum_{\xi \neq \eta} \beta_{\xi\xi\xi} \beta_{\eta\eta\xi} + \frac{1}{35} \sum_{\xi \neq \eta} \beta_{\eta\xi\xi}^2 \\ & + \frac{4}{105} \sum_{\xi \neq \eta \neq \zeta} \beta_{\xi\xi\eta} \beta_{\eta\xi\zeta} + \frac{1}{105} \sum_{\xi \neq \eta \neq \zeta} \beta_{\eta\xi\xi} \beta_{\eta\zeta\xi} + \frac{4}{105} \sum_{\xi \neq \eta \neq \zeta} \beta_{\xi\xi\eta} \beta_{\xi\zeta\eta} \end{aligned} \quad (3)$$

$$\begin{aligned} \langle \beta_{zzx}^2 \rangle = & \frac{1}{35} \sum_{\xi} \beta_{\xi\xi\xi}^2 + \frac{4}{105} \sum_{\xi \neq \eta} \beta_{\xi\xi\xi} \beta_{\xi\eta\eta} - \frac{2}{35} \sum_{\xi \neq \eta} \beta_{\xi\xi\xi} \beta_{\eta\eta\xi} \\ & + \frac{8}{105} \sum_{\xi \neq \eta} \beta_{\xi\xi\eta}^2 + \frac{3}{35} \sum_{\xi \neq \eta} \beta_{\xi\xi\eta}^2 - \frac{2}{35} \sum_{\xi \neq \eta} \beta_{\xi\xi\xi} \beta_{\eta\eta\xi} \\ & + \frac{1}{35} \sum_{\xi \neq \eta \neq \zeta} \beta_{\xi\xi\eta} \beta_{\eta\zeta\xi} - \frac{2}{105} \sum_{\xi \neq \eta \neq \zeta} \beta_{\xi\xi\xi} \beta_{\eta\eta\zeta} - \frac{2}{105} \sum_{\xi \neq \eta \neq \zeta} \beta_{\xi\xi\eta} \beta_{\eta\zeta\xi} \\ & + \frac{2}{35} \sum_{\xi \neq \eta \neq \zeta} \beta_{\xi\xi\eta}^2 - \frac{2}{105} \sum_{\xi \neq \eta \neq \zeta} \beta_{\xi\xi\eta} \beta_{\eta\zeta\xi} \end{aligned} \quad (4)$$

The first hyperpolarizability values are consistent with convention *B* of Ref. [41].

3. Results and discussions

3.1. Structural and orbital character

In this paper, nine polynuclear lithium compounds were investigated (Fig. 1), which contain different conjugate bridges, donor and acceptor. It should be noted that compounds **1a–1e** have a positive charge, however the compounds **2a–2d** are neutral. The optimized ground-state geometries of these compounds show that each lithium atom is three-coordinated to oxygen atom. Moreover, the distances of these Li–O bonds are almost the same. The influence of different conjugate bridges or substituent groups on Li–O bonding length is very small. The optimized ground-state geometries are also close to the crystal structures (see the Supporting information, Table S1), which mean that our adopted method can reproduce experimental structures.

The diagrams for frontier molecular orbitals (FMO) of compounds **1a** and **2a** are displayed in Fig. 2. The highest occupied molecular orbital (HOMO) of compound **1a** is formally localized on methyls and oxygen atoms of the bottom part, and the lowest unoccupied molecular orbital (LUMO) is localized on the lithium and carbon atoms of the top part. However, the frontier molecular orbital characters of compound **2a** are distinctly different from those of compound **1a**. The HOMO of compound **2a** is mainly delocalized over each lithium atom, and the LUMO is localized on the lithium atoms of the center part and marginal carbon atoms. FMOs of the other compounds are similar to those of compounds **1a** and **2a**. The means that the large intramolecular charge transfer will come into being under the external electronic field and a large NLO response could be expected.

3.2. Electronic spectra

Time-dependent density functional theory (TD-DFT) has emerged as the currently most applied method for molecular computations due to its balance between accuracy and efficiency. In Table 1, we summarize the maximum absorption wavelength (excitation energy), oscillator strength, and major contribution for the studied compounds. The results show that increasing the

Table 1

Computed maximum absorption wavelengths (λ_{\max} in nm), oscillator strengths (*f*), and transition nature of the studied compounds.

Compounds	λ_{\max}	<i>f</i>	Major contribution
1a	217.59	0.0154	HOMO-4 → LUMO
1b	205.48	0.0480	HOMO-4 → LUMO
1c	267.44	0.0031	HOMO-2 → LUMO+1
1d	324.55	0.0085	HOMO-2 → LUMO
1e	343.72	0.0028	HOMO-1 → LUMO+3
2a	1073.71	0.4275	HOMO → LUMO
2b	1272.54	0.3264	HOMO → LUMO
2c	1356.91	0.2517	HOMO → LUMO+1
2d	1396.92	0.2386	HOMO → LUMO+2

size of the conjugate bridge or donor and acceptor substitution can lead to substantial bathochromic shift of the maximum absorption wavelengths. It should be noted that the excitation energies of compounds **1a–1e** is much larger than those of compounds **2a–2d**. In general, there is close relationship between excitation energy and energy gap (Eg). The larger Eg is; the larger excitation energy is. As a result, the Egs of compounds **2a–2d** are much smaller than those of compounds **1a–1e** (see the Supporting information, Table S2). These results are consistent with the red-shifted absorption wavelengths. The oscillator strength for an electronic transition is proportional to the transition moment and reflects the transition probability from the ground state to the excited state [42]. In general, oscillator strengths of compounds **2a–2d** are much larger than those of compounds **1a–1e**. This means that transition moment of our studied compound can be easily tuned, which will be in favor of enhancing NLO response. Here, compound **2d** was taken as an example to analyze the transition nature. The main contribution of the corresponding maximal absorption corresponds to the promotion of one electron from HOMO to LUMO+2. A crucial feature is that the HOMO are localized mainly on central part (Li₃O₆) and LUMO+2 on the peripheral phenyl groups (Fig. 3), which occurs charge transfer from central core to the peripheral phenyl groups.

3.3. Methods and basis sets

Many investigations have revealed that the optimized geometries at different levels or with different basis sets do not cause significant differences in the calculated polarizability and hyperpolarizability values [43,44,4]. However, the polarizability and hyperpolarizability tend to be very sensitive to basis sets especially to diffuse and polarization functions and methods [5,45–48]. As far as we know, no systematically theoretical investigation has been reported to polarizability and hyperpolarizability of the studied compounds. Thus, the proper choice of method and basis set is very important to obtain accurate polarizability and hyperpolarizability.

To our studied compounds, no experimental polarizability and hyperpolarizability values have been reported. Here, we use the results obtained from MP2 as a benchmark to test the reliability

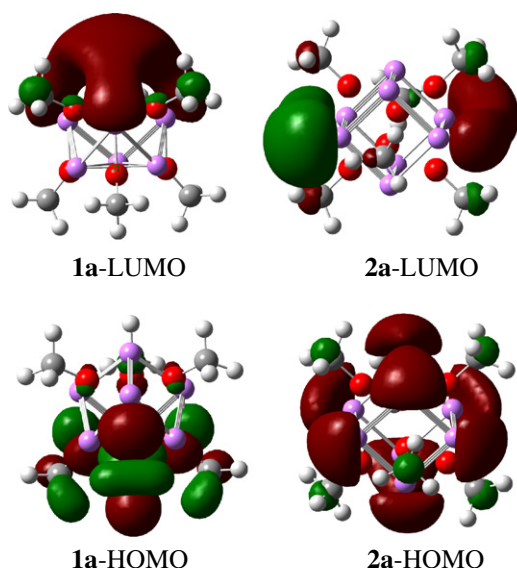


Fig. 2. HOMO and LUMO of compounds **1a** and **2a**.

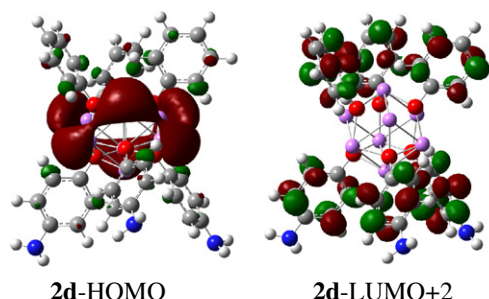


Fig. 3. Molecular orbitals involved in the main energy transition of compound **2d**.

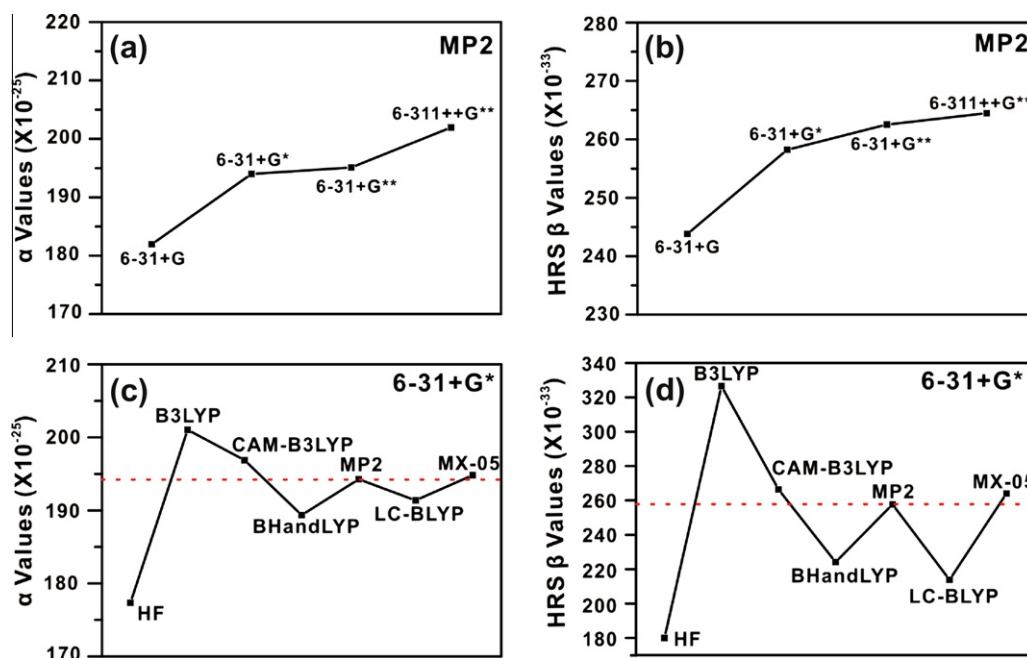


Fig. 4. The polarizability and hyperpolarizability values of compound **1a** obtained from different methods and different basis sets. (a and b) Are the results of MP2 method combined with different basis sets; (c and d) Are the results of different methods at 6-31+G* basis set level.

of the selected method and basis set. The compound **1a** was taken as an example to study the relationship between the polarizability and hyperpolarizability values and basis sets based on second-order Møller–Plesset (MP2) method. Four different basis sets (6-31+G, 6-31+G*, 6-31+G**, 6-311++G**) including diffuse functions and polarization functions were used and their results are shown in Fig. 4a and b. The polarizability and hyperpolarizability values become larger and larger with increasing the size of basis sets. However, the values obtained from 6-31+G* is much closer to the values obtained from 6-311++G**, especially to the hyperpolarizability. To reduce the computational cost, the 6-31+G* was used to calculate the polarizability and hyperpolarizability. Suponitsky et al. also found that 6-31+G* basis set is enough to their studied compounds [49].

Subsequently, we selected five different DFT functionals (B3LYP, CAM-B3LYP, LC-BLYP, BHandLYP, and MX-05) and Hartree–Fock (HF) method to test the influence on the polarizability and hyperpolarizability. These functionals have extensively been used to investigate the nonlinear optical properties [50–55]. The calculated results are shown in Fig. 4c and d. In comparison to the MP2 results, the HF method considerably underestimates polarizability and hyperpolarizability values as no correlation consideration in the HF method. B3LYP remarkably overestimates polarizability and hyperpolarizability values, which is in accordance with the conclusion in the literature [56]. It is interesting to find that the values obtained from CAM-B3LYP and MX-05 are much closer to the values of MP2. Thus, MX-05 combined with 6-31+G* basis set was used in the following discussion.

3.4. Polarizability and hyperpolarizability

Examining the physical mechanism concerning determination of the polarizability values is also important for the discussion of the hyperpolarizability values. The calculated diagonal polarizability tensors and average polarizability (α_s) values are given in Table 2. It should be noted that there is little difference among the relative magnitude of the three diagonal polarizability tensors. This is not like the most organic and metal–organic NLO chromophores

Table 2

The calculated static polarizability (10^{-25} esu) and first hyperpolarizability (10^{-33} esu) of the studied compounds.

Compounds	α_{xx}	α_{yy}	α_{zz}	α_s	β_{HRS}
1a	195.10	195.06	195.14	195.10	262.55
1b	504.24	503.50	499.85	502.53	512.00
1c	672.24	662.66	682.97	672.62	898.47
1d	699.88	689.87	792.25	727.33	3773.21
1e	803.03	802.86	851.37	819.08	6803.55
2a	1811.56	1802.63	1814.90	1809.70	
2b	3475.93	3491.90	3895.05	3620.96	
2c	2187.45	2200.96	2246.81	2211.74	
2d	2187.56	2187.56	705.42	2025.90	16336.35

typically feature dipolar molecules that are arranged in a donor–conjugate bridge–acceptor (D– π –A) motif whose molecular polarizability is dominated by the diagonal α_{xx} coefficient along the charge transfer axis. This means that the extent of charge transfer along the x, y, and z axes is almost the same. With increasing the size of the conjugate bridge, the α_s value remarkably increases. It should be noted that the effect of the donor and acceptor substitutions on the polarizability is relative small. Compared with between compounds **1a** and **2a**, the α_s of compound **2a** is almost ten times larger than that of compound **1a**. However, the structural difference between them is very small, which means that subtle structural modification can substantially enhance the polarizability.

Compounds **2a–2c** possess symmetric center and do not satisfy the pull–push electron requirement of the excellent second-order NLO materials. The static second-order polarizability is termed the zero-frequency hyperpolarizability and is an estimate of the intrinsic molecular hyperpolarizability in the absence of any resonance effect. Thus, first static hyperpolarizabilities of the other studied compounds are calculated and shown in Table 2. These compounds show calculated first hyperpolarizabilities (β_{HRS}) ranging from 262.55 to 16336.35×10^{-33} esu. This means that nonlinear optical response of the studied compounds can be effectively

tuned. For example, the first hyperpolarizability value of compound **2d** is nearly twenty times larger than that of compound **1c**. It should be noted that the effect of the donor and acceptor substitutions on the first hyperpolarizability is much larger than the polarizability. Moreover, the calculated first hyperpolarizability (β_{HRS}) value of compound **9** is about 100 times larger than the average second-order polarizability of the organic urea molecule [5] and three times larger than that measured for highly π -delocalized phenyliminomethylferrocene complex [57]. It indicates that the studied complex has excellent second-order nonlinear optical response.

From the complex SOS expression, the two-level model that linked between β_{CT} and a low-lying charge transfer transition has been established. For the static case, the following expression is employed to estimate β_{CT} :

$$\beta_{CT} \propto \frac{\Delta\mu f_{gm}}{E_{gm}^3} \quad (5)$$

where $\Delta\mu$ is the change of dipole moment between the ground and m th excited state, f_{gm} is the oscillator strength of the transition from the ground state (g) to the m th excited state (m) and E_{gm} is transition energy. Thus, the first hyperpolarizability caused by charge transfer (β_{CT}) is proportional to the optical intensity and inversely proportional to the cube of transition energy (E_{gm}). As a result, E_{gm} plays a key role in determining the first hyperpolarizability. According to the results of electronic spectra, the excitation energy (maximum absorption wavelength) decreases with the increasing the size of the conjugate bridge or donor and acceptor substitution (Table 1). This can be used to explain the variable trend of the NLO response.

4. Conclusion

We have investigated the electronic spectrum and the second-order nonlinear optics properties of polynuclear lithium compounds and elucidated structure–property relationships from the micromechanism. These compounds are based on aromatic subunits connected through polyhedral inorganic core (Li_7O_6 or Li_8O_6). A theoretical study of polynuclear lithium compounds has shown that these species display large calculated nonlinear optical responses. These compounds show the calculated first hyperpolarizabilities (β) ranging from 262.55 to 16336.35×10^{-33} esu, which means that subtle structural modification can substantially enhance the first hyperpolarizability. Charge transfer from central core to the peripheral phenyl groups plays a key role in the nonlinear optical response. Moreover, the effects of different functionals and basis sets on first hyperpolarizability were systemically investigated.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.comptc.2011.01.031.

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