



A quantum chemical study on the remarkable nonlinear optical and electronic characteristics of boron nitride nanoclusters by complexation via lithium atom



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ABSTRACT

Density functional theory (DFT) calculations have been carried out to study the electro-optical features of B₁₂N₁₂ and B₁₆N₁₆ nanoclusters by complexation via Li atom. The results reveal that the complexation process is energetically favorable. The electronic properties of these clusters are strongly sensitive to interaction with the Li atom. The HOMO–LUMO gaps of these nanoclusters are significantly narrowed due to the complexation via Li atom. Moreover it is observed that Li complexation enhances the first hyperpolarizabilities of B₁₂N₁₂ and B₁₆N₁₆ nanoclusters. The first hyperpolarizabilities remarkably increase in the range of 2975 to 130,837 a.u. Also the TD-DFT calculations are also performed to investigate the origin of first hyperpolarizabilities. To sum up, it is found that the Li atom complexation with these BN-clusters acts a key role in tuning their electronic and nonlinear optical properties. It seems that these systems could be introduced as promising innovative electro-optical BN-based materials.

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1. Introduction

In the last few decades the design and synthesis of nonlinear optical (NLO) materials have been attracting great interest due to their wide applications in optical communication, optical computing, dynamic image processing, telecommunications, information storage, optical switching and other laser devices [1–8]. Research on designing new high-performance NLO materials is being an intriguing issue for scientist [8–16]. Among many strategies for enhancing the NLO response of materials, introducing the diffuse excess electron, such as alkali metals, proposed an efficient approach to improve the NLO properties of different systems. It has been proposed that the excess electron is a kind of special anion with dispersivity, loosely bounding and with other fascinating features, which plays a pivotal role in the large first hyperpolarizabilities (β_0) of dipole-bound electron clusters [18]. For instance, it is reported that incorporating the alkali metal atom into organic calix [4]pyrrole [19], B₁₀H₁₄ basket [20], π -conjugated aromatic rings [21], C₆₀C₁₈ [22] Be₁₂O₁₂ and Mg₁₂O₁₂ [23] remarkably enhance first static hyperpolarizability (β_0). The first hyperpolarizability (β_0) is a third rank tensor and known as NLO response coefficient. Thus it seems that the dramatic effect of an excess electron on the

extraordinary β_0 of a cluster anion opens new perspectives for designing of novel NLO materials.

Boron nitride nanomaterials exhibit different desirable physical and chemical properties in comparison to their carbon counterparts. Recently fullerene-like cage of boron nitride nanostructures have attracted considerable attention due to their remarkable chemical and physical properties, particularly of wide gap semiconductors [24–28]. The geometries and stability of fullerene-like (BN)_n nanoclusters have been theoretically investigated by many researchers [29–33]. Fowler et al. [29] theoretically showed that B₁₂N₁₂ and B₁₆N₁₆ are magic stable BN fullerenes. Theoretical studies demonstrated that these clusters consist entirely of tetragonal and hexagonal BN rings. Oku et al. [34] have synthesized these magic clusters, detected by laser desorption time-of-flight mass spectrometry. They confirmed that B₁₂N₁₂ cluster is semiconductor which consists of square and hexagonal rings.

The applications of BN-based nanostructures in nonlinear optics have scarcely been reported. Recently Ma et al. have been investigating the influence of Li₂ trapped inside [n,0] boron nitride nanotube on their NLO responses [35]. Also the enhancement of second-order nonlinear optical response in boron nitride nanocone by Li atom doping is reported [36]. In the present study the influence of Li atom complexation with B₁₂N₁₂ and B₁₆N₁₆ nanoclusters on their electro-optical features is investigated through DFT and TD-DFT calculations. Due to the unique physiochemical properties of BN-based nanostructures, studying the

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first hyperpolarizability of BN clusters complexed with Li atom would be a valuable project.

2. Computational details

The geometries of all considered structures are fully optimized at B3LYP [37,38]/6-31 + G(d) [39–41] level of theory and the nature of the stationary points are checked by frequency analysis at the same computational level. The spin-unrestricted approach is applied to describe the geometry optimization, electronic structure and NLO properties of complexed nanoclusters via Li atom; whereas the restricted approach is used for the isolated clusters. The corresponding $\langle S^2 \rangle$ values for spin-unrestricted approach are in the range of 0.752–0.755 for these mentioned structures, which are very close to the value 0.750 for the pure doublet state, indicating that the spin contamination is negligible and the computational results are reliable. It is noteworthy that selecting a proper method to calculate the hyperpolarizability of a system is a challenging task. The quadratic configuration interaction including single and double substitutions (QCISD) and the second-order Møller–Plesset perturbation (MP2) methods are suitable to for calculating hyperpolarizability, but they are very costly for relatively larger systems [17,42]. On the other hand, the B3LYP method has overestimated the hyperpolarizabilities for some large systems [43]. Fortunately, a new density functional Coulomb-attenuated hybrid exchange-correlation functional (CAM-B3LYP) has been developed to overcome these limitations, and it is suitable to predict the molecular NLO properties of a large system [44]. It has been shown that this functional provides good results for electronic excitation energies [45–48], first [49], second hyperpolarizabilities [50] and even electric field-induced second harmonic generation [51]. Specifically, the CAM-B3LYP method was tested and found to be suitable for calculating hyperpolarizabilities of Li₂ trapped inside boron nitride nanotubes [35] and Li doped boron nitride nanocone [36]. Thus the CAM-B3LYP method could be satisfactory choice to explore the static hyperpolarizabilities of currently studied systems. The first hyperpolarizability is evaluated by an analytical CAM-B3LYP/6-311 + G(d) approach. Furthermore, the time-dependent density functional theory (TDDFT) calculations are performed at the CAM-B3LYP/6-311 + G(d) levels to obtain the crucial excited states of the related structures, and the differences of their dipole moments between the ground state and crucial excited state. All calculations are performed using Gaussian 09 quantum chemistry code [52] with default convergence criteria; the SCF convergence criteria are set to 10⁻⁸ Hartree on the density (SCF = Tight) as well as the convergence of geometric optimizations are adjusted to maximum force and root-mean-square (rms) force of 4.5 × 10⁻⁴ and 3.0 × 10⁻⁴ Hartree. Bohr⁻¹, respectively, and maximum and rms displacements of 1.8 × 10⁻³ and 1.2 × 10⁻³ Bohr, respectively.

The HOMO–LUMO gap (HLG) values are considered to explore electronic properties of the considered clusters. It is defined as follow:

$$HLG = (\varepsilon_L - \varepsilon_H) \quad (1)$$

where ε_H and ε_L are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, respectively.

The energy of a system in the weak and homogeneous electric field can be defined as [53,54]:

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

where E^0 is the molecular total energy without the electric field and F_α is the electric field component along α direction. The μ_α , $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ denote dipole, polarizability, and the first hyperpolarizability, respectively. The first hyperpolarizability (β_0) are noted as:

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (3)$$

in which

$$\beta_i = \frac{3}{5} (\beta_{iii} + \beta_{ijj} + \beta_{ikk}) \quad i, j, k = x, y, z \quad (4)$$

β_0 is the first hyperpolarizability, which is a third rank tensor and known as NLO response coefficient.

3. Results and discussions

The structures of B₁₂N₁₂ and B₁₆N₁₆ nanoclusters are optimized at B3LYP/6-31 + G(d) level of theory and depicted in Fig. 1. These nanoclusters consisted of tetragonal and hexagonal rings. It is clear from this figure that two kinds of individual B–N bonds are distinguishable for the considered structures. These different bonds are presented in Fig. 1. The bond lengths (l) of hh -bonds are 1.44 and 1.45 Å in B₁₂N₁₂ and B₁₆N₁₆ nanoclusters, respectively; whereas the corresponding hs -bonds have the lengths of 1.49 and 1.47 Å. Since the bond lengths of hs -bonds are larger than hh -ones, it seems that more p orbital participation is responsible for such increasing of hs -bonds than hh -ones.

The HOMO acts as electron donor and the LUMO largely acts as electron acceptor. The pictorial representations of the HOMO–LUMO distribution of the considered nanoclusters are also shown in Fig. 1. According to this figure, the HOMO is concentrated over the nitrogen atoms of the clusters as well as the LUMO is spread over the boron atoms. The obtained HOMO and LUMO energies together with HOMO–LUMO gap (HLG) values of these pristine clusters are listed in Table 1. The obtained HOMO–LUMO gap for the B₁₂N₁₂ and B₁₆N₁₆ nanoclusters are about 6.71 and 6.17 eV, respectively. The obtained HLG values are demonstrated the semiconductor characters of these clusters which is independent to the size of cluster. Indeed, the first hyperpolarizability (β_0) values of these clusters are calculated at CAM-B3LYP/6-311 + G(d) level and summarized in this table. The obtained results exhibit that both of these clusters have no NLO response due to their negligible value for first hyperpolarizability.

To continue, the electro-optical responses of B₁₂N₁₂ and B₁₆N₁₆ nanoclusters by complexation with lithium (Li) atom are investigated in details. To that end, the geometries of Li-cluster with all real frequencies are obtained at the B3LYP/6-31 + G(d) level of theory. Various initial locations for Li atom over the clusters are considered, including: over the boron or nitrogen atom, the hs - or hh -bond, the center of the hexagonal or tetragonal ring. After full relaxation, four and three distinguishable complexes are observed for Li over B₁₂N₁₂ and B₁₆N₁₆ nanoclusters, respectively. The corresponding relaxed structures are presented in Fig. 2. All these structures belong to Cs point group. In the case of B₁₂N₁₂ cluster the Li atom is located over the hs -bond, hh -bond, tetragonal or hexagonal ring which are specified as panels **a**, **b**, **c** and **d**, respectively, in this figure. According to Fig. 2 Li atom is located over hs -bond, hh -bond and hexagonal ring of B₁₆N₁₆ nanocluster, presented as panels **e**, **f** and **g**, respectively. The interaction distances are also depicted in this figure. In the case of **a**, **b**, **e** and **f** configurations in which Li atom located over B–N bonds, it is closer to nitrogen atom with interaction distances about 1.90 Å than boron atom with distance of about 2.20 Å. Moreover, the corresponding B–N bonds are elongated due to Li adsorption. The corresponding hs - and hh -bonds of B₁₂N₁₂ nanocluster are elongated to 1.67 Å in **a** configuration and 1.57 Å in **b** one. In the **e** and **f** configurations the corresponding hs - and hh -bonds are elongated to 1.63 and 1.59 Å, respectively. Thus Li complexation leads to structural deformation in clusters and this could be affected electro-optical features of the considered clusters.

The interaction energy (E_{int}) due to the complexation of nanoclusters with Li atom is defined as:

$$E_{int} = E_{Li-cluster} - E_{cluster} - E_{Li} \quad (5)$$

where $E_{Li-cluster}$ denotes the total energy of the adduct cluster with the Li atom. The term $E_{cluster}$ and E_{Li} are the total energy of isolated cluster

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