



Enhancement of second-order nonlinear optical response in boron nitride nanocone: Li-doped effect



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ARTICLE INFO

Article history:

Received 5 July 2013

Received in revised form

10 September 2013

Accepted 13 September 2013

Available online 23 September 2013

Keywords:

Electronic structure

DFT

frequency dependent

Li-doped nanomaterial

First hyperpolarizability

ABSTRACT

The unusual properties of Li-doped boron nitride nanomaterials have been paid further attention due to their wide applications in many promising fields. Here, density functional theory (DFT) calculations have been carried out to investigate the second-order nonlinear optical (NLO) properties of boron nitride nanocone (BNNC) and its Li-doped BNNC derivatives. The natural bond orbital charge, electron location function, localized orbital locator and frontier molecular orbital analysis offer further insights into the electron density of the Li-doped BNNC derivatives. The electron density is effectively bounded by the Li atom and its neighboring B atoms. The Li-doped BNNC molecules exhibit large static first hyperpolarizabilities (β_{tot}) up to 1.19×10^3 a.u. for Li@2N-BNNC, 5.05×10^3 a.u. for Li@2B-BNNC, and 1.08×10^3 a.u. for Li@BN-BNNC, which are significantly larger than that of the non-doped BNNC (1.07×10^2 a.u.). The further investigations show that there are clearly dependencies of the first hyperpolarizabilities on the transition energies and oscillator strengths. Moreover, time-dependent DFT results show that the charge transfer from BNNC to Li atom becomes more pronounced as doping the Li atom to BNNC. It is also found that the frequency-dependent effect on the first hyperpolarizabilities is weak, which may be beneficial to experimentalists for designing Li-doped BNNC molecules with large NLO responses.

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1. Introduction

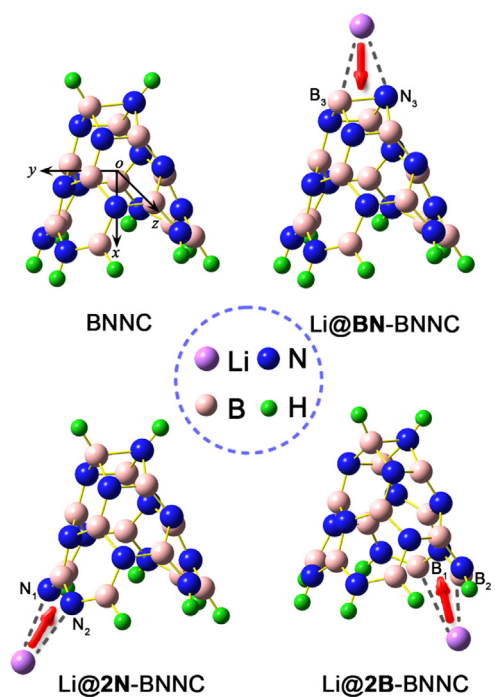
During the past 20 years, great effects have been devoted to design and synthesize high-performance nonlinear optical (NLO) materials for their potential applications in low-cost, high-performance photonic and electro-optical devices [1–10]. Up to now, the effective ways to enhance NLO responses mainly include enhancing the strength of the donor and acceptor [11], enhanced push–pull effects [12,13], twisted π -electron systems [14], introduction of a transition metal atom into the organic compounds [11,15–17], and so forth. Increasingly, recent studies of NLO responses have focused on the materials with Li-doped electroneutral/salt complexes [18–21]. These alkali-metal-doped model systems exhibit very large static first hyperpolarizabilities (β_{tot}). For example, the alkali-doped organic molecules Li@calix[4]pyrrole and the alkali molecule $\text{Li}^+(\text{calix-}[4]\text{pyrrole})\text{M}^-$ (M = alkali atoms) have large β_{tot} values (ranging from 10 969 a.u. to 35 934 a.u.) [18,21]. And the β_{tot} value of a very small compound (HCN...Li) with only four atoms is 13979 a.u. [22], which is comparable with that of traditional large donor/acceptor polyenes systems (ranging from 8818 a.u. to 15502 a.u.) [11]. It thus

demonstrates that doping alkali metals into proper organic complexant forms electroneutral and alkali molecules, which is an effective way to enhance static first hyperpolarizability [19].

The first attempts to estimate the magnitude of hyperpolarizabilities of lithiated organic molecules have been carried out by using semiempirical methods [23]. Papadopoulos et al. first investigated the lithiation effect of the conjugated benzenoid ring on the second hyperpolarizability [24]. Champagne et al. investigated the effect of charging on the second hyperpolarizabilities of polyacetylene chains by explicit doping alkali metal atoms [25]. Recently, the lithiation effects on the first hyperpolarizabilities of acene systems with planar π conjugation were investigated by Xu and co-workers [26–28]. Related theoretical studies on boron nitride nanotube (BNNT) have also been recently carried out [29–31]. The results show that BNNT is sensitive to external electron. Paying further attention to the mechanism of the electrical polarization property in boron nitride nanomaterials might open new perspectives to develop their further applications in nanotechnology.

From the above reports and appealing features of boron nitride nanomaterials, we are inspired to probe into the research of the novel boron nitride nanocones (BNNC) with large NLO responses. BNNC is one example for single layer nanostructures of BN and has already been experimentally synthesized and theoretically predicted [32,33]. Up to now, there are various techniques can be used to produce BNNCs, such as reactive ion etching (RIE) [34],

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Scheme 1. Molecular structures of BNNC and its Li-doped derivatives.

thermal annealing under lithium vapor [35] and chemical vapor deposition with boron and metal oxide as the reactant (BOCVD) [36]. Due to their unique interesting cone-shaped morphologies, greater rigidity, and easier mounting, BNNCs are more potential candidates for field emitters [37] and hydrogen storage materials [33,38] and so forth. However, there is less research on the NLO properties of Li-doped BNNC molecules. Can the first hyperpolarizability be increased when the Li atom doping on BNNC to form a new type of Li salts?

We have proposed a novel way to produce Li@BNNC molecules with good NLO values to answer this question. From the theoretical analyses before [39], it is noted that BNNCs can be generated by curling the white graphene with disclination angle $n \cdot 120^\circ$ in order to form the complete B–N bond. The 240° disclination is the smallest cone geometry ensuring the presence of B–N bonds only. Therefore, in this work, we first focus on the BNNC with 240° disclination angle and a suitable cone height (8.0 \AA) as complexant to design a new type of alkali-metal complexes with large β_{tot} values. The Li@BN-BNNC, Li@2N-BNNC and Li@2B-BNNC were formed by doping the Li atom to the top and two different bottom sides of BNNC, respectively (see Scheme 1). Significantly, it is our expectation that the doping effect on the first hyperpolarizability is great and quite different. Our investigation has focused on the molecular structure, electronic structure, frontier molecular orbital, and nonlinear optical response. The results may be beneficial in both designing high-performance NLO materials and understanding the origin of the interaction between the BNNC and the Li atom.

2. Computational details

It is well known that the choice of suitable method is crucial to generate reliable and accurate results. For calculation methods, the global hybrid generalized gradient approximation M06-2X functional was recommended by Truhlar and Zhao for calculation applications involving main group chemistry, valence and Rydberg electronic excitation energies, and aromatic–aromatic stacking interactions. The M06-2X functional is a highnonlocality functional with double the amount of nonlocal exchange (2X), which

is suitable in this work [40,41]. The optimized geometric structures of BNNC, Li@2N-BNNC, Li@2B-BNNC and Li@BN-BNNC with all real frequencies are obtained at the M06-2X/6-31+G(d) level. Furthermore, the natural bond orbital (NBO), Mayer and Wiberg bond order, electron location function (ELF), localized orbital locator (LOL) and vertical ionization potentials (VIP) are calculated at the same functional and basis set as that used to optimize the geometric structures. With regard to the calculation of the hyperpolarizability, choosing a proper method is important. The conventional DFT methods have been reported to provoke an overestimation of the hyperpolarizabilities [42,43]. The overestimation of the hyperpolarizabilities is expected due to the incorrect electric field dependence modeled by the conventional exchange functional treatments. Highly correlated coupled-cluster methods (such as CCSD, CCSD(T), or even higher CCSDT and CCSDTQ) are known to be generally reliable for calculating the hyperpolarizabilities of molecular systems. However, the use of such high-level methods is still limited to small and medium-sized systems due to the high computing cost. Because of the modest accuracy and computational cost, some hybrid DFT methods have been widely used to predict the optoelectronic properties of molecules. For example, the new hybrid meta exchange correlation functional M06-2X was employed to evaluate the static first hyperpolarizabilities for the long-range interaction system ($\text{Na@C}_{60}\text{C}_{60}\text{@F}$) [44] and the excess electron system (Li@BNNT) [30]. The results show that the static first hyperpolarizabilities of M06-2X method are close to those of MP2 method. To check the consistency of our calculations, the Coulomb-attenuated hybrid exchange–correlation functional (CAM-B3LYP) [45], which combines the hybrid qualities of B3LYP and the long-range correction presented by Tawada et al. [46], has been proposed specifically to calculate the first hyperpolarizabilities (Table S1, supporting information). It is clearly seen that two functionals display the same trend in β values. Thus, the β values are all evaluated at M06-2X/6-31+G(d) level throughout this work by analytical third energy derivatives, which is more efficient and less expensive [47]. The total static first hyperpolarizabilities, β_{tot} , for the studied molecules are defined as:

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

β_x , β_y , and β_z represent the components of the first hyperpolarizability tensors along x -, y -, and z -axis, respectively. The first hyperpolarizability component above is defined by the equation (Eq. (2)):

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} [(\beta_{ijj} + \beta_{jji})] \quad i, j = x, y, z \quad (2)$$

where β_{iii} is the diagonal tensor, β_{ijj} or β_{jji} are the off-diagonal tensors. Furthermore, to understand the influence of the dispersion (frequency-dependence) and the effect of the electron correlation on the NLO properties, the frequency-dependent first hyperpolarizabilities ($\beta(\omega)$) were evaluated by couple-perturbed (CP) DFT method with M06-2X functional.

To obtain more insight on the description of the trend of second-order NLO responses, time-dependent density functional theory (TD-DFT) was used to compute the excited states of the studied molecules applying the same theory level used for the calculation of the first hyperpolarizabilities. TD-DFT is one of the most successful and extensively used methods to describe the excited states in quantum chemistry owing to its efficiency and accuracy [48,49]. The hybrid M06-2x functional presents a higher percentage of Hartree–Fock (HF) exchange (54%) and is suitable for applications in many nanoscale molecular systems.

All of the calculations were carried out by using the Gaussian 09W program package [50]. The Mayer and Wiberg bond order, ELF, LOL were carried out using MultiWFN 2.5.2 [51].

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