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Muhammad Hussnain  
University of Agriculture Faisalabad

Rao Aqil Shehzad  
University of Agriculture Faisalabad

Shabbir Muhammad  
University of Agriculture Faisalabad

Javed Iqbal  
University of Agriculture Faisalabad  
https://orcid.org/0000-0003-0598-8401

Abdullah G. Al-Sehemi  
King Khalid University

Saleh S. Alarfaji  
King Khalid University

Khurshid Ayub  
COMSAT University

Muhammad Yaseen  
University of Agriculture Faisalabad

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Muhammad Hussnain, a Rao Aqil Shehzad, a Shabbir Muhammad, a,b Javed Iqbal, a,c Abdullah G. Al-Sehemi, d Saleh S. Alarfaji, d Khurshid Ayub, e Muhammad Yaseen, f

a Department of Chemistry, University of Agriculture Faisalabad, 38000, Faisalabad Pakistan.
b Department of Physics, College of Science, King Khalid University, Abha 61413, P.O. Box 9004, Saudi Arabia.
c Punjab Bio-energy Institute, University of Agriculture, Faisalabad-38040, Pakistan.
d Department of Chemistry, College of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia.
e Department of Chemistry, COMSAT University, Abbottabad Campus, KPK 22060, Pakistan.
f Department of Physics, University of Agriculture Faisalabad, 38000, Faisalabad Pakistan.

Email of Corresponding Authors: javedkhattak79@gmail.com; javed.iqbal@uaf.edu.pk; mshabbir@ku.edu.sa

Abstract

The present investigation highlights the 2-dimensional design of several interesting super alkali doped borophene derivatives for efficient nonlinear optical (NLO). Borophene (B_{36}) and super alkali units (Li_{3}O) whose combining effects and resulting NLO responses have been evaluated by orienting super-alkali clusters at various sites such as a hub, rim, and bridged around the B_{36} molecule. The charge analysis is characterized by frontier and natural bond orbital analysis, narrowed HOMO-LUMO band gap, better intramolecular charge transfers. Molecular electrostatic potential surfaces demonstrate enhanced optoelectronic features of these complexes that are viable owing to Li_{3}O adsorption. Singly doped and doubly doped complexes have been considered and their NLO properties have been calculated. Band gap energy reduces about three times when doped with two Li_{3}O. A considerably high figure of merit, first hyperpolarizability (β_{0}) values up to five digits 10611 a. u. for complex A proved that these systems can be utilized as promising candidates in various NLO applications.

Keywords: Nonlinear optical polarizability; first hyperpolarizability; borophene; super-alkali; molecular electrostatic potential.

1. Introduction
The most appealing tasks in contemporary research areas regarding nonlinear optical (NLO) materials, design, and fabrication are optoelectronic telecommunications, sensing [1], computing [2], modulators [3], switching devices [4], and information technology [5]. Due to asymmetric moieties enriched with excess electrons, the first hyperpolarizability can be enhanced such as second-order electric susceptibility per unit volume thus playing a significant role in the second harmonic generation (SHG) process, leading to better NLO responses [6-8]. Many stratagems available that are quite useful in fabricating optoelectronic materials with high performances regarding both theoretical and experimental viewpoints such as establishing \( \pi \)-conjugated bridge between donor and acceptor moieties (D-\( \pi \)-A) [9-12], by approaching bond length alteration (BLA) theory [13], employing multi-decker sandwiching clusters as fabricating units [14, 15], and doping or adsorbing alkali metals, transition metals or super alkali on different nanoclusters, are some of the most effective approaches [16-19].

Metals can donate their valence electrons with larger efficacy called super alkali metal [20]. In 1938, the first super alkali cation (Li\(_3\)O\(^+\)) was being observed as a part of crystal Li\(_3\)O\(^+\)NO\(_2\) [21]. In 1979, the isolated form of Li\(_3\)O was first spotted over the solid lithium oxide during mass spectrometric measurements [22]. The incorporation of super alkali and super halogen onto or into various compounds like organic fragments with push-pull chromophoric systems [23-25], metal-ligand complexes [26, 27], borophene (B\(_{40}\)) nanocage, and fullerene (C\(_{20}\)) [28] showed quite reasonable results for the first hyperpolarizability with a low band gap width between HUMO and LUMO that led to better non-linear responses. Thus, the incorporation of super atoms like super alkali opens a gateway to new and diverse implementation in various research facets like the NLO response. Inorganic fullerene and graphene-like structures remained the point of interest for many scientists during the past few decades.

Recently, a new group of compounds containing only one type of boron atom in its skeleton has been derived as borophene [29]. Borophene manifests varieties of planar, quasi-planar, cage-like, and other structures which have been confirmed by experimental and computational regimes. Among these, the borophene containing 36 boron atoms (B\(_{36}\)) having umbrella-like, slight out of plane symmetry, exhibiting very fine contrasting orderings of hexagonal and triangular units with a hexagonal hole present in the centre-C\(_6\)v symmetry, has been considered as the most stable cluster among its different analogues [30]. Borophene
(B$_{36}$) contributes little resemblance with other 2-D analogues like fullerene in terms of lattice constants or crystal symmetry [31] but shares most of its hexagonal two-dimensional layered structure with that of graphene in which the carbons atoms are being successively replaced by boron atoms. It is just a recently integrated metal attempted by Piazza et al.[30]. Moreover, it is experimentally synthesized and successfully grown on Al and Au single crystal substrates, respectively [32], possessing fine compromising electronic and optical characteristics. Its band structure exhibits highly anisotropic behavior [33], the strong bonding interactions between boron atoms aid borophene to withstand any mechanical stress, nominating it as a potential candidate to be utilized in 2D thin-film materials future technology [34, 35]. Because of its physical, chemical, optical, and thermal properties, borophene makes its way in countless research interests such as alkali metal ion batteries, Li-S batteries, hydrogen storage, supercapacitors, sensors, catalytic hydrogen evolution, oxygen reduction or evolution, CO$_2$ electro reduction cause and effects [36].

More recently, Solimannejad et al.[46] studied the interaction of borophene (B$_{36}$) with the alkali metal (Li) when placed at different sites of borophene and doping of first-row transition metal elements in its central hexagonal ring, respectively. This arrangement has been foreseen as an effective approach in designing and fabricating promising NLO material [37]. One unit of the super-alkali cluster (Li$_3$O) placed on the corner side from the center of sheet A, two on the corner of lower side B, two on the side-by-side from the center of sheet C, two at the void region of the sheet about center D, one at the void region of the sheet about center E, one at the parallel or side-by-side of the sheet about center F. From that viewpoint, the optimum concern of this study mainly deals with the following concerns: (1) investigations regarding the interaction of bowl-shaped borophene (B$_{36}$) with super-alkali cluster (Li$_3$O), when placed at various orientations, (2) its linear optical polarizability, and (3) nonlinear optical hyperpolarizability of the pure and doped borophene. The effect of doped Li$_3$O will be examined using different analyses such as density of states, natural bond orbital, frontier molecular orbitals, and molecular electrostatic potential. These analyses assist to compare the reliability and authenticity of the desired systems.

2. **Computational Methodology**

For performing all the calculations, Gaussian 09 package has been used [38]. All the moieties that come across in this benchmark study were optimized via density functional theory (DFT) using B3LYP functional with a 6-31G(d,p) basis set. The frequency
calculations were performed on the same level of theory for the sake of inspecting the nature of stationary points, which confirmed that these optimized structures correspond to real local minima i.e. exclusion of any imaginary frequencies was assured. The B3LYP is the most reliable functional found in the study of super alkali and super halogen doped compounds [39, 40]. Moreover, the density of states (DOS), natural bond orbital (NBO) charges, HOMO-LUMO band gap was estimated at the same computational levels. The density of states (DOS) analysis was performed with the help of PyMOlyze software [41]. The charge transfer phenomenon between borophene (B_{36}) and Li_{3}O was calculated by natural bond (NBO) analysis [42]. Interaction energies (E_{int}) have been calculated by the following equation [43].

\[ E_{\text{int}} = E_{\text{superalkali@B}_{36}} - (E_{B_{36}} + E_{\text{superalkali}}) \]  

(1)

Similarly, for calculation of dipole moment, average linear polarizability (\(\alpha_o\)), and first NLO hyperpolarizability the following equations were used [44].

\[ \mu = \mu_x^2 + \mu_y^2 + \mu_z^2 \]  

(2)

\[ \alpha_o = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \]  

(3)

\[ \beta_{\text{total}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \]  

(4)

Whereby

\[ \beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xxy} \]  

(4.1)

\[ \beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{xyy} \]  

(4.2)

\[ \beta_z = \beta_{zzz} + \beta_{xxx} + \beta_{yyz} \]  

(4.3)

Where equations 4.1, 4.2, and 4.3 are the 3×3 tensor components of the first hyperpolarizability and calculated through Gaussian suite of programs.

3. Results and Discussions

3.1. Molecular Geometries

The top and lateral views of borophene (B_{36}) nanosheet exhibiting slight out-of-plane umbrella-like quasi planar-C_{6v}-symmetry with a hexagonal hole present in the center. The optimized geometry was obtained utilizing the B3LYP/6-31G level of theory. The borophene (B_{36}) nanosheet results from intervening of three main types of boron atoms, the first six
innermost “hub” boron atoms ($B_h$) of the central hexagonal ring interlinking eighteen outer “rim” boron atoms ($B_r$) via twelve “bridged” boron atoms ($B_b$) lying in the center of those former ones, thus acting as a bridge holding the inner and outer layers of boron atoms in $B_{36}$ nano-skeleton [34]. The optimized geometries and the exact position of these three types of boron atoms which are the hub, rim, and bridge have been labeled in Fig. 1a. Elemental boron being an electron-deficient molecule exhibits peculiar behavior in terms of structure and chemical bonding [45].

Thus, in the bowl-shaped borophene, two different kinds of foreign B-B bond lengths were found, 1.678Å and 1.579Å. The obtained results are quite promising with the previously reported data [30]. Super-alkali cluster ($Li_3O$) is used to enhance the NLO response of pristine borophene molecules. For this purpose, various sites have been chosen around the quasi-planar $B_{36}$ molecule, starting from the super-alkali cluster on its top concave face to alternate position around the borophene nanosheet, from near to outer rim-corner atoms of borophene, single-sandwich, and fully sandwiched combinations. By setting super-alkali clusters on both concave and convex sides (compacting $B_{36}$ nanosheet between two super-alkali clusters) and by putting it in the left-right orientations. Their solo and the combined effect has been observed. The top and lateral views of optimized geometries with real-time interaction and vibrational frequencies have been depicted in Fig. 2.

### 3.2. Orbital analysis

The frontier molecular orbital (FMO) analysis has been carried out and the HOMO-LUMO visualization of pristine borophene molecule along with its density of states (DOS)
plot have been shown in Fig. 1b, band gap value for pristine borophene molecule comes out to be 1.918eV which agrees with the literature data. The larger band gap width for pristine B$_{36}$ molecules limits its use in optoelectronic implementations. In FMO diagram whereby redistribution of electronic charge density during excitation confirming charge transference. From Fig. 3, pristine-B$_{36}$ has a uniform electronic cloud in the ground state HOMO exhibiting
the equal distribution of atoms which distribute transversely in the excited state orbital LUMO. Complex A, B, C, D, E, and F have electronic density mainly on the Li$_3$O along with B$_{36}$ different than pristine-B$_{36}$. Such electronic distribution indicates the charge transfer from Li$_3$O to the B$_{36}$ group.

**Fig. 2.** The ‘Top and side view’ of optimized geometry, structures obtained for (Li$_3$O)$_n$@B$_{36}$, where n= 1 or 2, nanoclusters: (1) a; (2) b; (3) c; (4) d; (5) e; and (6) f.
To support the FMO analysis, the molecular electrostatic potential (MEP) has been performed which refers to the molecular electrostatic potential mapped onto the total electronic density surface available. It elaborates different properties of a molecule more efficiently such as electronic cloud delocalization, positions more vulnerable to attacking nucleophile or electrophile, charge transfer visualization, and electrostatic potential values at different points. A classic electrostatic potential mapped surface usually depicts positive (colored blue) and negative (colored red) potentials in which blue areas refer to electron-rich while red areas are pointed towards electron-poor regions. The MEP plots of the different studied complexes have shown in Fig. 4 along with the parent moiety B_{36} nanosheet. The central blue region of the B_{36} may arise because of empty p-orbitals associated with the elemental boron, it can be interpreted that the lithium-based super alkali clusters colored blue in the MEP diagrams highlight the transference of their excessive diffused electronic density from Li_{3}O cluster to quasi planar B_{36} nanosheet.

As obvious complexes with lower band gap energy values encounter greater intramolecular charge transfer (ICT) as compared to pristine-B_{36}. This charge transfer process is in absolute agreement with natural bond orbital (NBO) analysis. The total NBO charge that each super alkali cluster carries in its corresponding system is represented by [Q] and the positive value of the NBO charge reaffirming the fact that charge is being transferred from Li_{3}O to the borophene sheet.
3.3. Optical properties and thermodynamic stability

The distance of interaction between borophene nanosheet and super-alkali cluster kept in the range of 2.143-3.125Å. In this interactive distance, some of the super-alkali clusters tend to attach to the borophene sheet, some just altered the bond lengths, other develop bonding with each other and exert their combined effect on this boron-based nanocluster (see complex ‘e’ in Fig. 2). All these changes lead to structural abnormalities in sense of bond angles and bond lengths which in turn can affect the NLO properties of the considered systems. Among the different structures (A-F), complex A, B, and F displayed the narrowest band gap with notable energy of interaction in comparison with its other single super-alkali doped analogue. However, the interaction energy of complex C and D is greater than complex A, B, E, and F that have been compiled in Table 1. The ‘E$_{int}$’ values for single Li$_3$O based systems are -3.65eV and -2.65eV while for the systems containing two Li$_3$O molecules carry ‘E$_{int}$’ values range from -4.89eV to -7.77eV, higher interaction energy values for the systems with two Li$_3$O molecules suggest that these two units interact with borophene sheet, together exerting their effect jointly. All the ‘E$_{int}$’ values are negative which ensures the stability of the analyzed systems. The obtained results suggest that the interaction of Li$_3$O with surface interaction is corroborated.

The linear polarizability value ($\alpha_o$) of all the corresponding systems has been calculated and is gathered in Table 1. The enhanced $\alpha_o$ values of the studied complexes than the pristine B$_{36}$ molecule is evident of the fact that Li$_3$O adsorption has somewhat effect on

![Fig. 4. The MEP plot of the borophene and (Li$_3$O)$_n$@B$_{36}$, where n=1 or 2, nanoclusters.](image-url)
the structural as well as linear properties of the system too thus, granting pronouncing $\alpha_0$ values than most of the systems available in the literature. This data showed HOMO-LUMO alterations compromises finely with the fact available in the literature that nonlinear optical properties are more pronounced when a chemical moiety is placed near the outer rim boron atoms ($B_r$) of the $B_{36}$ molecule. Hence, it can be easily perceived from Fig. 2 that configurations carrying Li$_3$O units near the outer rim boron atoms ($B_r$) of borophene owned larger hyperpolarizability values as compared to other analogues in which Li$_3$O units are more confined to ‘$B_h$’ or ‘$B_b$’ boron atoms.

**Table 1.** The highest occupied molecular orbitals (HUMO) and lowest unoccupied molecular orbital (LUMO) energies and their gap in electron volts, linear polarizability values ($\alpha_0$) and first hyperpolarizability values ($\beta_0$) in atomic units, interaction energy values ($E_{int}$), total charge on super alkali clusters [Q] for all compounds at B3LYP/6-31G level of theory.

| Structures | HOMO (eV) | LUMO (eV) | $\Delta_{H-L}$ | $\alpha_0$ | $\beta_0$ | $E_{int}$ | [Q] |
|------------|-----------|-----------|----------------|------------|----------|-----------|-----|
| Pristine $B_{36}$ | -5.538 | -3.619 | 1.918 | 544.621 | 390.74 | — | — |
| A | -3.801 | -2.750 | 1.050 | 633.947 | 10611 | -3.65 | 1.407 |
| B | -4.121 | -3.052 | 1.069 | 684.326 | 4576.1 | -5.50 | 1.730 |
| C | -3.228 | -2.085 | 1.142 | 733.966 | 4283.5 | -7.32 | 1.354 |
| D | -4.829 | -3.699 | 1.129 | 603.132 | 1892.5 | -7.77 | 1.586 |
| E | -4.894 | -3.640 | 1.254 | 574.349 | 1222.4 | -2.65 | 0.831 |
| F | -4.438 | -3.516 | 0.921 | 629.155 | 1073.1 | -4.89 | 1.834 |

Materials exhibiting larger first hyperpolarizability values are suitable candidates in doubled frequency second harmonic generation (SHG) based NLO applications. For this purpose, corresponding materials should exhibit transparency under laser light used, besides the fact that it owes a greater NLO response. To make sure this statement ultraviolet-visible and near infra-red region analysis (UV-Vis-NIR) has also been carried out for all the studied complexes and their maximum absorption values have been provided in Table 2. From Fig. 5,
peaks showing maximum absorption values in the IR region and very weak absorption in the visible region of the electromagnetic spectrum. Hence, these materials are satisfactorily transparent for routinely encountered laser sources.

**Table 2.** The transition energies ($\Delta E$) in atomic units, oscillator strengths ($f_o$), change in dipole moment values ($\Delta \mu$) in Debye, assignments of orbitals involved in crucial transitions and absorption at maximum wavelength ($\lambda_{max}$) of all compounds at B3LYP/6-31G level of theory.

| Structures | $\Delta E$ | $f_o$ | $\Delta \mu$ | Assignments | Transition (% C.I.) | $\lambda_{max}$ (nm) |
|------------|-----------|-------|-------------|--------------|-------------------|-------------------|
| Pristine B$_{36}$ | 2.007 | 0.0010 | 2.85 | HOMO$\rightarrow$LUMO+4 | 53 | 944 |
| A | 1.011 | 0.0018 | 19.21 | HOMO$\rightarrow$LUMO+2 | 94 | 1302 |
| B | 1.081 | 0.0172 | 17.84 | HOMO$\rightarrow$LUMO+2 | 69 | 1791 |
| C | 1.560 | 0.0170 | 3.21 | HOMO$\rightarrow$LUMO+3 | 64 | 1454 |
| D | 1.657 | 0.0035 | 3.97 | HOMO$\rightarrow$LUMO+2 | 69 | 1219 |
| E | 1.635 | 0.0001 | 2.18 | HOMO-1$\rightarrow$LUMO+3 | 55 | 1317 |
| F | 1.669 | 0.0011 | 6.44 | HOMO$\rightarrow$LUMO+3 | 70 | 1786 |

**Fig. 5.** VIS-NIR spectra of all the studied complexes
3.4. **Total density of states (TDOS)**

To investigate electronic structures more deeply, density of states (DOS) spectra have also been approached. The DOS spectra represent the density of states versus energy intervals available for each energy level to be occupied. Doping of atoms is responsible for the formation of new HUMOs mainly contributing to the decreasing band gap for these considered systems, locating somewhere in between or at higher levels than that of pristine $\text{B}_{36}$ molecule. The constructed DOS spectra (Fig. 6) showed a significant interaction between super alkali cluster and $\text{B}_{36}$ nanosheet which implies enhanced HUMOs and lower LUMOs in such a way that leads to narrowed HOMO-LUMO energy gap as compared to pristine $\text{B}_{36}$ molecule.

![Graphs showing TDOS](image)

**Fig. 6.** Total density of states (TDOS) of the studied complexes 1)A; 2)B; 3)C; 4)D; 5)E; and 6)F.

3.5. **Origin of NLO hyperpolarizability**

NLO properties for borophene molecule have also been checked by the aid of B3LYP/6-31G level of theory and approximate negligible first hyperpolarizability value
ensures naught to NLO properties of pristine $B_{36}$ molecule. To be more concerned, a famous two-level model has been considered to describe the fluctuations between excitation energies, dipole moment, and first hyperpolarizability as [43]:

$$\beta_0 = \frac{3\Delta\mu f_o}{2\Delta E^3}$$  \hspace{1cm} (5)

Whereby, $\Delta\mu$, $f_o$, $\Delta E^3$, refers to change in dipole moment, oscillator strength, and the change in transition energy values due to crucial excitations from the ground state to an influential excited state. As obvious from the equation, a small change in excitation energy can alter the first hyperpolarizability ($\beta_0$) value to a remarkable extent, because of its third power reciprocated dependence in the relation. Thus, complexes with higher $\beta_0$ values own smaller excitation energies ($\Delta E$), larger dipole moments ($\Delta\mu$) and oscillator strengths ($f_o$) that are shown in Fig. 7. For instance, compound A possesses the lowest excitation energy value with the highest ‘$\beta_0$’ response whereas, compound F holds the lowest hyperpolarizability value with the greatest excitation energy value. Greater the charge transfer better will be the NLO responses.

![Graph showing reciprocal dependence](image_url)

**Fig. 7.** The first hyperpolarizability ($\beta$) and transition energy ($\Delta E$) showing reciprocal dependence.
4. Conclusion

Thus, in the current theoretical framework, it is found that drastic changes in structural, optical, and NLO properties have been observed by the intercalation of super-alkali clusters and borophene molecules. The intermolecular interactions between super-alkali clusters and borophene lead to better charge transfer properties with narrow HUMO-LUMO bandgaps as found in complex A, B, and F. A lower band gap energy is suitable for considerably high first hyperpolarizability values. The FMO, MEP, and NBO analyses with promising results assure that charge is being transferred from superalkali clusters to borophene molecules. Among all complexes, complex A showed the highest value of the first hyperpolarizability of about 10611 a. u., which is about 186% larger than the pristine $B_{36}$ molecule. The obtained results are predicting that optoelectronic and NLO properties of all these complexes are susceptive of Li$_3$O adsorption and remarkably larger first hyperpolarizability value ($\beta_o$) confirmed that corresponding materials can be used as an efficient candidate for designing the future NLO materials.

Declarations

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Availability of data and material: All data generated or analyzed during this study are included in this published article.

Authors’ contributions

1. Muhammad Hussnain: The acquisition, analysis, or interpretation of data; drafted the work or revised it critically for important intellectual content.

2. Rao Aqil Shehzad: The acquisition, analysis, or interpretation of data; drafted the work or revised it critically for important intellectual content; approved the version to be published;
and agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

3. **Shabbir Muhammad**: Made substantial contributions to the conception or design of the work; the acquisition, revised it critically for important intellectual content; approved the version to be published; and agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

4. **Javed Iqbal**: Made substantial contributions to the conception or design of the work; the acquisition, revised it critically for important intellectual content; approved the version to be published; and agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

5. **Abdullah G. Al-Sehemi**: The acquisition, analysis, or interpretation of data; drafted the work or revised it critically for important intellectual content.

6. **Saleh S. Alarfaji**: The acquisition, analysis, or interpretation of data; drafted the work or revised it critically for important intellectual content.

7. **Khurshid Ayub**: The acquisition, analysis, or interpretation of data; drafted the work or revised it critically for important intellectual content.

8. **Muhammad Yaseen**: The acquisition, analysis, or interpretation of data; drafted the work or revised it critically for important intellectual content.

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