DFT Study of Super Halogen Doped Borophene With Enhanced Nonlinear Optical Properties

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DFT study of super halogen doped borophene with enhanced nonlinear optical properties

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Abstract

The concern of the present study is to investigate the non-linear optical properties of super halogen doped borophene owing to its broad applications. The first principle study of the material for its non-linear optical properties elaborated its use for electrical and optical applications. The super halogen-based borophene in lithium ion-based batteries and medical appliances have made it one of the most potential materials for optoelectronics. First, hyperpolarizability (β_o) of pure and doped B_{36} is computed and the difference between their values was examined. The vertical ionization energy (VIE) was calculated for pure and doped systems. The interaction energy (E_{int}) for all combinations was computed. It would be expected to one of the best materials to have high capacity and resistance. For all the calculations and to calculate the HOMO and LUMO energy gap, the density functional theory (DFT) method was used. After observing all the above properties, it was predicted that these combinations are more beneficial and displayed the better nonlinear optical (NLO) for electronic devices.

Keywords: hyperpolarizability; nonlinear optics; optical properties; superhalogen; borophene

1. Introduction

Manufacturing and processing of non-linear optical materials is a goal of much significance due to their broad application in optical computing, signal processing and sensing applications in modern researches [1]. Until now several design approaches for effective NLO materials have been proposed; doping of metal atoms [2], using bond length alternation (BLA) theory [3] and decorating sp^2 hybridized carbon Nano-materials, etc[4]. The practical application of non-linear optical material is based on its stability and transparency in the laser wavelength applied. Inorganic compounds are well known to have better stability than organic compounds and much research is underway to explore super-halogens-based compounds that enhance inorganic non-linear optical materials [1, 5]. The potential to produce a new electrical and magnetic field that can alter its phase, frequency and

other physical properties due to interaction between incident laser light and electrical field that is only displayed by NLO material [6, 7].

The composition of any material strongly influences the interaction of light photons passing through it. Optical materials are very important to design the key components of optical systems and laser applications which are the main area of scientific study today. NLO materials produced new electromagnetic fields of different frequencies by giving applications in holographic imaging, optical data storage and frequency duplication [8]. Usually, normal light conduct is explained by optical materials. On the other side, NLO materials are typical materials that are concerned with the interaction of strong intensity laser light with the material. The non-linear response to the electric field of light by the polarization of NLO material alters the frequency of laser light [9]. Recently it has been discovered that species having excess electrons can display a significant NLO response where excess electron plays a role in enhancing first hyperpolarizability (β_o) [10]. Organic NLO small molecules typically face challenges in practical applications due to less thermodynamic stability under laser conditions so inorganic NLO materials are preferred due to higher physiochemical stability and mechanical strength. On the other hand, organic NLO materials also have some advantages such as flexibility and diversity [4, 11]. The second harmonic generation (SHG) optical process which usually gives results in doubling the input frequency normally occurs in the crystal is used to produce green light[12].

Among the different NLO materials preceded by the discovery of graphene, borophene is a hot concern of research among the Nanomaterials in the present era. It is a two-dimensional polymorph of boron, having hexagonal structures to stabilize its planar structure possessing metallic properties as compared to semiconducting bulk boron. Due to its anisotropic structure, high optical transparency is anticipated to be roughly 3ev with nearly 100% transmission as compared to graphene. Due to this, it has possible applications in photovoltaic and touch screens [13]. Depending on the density functional theory, researchers suggested multiple configurations of single atom layered borophene and examined the consequent thermodynamic stability. Through surface modification, the electronic properties of borophene can be altered. The thermal conductivity value of borophene is expected to be about 14.34 W/mK, highly lower than that of graphene which enhances its use in thermal management [14].

Unlike other allotrope materials, borophene has marked anisotropic properties for example Young's modulus estimated along the smoothest surface of borophene is higher than that of graphene. The anisotropic optical properties recorded on borophene sheets, on the

other hand, are quite interesting, as they possess high optical transparency. The 3D structure of borophene is believed to be metalloid used in the processing of semiconductors. Several mechanical values of borophene could be changed by chemical reactions; for example, electrochemical fluorination is susceptible to decrease coefficients on different forms of borophene. Due to behaving like a superconductor and showing good optoelectronic properties Nanodevices based on borophene Nanostructures could be applicable in different medical fields. Supercapacitor made with some layers of borophene has given incredible results till after 6000 discharge cycle giving applications in robotics and portable medical devices that need constant energy supply. Because of its high thermal stability and high chemical reactivity, it is used as a biosensor for the detection of gases for highly toxic compounds such as formaldehyde. X-ray production is a complex process that is reported to be energy-dependent. Borophene-based supercapacitor with a battery as a power source could be used in portable X-ray machines for the convenience of patients who are not able to move[15].

Electron affinity (EA) is the amount of energy needed to remove an electron from an anion that gives a governing role in the reactivity. Halogens have the highest electron affinity in the periodic table, but there exists a class of compounds that have electron affinities even greater than halogens observed first time by Bartlett and Lohmann. Several years later, Gutsev and Boldyrev gave the term superhalogens for these compounds[16]. Superhalogens comprised of metal atoms at the centre surrounded by halogen atoms having electron affinities larger than halogens [16, 17]for example electron affinity for BF4 is 6.86ev and for fluorine, it is 3.4ev[18]. Due to their high vertical detachment energy, super halogens have been analysed continuously for their applications in several areas such as in the processing of organic superconductors with enhanced properties [19]. Due to enhanced optical absorption, possessing adjustable band gap and low excitation binding energy they are fundamental compounds in the production of organic-inorganic hybrid perovskites to use in optoelectronics [20].

The general formula for superhalogens is MXk+1, where M is the main group or transition metal atom, X is a halogen atom, and k is the maximal formal valence of the atom M. The analysis of various new super halogen species concentrates on the study of larger molecular clusters that seem to be able to create firmly bound anions and thee efforts are being done to provide reliable data regarding the possible use of these compounds in optoelectronics and synthesis [21]. BF_4 and BeF_3 with vertical detachment energies (VDE) of 7.34 and 6.64 eV, respectively which are greater than corresponding chloride (3.60 eV) are

used as building blocks to produce super salts. As the electrons are delocalized in super atoms we think that compounds having super atoms can be anticipated to possess large polarizability (α) showing significant NLO properties[22].

Recently we designed super halogen doped 2D borophene and examine their first and second hyperpolarizability (β_o and γ_o) theoretically. Considerable changes in electronic and optical properties were observed and investigation has been carried out to investigate how NLO response varies with super halogen doped borophene having an increased number of halogen moieties. We tried to explain many details such as (1) how first hyperpolarizability and NLO properties could be enhanced after doping of super halogen on borophene, (2) what will be the effect on bandgap and other electronic properties, and (3) what will be changed in geometry after doping [23].

2. Computational details

All the calculations were performed using density functional theory (DFT). B3LYP with 6-31G (d,p) level of theory was used for the geometry of pure borophene (B_{36}) and super halogen (BF_4, BeF_3) doped borophene. B3LYP is a useful method for the calculation of different electronic and geometry of different compounds [24, 25]. The Swizard package was used for the simulation of UV-visible absorption of these molecules [26]. The energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO), interaction energies (E_i) was investigated by using the same computational level. The energy gap between (HOMO-LUMO) can be determined by the equation.

$$E_{H-L} = E_L - E_H \tag{1}$$

In this equation E_L represents the energy of lowest unoccupied molecular orbital (LUMO) and E_H represents the energy of highest occupied molecular orbital (HOMO). The interaction energy of the composite can also be calculated by the following method

$$E_i = E_{SH@B_{36}} - (E_{B_{36}} + E_{SH}) \tag{2}$$

In this equation, E_i displays the interaction energy of super halogen doped borophene, $E_{SH@B_{36}}$ is the energy of super halogen doped borophene, $E_{B_{36}}$ the energy of undoped borophene, E_{SH} energy of super halogen (BF_4, BeF_3). The equation to calculate vertical ionization energy is given

$$VIE = E(X^+) - E(X) \tag{3}$$

In this equation $E(X^+)$ is the energy of cat ion of super halogen doped borophene $(SH@B_{36})^+$ and $E(X)$ is the energy-neutral $SH@B_{36}$. Pymolyze software[27] was used to calculate the density of states (DOS) of all the structures. The calculations for the excited state were taken on the base of TD-B3LYP/631-G and utilized the same method to calculate the ground stated geometries and their absorption in the ultraviolet-visible was also checked. The B3LYP/6-31G (d, p) level of theory was utilized for the calculations of polarizability (α_o) first hyperpolarizability (β_o) of all the systems under study. The average polarizability (α_o), first-order polarizability (β_o) are defined as followed

$$\alpha_o = \frac{1}{3}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz}) \tag{4}$$

$$\beta_o = [\beta^2_x+\beta^2_y+\beta^2_z]^{1/2} \tag{5}$$

Where $\beta_x = \beta_{xxx}+ \beta_{xxy}+ \beta_{xxz}$

$\beta_y = \beta_{yyy}+ \beta_{yzz}+ \beta_{yxx}$

$\beta_z = \beta_{zzz}+ \beta_{zxx}+ \beta_{zyy}$

Gaussian 09 was used for all the calculations and GaussView 5.0 was used to view the results[28, 29].

3. Results and discussion

3.1 Geometrical parameters

The interaction of super halogen with borophene was investigated by using different combinations which are as following (a) super halogen BeF_3 was placed on the hollow structure of borophene sheet on one side and the double side (b). Similarly, the same process was repeated with the other super halogen which is BF_4 by placing it on a single side and a double side. In total considering all the above combinations, 4 combinations were obtained
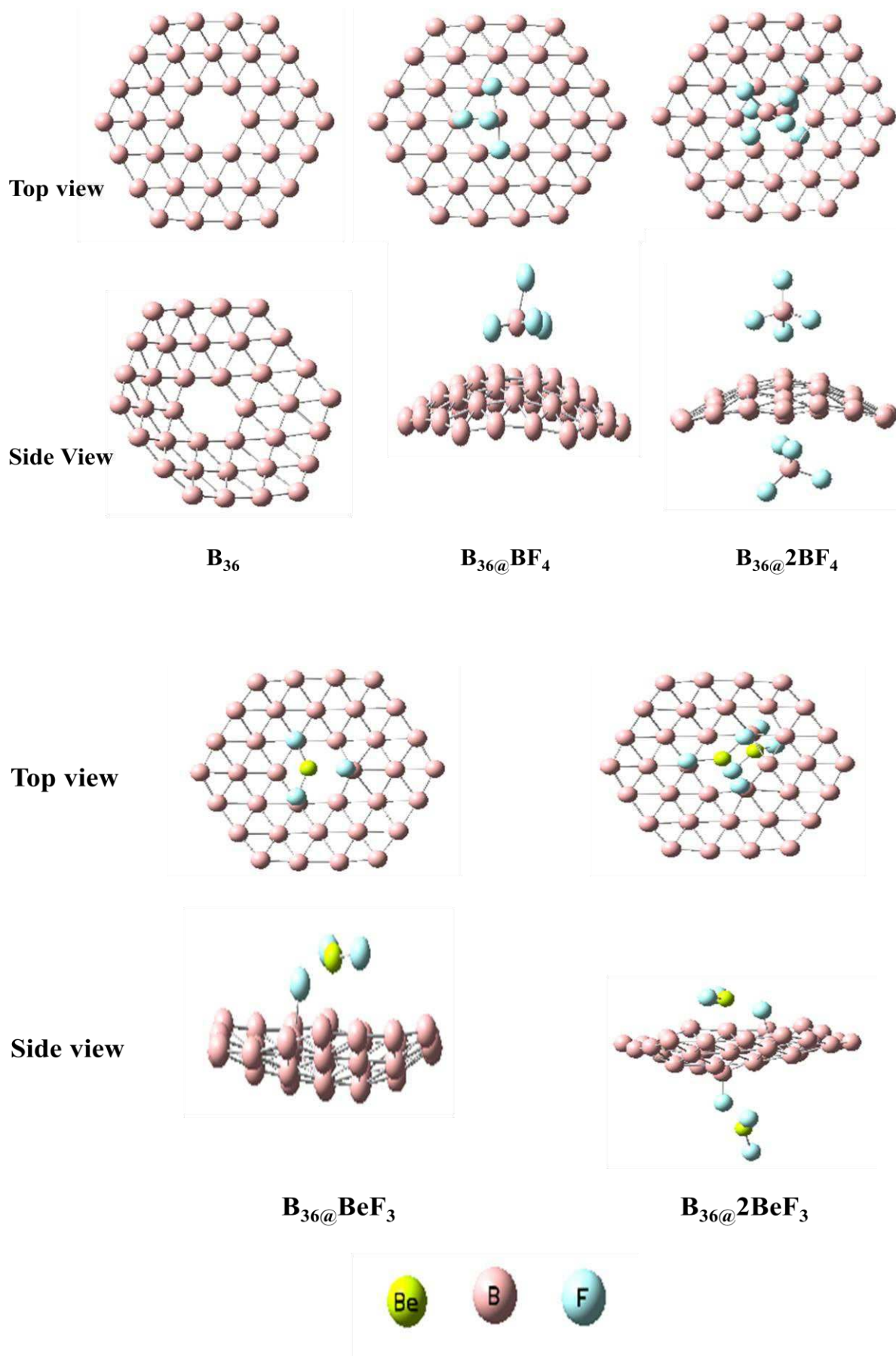
Fig .1. Front and side view of Optimized geometries of pure and super halogen doped borophene B_{36}.

There is a variation in the bond length when there is a comparison of bond lengths between pure borophene (B_{36}) and the sites where super halogens are doped. The bond distance between Boron and Fluorine is an area of hot concern due to charge transfer between borophene sheet and super halogen. NBO analysis of B_{36} doped with displays that super halogen (BeF_3, BF_4) exhibits donor accepter framework with the charge being transformed from borophene which acts as a donor to superhalogen which attracts electron density and accepts as acceptor. The bond length between B-B after the optimization of borophene was observed at 16.6 nm on average. After the doping of super halogen bond length changes from 16.6 nm to 16.8nm, 16.9 nm, 17nm and 17.2nm in $B_{36}@BF_4$, $B_{36}@2BF_4$, $B_{36}@BeF_3$and $B_{36}@2BeF_3$ respectively.
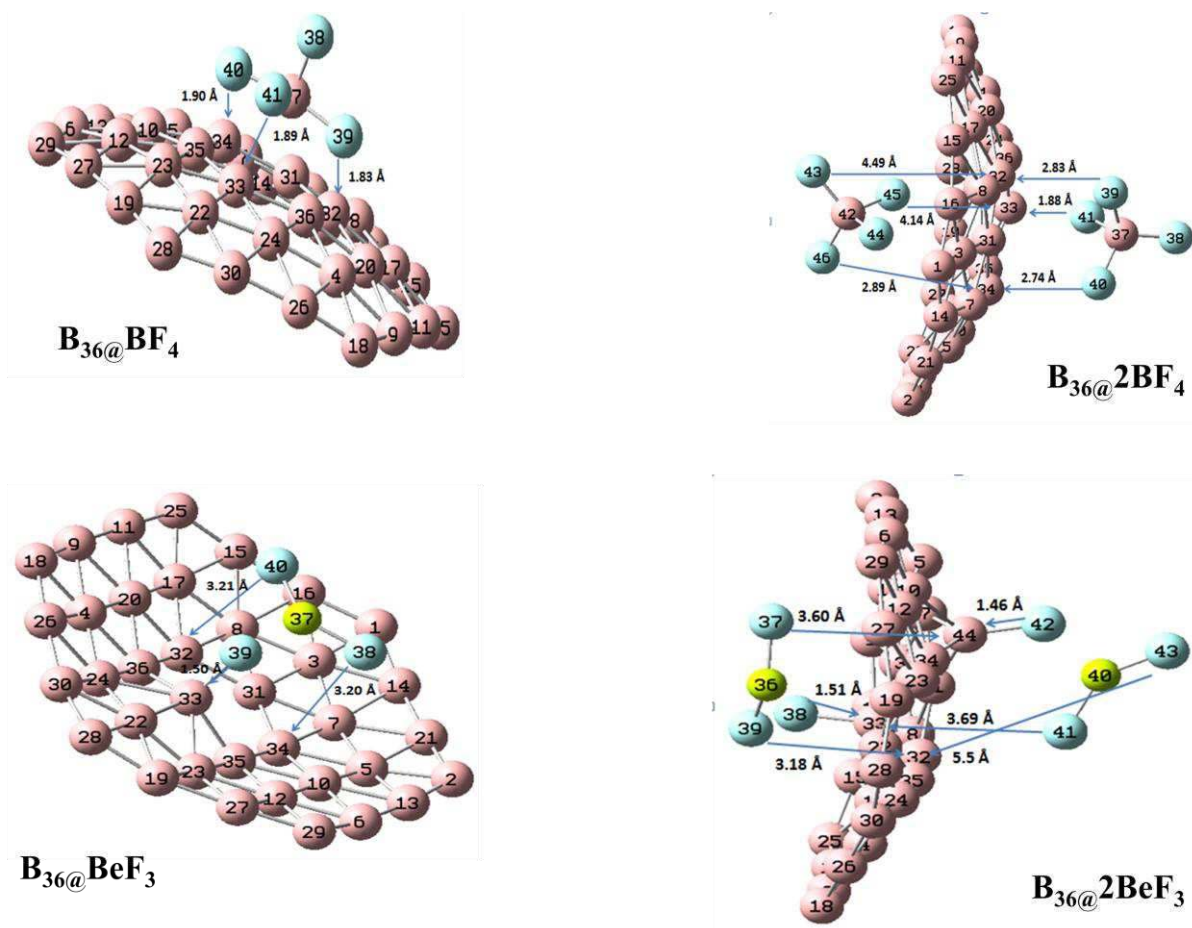

Fig.2. The average distance between borophene and super halogen

Thermodynamic stability and synthetic utilization are the crucial applications of NLO materials. So, interaction energy (E_{int}) and vertical ionization energies of all the complexes

were calculated and are reported in Table 1. The vertical distance between borophene and doped complex ranges from 4.040Å to 3.01Å before relaxation. After optimization, this distance resides in an interactive range of 2.64 Å, 3.17Å, 3.14Å and 1.90Å in $B_{36@}BeF_3$, $B_{36@}2BeF_3$, $B_{36@}2BF_4$ and $B_{36@}BF_4$ on average respectively.$B_{36@}BF_4$ displays the minimum distance between the doped moieties showing maximum interaction and maximum chemisorption of superhalogen on borophene sheet. Interaction energy defines the stability of complexes; thus the greater value of interaction energy tells how strong interaction is present between borophene sheet and superhalogen displaying superhalogen is chemisorbed on borophene surface. These values are ranging from 6.03eV to 5.53eV indicating all the complexes under study are highly stable with$B_{36@}BF_4$having the highest stability.

Table 1.Energy of HOMOs (in eV), energies of LUMOs (in eV) HOMO-LUMO energy gap (in eV), vertical ionization energies (VIE in eV) and interaction energies (atomic unit) of pure and superhalogen (BeF_3, BF_4) doped borophene (B_{36}).

Molecule	HOMO (eV)	LUMO (eV)	Eg (eV)	VIE (eV)	E_{int} (eV)
B_{36}	-5.53	-3.61	1.92	5.53	
$B_{36@}BeF_3$	-5.79	-4.64	1.15	5.79	-0.94
$B_{36@}2BeF_3$	-6.04	-4.85	1.19	6.03	-1.44
$B_{36@}BF_4$	-5.57	-4.64	0.93	5.57	-15.51
$B_{36@}2BF_4$	-5.71	-4.44	1.27	5.71	-1.90

Superhalogens are molecules with high electronegativity than those of simple halogens and have a negative charge before doping. When they are doped with the borophene they deprived borophene of its electronic density exhibiting that there is a charge transfer between superhalogen and borophene. The electronic properties of complexes were also investigated. The values for linear polarizability and maximum absorption are given in Table 2.

Table 2. Polarizabilities (α_o in a.u), first hyperpolarizability (β_o in a.u) dipole moment (Debye) excitation energy (ΔE in eV), oscillator strength (f_o) and orbital transition.

Molecule	λ_{max} (nm)	α_{iso} (a.u)	α_{aniso} (a.u)	β_{static} (a.u)	μ (D)	ΔE eV	f_o	%C. I	Transition
B_{36}	951	544.66	552.33	389.80	2.85	2.0076	0.0010	52.4	H→L+4
$B_{36}@BeF_3$	912	552.71	535.75	380.81	4.56	1.817	0.0085	52.9	H→L+3
B36@2BeF	857	544.76	482.46	466.72	1.63	2.271	*0.0209*	40.5	H-1→L+2
$B_{36}@BF_4$	1240	604.47	523.55	20727.3	1.59	1.42	0.0143	69.9	H-2→L+1
$B_{36}@2BF_4$	1385	563.74	488.84	438.46	2.093	2.064	0.0146	41.7	H-1→L+2

λ_{max} represents maximum absorption of complexes for ultraviolet and visible light. α_{iso} is isotropic linear polarizability and implies the dependence of potential energy on the orientation of the electronic cloud for the collision axis [8]. Second-order polarizability also known as the first hyperpolarizability is a third rank tensor defined by $3\times3\times3$ matrix and owing to the absence of resonance effect, it estimates the intrinsic molecular hyperpolarizability. f_o is oscillator strength which is a dimensionless quantity and represents the probability of absorption and emission of electromagnetic radiation during the transition between the energy levels of an atom. ΔE represents the energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital in electron volt with percent transition of charge from HOMO to LUMO. It can be seen from table 2 that $B_{36}@BF_4$ exhibits a significant value of second-order polarizability with a high value of oscillator strength having the highest value of charge transfer from HOMO to LUMO.

3.2 Electronic characteristics

Due to having applications in optoelectronics, borophene is considered a promising NLO material. To enhance the conducting properties of borophene it is doped with superhalogen (BeF_3, BF_4). The calculations show that the energy bandgap is altered when doping of borophene is done and therefore, the energy gap between HOMO and LUMO decreases from 1.92 eV in pure borophene to a range of 1.27-0.93 eV in superhalogen doped

borophene complexes. Results computed for the density of states in Figure.3 reveal how the HOMO-LUMO energy gap is varied after doping.
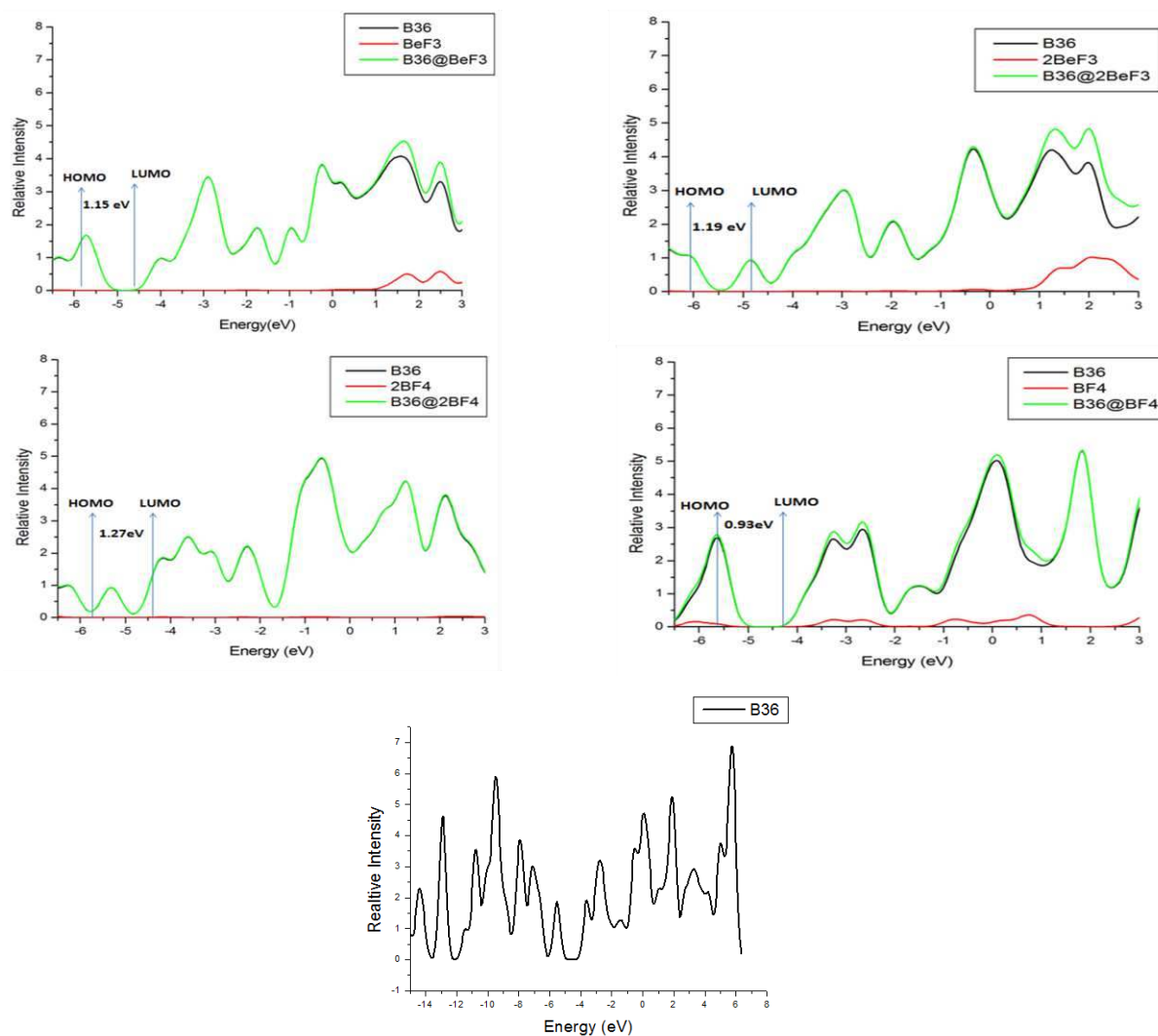

Figure.3. The density of states of pure and superhalogen doped borophene

The HOMO-LUMO energy gap of pure and superhalogen doped borophene can be seen in the density of states (DOS) plot graph. The HOMO-LUMO of doped systems is in between the original HOMO –LUMO of undoped systems. The excess number of electrons in the super halogens generated new HOMO and LUMO orbitals having an energy gap less than the original one. This study shows that doping the superhalogens created the productive material for conduction having less energy gap than that of undoped borophene. Figure 4 shows the frontier molecular orbital (HOMO-LUMO) and electron density distribution.

Frontier Molecular orbitals (FMOs)

B_{36}

$B_{36@}BeF_3$

$B_{36@}2BeF_3$

$B_{36@}BF_4$

$B_{36@}2BF_4$
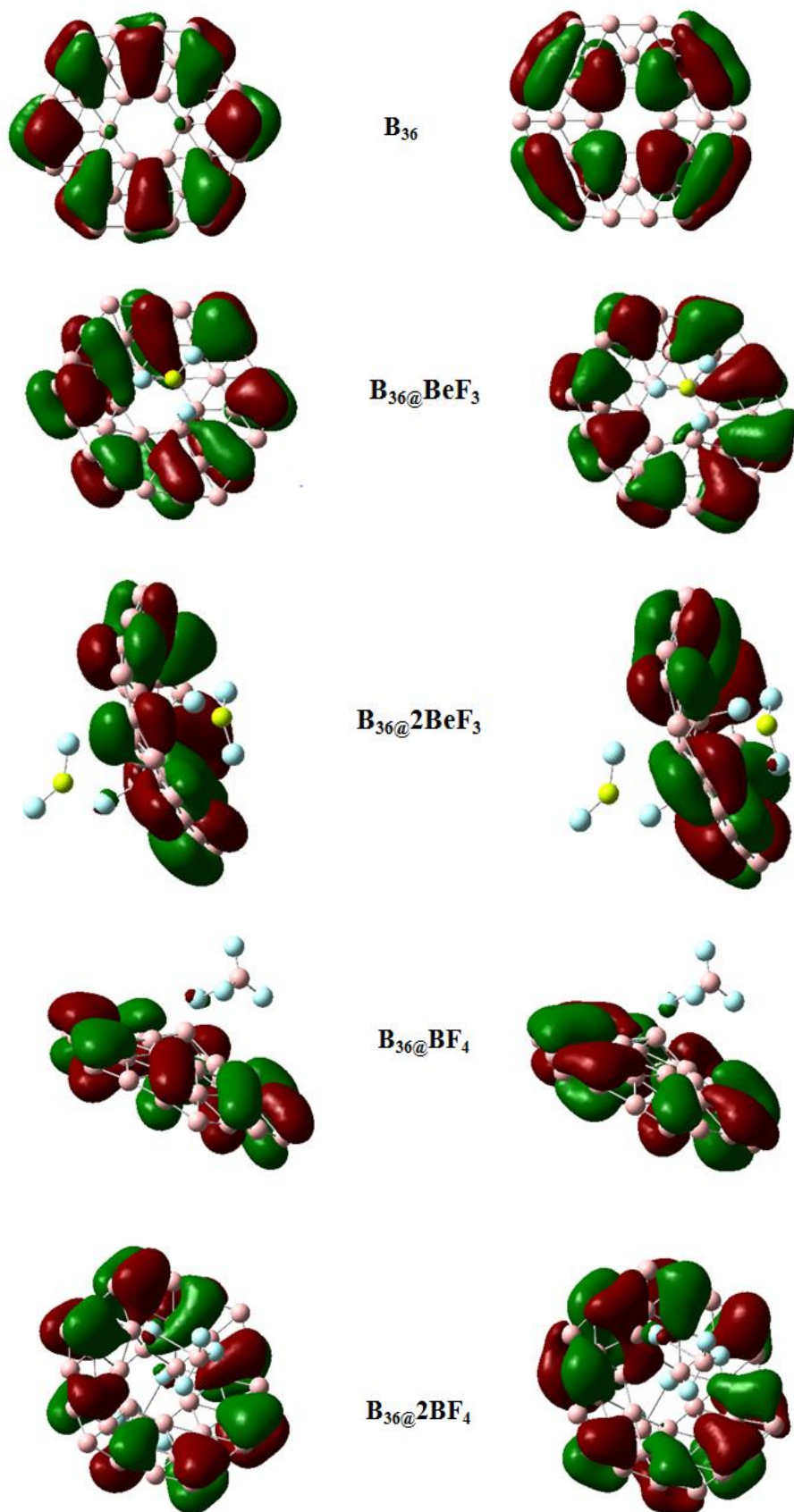
Figure.4 (FMOs) HOMO and LUMO of pure and super halogen doped borophene

3.3 Transition characteristics

The values for linear polarizability and first hyperpolarizability were calculated previously. The value of polarizability for pure borophene B_{36} is 544.66 a.u for α_{iso} and 533.4 a.u for α_{aniso}. After doping superhalogen a slight increase in polarizability was observed. The hyperpolarizability values are 389.80, 380.81, 466, 20727.3 and 438.46 for B_{36}, $B_{36}@BF_3$, $B_{36}@2BF_3$, $B_{36}@BF_4$ and $B_{36}@2BF_4$respectively. Hyperpolarizability values decreased in order of $B_{36}@BF_4 < B_{36}@2BF_3 < B_{36}@2BF_4 < B_{36} < B_{36}@BF_3$. The highest value reported for the first hyperpolarizability of the superhalogen doped 5 member carbon ring compound is 6 $\times 10^4$[30]. Doping superhalogen on borophene increases its NLO response. Moreover doping of superhalogen to study its non-linear response was also reported earlier in literature[23, 31].

3.4 Origin of Non-linearity

To investigate the influence of superhalogen on non-linearity of complex system two-level model is as follows [32]

$$\beta_o \propto \Delta\mu f_o / \Delta E^3 \qquad (6)$$

In equation 6, f_o is the oscillator strength, ΔE is the excitation energy of the critical excited state and $\Delta\mu$ the difference between the ground state and the critical excited state. The two-level equation shows β_o is directly proportional to $\Delta\mu$ and f_o is inversely proportional to ΔE^3 which is the third power of excitation energy.Table2 shows the calculated values of f_o and ΔE of all systems. ΔE values in table 2 tell that its value decreases in the order of $B_{36}@2BeF_3 < B_{36} < B_{36}@2BF_4 < B_{36}@2BeF_3 < B_{36}@BF_4$. In this investigation, $B_{36}@BF_4$ displayed the lowest ΔE value, the minimum energy difference between HOMO and LUMO due to which it has a maximum transition from HOMO to LUMO which is 69.9% and exhibited maximum interaction energy which is -15.51 eV. The isotropic polarizability (α_{iso}) of pure and doped systems was also computed and was compared to pure borophene. These values increase ranging from 0.01% to 11% with maximum value for $B_{36}@BF_4$. Similarly, anisotropic polarizability was also computed and analysed. These values decrease in the range of 552.33-482.46 a.u from pure to doped systems. This increase of isotropic polarizability and decrease of anisotropic polarizability indicates the independence of directional behaviour in these systems.
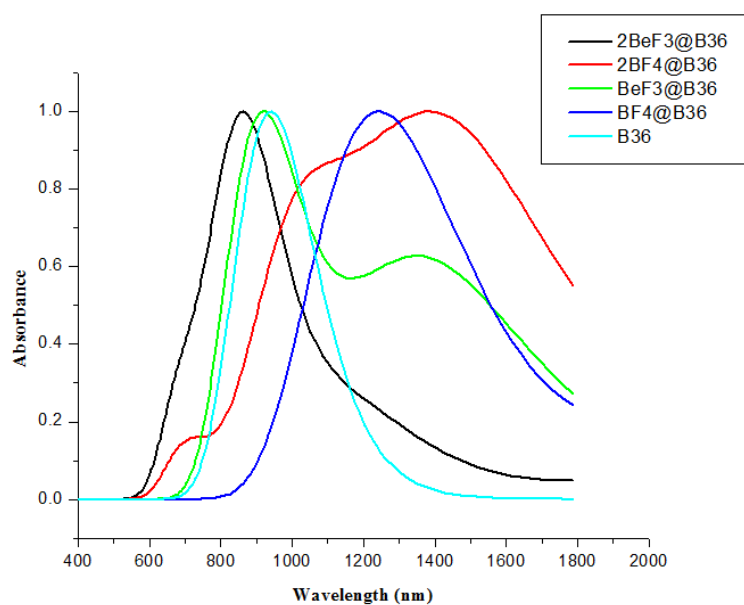
Figure.5. Infrared spectra of pure and superhalogen doped borophene

Figure 5 displays the ultraviolet-visible near-infrared (UV-Vis-NIR) absorption analysis of pure and super halogen doped borophene. The absorption values are 857nm, 912nm, 951nm, 1240nm and 1385nm for $B_{36}@2BeF_3$, $B_{36}@BeF_3$, B_{36}, $B_{36}@BF_4$ and $B_{36}@2BF_4$ respectively. The peeks having week adsorption in the visible and ultraviolet region display valuable transparency for the routinely used laser. In the deep ultraviolet region (<300nm), these systems also exhibit complete transparency. Because of these reasons, these complexes are reported to be new members of NLO material in the deep ultraviolet region. In pure form, it absorbs 951nm energy which is less energy to cross the energy barrier for conduction from HOMO to LUMO. After doping the superhalogen cluster it absorbs at higher values indicating it requires much less energy to cross the energy gap from HOMO to LUMO. In some composites, it also requires more energy than pure borophene.

3.5 Molecular Electrostatic potential (MSEP)

Molecular electrostatic potential (MESP) projection map for superhalogen doped borophene compounds was calculated using the B3LYP/6-31G* method. It gives a 3-D visual to understand the total electrostatic potential effect. It is a very helpful tool to investigate molecular structure and physicochemical properties. The red color in the MSEP indicates the negative region which is electron-rich and the blue color indicates the electron-poor region which is electron deficient. However green color indicates the neutral electrostatic potential

[33]. Borophene possessed electron deficiency because it is doped with highly electronegative electron-rich superhalogen which takes the electron density of borophene, so electron density is transferring from borophene to electronegative superhalogen.
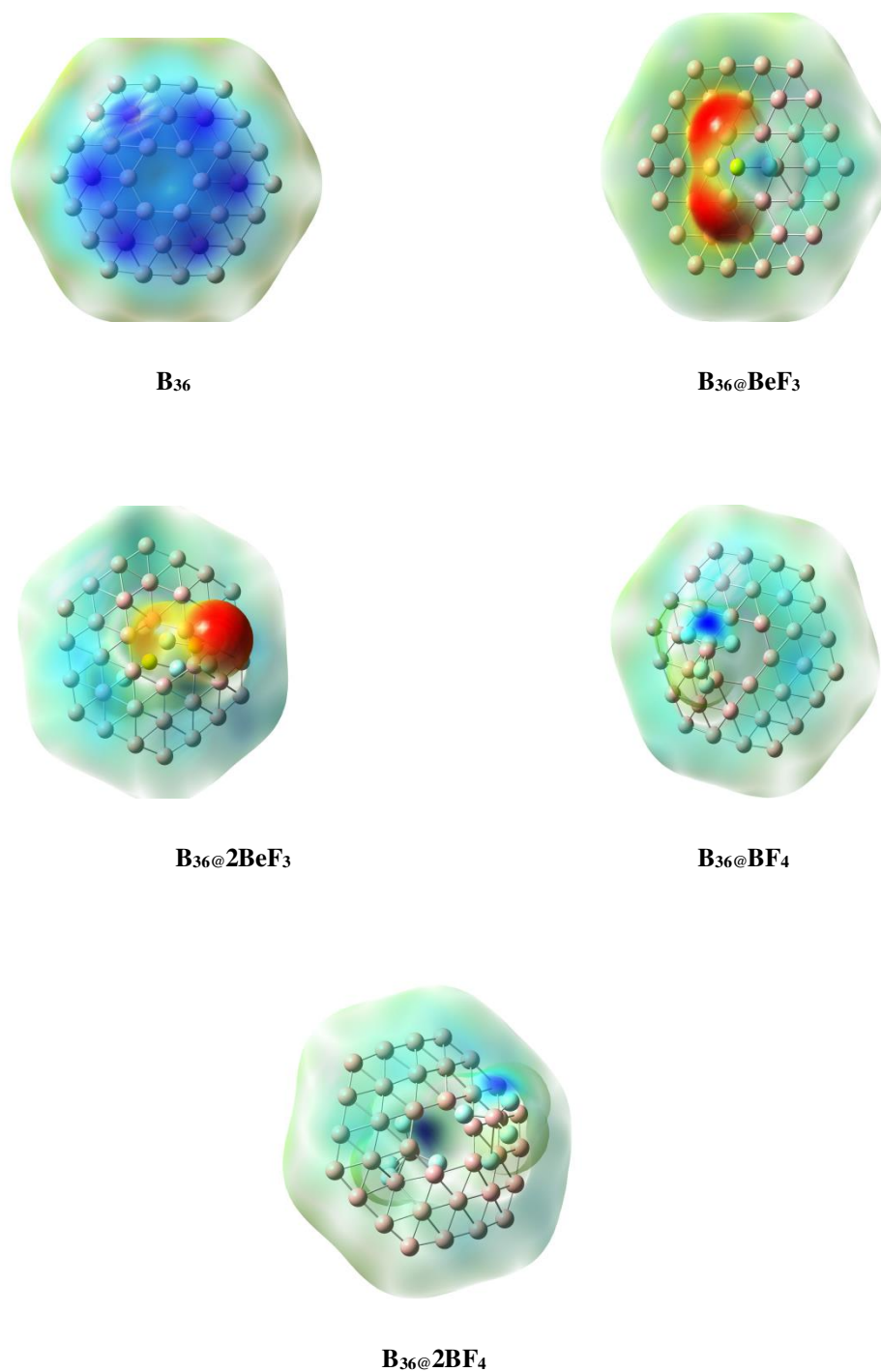

B_{36}

$B_{36}@BeF_3$

$B_{36}@2BeF_3$

$B_{36}@BF_4$

$B_{36}@2BF_4$

Figure 6.Molecular electrostatic potential diagram of pure and superhalogen doped borophene

4. Conclusions

Borophene (B_{36}) sheet doped with superhalogen (BeF_3, BF_4) was investigated for its non-linear optical properties on the base of density functional theory (DFT). The high vertical ionization energy and interaction energies display that these complexes exhibit thermodynamic stability. The HOMO-LUMO energy gap was reduced E_{H-L} when borophene was doped with superhalogen. $B_{36@}BF_4$ displayed the highest values for interaction energies and the lowest energy gap. A significant change occurred in the NLO characteristics due to a reduction in the HOMO-LUMO energy gap and consequently, $B_{36}@BF_4$ showed a higher value for first hyperpolarizability (β_o). Since borophene is considered to an anisotropic material so its NLO properties may change by changing the position of superhalogen. Due to the low bandgap and strong interaction energies, $B_{36}@BF_4$ displayed enhanced NLO properties as compared to other complexes under study. Finally, we expect that the interaction of superhalogen with considered borophene provides a promising application for the development of high-performance NLO materials.

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Code availability:

N/A

Authors' contributions:

Muhammad Ishaq: Writing the paper, the acquisition, drafting, analysis, working and interpretation of data.

Rao Aqil Shehzad: Substantial contribution to research design, the acquisition, analysis and interpretation of data, and approval of the submitted and final version.

Khurshid Ayub: Substantial contribution to research design, the acquisition, analysis and interpretation of data, and approval of the submitted and final version.

Javed Iqbal*: Substantial contributions to research design, the acquisition, analysis and interpretation of data

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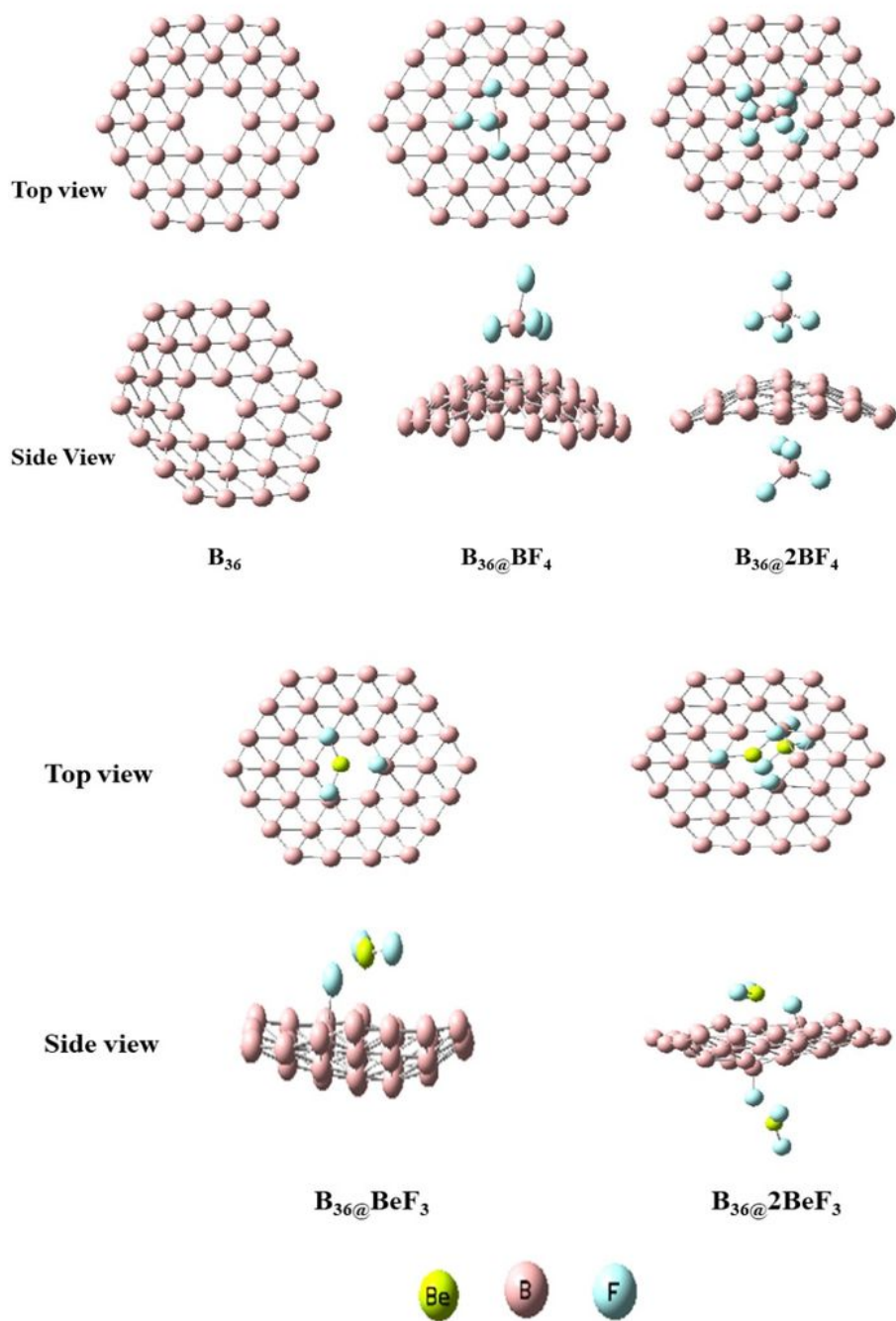
Figures

Figure 1

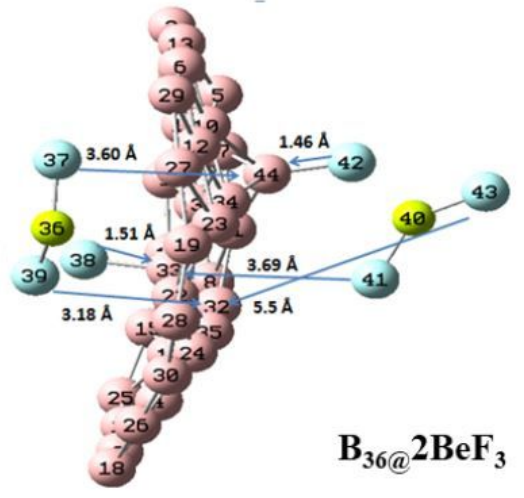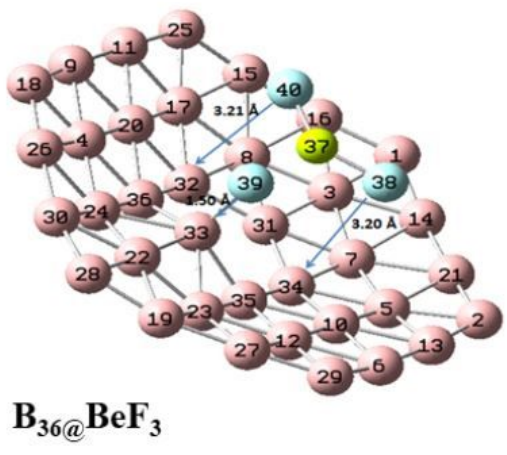Front and side view of Optimized geometries of pure and super halogen doped borophene B36.
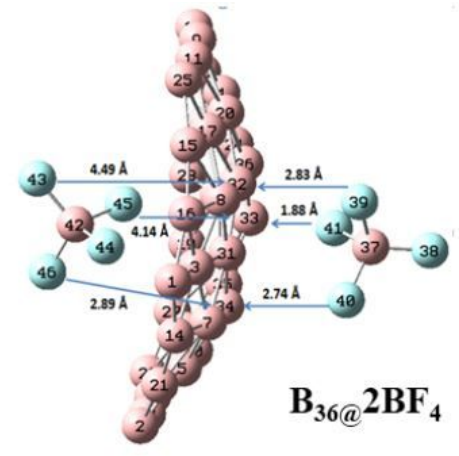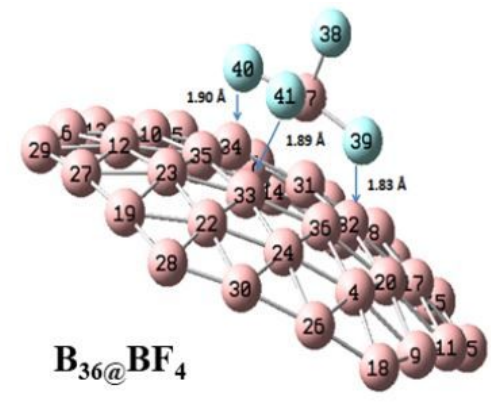
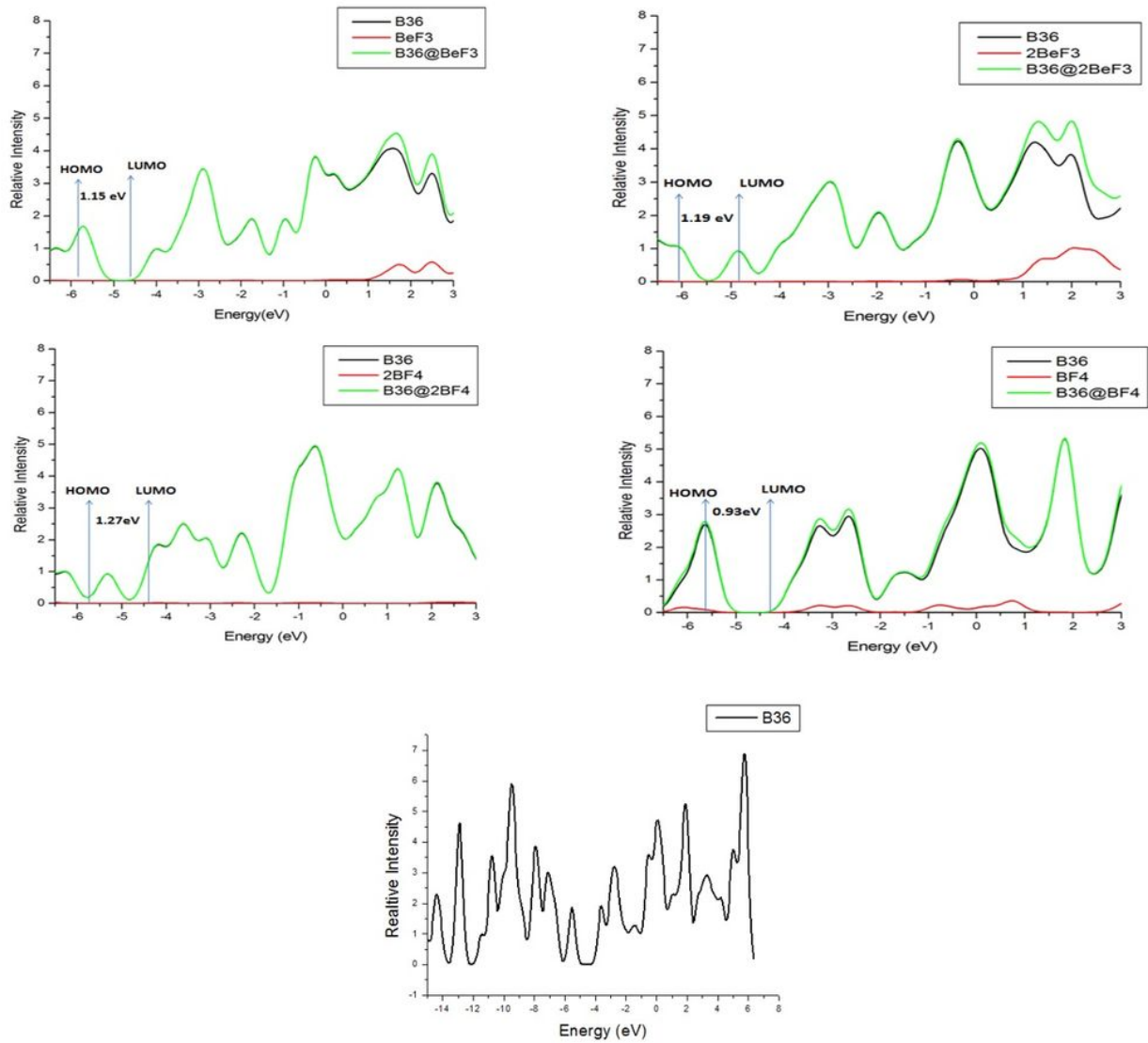**Figure 2**

The average distance between borophene and super halogen

Figure 3

The density of states of pure and superhalogen doped borophene
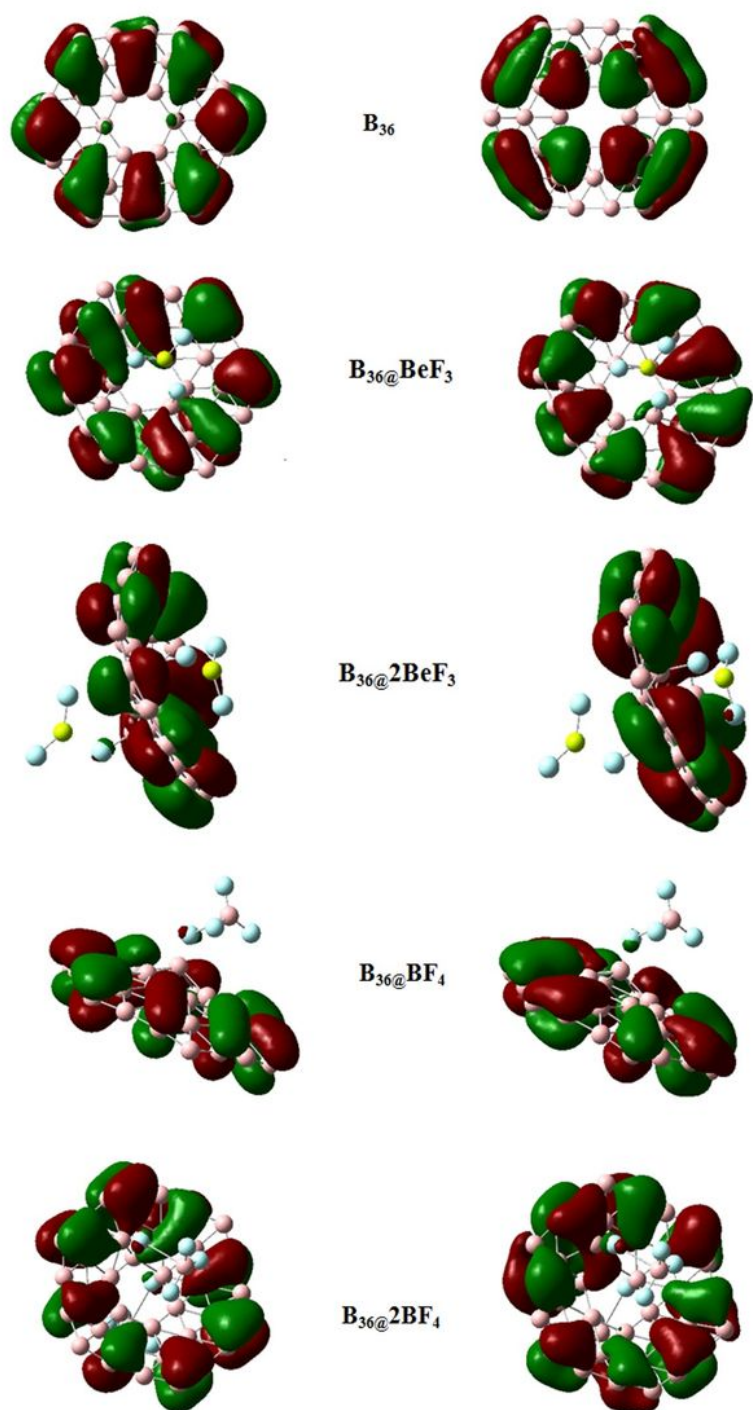
Figure 4

(FMOs) HOMO and LUMO of pure and super halogen doped borophene
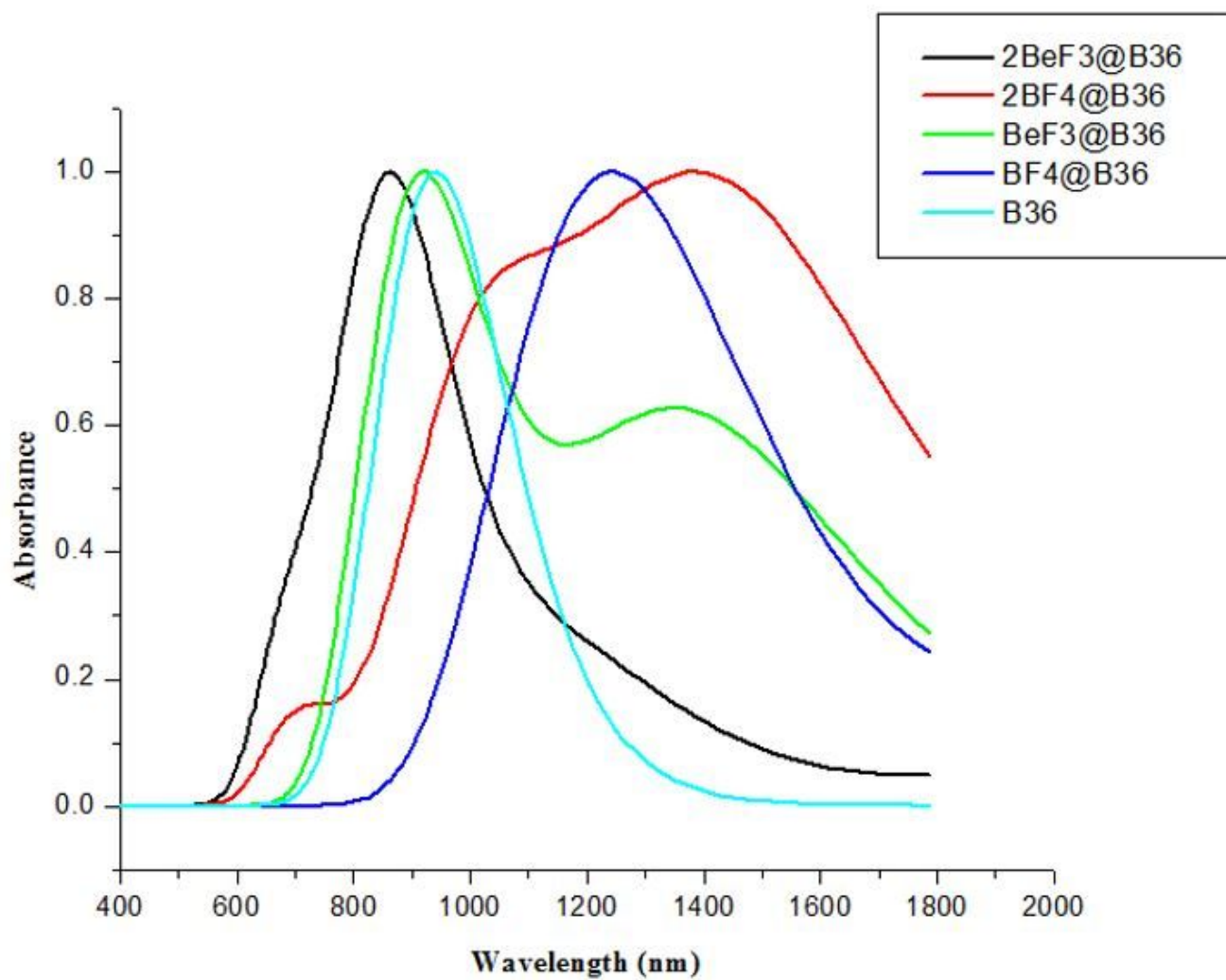
Figure 5

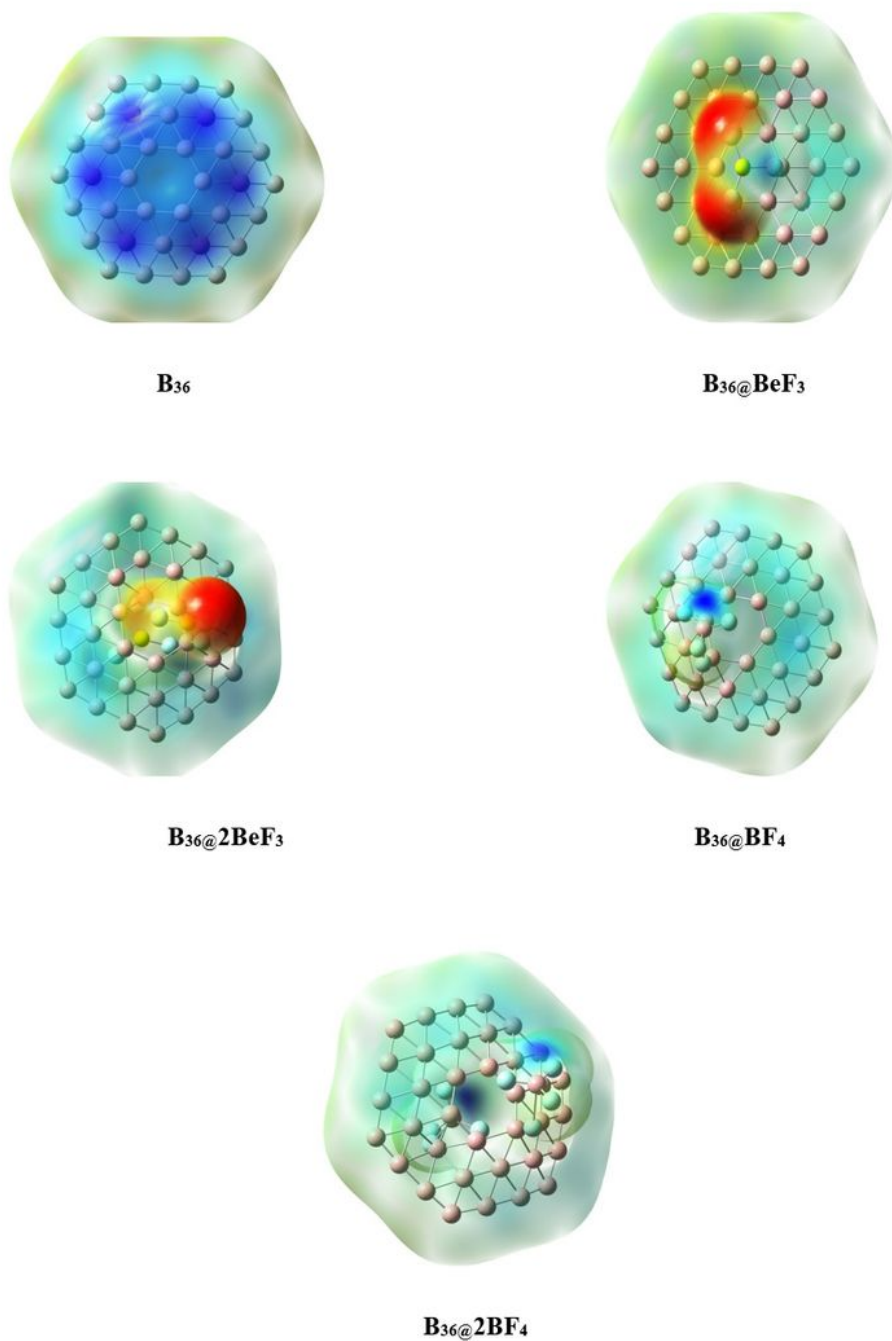Infrared spectra of pure and superhalogen doped borophene

Figure 6

Molecular electrostatic potential diagram of pure and superhalogen doped borophene

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