

A COMPARATIVE STUDY: INTERACTION OF GROUP IIA ANA HYDROGEN IN THE CATIONIC STATE INSIDE B₁₆N₁₆ FULLERENE LIKE NANOSTRUCTURE

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ABSTRACT

Interaction of three alkaline earth cations and proton inside of B₁₆N₁₆ nanofullerene like structure was investigated using density functional theory. interaction energies and band gaps of three members of group IIA and Hydrogen in the form of cationic within B₁₆N₁₆ i.e. Be²⁺@B₁₆N₁₆, Mg²⁺@B₁₆N₁₆, Ca²⁺@B₁₆N₁₆ and H⁺@ B₁₆N₁₆ by DFT/ B3LYP/6-311G (D, P) with Gaussian 09 software in the Gaseous phase. Among the structures, the most and the least amount of Interaction energy are related to cationic Beryllium and Calcium that are located within B₁₆N₁₆ respectively. By placing three cationic alkaline earths metals of the group IIA within the B₁₆N₁₆ structure, decreasing in the energy gap of them happens and this decreasing in the energy gap of them is not so impressive. But decreasing in the energy gap of H⁺@B₁₆N₁₆ is so impressive. The sensitivity according to percent i.e. S_{Mn+} (%) for structures in via of kind atoms within B₁₆N₁₆ is: H⁺@B₁₆N₁₆ > Mg²⁺@B₁₆N₁₆ > Be²⁺@B₁₆N₁₆ > Ca²⁺@B₁₆N₁₆ or H⁺ > Mg²⁺ > Be²⁺ > Ca²⁺. So that, the cationic alkaline earth's metal of the group IIA inside the B₁₆N₁₆ structure is likely placed in the category of insulators and H⁺@B₁₆N₁₆ is likely a semiconductor.

Keywords: B₁₆N₁₆ Fullerene Like Nanostructure; Density Functional Theory; Interaction; Group IIA Cations, Proton; Band Gap; Semiconductor, Insulator, Sensitivity

INTRODUCTION

Hydrogen, the third most abundant element on the earth's surface, has the potential to meet the energy needs of the mobile industry. Its economical use as an alternate energy has substantial difficulties to overcome (Oku *et al.*, 2004). Among these, the most difficult challenge is to find materials that can store hydrogen with large gravimetric and volumetric density and operate under ambient thermodynamic conditions. Nanotubes and nanoclusters have attracted great interest in recent years (Chakraborty *et al.*, 2012). Their high surface/volume ratio has significant implications with respect to energy storage. Carbon nanotubes, nano-magnesium based hydrides, complex hydride/carbon nano-composites, boron nitride nanotubes (BNNTs), TiS₂/MoS₂ nanotubes, etc. are considered to be potential candidates for storing large quantities of hydrogen (Beheshtian *et al.*, 2012). The use of hydrogen as a fuel source depends on its effective and safe means of storage (Struzhkin *et al.*, 2007). Hydrogen is extremely reactive in nature and therefore is not easy to control. It readily participates in combustion process. Boron Nitride (BN) is a compound of Boron and Nitride with a chemical formula BN. BN fullerene like materials would store H₂ molecule easier than carbon fullerene materials, and its stability for high temperature would be good.

Boron nitride (BN) Nanomaterials is expected to have vast variety applications as electronic devices, high heat-resistance semiconductors (Li, 2006). And insulator lubricants because of providing convenient stability at high temperatures with high electronic insulation in air and also hydrogen storage materials (Chakraborty *et al.*, 2012).

The purpose of the present work is to investigate interaction energy and band gap of three members of group IIA and Hydrogen in the form of cationic within B₁₆N₁₆ i.e. Be²⁺@B₁₆N₁₆, Mg²⁺@B₁₆N₁₆, Ca²⁺@B₁₆N₁₆ and H⁺@B₁₆N₁₆ by DFT/ B3LYP/6-311G (D, P) with Gaussian 09 software in the gaseous phase. We have calculated the HOMO-LUMO and band gap and interaction energies, dipole moments and charge transfers. In the next stage we compare these members from the view point of interaction energy and band gap energy (Boshra *et al.*, 2011). According to this work, it can be seen by placing these

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cationic alkaline earth metals within B₁₆N₁₆ nanostructure, decreasing in the energy gap of H⁺@B₁₆N₁₆ is so impressive but decreasing in the cationic energy gap of the alkaline earth metal of the group IIA within B₁₆N₁₆ structure is not so impressive. So these structures are likely placed in the category of insulators but H⁺@B₁₆N₁₆ is likely a semiconductor.

MATERIALS AND METHODS

All computations were performed at DFT/ B3LYP/6-311G (D, P) level of density functional theory with the Gaussian 09 program packages. The convergence criteria for structure optimizations and energy calculations in this work were set to default values in the package. The interaction energy of Mⁿ⁺ (Mⁿ⁺: H⁺, Be²⁺, Mg²⁺, Ca²⁺) cations within the pure B₁₆N₁₆ cluster was obtained using the following equation (Beheshtian *et al.*, 2012).

$$E_{\text{int}} = E(\text{B}_{16}\text{N}_{16}/\text{M}^{n+}) - E(\text{B}_{16}\text{N}_{16}) - E(\text{M}^{n+}) \quad (1)$$

Where E (B₁₆N₁₆/ Mⁿ⁺) is the total energy of B₁₆N₁₆/ Mⁿ⁺ complex and E (B₁₆N₁₆) or E (Mⁿ⁺) is referred to the energy of an isolated B₁₆N₁₆ molecule or cations of Mⁿ⁺ (Mⁿ⁺: H⁺, Be²⁺, Mg²⁺, Ca²⁺), respectively. According to the definition, negative values of E_{int} correspond to exothermic interaction process. E_{int} have been given in Table 1. In the following.

The E_g (eV) of the nanostructure has significant change (ΔE_g = 4.93 eV in the H⁺@B₁₆N₁₆ in respect to B₁₆N₁₆ (Table 2). This occurrence is expected to bring about obvious change in the corresponding electrical conductivity because it is well known that the E_g (eV) (or band gap in bulk materials) is a major factor determining the electrical conductivity of a material and a classic relation between them is as follows:

$$\sigma \propto \exp\left(\frac{-E_g(\text{eV})}{2kT}\right) \quad (2)$$

Where σ is the electrical conductivity and k is the Boltzmann's constant. According to Eq. (2), the smaller E_g (eV) at a given temperature leads to the higher electrical conductivity. However, the E_g (eV) of H⁺@B₁₆N₁₆ complex is substantially reduced compared to that of the pristine cluster (B₁₆N₁₆). Since the conductivity is exponentially correlated with negative value of E_g (eV), it is expected that it become larger with reducing the E_g (eV). However the electrical conductivity of a sensor is more due to the gas adsorption process, it more easily is diagnosed and its efficiency is high. Mathematically, the sensor sensitivity is defined as follows:

$$S = \left| \frac{\Delta R}{R_0} \right| * 100 \quad (3)$$

ΔR is changes in the Resistance; R₀ is the initial Resistance of the sensor.

In our calculations, the energy gap and its changes are measurable on the other side, the Resistance is directly related to the energy gap, and thus the sensitivity is defined as:

$$S = \left| \frac{\Delta E_g}{E_{g0}} \right| * 100 \quad (4)$$

ΔE_g is changes in the energy gap; E_{g0} is the initial energy gap.

It is seen that the sensitivity of sensor increases with increasing of changes in the energy gap (ΔE_g), and with reduction of band gap (E_g).

RESULTS AND DISCUSSION

We optimized B₁₆N₁₆ molecule and Mⁿ⁺ (Mⁿ⁺: H⁺, Be²⁺, Mg²⁺, Ca²⁺) cations with B3LYP /6-311G (d, p) level of density functional theory. We carried out full structural optimization of the B₁₆N₁₆, H⁺@B₁₆N₁₆, Be²⁺@B₁₆N₁₆, Mg²⁺@B₁₆N₁₆ and Ca²⁺@B₁₆N₁₆ Nanostructures to examine the energetic, structural, and electronic properties. Optimized structures of stable B₁₆N₁₆ molecule, H⁺@B₁₆N₁₆, Be²⁺@B₁₆N₁₆, Mg²⁺@B₁₆N₁₆ & Ca²⁺@B₁₆N₁₆, shown in Figure1. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is also desired structures shown in Figure 1. The density states for B₁₆N₁₆ Nanostructure and The density states for Mⁿ⁺ (Mⁿ⁺: H⁺, Be²⁺, Mg²⁺, Ca²⁺) within B₁₆N₁₆ Nanostructure have been given in Figure 2. The HOMO–LUMO gap (eV) upon the interaction process, The interaction energy (E_{int}), Dipole Moment (Debye), charge transfer (electron) for all structure have been given in Table 1.

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Table 1: The HOMO–LUMO gap (eV) upon the interaction process, the interaction energy (E_{int}), Dipole Moment (Debye), charge transfer (electron)

structures	E_{int} (eV)	HOMO	LUMO	Gap(eV)	Dipole	Q_{Mn+}	Diameter(A°)	B-N
$B_{16}N_{16}$	-	-0.290	-0.052	6.48	0.007	-	5.89	1.43
$H^+@B_{16}N_{16}$	-4.018	-0.425	-0.368	1.55	0.108	-0.183	5.95	1.43
$Be^{2+}@B_{16}N_{16}$	-10.68	-0.564	-0.350	5.81	4.278	0.051	5.85	1.43
$Mg^{2+}@B_{16}N_{16}$	-4.15	-0.572	-0.351	5.60	0.048	-0.220	5.97	1.43
$Ca^{2+}@B_{16}N_{16}$	-1.01	-0.565	-0.348	5.91	0.025	-0.717	5.85	1.44

E_g (eV): HOMO-LUMO gap = Gap(eV)

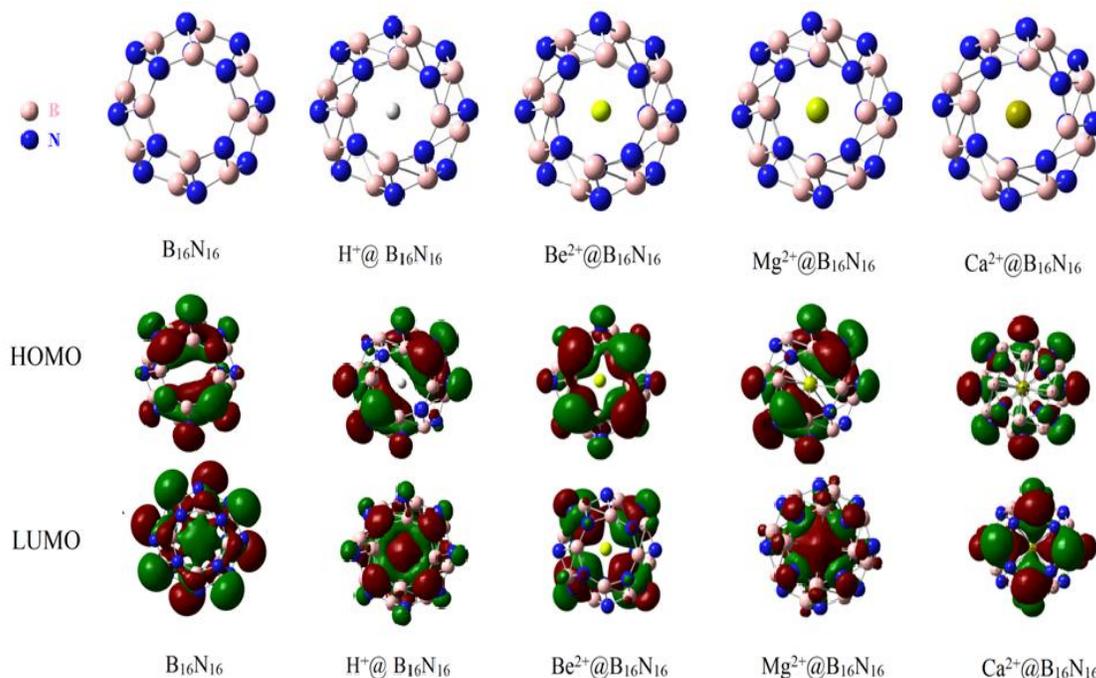


Figure 1: The Optimized structures from left to right respectively for $B_{16}N_{16}$ & M^{n+} (M^{n+} : H^+ , Be^{2+} , Mg^{2+} , Ca^{2+}) within $B_{16}N_{16}$ Nanostructure are respectively in the up, HOMO and LUMO MOs are from left to right for $B_{16}N_{16}$ & M^{n+} (M^{n+} : H^+ , Be^{2+} , Mg^{2+} , Ca^{2+}) within $B_{16}N_{16}$ Nanostructure respectively in the below

As it is seen from Table.1 all the interaction energies have negative signs. According to the definition, negative values of E_{int} correspond to exothermic interaction process and positive values of E_{int} correspond to endothermic interaction process. So here we have exothermic interaction process. If we compare these structures in via of exothermic interaction process, we have: $Ca^{2+}@B_{16}N_{16} < H^+@B_{16}N_{16} < Mg^{2+}@B_{16}N_{16} < Be^{2+}@B_{16}N_{16}$; so we see that $Ca^{2+}@B_{16}N_{16}$ and $Be^{2+}@B_{16}N_{16}$ have the least and the most values of interaction energy in via of exothermic process respectively and the two other structures are placing between $Ca^{2+}@B_{16}N_{16}$ and $Be^{2+}@B_{16}N_{16}$. With comparison values and signs of the interaction energy of the three cations of group IIA and hydrogen cation can be compared these structures in via stability. So we probably will have this respective: $Be^{2+}@B_{16}N_{16} > Mg^{2+}@B_{16}N_{16} > H^+@B_{16}N_{16} > Ca^{2+}@B_{16}N_{16}$ in via stability. If we construct these structures among them the $Be^{2+}@B_{16}N_{16}$ will have the most stable structure and $Ca^{2+}@B_{16}N_{16}$ will have the least stable structure and again the two other will be placed between of two i.e. $Be^{2+}@B_{16}N_{16}$ and $Ca^{2+}@B_{16}N_{16}$ from the point of stability.

According to Table.1, charge transfer in all structures has a negative value except in $Be^{2+}@B_{16}N_{16}$ and it has happened from $B_{16}N_{16}$ nanostructure to cations except in Be^{2+} , in other words can be understood that

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the electron cloud density around cations except in Be^{2+} is more than the other side. The most negative charge transfer has occurred in Ca^{2+} cation within $\text{B}_{16}\text{N}_{16}$ i.e. in $\text{Ca}^{2+}@\text{B}_{16}\text{N}_{16}$ and the least charge transfer has occurred in $\text{Be}^{2+}@\text{B}_{16}\text{N}_{16}$.

According to Table.1 it is also seen that there has been significant reduction in the band gap of proton inside $\text{B}_{16}\text{N}_{16}$. If we compare these structures from the view point of band gap energies; we have this respective: $\text{H}^+@\text{B}_{16}\text{N}_{16} < \text{Mg}^{2+}@\text{B}_{16}\text{N}_{16} < \text{Be}^{2+}@\text{B}_{16}\text{N}_{16} < \text{Ca}^{2+}@\text{B}_{16}\text{N}_{16} < \text{B}_{16}\text{N}_{16}$. Among the four structures, proton inside $\text{B}_{16}\text{N}_{16}$ i.e. $\text{H}^+@\text{B}_{16}\text{N}_{16}$ and Calcium cation within $\text{B}_{16}\text{N}_{16}$ i.e. $\text{Ca}^{2+}@\text{B}_{16}\text{N}_{16}$ have the least and the most of band gap in comparative to pristine $\text{B}_{16}\text{N}_{16}$ respectively. By placing three cations of the alkaline earth metals of group IIA within the $\text{B}_{16}\text{N}_{16}$ structure, decreasing in the gap energy of them is not so significantly but this decreasing in the energy gap of $\text{H}^+@\text{B}_{16}\text{N}_{16}$ is so impressive. So that, $\text{H}^+@\text{B}_{16}\text{N}_{16}$ is likely a semiconductor, these cationic alkaline earth metals structures are likely placed in the category of insulators when they match with $\text{B}_{16}\text{N}_{16}$ and they can construct endofullerene Nanostructure that their properties differ from the pristine $\text{B}_{16}\text{N}_{16}$. The values of energy levels of HOMO and LUMO in all structures have been increased in comparison to pristine $\text{B}_{16}\text{N}_{16}$ Nanostructure. The change of HOMO energies is small for H^+ within $\text{B}_{16}\text{N}_{16}$ Nanostructure in comparison to the alkaline earth metals within $\text{B}_{16}\text{N}_{16}$. Dipole Moment of the cationic alkaline earth metals and proton structures has been increased in respect to $\text{B}_{16}\text{N}_{16}$. It can also be seen that $\text{Be}^{2+}@\text{B}_{16}\text{N}_{16}$ has the highest dipole moment among the four structures.

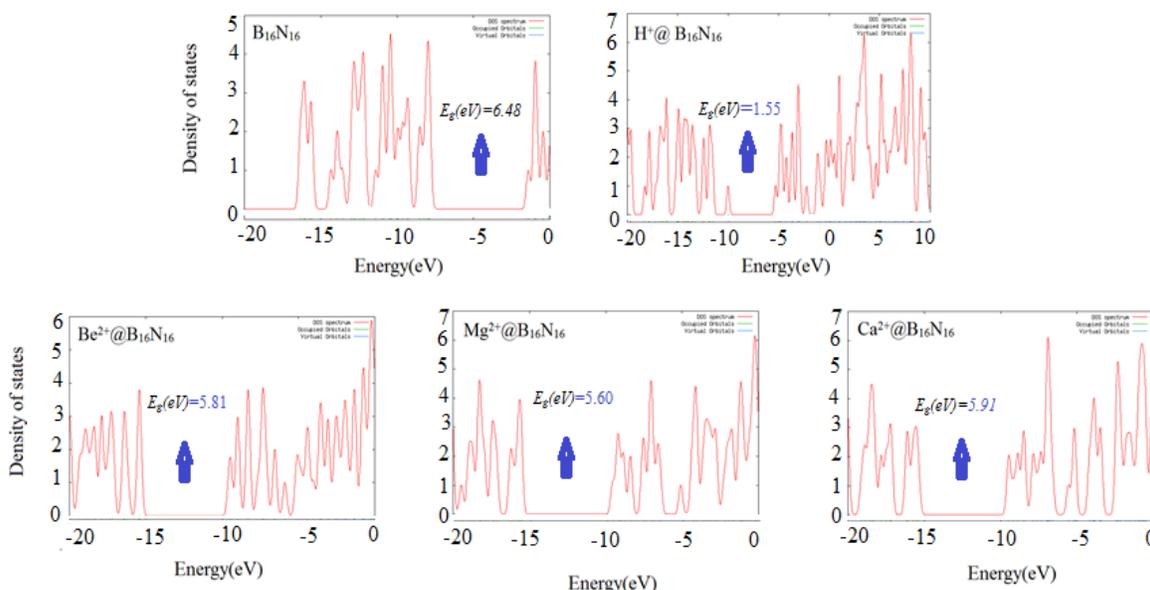


Figure 2: The Density states for $\text{B}_{16}\text{N}_{16}$ & M^{n+} (M^{n+} : H^+ , Be^{2+} , Mg^{2+} , Ca^{2+}) inside $\text{B}_{16}\text{N}_{16}$ Nanostructure respectively

Table 2: The HOMO–LUMO gap (eV) upon the interaction process, ΔE_g (eV), sensitivity in via percent (%)

Structures	Gap(eV)	ΔE_g (eV)	$S_{M^{n+}}$ (%)
$\text{B}_{16}\text{N}_{16}$	6.48	-	
$\text{H}^+@\text{B}_{16}\text{N}_{16}$	1.55	4.93	76.08
$\text{Be}^{2+}@\text{B}_{16}\text{N}_{16}$	5.81	0.67	10.34
$\text{Mg}^{2+}@\text{B}_{16}\text{N}_{16}$	5.60	0.88	13.58
$\text{Ca}^{2+}@\text{B}_{16}\text{N}_{16}$	5.91	0.57	8.79

ΔE_g (eV): Change of E_g upon the M^{n+} interaction

$S_{M^{n+}}$ (%): is the sensitivity of cations inside the $\text{B}_{16}\text{N}_{16}$ in terms of Percent

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According to the Table.2 & Figure 1 & Figure 2, by placing three atoms of group IIA inside $B_{16}N_{16}$, there is not so significant reduction in the energy gap of alkaline earth metals within $B_{16}N_{16}$ but decreasing in the energy gap of $H^+@B_{16}N_{16}$ is so impressive. So that, it is seen from table.2 the energy gap of $H^+@B_{16}N_{16}$ has been reduced to $E_g = 1.55(eV)$ from pristine value $E_g = 6.48$ in pristine $B_{16}N_{16}$ and this reduction is equal about ($\Delta E_g = 4.93(eV)$).

This reduction is very significant, so that $H^+@B_{16}N_{16}$ is probably placed in the category of semiconductors. After proton in the second order much reduction of energy gap is related to Mg^{2+} within $B_{16}N_{16}$. Be^{2+} the cationic alkaline earth metal within $B_{16}N_{16}$ have the third order of reduction in band gap in respect to pristine $B_{16}N_{16}$.

Among the studied structures, $Ca^{2+}@B_{16}N_{16}$ has so much energy gap. The sensitivity according to percent i.e. S_{Mn+} (%) for structures in via of kind atoms inside $B_{16}N_{16}$ is: $H^+@B_{16}N_{16} > Mg^{2+}@B_{16}N_{16} > Be^{2+}@B_{16}N_{16} > Ca^{2+}@B_{16}N_{16}$ or $H^+ > Mg^{2+} > Be^{2+} > Ca^{2+}$. So that if the three alkaline earth metals cations i.e. Be^{2+} , Mg^{2+} , Ca^{2+} and H^+ cations construct the endofullrenes with $B_{16}N_{16}$, They probably will placed in the range of insulators and semiconductor respectively.

Comparison between the energy gap of the three cations of group IIA and hydrogen cation with $B_{16}N_{16}$ structure is shown in Figure 2.

There are changes in HOMO and LUMO molecular orbitals structures in comparison with the $B_{16}N_{16}$, with the exception in the HOMO of $H^+@B_{16}N_{16}$ and $Mg^{2+}@B_{16}N_{16}$ (Figure 1).

According to the Table 1 in all structures have changes in the size of the diameters of the rings in respect to pristine $B_{16}N_{16}$. In the first and third structures it begins to increase in the second and later structures, the diameter of the ring decreases in respect to pristine $B_{16}N_{16}$. $Mg^{2+}@B_{16}N_{16}$ has the most size of the diameter of the ring. Comparison the interaction energy (E_{int}), Dipole Moment (Debye), charge transfer (electron) of the three cations of group IIA and proton within $B_{16}N_{16}$ nanostructure has been shown in Figure 3. Comparison the HOMO and LUMO energies, the energy gap, sensitivity of three cations of group IIA and proton inside $B_{16}N_{16}$ nanostructure have been demonstrated in Figure 4.

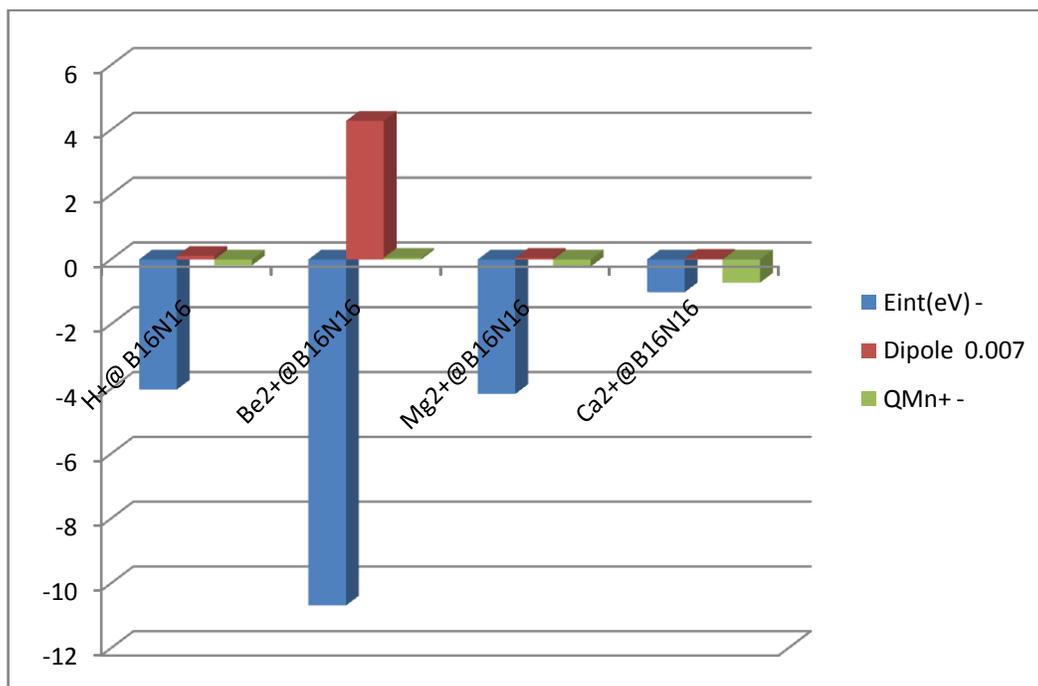


Figure 3: Comparison the interaction energy (E_{int}), Dipole Moment (Debye), charge transfer (electron) of the three cations of group IIA and proton within $B_{16}N_{16}$ nanostructure

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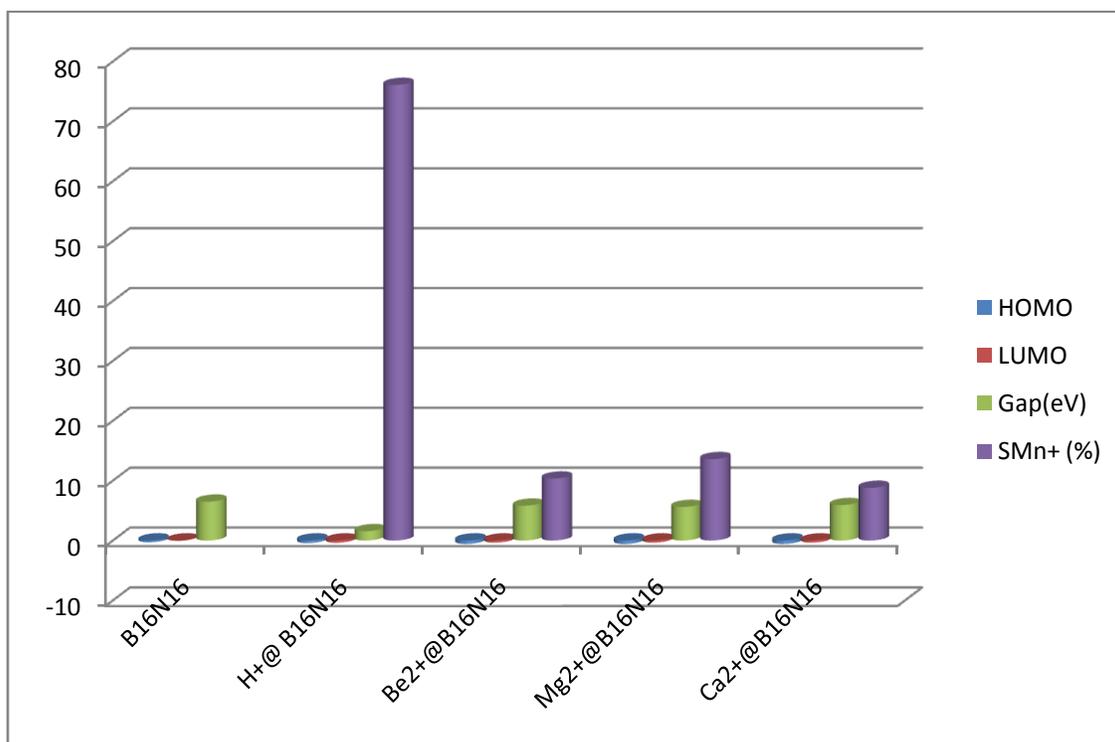


Figure 4: Comparison the HOMO and LUMO energies, the energy gap, sensitivity of three cations of group IIA and proton within B₁₆N₁₆ nanostructure

Discussion

This study showed that in all structures the charge transfer has happened from the B₁₆N₁₆ to the atoms except in Be²⁺@ B₁₆N₁₆. Minimum and maximum charge transfers have occurred in Be²⁺@ B₁₆N₁₆ and Ca²⁺@ B₁₆N₁₆ respectively. Dipole moments of the cationic alkaline earth metal and proton structures are more than B₁₆N₁₆ and this increasing is the most in the Be²⁺@ B₁₆N₁₆. The smallest dipole moment belongs to Ca²⁺@ B₁₆N₁₆.

Conclusion

By placing cations of the group IIA and Hydrogen cation inside B₁₆N₁₆ structure, significant decreasing in the energy gap happens but this decreasing in the energy gap of cationic alkaline earth metals is not very impressive so these structures are likely categorized as the insulators, the structure of the H⁺@ B₁₆N₁₆ has the least energy gap so it is likely categorized as a semiconductor. The value of HOMO and LUMO energy levels of structures increase in compared to B₁₆N₁₆. There is a change in HOMO and LUMO molecular orbitals of the structures with the exception in the H⁺@ B₁₆N₁₆ and Mg²⁺@ B₁₆N₁₆.

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