



Adsorption of the guanine molecule over the pristine, Nb-, and Au-doped boron nitride nanosheets: a DFT study

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Abstract

A theoretical study has been conducted onto the pristine, Nb-, and Au-doped boron nitride (BN) nanosheets using DFT calculations with the B3LYP-D3 method in order to evaluate their stabilities and electronic properties. The interaction of the guanine molecule with these clusters was also examined in order to determine their adsorption properties. The calculations show that the HOMO-LUMO energy gap (E_g) of the BN nanosheet was strongly decreased upon its doping with Nb and Au atoms, implying a strong enhancement in its surface reactivity. The interaction of the guanine with the BN nanosheet was found to be weak, which leads a slight variation in its energy gap; therefore, a low sensitivity of this nanosheet toward the guanine molecule was observed. The guanine adsorption over the NbBN cluster is very strong, and the calculated adsorptions energies are in the range of -36.7 to -60.2 kcal mol⁻¹, suggesting a great chemical adsorption. For the AuBN cluster, the guanine molecule has been chemisorbed onto its surface with adsorption energies which vary from -24.2 to -38.4 kcal mol⁻¹, which are lower than those obtained for the NbBN cluster. Upon adsorption process, the energy gap of the NbBN cluster was greatly increased, which leads to a decrease in its electrical conductivity; thereby, it cannot be a suitable sensor for the detection of the guanine molecule. On the contrary, the energy gap of the AuBN cluster was reduced by the effect of the guanine adsorption on its surface, indicating an increase in its electrical conductivity; thus, the AuBN cluster possesses a great electronic sensitivity to the guanine molecule. Based on the transition state theory, the recovery time of the guanine desorption from the AuBN cluster was estimated of 27.6 s, reflecting that the Au-doped BN nanosheet could be employed as an appropriate nanosensor for the guanine molecule detection with a short recovery time.

Keywords DFT · Au-doped BN nanosheet · Guanine · Adsorption · Electronic sensitivity

Introduction

Small metal clusters dispersed over different supports have received great deal of interest in heterogeneous catalysis, due to their excellent catalytic properties in comparison with the bulk metal [1–6]. The reactivity of these nanocatalysts is largely influenced by the method of preparation, cluster size, geometry, and the metal composition [7–10]. The nature of the support plays also a crucial role in the reactivity of the nanocatalysts [11, 12]. For example, in the dehydrogenation of 2-octanol, the rhenium clusters supported on Al₂O₃ are found to be more active than those supported on SnO₂, and

the catalytic activity of the particles was multiplied by 5.2 when Al₂O₃ support was replaced by SnO₂ [11]. This difference in reactivity is strongly related to the nature of the interaction (strong or low) between the clusters and the surface of the support. The graphene and its analogous such as boron nitride (BN) sheet are widely employed as an effective support for the metal clusters in order to enhance their catalytic properties in many heterogeneous reactions [12–16]. As an example, Rh nanoparticles dispersed over the surface of the graphene (Rh/Gr) show great catalytic activity in dehydrogenation of ammonia borane as compared to other classical supports such as SiO₂, C and Al₂O₃. The calculated specific activity (TOF) of the Rh/Gr nanocatalyst in the above reaction was found 2 times higher than that found for the Rh/Al₂O₃ one [12]. The BN nanosheet and its analogous have also been largely employed as the drug delivery vehicles [17–19]. For example, the BN nanosheet was successfully used for the adsorption of pharmaceutical drugs such as levofloxacin,

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tetracycline and curcumin [17]. Also, the boron carbonitride nanosheet was found as a suitable vehicle for the paclitaxel drug [18].

BN sheet was considered a novel structure of B and N atoms which can be employed as an adequate material support for the metal nanoclusters in order to obtain an efficient nanocatalyst for many chemical reactions such as the oxidation of alcohols, reduction of 4-nitrophenol and hydrogen generation from ammonia borane [14–16, 20]. The reactivity of the nanoparticles supported on BN sheet for the above reactions has been found to be very high in comparison with that of the classical nanocatalysts. This great catalytic activity of the nanocatalyst was ascribed to the high specific surface area of the BN nanosheet which facilitate the dispersion of the metal clusters over its surface, thereby leads to a better reactivity of the nanocatalyst in these reactions.

The doping of the BN nanosheet by a TM atom is an efficient way to improve significantly their chemical stability, electronic and catalytic properties. The experimental studies show that the reactivity of the BN nanosheet was greatly increased when the metal clusters of small size are dispersed over its large surface [21–24]. For example, the BN sheet which was synthesized in the presence of the ethylene glycol has been found an appropriate support for the Ag, Au and Pt nanoparticles. These nanoparticles supported over the BN sheet are found to be very active in the reduction of p-nitrophenol at mild conditions [23]. The Cu₂O/BN nanocatalyst which was obtained by the dispersion of the Cu₂O particles over the surface of the BN sheet show superior catalytic activity in the reduction of p-nitrophenol to p-aminophenol in comparison with that obtained for the Cu₂O particles and the pure BN nanosheet [21].

Ni nanoparticles deposited on BN sheet were prepared by reduction of Ni²⁺ by NaBH₄ in aqueous medium at room temperature and their catalytic performances were tested in the hydrolysis reaction of ammonia borane [24]. The results show that the obtained Ni nanoparticles are found well dispersed on the surface of the BN sheet and their catalytic activity in the hydrogen production from hydrolysis of ammonia borane was found to be much higher than that found for the Ni nanoparticles and the pure BN sheet. Furthermore, the recyclability test demonstrates that the Ni/BN nanocatalyst could retain 83% of its reactivity after five cycles of hydrolysis reaction.

A high catalytic activity was obtained in Suzuki-Miyaura reaction for the Pd-Fe nanoparticles supported over the surface of the BN sheet [22]. This great reactivity of these nanocatalysts was attributed to the synergetic effect, which is due to the Pd-Fe core-shell configuration and their interaction with the BN nanosheet. Moreover, when the BN sheet was replaced by the oxide graphene (GO), the results show that the reactivity of the Pd-Fe/GO nanocatalyst was found lower than that of the Pd-Fe/BN nanocatalyst. This finding

reflects that the BN sheet employed as support for the metal nanoparticles is an appropriate way to obtain an efficient nanocatalyst for many catalytic reactions.

In the last decade, the theoretical studies were focused onto the properties of the TM-doped of the BN nanosheet, which are extensively employed either as vehicles for the drug delivery or as active nanocatalysts for different catalytic applications. These nanoclusters formed by the doping of the BN nanosheet with TM atoms have also been studied computationally in order to better understand their electronic properties and sensitivity toward the toxic molecules [25]. For example, Vessaly et al. [25] have studied theoretically the adsorption of SO₂ over the pristine and the Si- and Al-doped BN nanosheets using B3LYP/6-31G level of theory, and the obtained results by them indicate that the BN nanosheet which is doped with Al and Si possess a great sensitivity toward SO₂ molecule, while the pure BN sheet was found to be insensitive to SO₂, and thereby this molecule cannot be detected by the BN sheet as a toxic molecule in a polluted environment. Also, due to its high surface area and great reactivity which are reported in several experimental studies, the BN nanosheet play a crucial role as an effective support in several catalytic reaction mechanisms which takes place on the catalyst surface [26, 27]. Also, the BN nanosheet has been mainly employed as vehicles for the drug delivery in biological environments [28–30]. As an example, Lin et al. [29] have investigated the interaction of the guanine, adenine, thymine and cytosine and uracil with the pure BN nanosheet. The calculated adsorption energies are in the range of 11.5 to 15.9 kcal mol⁻¹, indicating a physical adsorption. The results exhibit also that the nature of these nucleobases remains unchanged after interaction with BN sheet, suggesting that the BN nanosheet could be considered promising nanocarriers for these molecules in the biological systems. The adsorption of DNA nucleobases such as guanine and adenine over the BN sheet and graphene has been studied by Lee et al. [28] using DFT (PBE-vdW) calculations. The obtained results reveal that the binding energies range from 21.4 to 27.2 kcal mol⁻¹, reflecting a physisorption process. The reduction of NO over Si-doped BN sheet in the presence of CO molecule was investigated by PBE/DNP level with the empirical dispersion terms [27]. The doping of BN nanosheet with Si atom increases its surface reactivity, thus the Si atom in the cluster can plays a crucial role in the mechanism of the NO reduction. The formation of the N₂O molecule from (NO)₂ dimer over the Si/BN catalyst has been found to be the most likely mechanism for this reaction. The activation barrier for the reduction of NO is of 9.0 kcal mol⁻¹. Moreover, the remaining oxygen atom attached to the surface of the cluster is then removed by its reaction with CO gas to form the desorbed CO₂ gas. This formation of CO₂ molecule from CO requires a little activation energy of 7.8 kcal mol⁻¹.

In this work, a theoretical study was performed on the pristine, Nb-, and Au-doped BN nanosheets using DFT

calculations at the B3LYP-D3 method in order to investigate their stability and electronic properties. The electronic sensitivity of these clusters toward the guanine molecule has also been examined and the obtained results were analyzed and discussed.

Theoretical method

DFT calculations with the B3LYP-D3 level of theory were carried out using the Gaussian09 package [31–34] in order to evaluate the stability and electronic properties of the pristine, Nb-, and Au-doped BN nanosheet. The interaction of the guanine molecule with the BN, NbBN, and AuBN clusters has also been investigated with the same method in aim to examine their adsorption properties and electronic sensitivity. The B3LYP hybrid functional with the Grimme's dispersion (D3) correction were often used in the studies of the stabilities, electronic and adsorption properties of the nanomaterials and yielded acceptable results which are well close to the experimental data [35, 36]. Meanwhile, the LanL2DZ effective core potential (ECP) basis set was used for the Nb and Au atoms, and the 6-311G(d,p) basis set has been employed for the B, N, O, C, and H atoms [37, 38]. These two kinds of basis sets were chosen for their accuracy in which the theoretical values obtained for the studied nanostructured systems are well matched with the experimental results [39–42].

The BN nanosheet employed in our study is containing 23 atoms of boron, 23 atoms of nitrogen and 18 atoms of hydrogen which are attached to the boron or nitrogen atoms at the end of the BN cluster. The Nb- and Au-doped BN nanosheets have been constructed through of a substitution of a B atom of the BN nanosheet by an Au or Nb atom in order to improve their surface reactivity.

Fukui function (f^+) was also calculated in order to determine the active sites on the surface of the NbBN and AuBN clusters. The higher values of f^+ correspond to the active sites which may be involved in a chemical reaction. In other words, this function is able to predict the active sites existing on the surface of the studied clusters which could interact with the nucleophilic sites of a molecule. So, the Fukui function f^+ for a nucleophilic attack is defined as [43]:

$$f^+(r) = \rho_{N+1}(r) - \rho_N(r) \quad (1)$$

where $\rho_K(r)$ ($K = N$ and $N + 1$) represent the electron density at r in a cluster of a K -electron.

In order to obtain the most stable adsorption configurations, several positions and many orientations of the guanine above the surface of the BN, NbBN, and AuBN clusters were optimized. When the guanine molecule was adsorbed onto the surface of the clusters, it is important to know the nature of the

interaction between both species by calculating the adsorption energy (E_{ads}) which is given by the following equation.

$$E_{\text{ads}} = E_{\text{MBN/guanine}} - E_{\text{MBN}} - E_{\text{guanine}} + E_{\text{BSSE}} \quad (2)$$

where E_{MBN} and $E_{\text{MBN/guanine}}$ are the total energies of the metal-doped BN nanosheet and the complexes formed through their interaction with the guanine molecule, respectively. E_{BSSE} is the energy of the basis set superposition error.

Similar expression was used to evaluate the adsorption energy (E_{ads}) of the adsorbed guanine molecule over the surface of the pure BN nanosheet.

$$E_{\text{ads}} = E_{\text{BN/guanine}} - E_{\text{BN}} - E_{\text{guanine}} + E_{\text{BSSE}} \quad (3)$$

where $E_{\text{BN/guanine}}$ is the total energy of the adsorbed guanine on the pure BN nanosheet.

The electronic sensitivity of the BN, NbBN, and AuBN clusters to the guanine molecule for a given temperature (T) has also been computed using Eq. (4). According to Eq. (4), the energy gap (E_g) of the cluster has been directly related to its electrical conductivity (σ). For example, when the E_g of the cluster decreases due to the adsorption of the guanine molecule on its surface, its electrical conductivity rises, which can be converted to an electrical signal. Therefore, the cluster will be a promising candidate to be a good nanosensor for the detection of the guanine molecule.

$$\sigma = A T^{3/2} \exp(-E_g/2kT) \quad (4)$$

where A is a constant (electrons/m³ K^{3/2}), k is the Boltzman's constant, and E_g is the energy gap.

The recovery time of a molecule which is adsorbed over the surface of a cluster is an important criterion for the choice of a nanosensor. The desorption of a molecule which is greatly chemisorbed to the surface of the cluster requires a long recovery time. Thus, the clusters which are strongly attached to the molecules are not appropriate nanomaterials for the nanosensor applications. Experimental study indicates that the recovery of a nanosensor is achieved either by heating to high temperatures or by exposing to UV light. On the basis of the transition state theory, the recovery time of a molecule over the surface of a cluster can be estimated from Eq. (5), in which it was proven that there is a direct relationship between the adsorption energy (E_{ads}) and frequency (ν) with the recovery time (τ).

$$\tau = \nu^{-1} \exp(-E_{\text{ads}}/kT) \quad (5)$$

where T , k , and ν are the temperature (K), the Boltzman's constant ($\sim 2.0 \cdot 10^{-3}$ kcal mol⁻¹ K⁻¹), and the attempt frequency (s⁻¹), respectively. E_{ads} is the adsorption energy of the molecule over the surface of the cluster.

Results and discussion

The electronic properties of the pristine and the Nb- and Au-doped BN nanosheets

The geometries of the pristine and the Nb-, and Au-doped BN nanosheets were optimized, and the most stable configurations obtained are shown in Fig. 1. The density of states (DOS), molecular electrostatic potential (MEP), energies of HOMO and LUMO states (E_H and E_L), energy gap (E_g), charge on metal atom (q_M), electric dipole moment (β), chemical hardness (η), and the softness (s) have been calculated, and the results predicted are presented in Fig. 2 and Table 1. The calculated length of the B-N bond in the pure BN sheet was found to be 1.45 Å, which is in good agreement with the values reported by the other researchers [44, 45]. When a B atom of BN sheet was replaced by an Au or Nb atom, a small deformation in the geometry of the pure BN nanocage was observed, in which the metal atom was slightly taken out of the surface of the cage after the formation of the metal-doped cluster. The distance of the newly formed M-N bond in the Au- and Nb-doped BN clusters is found to be 2.11 and 2.02 Å, respectively, which are larger than that of the value obtained for the B-N bond in the pure BN nanosheet. The binding energy (E_b) of the BN sheet was found to be -5.431 eV, indicating that this nanosheet has a great stability. Doping of the BN nanosheet by an Au or Nb atom has slightly decreased its binding energy and the calculated E_b values are -5.336 eV and -5.327 eV for the AuBN and NbBN clusters, respectively. Upon doping, the values of E_b are found to be very negative, which reflect a high stability for the formed clusters. These results are confirmed by the positive harmonic vibration frequencies which were obtained for both clusters, where the calculated values range from 21.5 and 21.9 cm^{-1} to 47.2 and 45.6 cm^{-1} for the NbBN and AuBN clusters, respectively.

The energies of the HOMO and LUMO orbitals of the pristine are -6.573 and -0.541 eV, respectively, thereby a gap energy of 6.032 eV, suggesting that a semiconductor behavior can be manifested in this nanomaterial despite its large-band gap. Moreover, this estimated value (E_g) for the BN sheet is in excellent agreement with the experimental

values reported in the literature which vary between 3.6 and 7.1 eV [46]. The electronic properties of the BN nanosheet were strongly modified when a B atom was replaced by an Au or Nb atom (see Table 1). For example, the value of E_g was decreased from 6.032 eV in the BN sheet to 1.495 and 2.701 eV in the Nb- and Au-doped BN nanosheets, respectively. So, the variation in E_g (ΔE_g) after substitution of a B atom by Nb and Au atoms was found to be 75.2 and 55.2%, respectively, implying a deep alteration in the surface reactivity and electronic properties of the BN nanosheet upon doping. Therefore, the stability of the BN nanosheet has been strongly decreased after its doping with an Au or Nb atom. In other words, the doping with metal atom greatly enhances the reactivity of the pure BN sheet. That is to say, the AuBN and NbBN clusters are found to be more reactive than the BN sheet, thus their interaction with the nucleophilic centers of a molecule is done more easily than the pure BN sheet. This increase in reactivity was confirmed by the values of the chemical hardness (η) and the softness (s) of the BN nanosheet which were calculated before and after metal doping. The values of η were sharply diminished after metal doping (η decreases from 3.016 in the BN sheet to 0.748 and 1.351 eV in NbBN and AuBN nanoclusters, respectively). In cluster science, the chemical hardness is an important parameter that characterizes the chemical stability of the cluster [47–49]. A large η value indicates a higher stability, while a little η value suggests a higher chemical reactivity. The calculations of the softness indicate a reverse trend compared to the hardness, where the values are increased from 0.166 $(\text{eV})^{-1}$ in BN sheet to 0.370 and 0.668 $(\text{eV})^{-1}$ in AuBN and NbBN clusters, respectively, confirming that the reactivity of the BN nanosheet was sharply enhanced after doping with Au and Nb atoms. Furthermore, these results are in excellent agreement with the obtained values for the energy gap and the chemical hardness.

The AIM charges analysis of the BN nanosheet exhibits a sizable charge of 0.382 |e| was transferred from the bore to the nitrogen atoms in the pure BN nanosheet, implying the existence of a strong ionic interaction between the B atoms and the N atoms in the BN nanosheet. This strong interaction between both atoms indicates a great chemical stability of the BN sheet, which is consistent with the calculated values for the binding

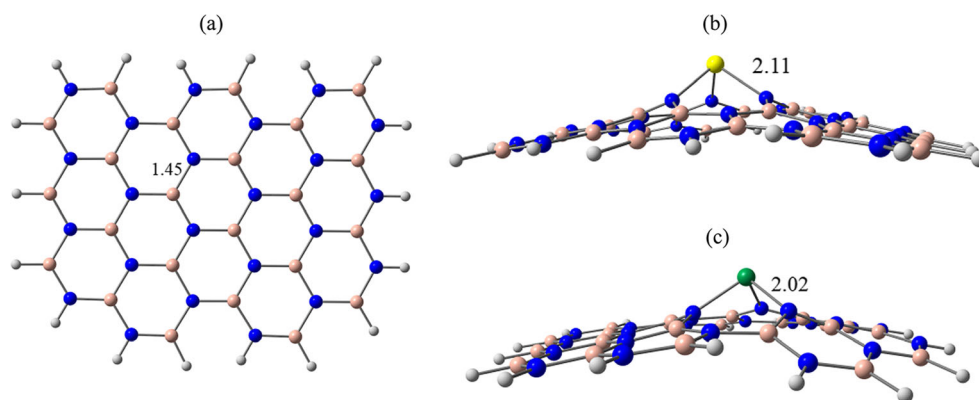
Table 1 The M-N bond distance (d), binding energy (E_b), energies of HOMO and LUMO states (E_H , E_L), energy gap (E_g), charge on metal atom (q_M), dipole moment (β), chemical hardness (η), and softness (s) of the pure and Nb and Au-doped BN nanosheet

Cluster	d (Å)	E_b (eV/atom)	E_H (eV)	E_L (eV)	E_g (eV)	q_M (e)	β (D)	η^* (eV)	s^* (eV^{-1})
BN	1.45	-5.431	-6.573	-0.541	6.032	+0.382**	0.217	3.016	0.166
NbBN	2.02	-5.327	-3.540	-2.045	1.495	+1.064	0.936	0.748	0.668
AuBN	2.11	-5.336	-6.313	-3.611	2.701	+0.287	0.938	1.351	0.370

* The chemical hardness was calculated by $E_L - E_H / 2$ and the softness was estimated by $1/2 \eta$

** Charge on B atom in BN sheet which was substituted by Au or Nb atom

Fig. 1 The optimized geometries of the (a) pristine, (b) Au-, and (c) Nb-doped BN nanosheets



energy, the chemical hardness and the softness. The direction of the charge transfer in BN sheet has also been confirmed by MEP isosurface (see Fig. 2), where the N atoms are greatly negatively charged (red color), and the B atoms are positively charged (blue color). The analysis of charges shows also that a large quantity of charge was transferred from metal atom to nearest N atoms in the NbBN and AuBN clusters. The charge predicted over the Nb and Au atoms were found to be +1.064 and +0.287 |e|, respectively. The positive charge on Nb and Au atoms in the clusters (blue color) has also been confirmed by MEP analysis (Fig. 2). These results indicate that the Nb and Au atoms in the clusters could be considered electrophilic sites, which can easily attacked by the nucleophilic centers of a molecule as the guanine. In order to determine the reactive sites onto the surface of the NbBN and AuBN clusters, the condensed Fukui function (f^+) was calculated, and the results obtained are illustrated in Fig. 3. Theoretically, the electrophilic sites existing over the surface of the cluster which are susceptible to be attacked by the nucleophilic sites of a molecule such as the guanine could be described by the high positive value of f^+ . In other words, the higher values of f^+ correspond to the most favorable sites in the clusters which are able to interact with the nucleophilic centers of the guanine molecule. As it was shown in Fig. 3, the isosurface of f^+ indicates that the highest f^+ values were predicted for the Nb and Au atoms, respectively, suggesting that the two atoms could be considered the most favorable adsorption sites over the surface of the clusters; thereby, they are susceptible of interacting easily with the nucleophilic centers of the guanine. Moreover, the value of f^+ for the Au atom ($f^+ = 0.152$) in the AuBN cluster is lower than that obtained for the Nb atom ($f^+ = 0.397$) in the NbBN cluster, suggesting that the Nb atom in NbBN cluster is substantially more reactive than the Au atom in AuBN cluster. The results show also that the electric dipole moment (β) of the BN nanosheet is slightly increased upon its doping with Nb and Au atoms (see Table 1). It increases from 0.217 D in the pure BN nanosheet to 0.936 and 0.938 D in the NbBN and AuBN nanoclusters, respectively.

Adsorption of the guanine over the BN nanosheet

In this section, we have studied the reactivity of the BN nanosheet toward the guanine molecule. In order to determine the optimized configurations of the adsorbed guanine molecule over the BN nanosheet, different orientations of the molecule onto the surface of the cluster were tested. Upon optimizations, two most stable complexes have been obtained (A and B), and their optimized geometries, structural parameters and electronic properties are reported in Fig. 4 and Table 2. The electron densities of the HOMO and LUMO orbitals of the two complexes have also been shown in Fig. 4. As one can see from Fig. 4, for both states, the guanine molecule was adsorbed parallel to the surface of the BN nanosheet. The interaction distances between the guanine molecule and the surface of the BN cluster are 3.27 and 3.36 Å for the A and B configurations, respectively (Table 2). These large distances suggest that the adsorption of the guanine over the surface of the BN sheet is weak. The calculated adsorption energies (E_{ads}) are -15.2 and -14.9 kcal mol $^{-1}$ for the A and B complexes, respectively, indicating a physical adsorption. The interaction of the guanine molecule with the B $_{40}$ nanocage has been investigated by Cheng et al. [50] by using the PBE/DNP method. Upon optimizations, they found five most stable complexes with adsorption energies which vary from -23.6 to -36.3 kcal mol $^{-1}$, and which are higher than the values obtained in our study. On the contrary, the computed adsorption energy by Lin et al. [29] for the interaction between the guanine and the h-BN nanosheet ($E_{\text{ads}} = 15.9$ kcal mol $^{-1}$) was found almost equal to the values predicted in our calculations. The energies of the HOMO and LUMO states, energy gap (E_g), charge transfer (q_{CT}) and the dipole moment (β_T) of the formed complexes upon interaction between the BN nanosheet and the guanine molecule were computed and the values obtained are listed in Table 2. The thermodynamic parameters such as entropy change (ΔS), enthalpy change (ΔH) and Gibbs free-energy change (ΔG) for the complexes were also calculated and the predicted values are summarized in the same table. As it was presented in Table 2, the values of ΔH

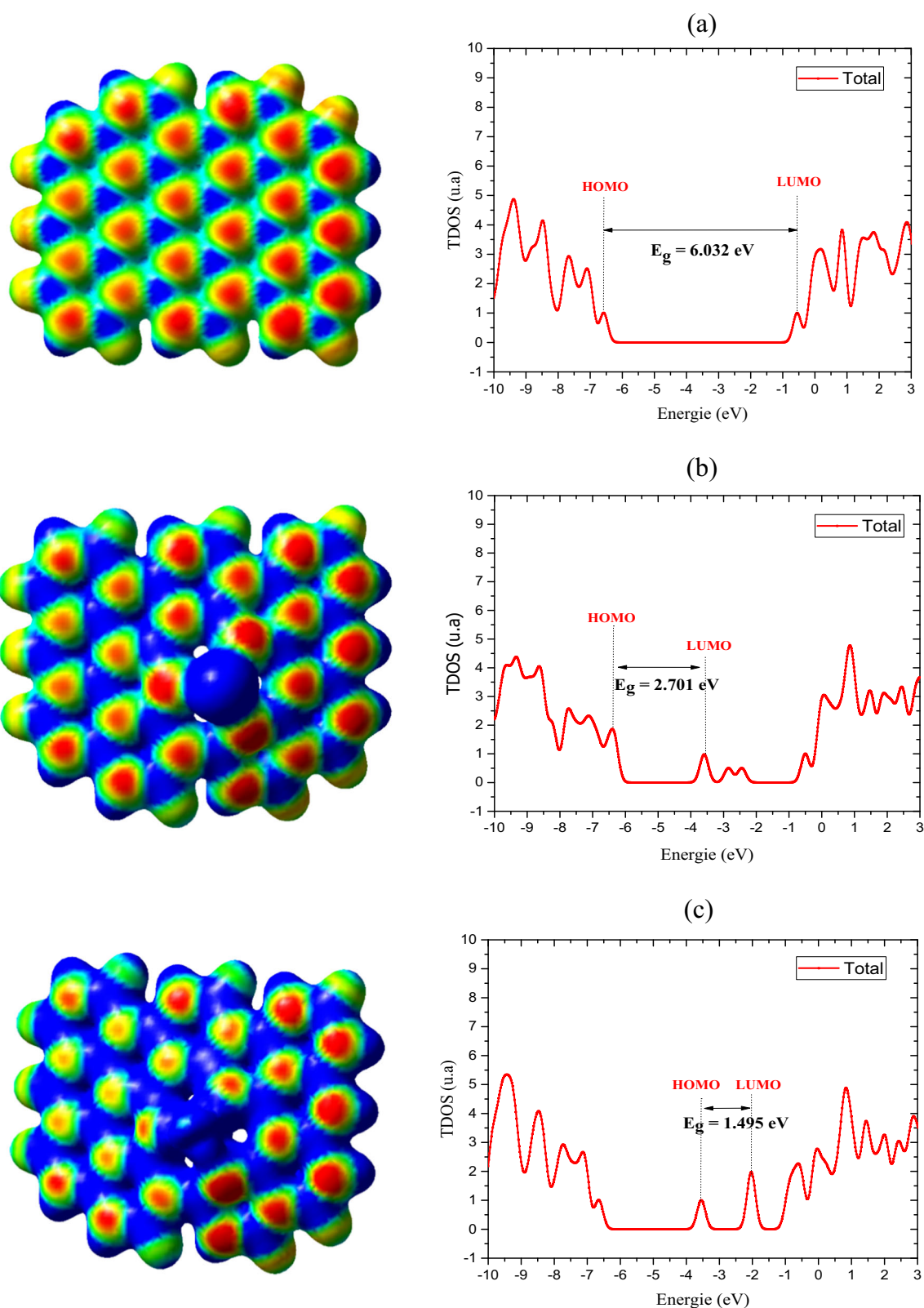
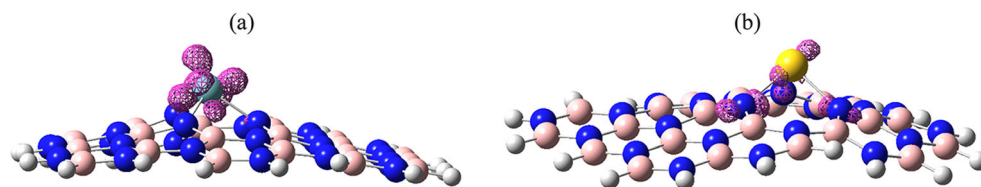


Fig. 2 Molecular electrostatic potential maps (MEP) and density of states (DOS) of the (a) pristine, (b) Au-, and (c) Nb-doped BN nanosheets

and ΔG are found to be more negative, indicating that the complexation process between the cluster and the guanine molecule is exothermic and thermodynamically spontaneous.

The results show also that the HOMO-LUMO energy gap of the BN nanosheet was slightly influenced by the adsorption of the guanine molecule over its surface, and the variation in E_g

Fig. 3 The isosurface of f^+ of the Nb- and Au-doped BN nanosheets



(ΔE_g) is 14.9% and 13.2% for the configurations A and B, respectively.

The HOMO and LUMO orbitals of the complexes which were formed upon the adsorption of the guanine over the surface of the BN nanosheet (A and B) were calculated and the obtained results are given in Fig. 4. For the two configurations A and B, the results clearly indicate that the distribution of HOMO is mostly localized over the guanine molecule, whereas the density of LUMO is principally located on the surface of BN nanosheet. This result suggests that the guanine molecule was strongly interacted with the LUMO level of the cluster. Moreover, the results show that small charges were transferred from the BN cluster to the guanine molecule, reflecting a weak adsorption process (Table 2). The AIM charges analysis shows that the quantity of charge transferred between both species is 0.001 and 0.010 $|e|$ for the A and B complexes, respectively (Table 2).

The EDD isosurfaces for both complexes (A and B) were calculated and the results are presented in Fig. 5. Accordingly to Fig. 5, the electron density accumulation between the surface of the BN nanosheet and the guanine molecule is almost negligible, confirming the above results which indicate a weak physical adsorption of the guanine over the surface of the BN nanosheet.

Adsorption of the guanine molecule over the AuBN nanosheet

To study the electronic sensitivity of the Au-doped BN nanosheet toward the guanine molecule, we have examined its interaction with the surface of the AuBN cluster. In order to find the most stable configurations of the formed complexes after adsorption process, several initial geometries were fully optimized and analyzed. Before optimizations, the guanine molecule was located above the surface of the AuBN cluster through their nucleophilic sites (oxygen and nitrogen atoms), where each site of the above molecule has a large tendency to attack the electrophilic site (Au atom) of the cluster. Another

configuration, where the guanine molecule was adsorbed parallel to the surface of the AuBN cluster has also been considered in our calculations. As it was mentioned above, the Au atom of the AuBN cluster represents an active site which can easily interact with the nucleophilic sites of the guanine molecule. Upon full optimizations, five stable complexes namely, C, D, E, F and G were predicted (Fig. 6), and their electronic and adsorption properties are reported in Table 3. The calculations show that the interaction between the guanine molecule and the Au-doped BN nanosheet is very strong, and the calculated adsorption energies are in the range of -24.2 to -38.4 kcal mol^{-1} (Table 3). Moreover, for all the formed complexes, the interaction between both species was carried out without deformation of the guanine molecule, suggesting that the fundamental nature of the guanine molecule remains unchanged after adsorption process. This finding is very important for the nanomaterials which could be employed as promising nanocarriers for this molecule.

In the complex C, the guanine molecule is adsorbed onto the Au atom of the AuBN cluster by the lone electron pairs of the nitrogen atom that belongs to the 5-membered ring of the guanine. The interaction between both species is found to be very strong, and the calculated adsorption energy (E_{ads}) of this state is -32.9 kcal mol^{-1} , indicating a chemisorption process. The newly Au-N bond distance which was formed after interaction between the guanine and the AuBN cluster is of 2.15 Å. For the complex D, the same atom of the nitrogen has also been sharply chemisorbed over the Au atom of the AuBN cluster to form a second stable geometry which is completely different (orientation parallel with respect to the surface of the AuBN cluster) than that obtained for the complex C (see Fig. 6). The length of the Au-N bond which was formed upon adsorption process in complex D is 2.17 Å and the calculated adsorption energy was found to be -33.3 kcal mol^{-1} , which is slightly higher than the value predicted for the complex C, indicating that this geometry is more stable than that found for the complex C. The guanine adsorption over the surface of the AuBN cluster through its nitrogen of $-\text{NH}_2$ has also been

Table 2 The interaction distance (d), energies of HOMO and LUMO states (E_H , E_L), energy gap (E_g), charge transfer (q_{CT}), dipole moment (β_T), adsorption energy (E_{ads}), and thermodynamic parameters (ΔH , ΔS , and ΔG) for the complexes A and B

Complex	d (Å)	E_H (eV)	E_L (eV)	E_g (eV)	q_{CT} (e)	β_T (D)	E_{ads} (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1})	ΔG (kcal mol^{-1})
A	3.27	-5.835	-0.700	5.134	-0.001	5.326	-15.2	-19.1	-41.3	-6.8
B	3.36	-5.833	-0.595	5.237	-0.010	5.087	-14.9	-20.0	-39.6	-8.2

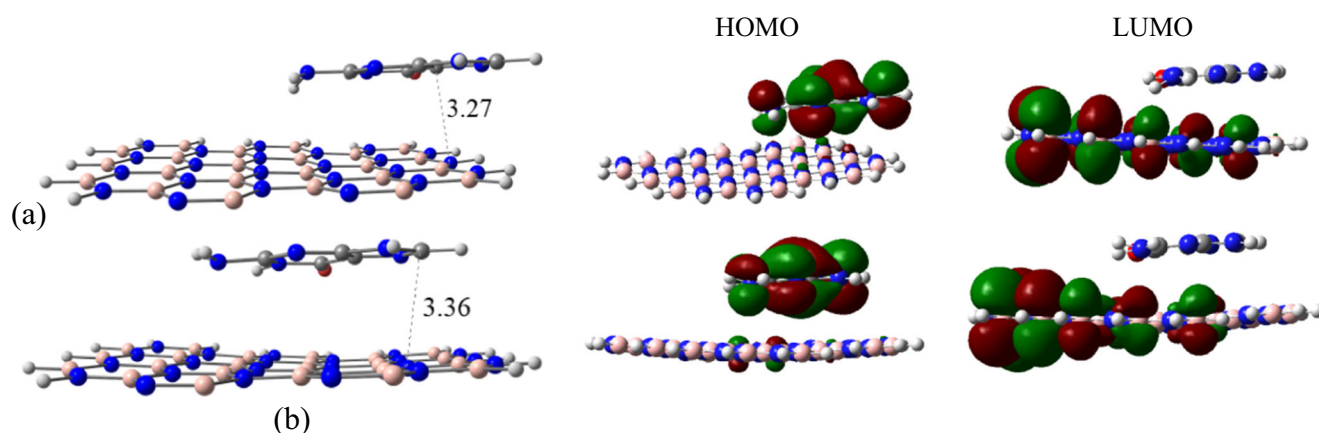


Fig. 4 The optimized geometries of the complexes formed from the guanine adsorption over the surface of the BN nanosheet (A and B complexes) and their HOMO and LUMO orbitals

predicted in our optimizations (complex E) and the calculated E_{ads} value ($-24.2 \text{ kcal mol}^{-1}$) is lower than the values predicted for the above configurations (C and D). The distance of the Au-N bond is 2.26 \AA , which is a bit greater than the values estimated for the configurations C and D, respectively. For the complex F, the interaction was carried out between the Au atom of the cluster and the N atom that belongs to the 6-membered ring of the guanine with an adsorption energy of $-38.4 \text{ kcal mol}^{-1}$. The highest E_{ads} value was obtained for this complex in comparison with the values calculated for the other configurations, indicating a very strong chemical adsorption between the N atom of the guanine and the Au atom of the AuBN cluster. The distance of the Au-N bond which was formed in the complex F after chemisorption process is only 2.17 \AA .

For the complex G, the guanine molecule was chemisorbed with an orientation parallel to the surface of the AuBN cluster. This result exhibits that the interaction between the Au atom of the AuBN cluster and the π -electrons of the six-membered ring of the guanine is a chemical adsorption in nature. The calculated E_{ads} for this configuration was found to be $-25.3 \text{ kcal mol}^{-1}$, which is much higher (~ 3.5 times) than the values predicted for the two complexes A and B (see Table 1) where the guanine was adsorbed parallel to the surface of the pure BN nanosheet. Moreover, the results suggest that the substitution of a B atom of the BN nanosheet by an Au atom was greatly improved its surface reactivity; thus, the Au atom is considered an electrophilic site that will be attacked by the nucleophilic centers of the guanine molecule. The estimated length between the guanine molecule and the surface of the

cluster is 2.37 \AA , which is a bit lower than the values predicted for the configurations A and B.

Also, it is important to note that the adsorption of the guanine over the surface of the AuBN cluster by its oxygen atom was also optimized, and the results indicate that the obtained complex from this initial geometry was found identical to that of the complex C. The results show also that the length of the Au-N bond in the AuBN cluster for the complexes formed by its interaction with the guanine molecule was found to be between 2.03 and 2.08 \AA , which is a bit lower than that of the isolated AuBN cluster, indicating that the guanine adsorption onto the surface of the AuBN cluster did not significantly alter their structural parameters. The calculations show also that the values of ΔH for the formed complexes are in the range of -26.7 to $-42.4 \text{ kcal mol}^{-1}$, and the values of ΔG vary from -14.0 to $-28.8 \text{ kcal mol}^{-1}$, reflecting that the formation process of the complexes is exothermic and thermodynamically realizable at normal conditions.

A great change in the energies of HOMO and LUMO orbitals (E_{H} and E_{L}) was clearly observed (Table 3) for the complexes which were formed after the adsorption of the guanine molecule over the AuBN cluster. The energies of HOMO and LUMO states of all the studied complexes (C-G) were shifted to the less negative values. For example, the HOMO and LUMO levels shift from -6.313 and -3.611 eV for the AuBN cluster to -5.297 and -2.870 eV for the complex C, thereby a variation in E_{H} and E_{L} of 16 and 20%, respectively. Based on the energies of HOMO and LUMO orbitals, the E_{g} of the complexes were calculated, and the values obtained are listed in Table 3. As it was shown in this table, the electronic

Fig. 5 The electron density difference (EDD) isosurfaces for the complexes A and B. The pink and yellow represent the electron density gain and loss regions, respectively

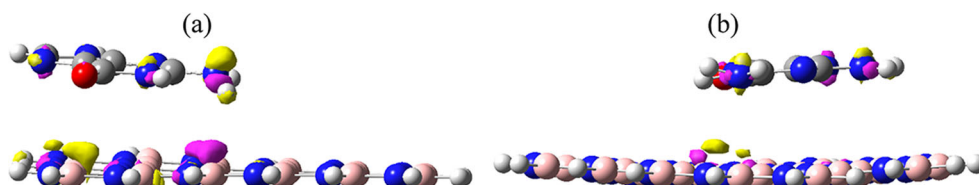


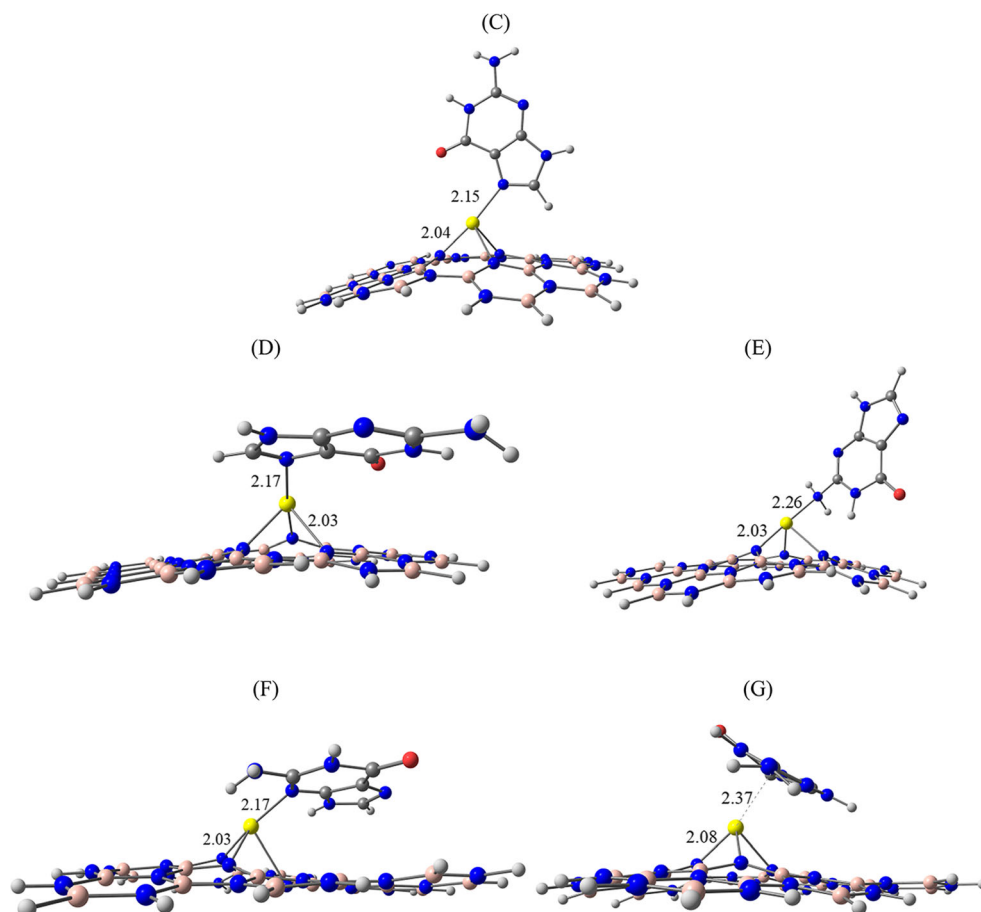
Table 3 The interaction distance (d), energies of HOMO and LUMO states (E_H , E_L), energy gap (E_g), charge transfer (q_{CT}), dipole moment (β_T), adsorption energy (E_{ads}), enthalpy change (ΔH), entropy change (ΔS), and Gibbs free-enthalpy change (ΔG) for the formed complexes from the interaction of the guanine molecule with the surface of the clusters

	d (Å)	E_H (eV)	E_L (eV)	E_g (eV)	q_{CT} (e)	β_T (D)	E_{ads} (kcal mol ⁻¹)	ΔH (kcal mol ⁻¹)	ΔS (cal mol ⁻¹)	ΔG (kcal mol ⁻¹)
AuBN complex										
C	2.15	-5.297	-2.870	2.427	+0.192	13.941	-32.9	-35.3	-38.0	-24.0
D	2.17	-5.414	-2.951	2.463	+0.183	10.070	-33.3	-38.3	-42.8	-25.6
E	2.26	-5.884	-3.520	2.364	+0.152	6.839	-24.2	-26.7	-42.4	-14.0
F	2.17	-6.037	-3.569	2.469	+0.727	3.201	-38.4	-42.4	-45.8	-28.8
G	2.37	-5.744	-3.325	2.419	+0.210	5.664	-25.3	-30.9	-44.9	-17.5
NbBN complex										
H	2.39	-3.443	-1.801	1.642	-0.682	15.563	-60.2	-64.2	-38.9	-52.6
I	2.31	-3.383	-1.699	1.684	-0.045	5.812	-57.2	-61.1	-36.5	-50.2
J	2.27	-4.373	-1.669	2.704	-0.181	5.603	-50.5	-63.1	-46.0	-49.4
K	2.34	-4.146	-1.569	2.577	+0.025	5.113	-36.7	-40.8	-28.9	-32.2
L	2.55	-4.198	-2.024	2.174	-0.079	4.106	-42.1	-47.1	-34.4	-36.9

properties of the AuBN cluster were largely influenced by the interaction of the guanine molecule onto its surface. The guanine adsorption over the surface of the AuBN cluster has considerably modified the energies of HOMO and LUMO states of the cluster, thereby its energy gap (E_g). As an

example, the energy gap was decreased from 2.701 eV in the AuBN cluster to 2.364 eV in the complex E, thereby a variation in E_g of 0.337 eV. Based on Eq. (4), the decrease in E_g of the cluster greatly raised its electrical conductivity, thus it can generate an electrical signal. This result suggests that

Fig. 6 The most stable complexes obtained upon the interaction of the guanine molecule with the surface of the AuBN cluster (C, D, E, F, and G)

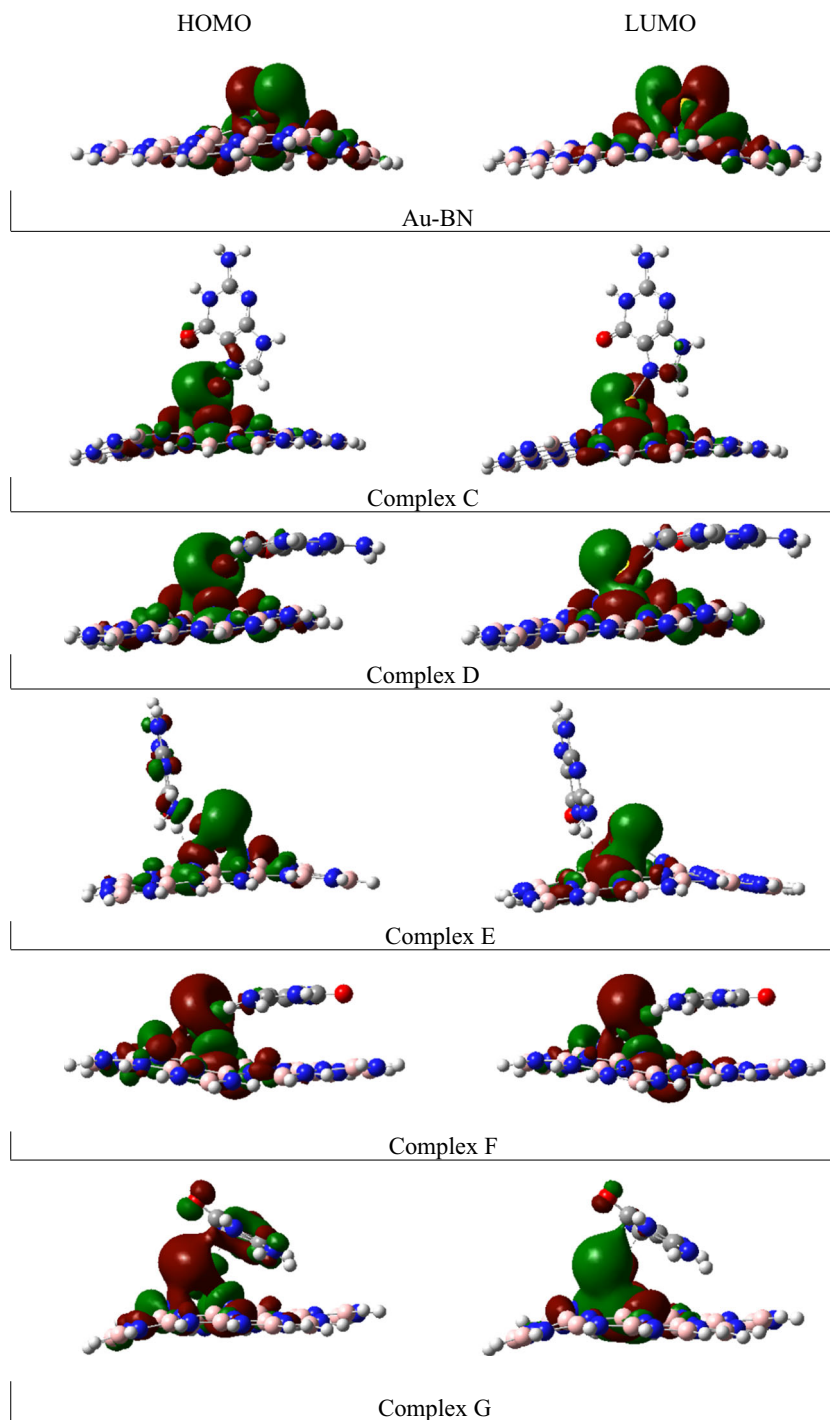


this cluster could be an appropriate nanosensor for the guanine molecule detection.

The spatial orientations of the HOMO and LUMO orbitals of the cluster and their complexes formed after its interaction with the guanine molecule are depicted in Fig. 7. As one can see from this figure, the HOMO and LUMO states for the AuBN cluster are completely localized on the Au atom. When the guanine molecule is chemisorbed over the surface of the AuBN cluster, the electron density is mostly located on

the Au atom of the cluster and around the chemical bond that bind the cluster with the guanine molecule. Also, a low distribution of the electron density was observed onto the guanine molecule. This result suggests a strong interaction between the AuBN cluster and the guanine molecule confirming a chemisorption process for all the studied complexes. This result was also supported by the spin density of the complexes (not shown), which exhibit a large localization of electrons between the Au atom of the AuBN cluster and the guanine,

Fig. 7 Frontier molecular orbitals (FMO) plots of the Au-doped BN nanosheet and their formed complexes through its interaction with the guanine molecule (C, D, E, F, and G)



implying a great chemical adsorption between both species. In order to investigate the nature of the formed bonds in the complexes upon the interaction of the guanine with the AuBN cluster, the electron density difference (EDD) isosurfaces were calculated for the formed complexes and the results obtained are illustrated in Fig. 8. The results show that the electron density was greatly accumulated around the Au atom of the cluster and the guanine molecule, indicating a great chemical adsorption between both species. This finding was confirmed by the highest E_{ads} values which are obtained for the complexes, indicating a chemisorption process.

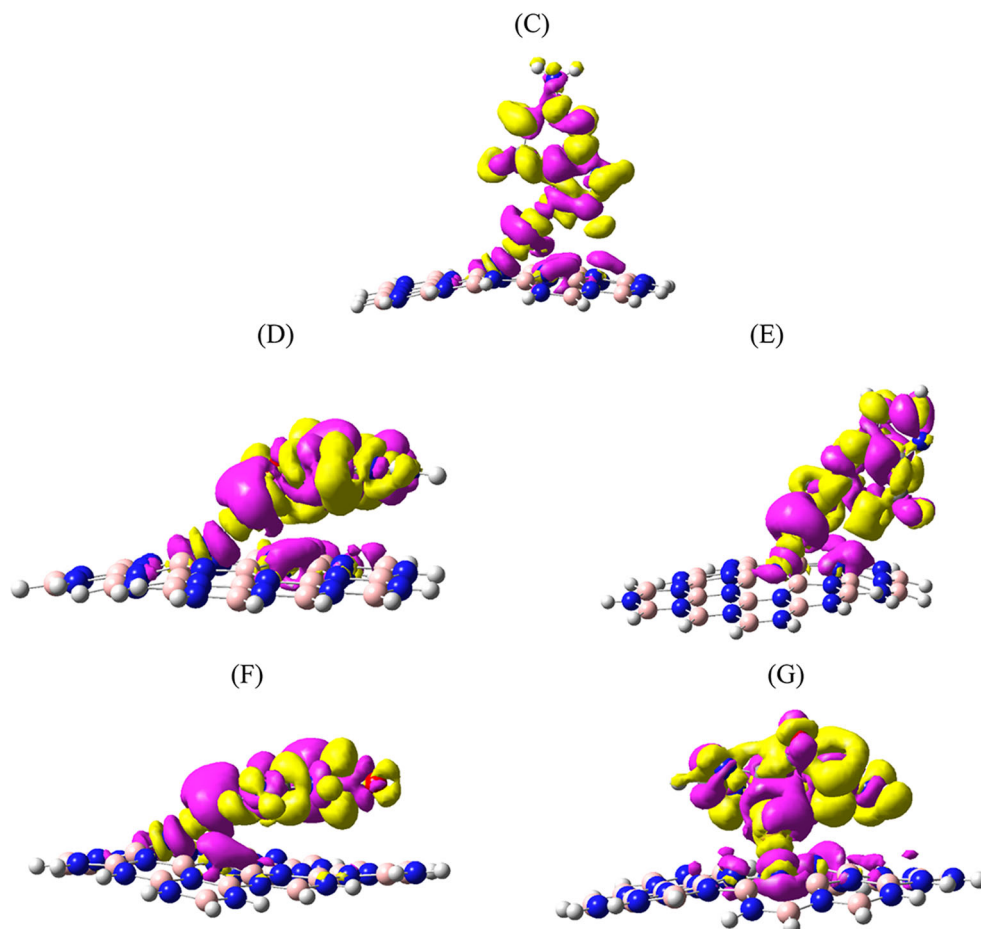
In order to determine the quantities of charge transferred between the AuBN cluster and the guanine molecule during the formation of the complexes, AIM charges on each atom for all the considered complexes were calculated and analyzed. The values obtained are summarized in Table 3. As it was reported in this table, a sizable charge was transferred from the guanine molecule to the AuBN cluster in all the studied configurations and the calculated q_{CT} values for the complexes range from 0.152 to 0.727 |e|. The large charge transferred between both species reflects a strong adsorption of the guanine molecule over the surface of the AuBN cluster. The adsorption of the guanine over the AuBN cluster affects

also its electric dipole moment. The results indicate that the β_{T} values of the formed complexes after interaction between the cluster and the guanine were largely augmented, and the calculated values are in the range of 3.201 to 13.941 D. The highest β_{T} value was obtained for the complex C.

Adsorption of the guanine molecule over the NbBN nanosheet

In this section, we have investigated the interaction of the guanine with the surface of the NbBN cluster in order to evaluate its electronic sensitivity. In the same way as above, we placed the guanine molecule on the surface of the NbBN cluster with different orientations in aim to obtain the most stable adsorption configurations. After full optimizations, five stable complexes were obtained (H, I, J, K, and L configurations), in which their geometries are completely different to those obtained for the AuBN complexes which are formed from the AuBN cluster (see Figure S1). The interaction distance, energies of the HOMO and LUMO states (E_{H} , E_{L}) energy gap (E_{g}), adsorption energy (E_{ads}) and thermodynamic parameters (ΔH , ΔS , and ΔG) of the complexes were summarized in Table 3. As shown from this table, the adsorption of the

Fig. 8 The electron density difference (EDD) isosurfaces for the complexes C, D, E, F, and G



guanine onto the surface of the NbBN cluster was carried out without deformation of the molecule and the calculated adsorption energies vary from -36.7 to -60.2 kcal mol $^{-1}$, which are larger than those computed for the guanine adsorption over the AuBN cluster, except for the K configuration, where E_{ads} was found a bit lower in comparison with that predicted for the complex F (-38.4 kcal mol $^{-1}$). This great adsorption between the guanine and the NbBN cluster reflects that the NbBN cluster is more reactive than the AuBN cluster, confirming the above results obtained for the chemical hardness, softness and Fukui function. For the complex H, the guanine adsorption over the surface of the NbBN nanosheet occurs by its oxygen atom with an adsorption energy of -60.2 kcal mol $^{-1}$, which is much greater than that found for the other complexes. The calculated length of the Nb-O bond in the formed complex (H) upon chemisorption process is 2.39 Å. Unlike the interaction between the AuBN cluster and the guanine molecule, the charge transfer in this case occurs from the NbBN cluster to the guanine for all the studied complexes, except for the K complex, where a low charge of 0.025 |e| was transferred from the guanine molecule to the NbBN cluster. This configuration corresponds to the lowest E_{ads} value (-36.7 kcal mol $^{-1}$) in comparison with the estimated values for the other complexes. The calculated E_{ads} are -57.2 , -50.5 , and -42.1 kcal mol $^{-1}$ for the I, J, and L configurations, respectively, suggesting a great chemisorption between the guanine and the NbBN cluster. The quantity of charge transferred between both species is of 0.682 , 0.045 , 0.181 and 0.079 |e| for the configurations H, I, J, and L, respectively. The interaction distance between the guanine molecule and the surface of the NbBN cluster for the complexes I, J, K and L varies between 2.27 and 2.55 Å (Table 3).

It is interesting to note also that when we optimized the configuration where the guanine molecule was chemisorbed through its nitrogen atom of $-\text{NH}_2$ group, the calculations revealed that the optimized geometry of the complex was found similar to that of the complex K. The results show also that the calculated distance of the Nb-N bond in the NbBN cluster after its interaction with the guanine molecule is in the range of 2.00 to 2.06 Å, which is remained almost unchanged with respect to the value calculated for the isolated NbBN nanosheet, implying that the strong interaction of the guanine over the surface of the NbBN cluster has not modified their structural parameters. The results indicate also that the calculated values of ΔH and ΔG for the complexation process are negative, indicating that the complexation process of the guanine over the surface of the NbBN cluster was found to be exothermic and thermodynamically feasible at ambient temperature ($T = 298.15$ K) and pressure (1 atm).

The change in the energies of frontier molecular orbitals (FMO) for the complexes which are formed from the interaction of the guanine with the NbBN cluster was clearly observed (Table 3). As it was reported in Table 3, the energies

of HOMO orbitals for the configurations J, K and L are shifted to the more negative values, while for the configurations H and I, the values of HOMO orbitals are shifted to the less negative values. On the other hand, the energies of LUMO orbitals of all the studied complexes were shifted to the less negative values, except for the complex L where its energy of LUMO level remains almost unchanged. As an example, the HOMO level shifts from -3.540 in NbBN cluster to -4.146 eV in complex K, whereas the LUMO level shifts from -2.045 to -1.569 eV. Based on the energies of HOMO and LUMO states, the energy gaps (E_g) of these complexes are calculated, and the values obtained are reported in Table 3. From this table, it was found that the guanine adsorption over the surface of the NbBN cluster was sharply affected their electronic properties. In contrast to the results obtained for the AuBN cluster, the energy gap of the NbBN nanosheet was largely increased when the guanine molecule was adsorbed on its surface. The variation in energy gap (ΔE_g) for the configurations J, K, and L is 80.9% , 72.4% and 45.5% , respectively, whereas for the configurations H and I, the calculated ΔE_g is small ($\Delta E_g < 13\%$). This result indicates that the Nb-doped BN nanosheet is very sensitive to the adsorption of guanine onto its surface. Accordingly to Eq. (4), the electrical conductivity of the NbBN cluster was sharply reduced when the guanine molecule was strongly chemisorbed over its surface; thereby, the NbBN cluster can be considered not suitable nanosensor for the detection of the guanine molecule.

The spatial orientations of the HOMO and LUMO levels of the NbBN cluster and their interaction with the guanine molecule are depicted in Figure S2. From this figure, the results indicate that the HOMO and LUMO orbitals are mostly localized on the Nb atom for the NbBN nanosheet. When the guanine molecule was chemisorbed over the NbBN cluster, the density of HOMO remains unchanged, and the electron density is completely located around the Nb atom of the cluster. The LUMO orbitals are mainly localized over the Nb atom of the cluster and the guanine molecule. This result suggests a strong chemisorption process between the Nb atom of the NbBN cluster and the guanine molecule in all the formed complexes. This finding has also been confirmed by the spin density which was calculated for the complexes (not shown), which exhibits a large localization of electrons between the Nb atom of the cluster and the guanine molecule.

In order to investigate the nature of the formed bonds in the formed complexes through the interaction of the guanine with the NbBN cluster, the EDD isosurfaces were calculated and the results predicted are shown in Figure S3. As an example, for the configuration H, the EDD isosurface reveals that the electron density is mainly accumulated around the Nb-N bond, reflecting a great chemical adsorption between the guanine molecule and the Nb atom of the NbBN cluster (chemisorption process). Identical results were obtained for the other complexes (I, J, K, and L), where the electron density

accumulation has also been mostly observed between the surface of the NbBN cluster and the guanine molecule, suggesting a strong chemical adsorption. The results exhibit also that the electric dipole moment (β_T) of these complexes was augmented after the adsorption process (Table 3), and the highest β_T value was predicted for the complex H (15.563 D), where the chemisorption of the guanine over the surface of the NbBN cluster was carried out by its oxygen atom.

Recovery time

A shorter recovery time can be obtained if the interaction between the cluster and the guanine molecule is not strong. The great adsorption makes the desorption of the molecule from the cluster surface very hard, which leads to long recovery time. Therefore, the cluster does not become a suitable nanomaterial for nanosensor applications. In other words, the strong adsorption between the molecule and the cluster reduces the efficiency and significance of the cluster as a nanosensing. Using an attempt frequency of 10^{14} s^{-1} to desorb the guanine molecule which is attached to the surface of the AuBN clusters, the recovery time at 540 K was estimated to be 27.6 s which is considered a short time for the desorption of the guanine from the cluster surface. Therefore, the AuBN cluster can be viewed as a good nanosensor for the detection of the guanine molecule with a short recovery time. Also, it is interesting to say that the recovery time could be greatly reduced when the temperature was raised. So, the higher temperatures facilitate the desorption process of the guanine molecule through the surface of the AuBN cluster. Unfortunately, there is no experimental or theoretical results to compare with our theoretical values obtained in this work. Thus, this theoretical study could be a window for experimenters to draw attention to the AuBN cluster as a nanosensor for the detection of the guanine molecule or other drug molecules.

Conclusions

In the present work, the stability and electronic properties of the pristine, Nb-, and Au-doped BN nanosheet were investigated using DFT calculations with the B3LYP-D3 level of theory. The interaction of the guanine molecule with the surface of these clusters has also been examined. The results show that the HOMO-LUMO energy gap of the BN nanosheet has been greatly decreased upon its doping with Nb and Au atoms, suggesting a great enhancement in its reactivity. This finding was supported by the calculated values of the hardness (softness) for the AuBN and NbBN clusters which are found to be lower (greater) than that obtained for the pure BN nanosheet, reflecting an increase in their surface reactivity. Moreover, the condensed Fukui function indicates that the Nb and Au atoms in the clusters are considered the most

favorable adsorption sites for a nucleophilic attack. The calculations show also that the interaction between the BN nanosheet and the guanine is weak (physical adsorption), and the calculated adsorption energies are -15.2 and $-14.9 \text{ kcal mol}^{-1}$ for the complexes A and B, respectively. The variation in E_g of the BN nanosheet after its interaction with the guanine molecule was found to be 14.9 and 13.2% in the A and B states, respectively, implying a low sensitivity of this cluster toward the guanine molecule. The interaction of the guanine with the NbBN and AuBN clusters has also been investigated. The results indicate a strong adsorption of the guanine molecule over the surface of the NbBN cluster with adsorption energies which vary between -36.7 and $-60.2 \text{ kcal mol}^{-1}$, indicating a great chemisorption process. The energy gap of the NbBN cluster was greatly raised when the guanine molecule was chemisorbed on its surface; thereby, its electric conductivity was sharply reduced; thus, this cluster could not be a good nanosensor for the detection of the guanine molecule. The guanine adsorption onto the surface of the AuBN cluster is considered a chemical adsorption with adsorption energies ranging from -24.2 to $-38.4 \text{ kcal mol}^{-1}$, which are lower in comparison with those obtained for the guanine adsorption onto the surface of the NbBN cluster. Contrary to the NbBN cluster, the energy gap of the AuBN cluster has been reduced upon its interaction with the guanine molecule, which leads to an increase of its electrical conductivity, thus an electrical signal can be generated. So, the AuBN cluster could be employed as an appropriate nanosensor for the guanine molecule detection. Moreover, the calculations show that the recovery time of the guanine molecule which was attached to the surface of the AuBN cluster is found to be 27.6 s, which is considered a very short recovery time. This suggests that the desorption of the guanine from the cluster surface occurs easily with a short recovery time. The AIM charges analysis reveals that the charge is transferred from the NbBN cluster to the guanine molecule (except for the configuration K), and the calculated values predicted are in the range of 0.025 to 0.682 |e|. On the contrary, for the complexes formed between the AuBN cluster and the guanine, the charge transfer occurs from the molecule to the cluster, and the amounts of charge transferred between both species varies from 0.152 to 0.727 |e|. The calculations show also that the dipole moments of the clusters (BN, NbBN, and AuBN) were increased after their interaction with the guanine molecule.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11224-021-01785-z>.

Code availability Not applicable.

Data availability Data can be obtained through the corresponding author from email.

Declarations

Conflict of interest The authors declare no competing interests.

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