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THE INTERACTION OF ZINC OXIDE NANOCLUSTERS WITH ADENINE BASE: A THEORETICAL STUDY FOR ADENINE CHEMICAL SENSOR

Nghiên cứu lý thuyết sự tương tác của zinc oxide nanocluster với base adenine - ứng dụng cho cảm biến

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ABSTRACT

A theoretical study on the adsorption of adenine onto $(ZnO)_n$ clusters (n = 5, 6) has been performed using the hybrid density functional B3LYP in conjunction with the 6-311+G(d) and aug-cc-pVDZ-PP basis sets. Three equilibrium geometries of dimers were found based on the results of interactions between adenine and each $(ZnO)_n$ clusters (n = 5, 6) These complexes are stabilized by Zn-N bonds and N/C-H···O hydrogen bonds. In addition, bonding formation was characterized by natural bond orbital (NBO) and atoms in the molecule (AIM) theories at the same computational level. The potential application of this material as a sensor to detect adenine is also investigated. This study contributes to a deeper understanding of the structural shape, stability, and interaction characteristics of $(ZnO)_n$ clusters with the biomolecule base adenine, thereby paving the way for their promissing applications in the fields of biomedical nanotechnology.

Keywords: *AIM, electron density, NBO, sensor, Zinc oxide.*

TÓM TẮT

Quá trình hấp phụ của adenine trên cluster $(ZnO)_n$ (n = 5, 6) được nghiên cứu bằng lý thuyết phiếm hàm mật độ với phiếm hàm lai B3LYP cùng các bộ hàm cơ sở 6-311+G(d) và aug-cc-pVDZ-PP. Đối với mỗi kích thước của n = 5, 6, ba đồng phân của phức được tìm thấy. Phức chất được làm bền bởi liên kết Zn-N và các liên kết hydrogen N/C-H···O. Tính chất của các liên kết hình thành được phân tích một cách chi tiết bởi các lý thuyết AIM và NBO tại cùng mức lý thuyết. Tiềm năng ứng dụng của vật liệu này trong việc sử dụng làm cảm biến phát hiện adenine cũng được khảo sát. Nghiên cứu này góp phần hiểu sâu hơn về hình dạng cấu trúc, độ bền, đặc trưng tương tác của các cấu trúc cluster $(ZnO)_n$ với base adenine, một loại phân tử sinh học, tạo tiền đề cho các ứng dụng tiềm năng của chúng trong các lĩnh vực công nghệ nano y sinh.

Tù khóa: *AIM, mật độ electron, NBO, cảm biến, Zinc oxide.*

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1. Introduction

Zinc oxide (ZnO) is classified as a semiconductor in group II-VI with a direct wide band gap (3.37 eV) and a large exciton binding energy (60 meV). Therefore, ZnO material has been attracting the attention of many researchers due to its unique physical and chemical properties, such as high chemical stability, wide radiation absorption range, and the ability of exciton recombination even at room temperature. Its potential applications include fluorescence, photocatalysis, gas sensing, electrochemistry, and solar cells [1], [2]. It is an important material in the ceramics industry because of its hardness, rigidity, and piezoelectric constant, while the low toxicity, biocompatibility, and biodegradability make it a material of interest in biomedicine and in pro-ecological systems [3]. On the other hand, ZnO nanoparticles can kill cancer cells and activate human T cells, suggesting the biotherapeutic functionality of this novel material [4]. Inorganic nanostructures interacting with biological molecules to produce novel hybrid materials are important for future advancements in biomedical nanotechnology. Particularly, the combination of ZnO with biomolecules is intriguing since it opens up opportunities for novel bio- and nanotechnological applications. [5]. The interaction of DNA nucleotides at different levels in theoretical research is one of the effective measures to investigate the changes in physical properties of materials used in biosensor [6], [7]. Notably, the adsorption energy of adenine, guanine, thymine, and cytosine on ZnO-Graphene increased by more than 50 % compared to their adsorption energy on pure graphene [8]. In 2011, Shewale *et al.* carried out an investigation on the interaction of the nucleotide bases of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) with a $(ZnO)_{12}$ cluster using density functional theory [4] and found that the interaction strength, expressed in terms of the binding energy, reaches the highest value at the ring nitrogen site for all nucleobases in the the sequence guanine < thymine < uracil < adenine < cytosine. Besides, the interaction between the ZnO-clusters and nucleobases is dominated by the covalent and weak vdW forces. In 2014, Chandraboss *et al.* investigated the electronic structure of guanine interacting with different-sized ZnO clusters by DFT theory and reported that the $(ZnO)_n$ cluster preferentially binds to the nitrogen atom in the ring position with unbonded electron pairs compared to other nitrogen atoms in a different position of the base [9].

Although ZnO nanoparticles have many potential applications in biomedicine, only a few studies have been reported on the interaction of ZnO nanoparticles with biological molecules. Recently, Yong *et al.* indicated that the $(ZnO)_n$ is a potential candidate for gas sensors with high sensitivity [10]. On the other hand, the detection of adenine molecules at very low concentrations is of great importance for both biological and medical applications [11]. In this context, we perfomed a theoretical investigation using density functional theory calculations to study the interaction of clusters $(ZnO)_n$ (n = 5, 6) with adenine molecules with the aim of adding and clarifying the structural shape, stability, and interaction characteristics of $(ZnO)_n$ clusters with biomolecules. Futhermore, the potential

use as a sensing material of cluster $(ZnO)_n$ (n = 5, 6) with adenine was also explored and evaluated based on the obtained results.

2. Computational methods

Density functional theory (DFT), with its economic advantage in both cost and computational time over other methods, attracted substantial attention and has been widely used in quantum computations to predict the structure, stability, and electron properties of ZnO metal oxide clusters in recent years. In the present report, the calculations were conducted using Becke's three-parameter B3 with the Lee, Yang, and Parr (LYP) correlation functional [12]. The B3LYP hybrid functional yields reasonable results for small clusters in earlier studies and has been reliable for predicting energy gap values for a variety of metal oxides. This choice of the B3LYP method with moderate computational cost has been tested to yield good results in previous studies on $(ZnO)_n$ clusters [9], [13], [14]. Therefore, in this study, the geometrical parameters of the equilibrium structures were fully optimized using the B3LYP functional. The correlation consistent 6-311+G* basis set was applied to generate atomic orbitals of C, H, N, and O atoms, and the aug-cc-pVDZ-PP basis set was used for the Zn atom. All electronic structure calculations were carried out using the Gaussian 09 suite of programs [15]. The adsorption energy, which is also the binding energy between cluster and adenine, reported herein is calculated using the equation (1):

$$E_b = E_{adenine} + E_{(ZnO)_n} - E_{complex} \quad (1)$$

where E is the total energy including zero−point energy (ZPE) of the structure. The larger the value of the binding energy E_b, the stronger the affinity of the $(ZnO)_n$ clusters with adenine, and the easier the interaction is to form.

The NBO analysis was performed using the 3.1 program as implemented in the Gaussian 09 package at the same calculation level. The hyperconjugation interaction energy $E^{(2)}$ associated with each donor and acceptor is estimated using second-order perturbation theory analysis of the Fock matrix on the NBO basis as in equation (2):

$$E_{i\to j}^{(2)} = q_i \frac{\left|F_{ij}\right|^2}{\left(\varepsilon_j - \varepsilon_i\right)} \quad (2)$$

where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements and F_{ij} is the of-diagonal NBO Fock matrix element.

The electronic density ($\rho(\mathbf{r})$) and its ($\nabla^2\rho(\mathbf{r})$) for critical points of interactions in the structures are identified using the quantum theory of atoms in the molecule (AIM) and carried out at the same level of theory[16].

3. Results and discussion

3.1. Geometric structures of adenine, Zn_5O_5, and Zn_6O_6

The molecular structure with numbered atoms of the adenine is presented in Figure 1. Both values of bond lengths and bond angles of adenine at B3LYP/ 6-311+G* and the measured results from the high-resolution X-ray and neutron diffraction experimental methods are listed in Table 1 [17].

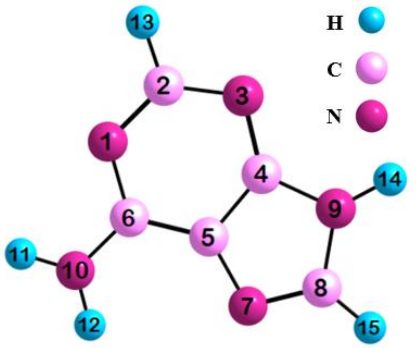


Figure 1. The optimized molecular structure with atom numbered of adenine at B3LYP/6-311+G* level

The optimized geometrical parameters obtained at B3LYP/6-311+G* level are listed in Table 1 and corresponding to atom numbering scheme given in Figure 1. The available experimental data are also included in Table 1 for comparison.

Table 1. The optimized geometrical parameters for adenine at B3LYP/6-311+G* level of theory

Bond length (Å)	This study	Exp. [17]	Bond angle (°)	This study	Exp. [17]
C7-N8	1.308	1.311	C6-N1-C2	118.6	118.6
C8-N9	1.380	1.373	N1-C2-N3	128.6	129.3
C4-N9	1.377	1.374	C2-N3-C4	111.5	110.6
C5-N7	1.385	1.388	C4-C5-C6	116.0	117.0
C4-C5	1.397	1.383	C4-C5-N7	111.3	110.7
N3-C4	1.336	1.344	N7-C8-N9	113.3	113.8
C2-N3	1.334	1.331	C8-N9-C4	106.7	105.8
N1-C2	1.341	1.339	N9-C4-C5	104.5	105.8
N1-C6	1.343	1.351	N3-C4-N9	128.8	127.4
C6-N10	1.352	1.335	C6-C5-N7	132.7	132.3
C5-C6	1.409	1.406	N1-C6-N10	118.9	118.6

As can be seen from Table 1, the calculated results of adenine molecule at the B3LYP/ 6-311+G* level agree well with obtained experimental values for X-ray diffraction proving the reliability of the quantum approach used.

For each size of $(ZnO)_n$ (n = 5, 6), it was found that there are 4 of the most stable isomers, which are shown in Figure 2. In order of increasing relative energy, they are denoted **5A**, **5B**, **5C**, and **5D** and **6A**, **6B**, **6C**, and **6D** corresponding to n = 5 and n = 6, respectively. Besides, the symmetry point group and relative energy in eV of each structure are also shown in parentheses.

For n = 5, a planar ring structure with D_{5h} point group is found to be the most stable structure (**5A**). In this planar ring, the Zn-O bond lengths are 1.774 Å and is close to the value reported in Ref. [18] (1.780 Å, obtained at B3LYP/LanL2DZ). The remaining isomers have the same C_s point group, C_s. The next isomer (**5B**) is a three-dimensional structure and the relative energy between these two structures is found quite high, being 2.504 eV. These are also the two the lowest isomers of Zn_5O_5 that Mingyang Chen and co-worker found in a previous study [19]. The optimized geometry results in Figure 2 showed that planar the structure **6A** is again found to be the most stable isomer with D_{6h} symmetry. We also found the angle of 179.8° and the bond length of 1.772 Å for **6A** structure agree well with the previous cases reported [18]–[21].

In this work, to study the interaction between $(ZnO)_n$ (n = 5, 6) and adenine, we chose the lowest-energy isomers **5A** and **6A** as initial reactants together with adenine.

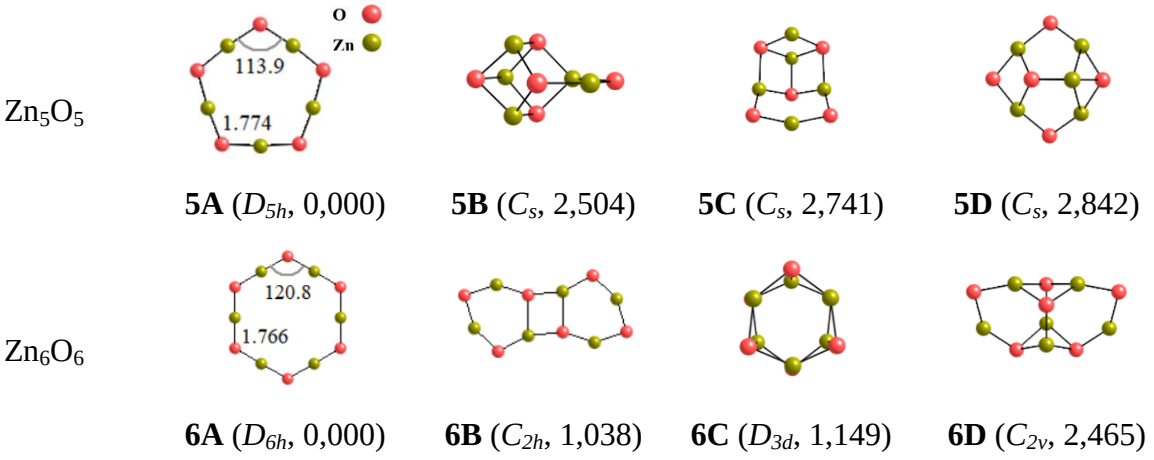
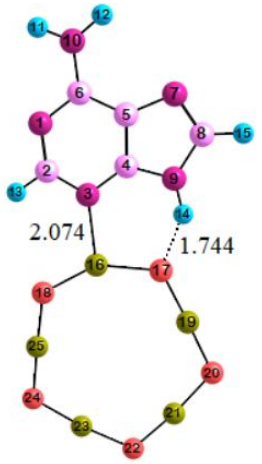


Figure 2. The lowest-energy structures of the clusters Zn_5O_5 and Zn_6O_6 and their bond length (Å), and bond angle (°). The symmetry point group and relative energy (eV) are given in brackets.

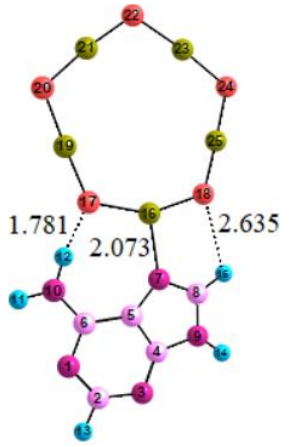
3.2. The interaction between adenine with Zn_5O_5 and Zn_6O_6 clusters

To further understand the properties of the interaction of Zn_5O_5 and Zn_6O_6 with adenine, the adsorption configuration of adenine on the Zn_5O_5 and Zn_6O_6 clusters was optimized at B3LYP/ H,C,N,O (6-311+G*), Zn (aug-cc-pVDZ-PP) level and shown in Figure 3.

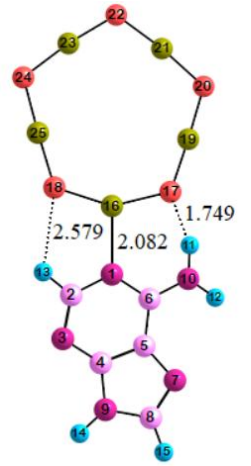
Zn_5O_5 and Zn_6O_6 are considered to approach adenine toward possible binding sites including H11, H12, H13, H14, and H15 or N1, N3, and N7 of adenine via Zn-site or O-site. Interestingly, the similar preferential site (N-sites) was found in previous studies on the interaction of the adenine with *cis*-$[Pt(NH_3)_2Cl_2]$ [22] và Ag_4 [23]. Three dimer structures were yielded after considering numerous possibilities for the optimization starting points where the adenine comes in contact with the cluster. Each dimer is symbolized hereafter by $\mathbf{A_i}$ (Zn_5O_5-Adenine) or $\mathbf{B_i}$ (Zn_6O_6-Adenine) (i = 1 ÷3), respectively (see Figure 3).



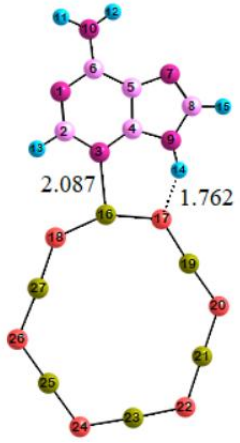
A1 (115.3; 0.000)



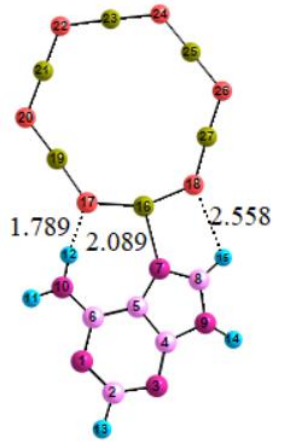
A2 (108.3; 0.073)



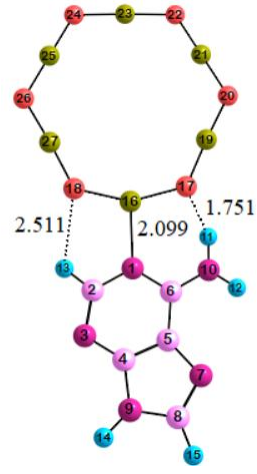
A3 (107.4; 0.082)



B1 (105.9; 0.000)



B2 (99.5; 0.066)



B3 (98.8; 0.074)

Figure 3. Some of the lowest-energy structures of the complexes of Zn_5O_5-Adenine and Zn_6O_6-Adenine. The bond length (Å). The binding energy (E_b, kJ/mol) and relative energy (E_{rel}, eV) are in brackets.

It can been seen that planar ring structures are the most stable configuration that is similar to the results found by Chandraboss *et al.* in the study on the interaction of small clusters $(ZnO)_n$ (n= 2, 3, 4) with base adenine [9]. As can be seen from Figure 3, the order for the interaction strength is as follows: **A1**-**A2**-**A3** and **B1**-**B2**-**B3**. The binding energy of Zn_5O_5 is higher somewhat than that of Zn_6O_6. Concretely, **A3** is the less stable configuration among Zn_5O_5-Adenine complexes while **B1** is the most stable among Zn_6O_6-Adenine complexes. However, the E_b of **A3** is 1.5 kJ/mol higher in energy than that of **B1**. Besides, the E_b of **A1** is 115.3 kJ/mol which is close to the value 115.4 kJ/mol previously reported for interaction between adenine and Ag_4 [23] but it is 27.5 kJ/mol less than that found between $Zn_{12}O_{12}$ and adenine [4].

3.3. Analysis of AIM and NBO

As displayed in Figure 3, the H···O contact distance in the N/C–H···O

interactions of complexes are in the range 1.744 – 2.635Å, which are all smaller than the sum van der Waals radius of the two H and O atoms participating in the interaction being 2.720 Å. Therefore, we predict that there is the formation of hydrogen bonds in the $(ZnO)_n$-Adenine complexes. The "atoms in molecules" topological analysis (AIM) of the electron density provides for further understanding of the nature of the interactions of complexes. Various properties at bond critical points such as Electron Density ρ(r), Laplacian $\nabla^2\rho(r)$, kinetic energy density G(r), potential energy density V(r), energy density H(r) in a.u., and the hydrogen bond energy (E_{HB}, kJ/mol) of **A1**, **A2**, **A3** and **B1**, **B2**, **B3** are presented in Table 2. The Table 2 show that the ρ(r) values at BCPs for Zn-N are in the range 0.0703 – 0.0736 a.u. and are larger than the ρ(r) value at BCPs for N/C-H···O only from 0.0076 to 0.0422 a.u. The values of charge density reveal that Zn-N interactions played a major role in complex stabilization. The ρ(r) values at BCPs for Zn-N interactions in complexes decrease in the following order **A1** > **A2** > **A3** and **B1** > **B2** > **B3**. Besides, the charge densities at BCPs for Zn-N interaction of **A1-A2-A3** are larger than those of **B1-B2-B3** indicating the interaction formation between adenine and Zn_5O_5 is stronger than that of Zn_6O_6. This result is consistent with the analysis of binding energy E_b, the larger the value of E_b, the larger the charge density values at BCPs.

Table 2. Electron density ρ(r), Laplacian $\nabla^2\rho(r)$, kinetic energy density G(r), potential energy density V(r), energy density H(r) (a.u.) and hydrogen bond energy E_{HB} (kJ/mol) at BCPs

Structures	Bonds	ρ(r)	H(r)	$\nabla^2\rho(r)$	G(r)	V(r)	E_{HB}
A1	N-H···O	0.0422	-0.0024	0.1422	0.0379	-0.0403	-36.3
	N-Zn	0.0736	-0.0142	0.2989	0.0889	-0.1031	
A2	N-H···O	0.0378	-0.0013	0.1310	0.0341	-0.0354	-32.2
	N-Zn	0.0729	-0.0137	0.3017	0.0891	-0.1028	
	C-H···O	0.0076	0.0013	0.0311	0.0065	-0.0052	-4.0
A3	N-H···O	0.0410	-0.0021	0.1410	0.0373	-0.0394	-35.1
	N-Zn	0.0730	-0.0140	0.2929	0.0872	-0.1012	
	C-H···O	0.0082	0.0012	0.0309	0.0066	-0.0054	-4.6
B1	N-Zn	0.0714	-0.0130	0.2900	0.0855	-0.0984	
	N-H···O	0.0408	-0.0019	0.1382	0.0364	-0.0383	-35.0
B2	N-H···O	0.0374	-0.0012	0.1289	0.0334	-0.0347	-31.8
	N-Zn	0.0703	-0.0122	0.2899	0.0847	-0.0970	
	C-H···O	0.0089	0.0013	0.0345	0.0073	-0.0059	-5.2
B3	N-H···O	0.0411	-0.0022	0.1405	0.0373	-0.0394	-35.3
	N-Zn	0.0703	-0.0125	0.2815	0.0829	-0.0955	
	C-H···O	0.0095	0.0012	0.0344	0.0074	-0.0062	-5.7

Through the investigation of a series of different complexes with hydrogen bonds, eight different criteria were proposed by Popelier for hydrogen bond formation, in which three are most often applied: i) a bond critical point (BCP) must be present to classify an interaction as a hydrogen bond; ii) the electron density ρ(r) at BCP should be within the range 0.002 – 0.04 a.u.; and iii) $\nabla^2\rho(r)$ at the BCP should be between 0.02 and 0.15 a.u. [24]. Hydrogen bonds are considered to be very strong if the bond energy is in the range of 15 – 40 kcal/mol. The strength of the hydrogen bond is considered medium and weak if the bond energy is in the corresponding range, respectively 4 – 15 và 1 – 4 kcal/mol [25]. The hydrogen binding energy (E_{HB}) is also calculated according to S. Emamian's formula based on the distribution of electron density at the BCPs of the bond with $E_{HB}(\text{kcal/mol}) = -223.08 \times \rho(r)/\text{a.u.} + 0.7423$ [26].

From these criteria, it can be seen the structures **A2**, **A3,** and **B2**, **B3** not only contain the N-Zn and N-H···O bonds which are similar to that of **A1** and **B1,** but also present the type of C-H···O hydrogen bonds. The existence of an atomic interaction line in an equilibrium geometry and the appearance of critical points satisfy both necessary and sufficient conditions for these interaction formations. Remarkably, the ρ(r) values in BCPs of N-Zn are quite large, in the range 0.0703 – 0.0736 a.u. Meanwhile, these values in the hydrogen bonds are all small, for N-H···O bonds it is about 0.0374 – 0.0422 a.u., and for C-H···O it is only in the range 0.0076 – 0.0095 a.u. These results are proportional to the bond energy of C-H···O bonds in complexes which is only about 4.0 – 5.7 kJ/mol (corresponds to the average hydrogen bond energy level). These values are much smaller than the binding energy of N-H···O bonds in the range of 31.8 - 36.3 kJ/mol, which belongs to strong hydrogen bond type. The ρ(r) values at BCPs for Zn-N and N-H···O bonds in complexes decrease in the following **A1 > A2 > A3** and **B1 > B2 > B3**. Linear relationships are found between the magnitude of ρ(r) and the length of the hydrogen bond. The larger the value of E_{HB}, the larger the charge density values at BCPs.

The relative energy of either three isomers $\mathbf{A_i}$ of Zn_5O_5 or three isomers $\mathbf{B_i}$ of Zn_6O_6 are very close with the range of only 0.074 – 0.082 eV. Characterized binding energies are 7,9 kJ/mol for the case of **A1** and **A3** as well as 7.1 kJ/mol for the case of **B1** and **B3**. Therefore, they have almost the same stability, indicating their possible coexistence. This suggests that the interaction ability of $(ZnO)_n$ clusters with either H11, H12, H13, H14, and H15 or N1, N3, and N7 of adenine are the same.

To further explore the interaction formation in complexes, NBO analysis was perfomed using the second-order perturbation theory (the second-order stabilization energy is a measure of the strength of the electron donor-acceptor interaction) at the same calculation level (B3LYP/ H, C, N, O (6-311+G*), Zn (aug-cc-pVDZ-PP)). Analysis of NBO presented in Table 3 indicates the positive values of electron density transfer (EDT) is 0.106, 0,103, and 0.109 a.u. for adenine moiety of **A1**, **A2,** and **A3**, respectively; and 0.103, 0.098, and 0.104 for that of **B1**, **B2** and **B3**, respectively. These results point out the electron density is transferred strongly from adenine moiety to $(ZnO)_n$ upon complexation. The electron transfer tends to

occur more strongly for the smaller cluster Zn_5O_5. This is consistent with the binding energy of adenine with Zn_5O_5, which is larger than with Zn_6O_6 as analyzed above. This can be easily explained by the much larger values of the electron transfer process from LP(O) of $(ZnO)_n$ to antibonding orbital BD*(N/C – H) of adenine. Besides, the hyperconjugative interaction energy $E^{(2)}$ (kJ/mol) of electron delocalization LP(O)→σ*(N-H) of Zn_5O_5/Zn_6O_6 cluster with adenine are all large in the range of 58.2 – 65.7 kJ/mol, which as compared to the process LP(O)→σ*(C-H) being 0.9 to 1.5 kJ/mol. Remarkably, the values of $E^{(2)}$ of LP(O)→σ*(C-H), at B3LYP/ H, C, N, O (6-311+G*), Zn (aug-cc-pVDZ-PP) are neglegible in **A2** and **B2**. The hydrogen formation of C-H···O in **A2** and **B2** was observed only through AIM analysis as discussed above.

Table 3. The electron density transfer (EDT) on adenine, hyperconjugative interaction energy $E^{(2)}$ (kJ/mol) of electron transfer for hydrogen bond formation in adenine adsorbed complexes by NBO analysis

Structure	EDT (a.u.)	Electron transfer	Hyperconjugative interaction energy $E^{(2)}$ (kJ/mol)
A1	0.106	LP(O17) → BD*(N9-H14)	65.3
A2	0.103	LP(O17) → BD*(N10- H12)	58.2
A3	0.109	LP(O17) → BD*(N10- H11)	63.0
		LP(O18) → BD*(C2- H13)	0.9
B1	0.103	LP(O17) → BD*(N9-H14)	62.3
B2	0.098	LP(O17) → BD*(N10- H12)	58.7
B3	0.104	LP(O17) → BD*(N10- H11)	65.7
		LP(O18) → BD*(C2- H13)	1.5

3.4. The possibility of the Zn_5O_5 and Zn_5O_6 as sensors for adenine

Since **A1** and **B1** are the isomers with the highest binding energies, these structures will be further analyzed to preliminarily evaluate their potential application as sensors for adenine. As analyzed above, the binding energy of Zn_5O_5 and Zn_5O_6 with adenine base during the adsorption process is not large, only from 48.3 to 115.6 kJ/mol, so they can be desorbed when stimulated by heat or exposed to light. To clarify this issue, the recovery time of the adsorption of adenine base molecules onto clusters of Zn_5O_5 and Zn_5O_6 was computed based on the transition-state theory. Accordingly, the larger the binding energy (E_b), the longer the recovery time (τ). These quantities are related to each other through the equation (3) [10]:

$$\tau = \frac{1}{v_0}.\exp\left(\frac{E_b}{k_B T}\right) \quad (3)$$

where T is temperature; k_B is Boltzmann constant; v_0 is frequency of light.

For example, at T = 298K, with wavelengths in the visible region 500 nm, the recovery time of **A1** is approximately 77.1 h which is consistent with its binding energy (115.4 kJ/mol). When the temperature increases (T = 373 K), the recovery time is much quicker, it is about 23.8 s for **A1**, and 1.2 s for **B**1.

Next, the sensitivity of Zn_5O_5 and Zn_6O_6 clusters to the presence of adenine was explored by examining the change of band gap energy (ΔE_g). This quantum index is determined by the formula (4) [27]:

$$\Delta E_g = \frac{|E_{g2} - E_{g1}|}{E_{g1}} \times 100\% \quad (4)$$

where E_{g1} and E_{g2} are band gap energy (which is the difference of the energies of the HOMO and LUMO) of Zn_5O_5, Zn_5O_6 clusters, and **A1**, **B1**. The results are reported in Table 4.

Table 4. Calculated HOMO energies (EHOMO), LUMO energies **(**ELUMO), HOMO-LUMO energy gap (Eg) in eV, change of energy gap (ΔE_g, %), and recovery time (τ, s)

Structure	E_{HUMO}	E_{LUMO}	E_g	ΔE_g(%)	τ (s), 298K	τ (s), 373K
5A	-7.682	-2.897	4.785			
6A	-7.524	-2.874	4.650			
A1	-6.885	-2.396	4.489	6.2	2.8×10^5	23.8
B1	-6.848	-2.483	4.366	6.1	6253	1.2

The kinetic activity and the electrical conductivity of material are closely related to the band gap energy E_g. The sensitivity of the adsorbent to the adsorbate depends strongly on the change of band gap energy (ΔE_g) [27]. The adsorption of adenine base molecules significantly changed the band gap energy of the Zn_5O_5, and Zn_6O_6 clusters. Accordingly, the values of E_g of both Zn_5O_5 and Zn_6O_6 clusters decrease from 4.785 and 4.650 eV to 4.489 and 4.366 eV, respectively, corresponding to the change in band gap energy being 6.2 and 6.1%. These changes will alter the electrical signal and thereby help detect adenine bases when Zn_5O_5, and Zn_6O_6 are used as sensors. The results of the recovery time (τ) as well as the band gap energy (ΔE_g) reveal that there is great potential for using the Zn_6O_6 cluster as manufacturing sensor devices for selective detection of adenine base material.

4. Conclusions

Using the DFT functional B3LYP in conjunction with the 6-311+G(d) basis set for C, H, N, and O and aug-cc-pVDZ-PP basis set for Zn, the electronic properties for the interaction between $(ZnO)_n$ (n = 5, 6) clusters and adenine are explored. Three planar geometries of dimers were found from the interactions with adenine of each $(ZnO)_n$ clusters (n = 5, 6), which is stabilized by Zn-N bonds and N/C-H···O. It has been seen that the the relative energy of these isomers is not too much and this indicated their possible coexistence. Both AIM and analysed NBO results show that the N-H···O hydrogen bonds in these complexes are the strong hydrogen bonds. Meanwhile, Zn_6O_6 material has the potential for application in manufacturing adenine detection sensors.

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