



The solvent (water) and metal effects on HOMO-LUMO gaps of guanine base pair: A computational study



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ABSTRACT

The most stable structures of guanine dimer and metal-mediated guanine base pair complexes were determined both in vacuum and solvent (water). Density functional theory (DFT) method is generally used in the calculations. The calculations of systems containing C, H, N, O is described by 6-311 + +G(d,p) basis set and LANL2DZ basis set is used for transition metals. Some geometrical parameters, the LUMO, HOMO energy levels and energy gaps of compounds are calculated. Hydrogen bond stabilization energies in dimer and charge transfer in metal complexes are also determined using NBO analysis. The solvent and metal effects on energy gaps of molecules are found. Cu-mediated guanine complex can be preferred for nanotechnological applications due to its good electronic properties.

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1. Introduction

Nucleic acids including purine and pyrimidine bases contain the genetic information for the development and function of living organisms [1,2]. In the recent years, DNA have used as a template in nonbiological contexts such as nanomaterials or nanostructures [3–9]. Among of these nanomaterials, metal-modified DNAs (M-DNAs) have drawn attention. M-DNAs can be obtained by treatment with double-stranded DNA of the metal ions [10–13]. In these compounds, transition metal are preferred instead of alkali or rare-earth metal because transition metals have a lot of functions especially in the nano-world [14]. Additionally, transition metals are expected to interact with the nucleobases by both chemical bonding and electrostatic interactions but other metals form complex by only electrostatic interactions [15–17]. Furthermore, metal ions have some properties such as electrical, optical and magnetic [18–20]. M-DNAs have also same properties like metals. Therefore, these compounds can be used as nanomagnets [21,22], nanowires [23,24] or catalysts in chemical reactions [25,26].

There are many theoretical and experimental studies on metal-DNA and natural base dimers [27–39]. One of experimental studies has been made by the Lee group. At high pH conditions, they reported that some divalent metal ions (as Co^{2+} , Ni^{2+} and Zn^{2+}) formed complexes with unmodified DNA [27,28]. Lee and co-

workers proposed that such metal–DNA complexes could be more conductive than DNA and useful for nanotechnological applications [27–30].

In the theoretical studies made by Brancolini and co-worker, they discussed electronic properties of GC and metal-mediated M^{n+} –GC complexes ($\text{M} = \text{Zn}, \text{Ag}, \text{Cu}$; $n = 1, 2$) with DFT method by analyzing geometrical details, energy levels of the frontier orbitals [31]. They reported that Cu-mediated GC complexes could be the best candidates with good conduction properties. They noted a decrease of the energy gap in complexes with Cu(I) and Ag(I). In addition to, there are many studies on mismatched base pairs in duplex DNA [32–39]. In the theoretical study made by Das and co-workers, the geometry of mismatched base pairs (TT, CC, AA, GG) and their adducts with ruthenium complexes was analyzed [32]. It was determined hydrogen bond stabilization energy in the base pairs and charge transfer in the metal complexes.

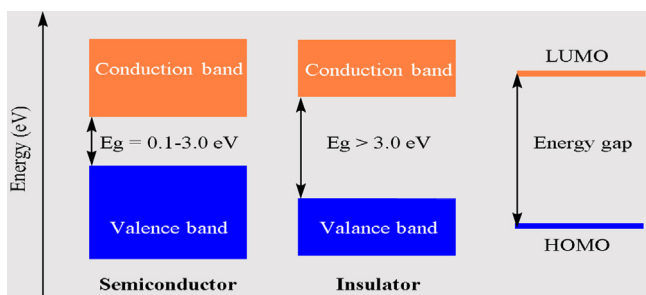
In this paper, firstly, the geometrical parameters and the energy levels of frontier orbitals of GG dimer are investigated. Then those of some metal-mediated GG complexes are examined. Effects on frontier orbitals of metal and solvent (water) are determined. Energy gaps of compounds are compared in detail with each other. Moreover, using NBO analysis, hydrogen bond stabilization energy in the base pair and charge transfer in the complexes are examined.

2. Computational details

Guanine dimer and metal-mediated guanine complexes were formed and the most stable structures of them were determined

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Scheme 1. The correlation between energy band diagram and HOMO-LUMO.

at B3LYP/6-311++G(d,p)(LANL2DZ) level in vacuum and solvent which is water. Dielectric constant of water is 78.3553. B3LYP is one of the hybrid DFT functions [40,41]. B3LYP method has been shown as a good method in calculations of transition metal-ligand systems [42]. HF and M062X methods were also used for dimer calculations. In all calculations, LANL2DZ basis set [43] was used for transition metals and 6-311++G(d,p) basis set was preferred for rest atoms. All calculations have been performed by using the Gaussian 09 and GaussView 5.0.9 [44,45]. Closed- and open-shell calculations were performed by using the restricted formalism and unrestricted formalism, respectively. The interactions of solute-solvent were taken into account by conductor-like polarizable continuum model (CPCM). Natural bond orbital (NBO) computations are performed with the NBO code included in Gaussian 09 program. The energy difference (E_{gap}) between lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) were calculated by using the Chemissian, version 4.43 program [46] (created in Chemissian based on Gaussian 09 calculations). The conductivity of single base pair or metal complexes can be examined by energy gap (Scheme 1) [47].

The energy gap is given as follows:

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$$

Also, according to Koopmans' theorem [48], ionization potential (I) is given as follows:

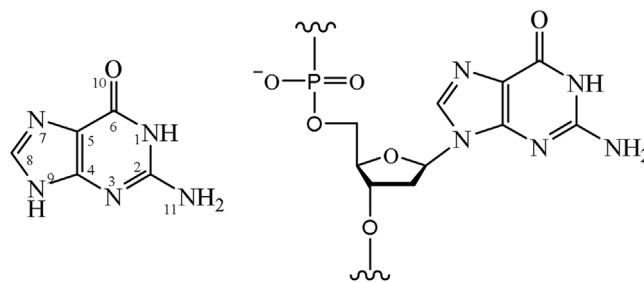
$$I = -E_{\text{HOMO}}$$

3. Result and discussion

3.1. Guanine base pair

Guanine is one of the purine bases in DNA and its structure is as given below. It binds from N atom (N9) to DNA chain (Scheme 2).

Mismatched guanine base pair can form geometry as shown in Scheme 3 in DNA duplexes in the absence of metal. Hydrogen bonds



Scheme 2. Guanine base and its binding to DNA chain.

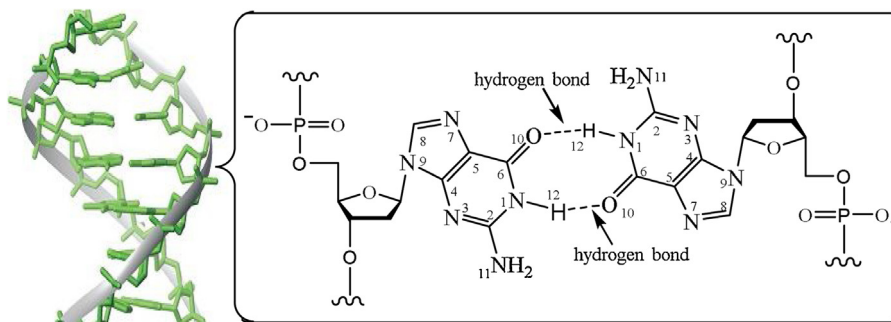
occur between the base pair. The binding type is similar to that of Watson-Crick base pairs formed from natural bases.

In the theoretical studies, it is generally focused on base pair or metal-base pairs because sugar and phosphate groups are not changed in DNA duplexes [31,42,49,50]. Thus, we will also focus on base and metal-base pairs.

The optimized geometry of GG base pair are obtained as in Fig. 1. Two hydrogen bonds (HB) formed between the base pair were shown. The strength of the hydrogen bonds can be evaluated by NBO analysis [32]. The stabilization energy $E^{(2)}$ of the N–H...O hydrogen bonding interactions have been computed via perturbation theory. The donor-acceptor interaction emerges owing to delocalization of electron density from the lone pair LP of the acceptor atom into the unfilled BD^* antibonding orbital of the donor atom. The LP– BD^* overlap occurs hydrogen bonding interaction and this is determined that the values of stabilization energy $E^{(2)}$ for LP of the O acceptor atom and the antibonding orbital BD^* of the H donor atoms in the GG pair. Average hydrogen bond stabilization energies $E^{(2)}$ of GG pair which are calculated by different methods are given in Table 1 (Table S1 (supporting information) gives more detailed information).

According to Table 1, the hydrogen bonds formed in water are generally longer than those formed in vacuum and hydrogen stabilization energy is inversely proportional with hydrogen bond distance. Additionally, the energy values and dihedral angle of the GG pair which are calculated by DFT method are given in Table 2. The frontier orbitals of the GG pair are also founded as in Fig. 2.

Referring to Fig. 2, HOMO-LUMO shapes are similar in vacuum and water. All atoms except the imine group contribute to the HOMO. All atoms except amino group contribute to the LUMO and LUMO also carries the hydrogen bond character. Referring to Table 2 and Fig. 2, it is seen that the E_{gap} value of GG pair in water is lower than those in vacuum. According to the E_{gap} values, conductivity of GG pair is low [47].



Scheme 3. The structure of GG base pair without metal in DNA duplex.

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