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A combined DFT/Green's function study on electrical conductivity through DNA duplex between Au electrodes

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Abstract

Electrical conducting properties of DNA duplexes sandwiched between Au electrodes have been investigated by use of first-principles molecular simulation based on DFT and Green's function to elucidate the origin of their base sequence dependence. The theoretically simulated effects of DNA base sequence on the electrical conducting properties are in qualitative agreement with experiment. The HOMOs localized on Guanine bases have the major contribution to the electrical conductivity through DNA duplexes.

1. Introduction

DNA has attracted much attention as a primary candidate for next-generation nanowires which possess outstanding qualities such as high self-organizing capability [1] and electrical conductance [2–4]. Although a number of experimental studies have been conducted, its electrical conducting properties remain to be fully elucidated in terms of the structural details. In particular, the effect on conductance of DNA base sequence was widely investigated [5–10]. Xu et al. [9] measured the conductance of the DNA duplexes whose base sequences are 5'-d(CGCGCGCG)₂-3' and 5'-d(CGCGATCGCG)₂-3' in aqueous solution. Their results indicated that the insertion of AT base pairs between GC base pairs of DNA duplex significantly decreases the electrical conductivity of DNA duplex.

A number of theoretical studies [11–36] have been performed to clarify the electrical conducting properties of DNA duplexes. Tada et al. [12] investigated the properties by using Green's function [37] based on empirical extended Hückel molecular orbital (MO) within the framework of Landauer theory [38]. Their results indicated that the electrical conductance of DNA duplex is sensitive to the configuration of the connection between DNA duplex and Au electrodes.

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Recently, we [35] attempted to elucidate the effect of environmental factors on the electrical conducting properties of DNA duplexes sandwiched between Au electrodes by using a combined method of classical molecular dynamics (MD) and Green's function based on extended Hückel MO calculations [39]. In that study, we successfully investigated the electrical conducting properties for a total of 1000 structures of DNA duplexes sandwiched between Au electrodes to clarify the effect of environmental factors, because the extended Hückel MO method has sufficient accuracy and high computational speed. The results clearly indicated that the electrical conductivity through DNA duplex depends most strongly on the surface structure of Au electrodes. However, the extended Hückel MO method was unable to account for the effect of DNA base sequence on the electrical conducting properties: the conductivity was experimentally shown to decrease when an AT base pair was inserted into GC rich domain of DNA duplex [9], the effect of which the extended Hückel MO failed to reproduce. By means of *ab initio* MO calculations [11], this reduction was earlier explained in terms of the difference ~ 0.2 eV in ionization energies between guanine and adenine bases. The extended Hückel MO calculations also failed to reproduce the difference in ionization energies, the calculated value for the former and the latter being 11.97 and 11.99 eV, respectively. Therefore, we conclude that although the extended Hückel MO method is useful for large systems, it is not adequate for investigating the effect of base sequence on the electrical conducting properties in DNA duplex.

In the present study, we employ density-functional theory (DFT) calculations to elucidate the effect of base sequence on the electrical conducting properties in DNA duplex. Because Au electrodes are metallic with no HOMO-LUMO energy gap, it is difficult to obtain SCF convergence for the DNA-duplex + Au-electrode system in DFT calculations. Therefore, we employ the DFT program SIESTA [40–42], which has been widely used in solid-state physics because of its established procedure in achieving SCF convergence. As a result, we have succeeded, for the first time, in calculating the electronic properties for an extended system consisting of a DNA duplex with four base pairs plus two Au electrodes to evaluate the effect of base sequence on the electrical conducting properties in DNA duplex.

2. Methods of calculations

We first obtained the most stable structures of DNA duplexes by means of classical MD simulations using the AMBER9 [43] program. In order to investigate the effect of DNA base sequence, we considered two types of DNA base sequences 5'-d(CGCG)₂-3' and 5'-d(CATG)₂-3', which model the central four base pairs of the experimental structures [9]. Counter ions (6 Na⁺ ions) were added to the PO₄⁻ proximity of DNA backbones to neutralize the negative charge of the backbones. Solvating water molecules within 8 Å distance from DNA duplex and Na⁺ ions were considered explicitly to obtain DNA structure in aqueous solution. The details of MD simulations are described in our previous study [35].

Subsequently, two Au electrodes were each attached to the 3' and 5' terminal bases of the DNA duplex along the helical axis as shown in Fig. 1. The helical axis was determined from the average of normal vectors of all DNA bases. The distance between DNA bases and Au electrode was set to 3.4 Å, which is comparable to the stacking distance between DNA bases. The structure of the electrode surface is that of Au(111) surface used in the experimental study [9]. This Au electrode is composed of 44 Au atoms and has 2 units of periodic cells, large enough to obtain the density of states for a semi-infinite Au electrode by using its periodicity in calculating the electrical conductivity. The relative positions of the two Au electrodes sandwiching the DNA duplex were taken from the previous study by Tada et al. [12]. In the present study, the optimization of the DNA-duplex + Au-electrode system was not performed at the DFT level, because it was not practical on our computers.

In order to evaluate the electrical conducting properties, the electronic states of the DNA-duplex + Au-electrode system must be calculated accurately. The extended Hückel MO method has often been used to calculate the electronic states of such a large system because of its low computational cost and sufficient accuracy. As indicated in our previous study [35], however, it is difficult to describe the base sequence dependence of electrical conductivity in DNA duplexes by the extended Hückel MO method, because the method fails to provide accurate ionization energies and other electronic properties for the four types of DNA bases. In contrast, the DFT has been shown to be more accurate in describing the electronic properties of the DNA bases. Earlier DFT and other *ab initio* MO studies, however, showed that it was difficult to achieve SCF convergence for systems involving large clusters of Au [44,45]. They therefore employed a small cluster composed of a few Au atoms as a model for Au electrode. In the present study, we employ the DFT program SIESTA [40–42] to overcome the convergence difficulty for systems involving large Au-cluster electrodes. The revised PBE functionals [46] for the exchange and correlation energies and the DZ (double zeta) basis sets were employed in the DFT calculations. In these DFT calculations, water molecules were not considered, due to the limitation of computational cost. The effect of the hydrating water molecules will be investigated in our future study.

To evaluate the electrical conductivity in DNA duplexes from the DFT-computed electronic states, we employed the program developed by Meunier and Sumpter [47] based on the nonequilibrium Green's function and Landauer theories. The conductance of molecule between electrodes is given by the following equation.

$$G = \frac{2e^2}{h} T(E_F)$$

Here, $T(E)$ is transmission function, E_F is Fermi energy. In this program [47], Retarded/Advanced Green's function $G^{R/A}$ and self-energy $\Sigma^{R/A}$ are evaluated from Hamiltonian obtained by the DFT calculations. Subsequently, transmission function $T(E)$ is calculated by the following Fisher and Lee Formula [48].

$$T(E) = \text{Tr}(\Gamma_L(E) G^R(E) \Gamma_R(E) G^A(E))$$

where $\Gamma_{L/R}$ describe the coupling of the conductor to the left/right electrodes and are given by

$$\Gamma_{L/R}(E) = i \left[\sum_{L/R}^R(E) - \sum_{L/R}^A(E) \right].$$

Additionally, we calculated the I–V (current-voltage) curve by the following integration of the transmission function $T(E)$ to compare the calculated and the experimental results.

$$I = \frac{2e}{h} \int_{E_F - eV/2}^{E_F + eV/2} T(E) dE$$

3. Results and discussion

3.1 Electronic properties

In order to evaluate the effect of base sequence on the electronic properties, we investigated spatial distributions and energy levels of molecular orbitals (MOs) near HOMO and LUMO for the DNA duplexes, CGCG and CATG. As shown in Table 1, the highest three occupied orbitals, HOMO- n ($n = 0-2$), are distributed in Guanine bases for both these DNA duplexes. This result is comparable to that obtained by Saito et al. [11], indicating that the hole (i.e., positive electric charge) transfer via Guanine bases plays an important role in the charge transport in DNA. In contrast, the lowest two unoccupied orbitals, LUMO and LUMO+1, are distributed on Na^+ as well as on Adenine and Thymine bases for the CATG duplex.

Fig. 2 displays the MO energy diagrams for those MOs near the Fermi level for the DNA-duplex + Au-electrode system. Each MO is partitioned into DNA bases (G, C, A and T), Na^+ and two Au electrodes in accordance with its spatial distribution. The Fermi energy (E_F) obtained from the HOMO and LUMO energies of Au electrode is 2.4 eV and represented by a broken line in Fig. 2. It is assumed that hole transfer occurs at levels lower than the Fermi level. As shown in Fig. 2, the MOs localized on G and C bases reside closer to the Fermi level than the MOs localized on A and T bases. Therefore, it is expected that these MOs localized on G and C bases contribute to the hole transfer through DNA duplex. However, it should also be noted that the MO immediately below the Fermi level is localized on the C base connected directly to the Au electrode. Therefore, Fig. 2 indicates that G bases mainly contribute to the hole transfer, and that the energy level of HOMO localized on G is higher in CGCG compared with that in CATG, resulting in greater hole transfer in CGCG.

3.2 Electrical conductivity

Fig. 3 shows density of states (DOS) and transmission probability for the CGCG and CATG duplexes sandwiched between Au electrodes. The horizontal axis in Fig. 3 represents the electron energy and the horizontal broken line indicates the Fermi level (E_F).

As shown in Fig. 3(a), DOS for both these DNA duplexes at the Fermi level are significantly low, indicating their semiconducting properties. The origin for this low DOS is related to the significant HOMO-LUMO energy gap in the DNA duplexes as displayed in Fig. 2. As a result, transmission probability also has a very low value at the Fermi level for both the DNA duplexes, as shown in Fig. 3(b).

In the hole transfer region (i.e., the energy range below the Fermi level), transmission probability in CGCG is one- to two-orders of magnitude higher than that in CATG. The origin of the low probability for CATG can be explained by the lower energy levels of HOMO- n ($n=0-2$) for CATG compared with those for CGCG displayed in Fig. 2. On the other hand, in the electron transfer region (i.e., the energy range above the Fermi level), the calculated transmission probability for electron transfer near the Fermi level is significantly - an order of magnitude - lower than that of hole transfer. Consequently, the hole transfer has a major contribution to charge transport through the DNA duplexes at energies near the Fermi level. This result is consistent with experiment [6].

As described above, the difference in MO energy levels of DNA duplexes directly affects the transmission probability as well as the DOS. Therefore, it is essential to describe electronic states by higher-level calculations such as the DFT. The present study indicates that the DFT provides sufficient accuracy in analyzing the conducting properties, such as the effect of DNA base sequence on the electrical conducting properties, whereas the extended Hückel MO used widely in previous theoretical studies does not.

The I–V curve was constructed by integrating the transmission probabilities at energies near the Fermi level in order to compare with experiment [9]. Fig. 4 shows the computed I–V curves for the CGCG and CATG duplexes, which clearly indicate that CGCG has greater electrical conductivity than does CATG. This result is in qualitative agreement with experiment [9]. However, the calculated current is nearly 30 times smaller than the experimental value (100–150 nA). As indicated in our previous study [34], the hydrating water molecules surrounding the DNA duplex may likely enhance the charge transfer rate through DNA duplex. In order to elucidate the effect of hydration, we are examining the electrical conductivity with an explicit inclusion of hydrating water molecules. Additionally, the structure of the molecule-electrode contact [49,50] must be addressed in order to obtain the electrical conductivity comparable in magnitude to the experimental values. The results of these investigations will be discussed in our future paper.

4. Conclusions

In the present study, we employed first-principles molecular simulation based on DFT and Green's function to examine the effect of DNA base sequence on the electrical conductivity through DNA duplexes. The results indicate that the electrical conductivity of the CGCG duplex is significantly higher than that of CATG in agreement with experiment [9]. We further elucidated that the HOMOs localized on Guanine bases make a major contribution to the electrical conductivity through DNA duplexes.

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Fig. 1.
Structures of the DNA-duplex + Au-electrode systems; (a) CGCG and (b) CATG

Fig. 2. Partition of MOs near the Fermi level of the DNA-duplex + Au-electrode systems into each component; (a) CGCG and (b) CATG. The broken horizontal line indicates the Fermi level (E_F).

Fig. 3.
(a) DOS and (b) transmission probability for the DNA-duplex + Au-electrode systems

Fig. 4.
I-V curves for the DNA-duplex + Au-electrode systems

Table 1

Spatial distributions and orbital energies (eV) of the MOs near HOMO and LUMO for the DNA duplexes with 5'-CGCG-3' and 5'-CATG-3' base sequences. Values in parentheses represent the contribution (%) of each part to MOs.

MOs	CGCG ^{*1}		CATG ^{*2}	
LUMO+3	Na ⁺ (59) C ₃ (17) Na ⁺ (16)	-1.50	Na ⁺ (70) A ₆ (20)	-1.46
LUMO+2	Na ⁺ (78) G ₆ (18)	-1.52	Na ⁺ (78) G ₈ (18)	-1.52
LUMO+1	Na ⁺ (78) G ₄ (20)	-1.56	Na ⁺ (68) T ₇ (18)	-1.64
LUMO	Na ⁺ (55) Na ⁺ (24) G ₂ (14)	-1.67	Na ⁺ (78) A ₂ (20)	-1.75
HOMO	G ₆ (82)	-2.83	G ₄ (96)	-2.88
HOMO-1	G ₄ (70) G ₂ (20)	-2.95	G ₈ (96)	-2.94
HOMO-2	G ₂ (70) G ₄ (16)	-2.97	G ₄ (94)	-3.40
HOMO-3	G ₈ (93)	-3.06	T ₃ (63) A ₆ (31)	-3.55

^{*1} 5'-C₁G₂C₃G₄-3'

3'-G₈C₇G₆C₅-5'

^{*2} 5'-C₁A₂T₃G₄-3'

3'-G₈T₇A₆C₅-5'