Theoretical study on enhancement of DNA conductivity by copper modification of mismatched base pairs

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Abstract. DNA is a potential material for nanodevices. Metallization is a promising way to improve its conductivity. Two copper modified mismatched base pairs were designed by H-by-Cu replacement. The conductivities of these base pairs were studied by density functional theory (DFT) combined with nonequilibrium Green's function (NEGF) method. Energy levels of copper modified mismatched base pairs were firstly compared with those of mismatched base pairs. The results show that HOMO-LUMO gaps are narrowed significantly by copper modification. This change indicates that the modification can enhance electronic properties of the studied systems. Then longitudinal charge transport properties of DNA fragments composed by repeating multilayers of base pairs were investigated with the measurable conductivity indices. The results prove that conductivities of the copper modified mismatched DNA can be significantly improved compared with those of the unmodified. More importantly, the mechanism of the enhancement of H-by-Cu replacement was revealed. This work may provide some theoretical supports for designs of DNA-based nanodevices.

1. Introduction

With the rapid development of integrated circuits, Moore's law will face enormous challenges in the not long future. The replacement of existing semiconductor materials with molecular materials becomes necessary [1]. Due to its natural double helix structure, excellent self-assembly and self-recognition characteristics, DNA has been the potential material to construct molecular devices. The electronic transport properties have attracted much attention [2-5]. Although in the past two decades there were many controversial results about conductivity of DNA, changed from insulators [3], semiconductor [4] to conductor [5], recently a consensus has been reached that natural DNA is a semiconductor [6]. To achieve the goal as molecular wires, DNA will thus require modifications for improving its conductivity [7]. Generally, there are two main methods for DNA modification: phosphoric acid skeleton modification and base modification [8]. Some papers have shown that base modification has more significant effect on the electronic properties of DNA [9-13].

Metallization is one of main modifications of bases [10]. Shionoya group [11-12] inserted Cu²⁺ and Hg²⁺ into DNA molecular materials by adjusting the position of corresponding ligands, forming one-dimensional metal ion arrays. This is the first synthesis of controllable DNA-based materials. Subsequently, many metal modifications emerged. Researches have shown that DNA can be transformed into conductors through reasonable bases metallization (e.g. Zn-DNA, Co-DNA, Fe-DNA and Cu-DNA) [13-14]. Therefore, it is possible to obtain excellent DNA-based nanowires by designing reasonable artificial DNA analogues. We have studied structures and electrical properties of
G₃CuT and A₂CuC base pairs mediated by H-by-Cu replacements for natural base pairs [15]. The results showed that the modified DNA base pair not only reduced the HOMO-LUMO energy gaps and ionization potentials, but also enhanced the charge transport properties.

Due to radiation and other damages, mismatched bases are also common forms of DNA bases [16]. Modifications of prior works were mainly aimed at metallization of natural bases. However, metallization of mismatched bases has not been reported previously. Inspired by the above works and considered the importance of mismatched DNA, we use G₃CuT and A₂CuC as modification scheme (shown in Figure 1). Electronic properties of the copper modified mismatched base pairs are compared with those of the natural DNA base pairs. More importantly, the measurable electronic parameters are applied to indicate the improvement of modification.

Figure 1. Geometries of isomeric base pairs and copper mismatched base pairs.

2. Computational methods

2.1. Calculations of structural and electronic properties

The relevant isolated base pairs (including isomeric base pairs of GisoT, AisoC, GTiso, ACiso and the copper-modified mismatched base pairs of G₃CuT, A₂CuC) were optimized. All optimizations and the electronic properties were carried out with Gaussian 09 software package [17], at the hybrid DFT/B3LYP [18-19] level of theory with the 6-311++G(p,d) [20] base set for H, C, N, O atoms and the LANDL2DZ [21] for Cu atom. All the calculations were performed with spin-restriction. The spin-unrestricted results were also checked. It is found the differences of electronic properties between them are neglectable.

2.2. Electronic transport calculations

Quantum transport properties of base pairs were calculated with ATK software package [22-23], which is based on density functional theory (DFT) and combined with nonequilibrium Green’s function(NEGF) technique. This method has been successfully applied to study some systems with weak interactions [15, 24].

For the longitudinal electronic calculation, the 6×6 cell electrodes were applied and the Monkhorst-Pack k-point sampling was set as 3×3×100. First, the multi-layer stacks of GisoT, AisoC and the copper-modified mismatched base pairs of G₃CuT, A₂CuC were constructed using the same structural parameters as those in B-DNA but without any further optimizations, i.e. the interplane-distance being 3.4 Å and the helical angle being 36°. For simplicity, the sugar-phosphate skeleton was removed and the NEGF-DFT calculations were performed on π-π stacked base pairs. The simplification of the
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3. Results and discussion

3.1. Geometric characters

Figure 1 provides the geometries of GisoT, GTiso, AisoC, ACiso, G3CuT and A2CuC, including isomeric base pairs and copper-modified-mismatched base pairs. The optimized geometric configurations show that the multi-copper modified base pairs G3CuT and A2CuC are both planar within chemical accuracy. The whole lengths of base pairs between the paired bases are elongated by about 1 Å due to H-by-Cu replacement. The enlargement mainly near the regions of Watson-Crick hydrogen bond, while changes far from the region of modifications are minor. Slightly mechanical strain may occur due to the length increase of base pairs. However, given the flexibility of the phosphate-sugar backbone of DNA, the small expansion would not affect the entire architecture of DNA duplexes constructed by the modified G3CuT and A2CuC.

3.2. Electronic properties

In order to better understand the effect of metal mismatch modification on conductivity of DNA, it is necessary to study changes of electronic properties caused by modification. Figure 3 shows energy levels of the related systems. For comparison, energy levels of the copper-modified-natural and natural base pairs are also provided.

It indicates that both of the LUMO energy levels of modified G3CuT and A2CuC are lower than those of their corresponding isomers analogues, and the HOMO of G3CuT is clearly higher than those of GisoT and GTiso, while the change of the HOMO of A2CuC is slight compared with AisoC and ACiso. The HOMO and LUMO of G3CuT are very similar to the natural copper-modified base pairs of G3CuC, and so does A2CuC to A3CuT.
Figure 3. Energy levels of isomeric, copper-modified-mismatched, copper-modified-natural and natural base pairs.

The variations of HOMO-LUMO gaps occur due to the changes of energy levels, especially the changes of HOMO and LUMO energy levels. The number near two-way arrow in Figure 3 shows the HOMO-LUMO gap value of the related systems, which is a representative indicator of electronic properties. The H-by-Cu replacement results in a significant reduction of HOMO-LUMO gap from 3.96 eV for GT\textsuperscript{iso} and 3.86 eV for G\textsuperscript{iso}T to a value of 2.51 eV for G\textsubscript{3Cu}T, with very near that of G\textsubscript{3Cu}C. Compared the gap of A\textsubscript{2Cu}C with that of the isomeric base pairs A\textsuperscript{iso}C and A\textsubscript{iso}C, a decrease also can be observed. The difference of gap for G\textsubscript{3Cu}C and A\textsubscript{2Cu}C reveals that the number of Cu ions is the key factor affecting the narrowing of HOMO-LUMO gap. The shrinking of HOMO-LUMO gaps demonstrates that the conductivity of the DNA fragments composed by copper modified mismatched base pairs can be enhanced. This has been proved in our previous studies [15]. This makes it much more possible to achieve DNA-based nanowires with good conductivity.

3.3. Longitudinal electronic transport

Figure 4. Longitudinal currents of isomeric base pairs, copper-modified-mismatched base pairs as a function of bias.

To deeply investigate the effect of copper modification on conductivity of DNA, the three-repeating-layer-stacked A\textsuperscript{iso}C, A\textsubscript{2Cu}C, G\textsuperscript{iso}T and G\textsubscript{3Cu}T were further studied. From the above analysis of
electronic properties, it can be predicted that the conductivity of G\textsuperscript{iso}T should be better than that of GT\textsuperscript{iso}, and so should A\textsuperscript{iso}C compared with AC\textsuperscript{iso}. Therefore, only the longitudinal transport properties of A\textsuperscript{iso}C, A\textsubscript{2Cu}C, G\textsuperscript{iso}T and G\textsubscript{3Cu}T were investigated in the following. Figure 4 shows the longitudinal I-V curves of the related systems under the bias range from 0 to 0.5 V. It can be clearly seen that the longitudinal conductivities of copper modified mismatched bases of A\textsubscript{2Cu}C and G\textsubscript{3Cu}T are significantly enhanced by almost two orders of magnitude compared with those of unmodified mismatched bases A\textsuperscript{iso}C, and G\textsuperscript{iso}T, respectively. Moreover, the enhancement of modification of mismatched GT is obviously larger than that of AC. This is consistent with the above prediction from the results of electronic properties.

In general, the current I can be explained as a function of the applied bias V by the Landauer-Büttiker formula [22]:

\[
I(V) = G_0 \int_{-\infty}^{\infty} n(E) T(E,V) dE
\]  

(1)

where \( G_0 = \frac{2e^2}{h} \) (quantum conductance), \( n(E) \) is the distribution function, and \( T(E,V) \) is the transmission coefficient for electrons with energy \( E \) for bias \( V \). \( n(E) \) can be expressed as

\[
n(E) = f(E - \mu_L) - f(E - \mu_R)
\]

(2)

where \( f \) is the Fermi function, \( \mu_L \) and \( \mu_R \) are the electrochemical potentials of each electrode. From the expression of \( n(E) \), it can be expected that only electrons with energies within a range around the Fermi level (\( E_f \)) contribute to the total current. A general approximation for this threshold is a range of \([ -\frac{V}{2}, \frac{V}{2} ]\), which is considered as the bias window.

Since the current is the integral of the transmission coefficient in the bias window, analysis of the transmission spectra will provide a clear understanding for the enhancement of copper modification to mismatched base pairs. Figure 5 shows the transmission spectra \( T(E,V) \) of the longitudinal transport junction model composed by gold electrodes and the four related species at zero bias in the energy range from -4 to +4 eV. The averaged Fermi level (\( E_f \)) is set as zero [22], which corresponds to the averaged value of the chemical potentials of the left and the right electrodes.

![Figure 5](image_url)  

**Figure 5.** Transmission spectra of G\textsubscript{3Cu}T, A\textsubscript{2Cu}C, G\textsuperscript{iso}T and A\textsuperscript{iso}C, junctions at zero bias for the longitudinal electronic transport model. The averaged Fermi level is set as zero.

To reveal the origin of transmission peaks, the eigenvalues of the molecular projected self-consistent Hamiltonian (MPSH) were calculated and shown on the top of each panel in Figure 5.
MPSH means orbital energy level of the inserted molecules between two electrodes. The solid dots represent the occupied molecular orbital energies (at the left side of Fermi level), and the hollow dots correspond to the unoccupied orbital energies (at the right side of Fermi level). The positions of most transition peaks match well with those of MPSH, indicating that these molecular orbitals provide charge transport channels.

Obvious differences can be observed between transmission spectra of copper modified and unmodified mismatched base pairs. Firstly, many new transmission peaks appear for the molecular junctions composed of copper modified base pairs G\textsubscript{3CuT}, A\textsubscript{2CuC}, so their whole transmission spectra are more broad and strong. For example, for the transmission spectrum of G\textsuperscript{isoT}, in the range of [-1, 1]eV, there are only three low and narrow peaks, while for that of G\textsubscript{3CuT}, the peaks at the left side of Fermi level become stronger with the coefficient up to 1.02 and three new peaks emerge at the right side of Fermi level. The increase of new transmission peaks indicates that there are more transport channels due to the insertion of copper ions for the mismatched base pairs. Moreover, with the H-by-Cu replacement, the transmission peaks have the trend to approach the Fermi energy level from both sides, thus the nonconductive platform between occupied and unoccupied orbitals become narrower. Most importantly, some new transmission peaks emerge near Fermi level in G\textsubscript{3CuT} and A\textsubscript{2CuC} junctions. These change trends of transmission spectra could reveal the reason why the conductivity of G\textsubscript{3CuT} and A\textsubscript{2CuC} junctions is significantly enhanced by copper modification.

In addition to clarifying the reason for the enhancement of conductivity by copper modification, the mechanism about the transport charge carrier also can be explained by analyzing the transmission spectra. For the mismatched base pairs of G\textsuperscript{isoT} and A\textsuperscript{isoC}, the transmission peaks assigned to occupied orbitals are relatively dense and high compared with the sparse unoccupied peaks. Therefore, the occupied orbitals assigned to these transmission peaks should be the main transport channels. Thus the corresponding charge carrier should be hole. With the H-by-Cu replacement, the transmission peaks at the right side of Fermi level obviously increase. But the positions of these peaks are not closer to Fermi level. This trend indicates that with the insertion of copper ions, the transport carrier could also be an electron although hole transport is still more possible.

4. Conclusions
In this work, a thorough theoretical investigation was carried out to reveal the effects of H-by-Cu replacement on the conductivity of mismatched base pairs. Firstly, the basic geometry of DNA was conserved after the copper modification. Secondly, the electronic properties of modified base pairs were improved indicated by the shrinkage of HOMO-LUMO gaps. Moreover, the results of the longitudinal charge transport align with that observation. I-V curve is a measurable parameter, which can be obtained from experiments. Most importantly, the mechanism of the improvement by copper modification was clarified by analyzing the transmission spectra. Preliminary results presented here show that copper modification could largely increase the conductivity of DNA composed by mismatched base pairs. This work may provide meaningful theoretical support to the exploration of DNA-based nanodevices by expanding the possible building blocks of DNA-based wires.

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