

Invited feature article

Role of base arrangements and intermolecular hydrogen bonding in charge-transfer states of thymine-adenine dinucleotide in aqueous solution

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ABSTRACT

Charge-transfer (CT) states of thymine-adenine deoxy-dinucleotide (TpdA) were studied by using the UV-vis spectroscopy, molecular dynamics simulations and time-dependent density functional theory. Two CT states emitting distinguished fluorescence are found in TpdA. They are derived from two base arrangements of adenine and thymine. Intermolecular hydrogen bonding interactions with water prevent the stacked bases from approaching too closely in the CT states. The thymine ring is planar in the CT states and the sugar of adenine should adopt C2-endo puckering. Without water, TpdA might form a photoproduct or relax to a CT state with a “boat-like” thymine ring.

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1. Introduction

Numerous studies have been aimed at characterizing the electronic states of DNA and their relaxation dynamics after absorption of ultraviolet radiation [1]. Time-resolved spectroscopies are used to probe the relaxation dynamics of excited states [2–4]. Theoretical calculations are able to give more information at the molecular level, such as the geometrical characteristics, electronic structures and their evolutions [5,6]. The initially populated $\pi\pi^*$ states might either relax to the ground state (S_0) by internal conversion in less than one picosecond or form excited-state complexes such as charge-transfer (CT) states, which exhibit much longer lifetimes [7,8]. In hetero-dinucleotides and hetero-oligomers, CT states are easily to form owing to the different oxidation potentials between nucleobases [2,9]. For thymine-adenine deoxy-dinucleotide in aqueous solution (TpdA, Fig. 1), two CT species with nanosecond lifetimes were found [10]. However, the origins of these CT states and their geometrical characters have not been determined. Elucidating these issues is beneficial to understand the role of high-order structures on the relaxation dynamics of DNA [11].

Owing to the large difference in the ionization potentials and electron affinities between adenine (A) and thymine (T) [9,12], T is

favoured to be electron acceptor while A is the donor in CT states. Previous theoretical studies on stacked TA suggest that the energy of the CT state in the Franck-Condon (FC) region is sensitive to the base arrangements and surrounding water molecules [5,13]. However, the relaxation of the CT state still needs to be explored by ab initio calculations, which has a correlation with the photochemical reactions of TpdA [14,15]. On the other hand, in most theoretical studies of DNA in aqueous solution, the intermolecular hydrogen bonding interactions with water are ignored [16,17]. These interactions have been turned out to be necessary to elucidate many photophysical and photochemical properties in liquid phase [18–21]. Thus, it is essential to consider the intermolecular hydrogen bonding in studying CT states of DNA.

In this study, by using the UV-vis spectroscopy, molecular dynamics (MD) simulations and ab initio calculations, we show that two CT species of TpdA are derived from different base arrangements. Intermolecular hydrogen bonding interactions with water is strengthened in the relaxations of the two CT states. Without these interactions, TpdA might relax to a CT minimum involving some $\pi\pi^*$ characters.

2. Experimental methods

Deoxy-adenosine (>99%, dA) and thymidine-5'-monophosphate (>99%, TMP) were purchased from Tokyo Chemical Industry (TCI, Shanghai, China). TpdA (>98%, Sigma-Aldrich) and an

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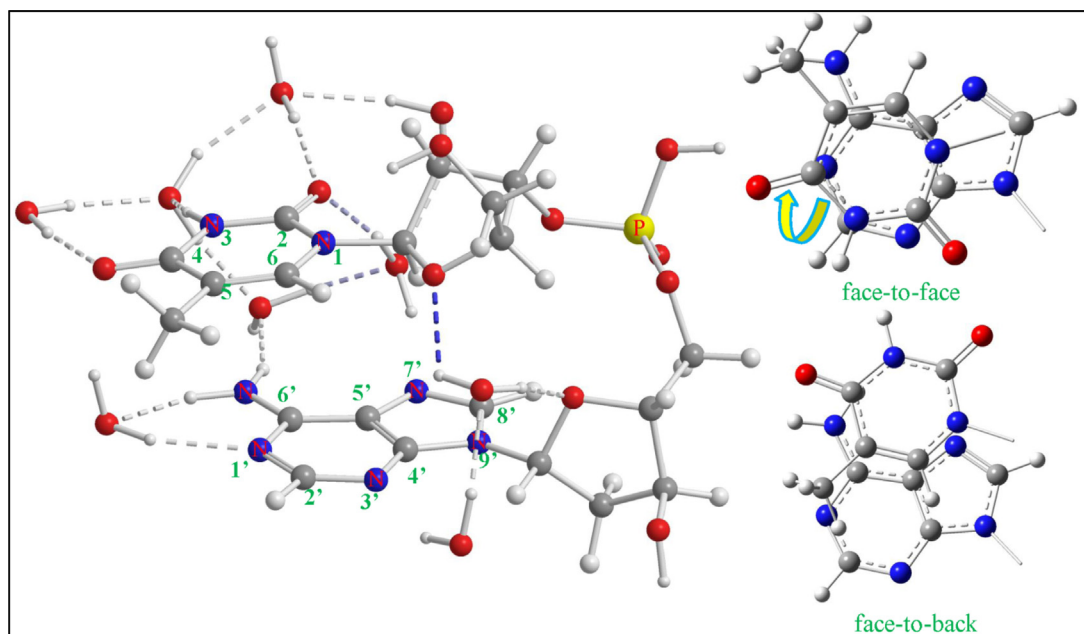


Fig. 1. Structure of thymine-adenine deoxy-dinucleotide hydrogen bonded with nine water molecules and top views of the face-to-face and face-to-back arrangements of adenine and thymine. The two base arrangements can be transformed by torsion of the thymine ring.

equimolar mixture of dA and TMP (dA+TMP) were dissolved in water without further purification. When using the $1\text{ cm} \times 1\text{ cm}$ quartz cuvette, the absorbance of the absorption maximum has a value lower than 1. Steady-state UV-vis spectra and emission spectra were measured on a Lambda 35 UV-vis spectrophotometer (Perkin-Elmer) and a Fluoromax-4 spectrofluorometer (Horiba-Jobin Yvon) at room temperature, respectively.

3. Computational details

All ab initio calculations were performed on the Gaussian 09 [22] program and the defaulted parameters were used. The hybrid M052X functional [23], which had been tailored to describe CT transitions and treat stacked systems correctly [17], was used in the density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. All geometry optimizations were calculated at the basis set 6-31g(d) level. And the extended basis set 6-31 + g(d, p) was used to calculate vertical excitation energies. Solvent effects were included using the default polarizable continuum model (PCM) [24]. Linear-response PCM (LR-PCM) and state-specific PCM (SS-PCM) were used to simulate the solvent response to electronic transitions [25,26]. Vertical absorption energies were calculated in a nonequilibrium solvent regime and vertical emission energies in an equilibrium solvent regime. The amount of transferred charges in the CT emissions was calculated based on the Mulliken population analysis. Firstly, the difference of the ground and excited states Mulliken atomic charges of adenine fragment was calculated as the amount of transferred charge of adenine in CT emissions. The amount of transferred charge of thymine fragment was also calculated like this. Then, the smaller value was chosen as the amount of transferred charge from adenine to thymine in CT emissions.

MD simulations were performed using the version 4.5 of GROMACS [27] program. The CHARMM27 force field [28] was employed. The initial geometry of TpdA for MD simulations was derived from a B-DNA structure (pdb ID: 3BSE) [29]. The TpdA molecule was solvated with 5034 spce [30] water molecules in a dodecahedron box with a size of 6.0 nm. A Nosé-Hoover thermostat [31,32] and a Parrinello Rahman barostat [33] were

used to simulate the system at 298 K and 1 bar. Restrained electrostatic potential charges (RESP) [34] were calculated under the PCM/M052X/6-31g(d) level and then used in the MD simulations. The total simulation time was 100 ns with a step size of 1 fs, and conformations were saved every 5 ps.

4. Results and discussion

4.1. The UV-vis spectral results

The UV-vis absorption and fluorescence spectra of TpdA and dA+TMP are shown in Fig. 2. Their absorption spectra are both peaked at 4.71 eV, while TpdA has obviously larger absorption intensity in the red region, induced by the CT states of TpdA [35]. The fluorescence spectrum of dA+TMP under 4.71 eV excitation shows a peak around 3.75 eV (Fig. 2 black solid line), which is the sum of the fluorescence spectra of adenine and thymine, as shown in Fig. S1 (Supplementary content†). As shown in Fig. 2, the fluorescence spectrum of TpdA under 4.71 eV excitation shows a broad peak at approximately 3.7 eV and a largely red-shifted peak at approximately 2.9 eV. Two CT species of TpdA were identified by Ballini et al. using the time-resolved fluorescence spectrum technique [10], and their emission spectra were peaked at 3.54 and 2.94 eV, respectively. As a result, the fluorescence spectrum of TpdA should comprise emissions from singlet $\pi\pi^*$ states of monomers (peaked at 4.71 eV) and the two CT states of TpdA (peaked at 3.54 and 2.94 eV), similar to the fluorescence spectrum of d(AT)₁₀ under 4.64 eV excitation [8]. As the excitation energy decreases, more CT states are populated due to their relatively low excitation energies compared to the singlet $\pi\pi^*$ states of monomers. Different excitation wavelengths also change the relative weights of the two CT species of TpdA, leading to the excitation wavelength dependent fluorescence spectra. As shown in Fig. 2, the fluorescence spectra excited by 4.43 and 3.38 eV are peaked at approximately 3.3 and 3.1 eV, respectively. They are the results of different weighted sums of the two CT states with their emission peaks at 3.54 and 2.94 eV, respectively [10]. A similar phenomenon has been observed in the fluorescence spectra of (dA)₂₀. Different excitation wavelengths change the relative

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