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Direct Measurement of the Dynamics of Excess Electron Transfer through Consecutive Thymine Sequence in DNA

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Supporting Information

ABSTRACT: Charge transfer in DNA is an essential process in biological systems because of its close relation to DNA damage and repair. DNA is also an important material used in nanotechnology for wiring and constructing various nanomaterials. Although hole transfer in DNA has been investigated by various researchers and the dynamic properties of this process have been well established, the dynamics of a negative charge, that is, excess electron, in DNA have not been revealed until now. In the present paper, we directly measured the rate of excess electron transfer (EET) through a consecutive thymine (T) sequence in nicked-dumbbell DNAs conjugated with a tetrathiophene derivative (4T) as an electron donor and diphenylacetylene (DPA) as an electron acceptor at both ends. The selective excitation of 4T by a femtosecond laser pulse caused the excess electron injection into DNA, and led to EET in DNA by a consecutive T-hopping mechanism, which eventually formed the DPA radical anion ($DPA^{\bullet-}$). The rate constant for the process of EET through consecutive T was determined to be $(4.4 \pm 0.3) \times 10^{10}$ s^{-1} from an analysis of the kinetic traces of the ΔO.D. during the laser flash photolysis. It should be emphasized that the EET rate constant for T-hopping is faster than the rate constants for oxidative hole transfers in DNA (10^4 to 10^{10} s^{-1} for A- and G-hopping).

Charge transfer in DNA has received great attention from many researchers over the past few decades from the biomedical and nanotechnological viewpoints. To apply DNA to molecular wire,[1a,b] the conductivity would be one of the most important characteristics, although there is confusion over the reported conductivity of DNA. That is, conductor-, semiconductor-, and insulator-like conductivities have been reported for DNA.[1] Thus, it is necessary to understand the mechanisms and dynamics of DNA-mediated charge transfer processes.

From the biomedical viewpoint, the oxidation and reduction of DNA are essential processes in various biological phenomena. It is well-known that the oxidation of DNA promotes oxidative damage, apoptosis, and cancer.[2] On the other hand, the reduction of DNA closely relates to the repair of damaged DNA such as a T−T cyclobutane lesion.[3] Understanding of oxidative and reductive charge transfers in DNA is key to explaining remote damage and the repair of DNA. Thus, a clarification of the charge transfer mechanism in DNA is very important. Furthermore, these mechanisms are very interesting when considered in the context of the charge transfer theory.

The detailed mechanisms and kinetic parameters of hole transfer in DNA have been studied.[4] It is, currently, widely accepted that both tunneling and hopping mechanisms are important for describing DNA hole transfer. The rate constants for hole transfers have been determined to be on the order of 10^4-10^{10} s^{-1}.[4] It should be emphasized that these rate constants are essential for various applications. For example, the detection of a single nucleotide polymorphism (SNPs) has been demonstrated based on estimated hole transfer rates.[4g]

In contrast to hole transfer, our understanding of the mechanism of EET in DNA is not sufficient.[5] The γ-ray radiolysis works by Sevilla et al. have revealed a contribution of both tunneling and hopping mechanisms in EET.[6] Carell et al. demonstrated EET from a photoexcited reduced flavin to a T dimer through DNA by excess electron hopping.[7a] EET by hopping mechanism has been also reported by several research groups employing product analysis.[7b−d] The processes whereby excess electron is injected into DNA have also been investigated by some groups using laser flash photolysis.[8]

Despite these studies, the rate constant of EET in DNA has not been determined. To determine the rate of EET through DNA, a laser flash photolysis study on a donor-DNA-acceptor system is necessary. Although we recently investigated EET in DNA hairpins using laser flash photolysis, the EET rate constant could not be determined due to a spectral overlap of radical ion species and the long DNA length.[9] In the present study, we directly measured the EET rate in DNA conjugated with tetrathiophene (4T) and diphenylacetylene (DPA) as the photosensitizing electron donor and acceptor, respectively, by femtosecond laser flash photolysis. To the best of our knowledge, this is the first determination of the EET rate constant in DNA.

In the present study, a 4T derivative (Figure 1a) was employed as the photosensitizing electron donor of the donor-DNA-acceptor system, because of its high electron donor ability. Since T has the highest reduction potential (E_{red} = −2.12 V vs NHE)[10] among the four natural nucleobases, T acts as the primal excess electron carrier in EET. By employing the oxidation potential (0.97 V)[11] and singlet energy (3.18 eV) of 4T, −0.09 eV of driving force for charge separation (ΔG_{cs}) with T was estimated.[12] A DPA derivative (Figure 1a) was employed as an acceptor, because its E_{red} (−1.98 V)[13] is higher than that of the four nucleobases. That is, a photoexcited 4T can donate an excess electron to DNA, from which DPA can accept the excess electron as indicated in Figure 1c. Employing 4T and DPA is also useful for following the reaction process by transient absorption spectroscopy, because the reaction intermediates expected for the donor-DNA-acceptor system can be distinguished using the

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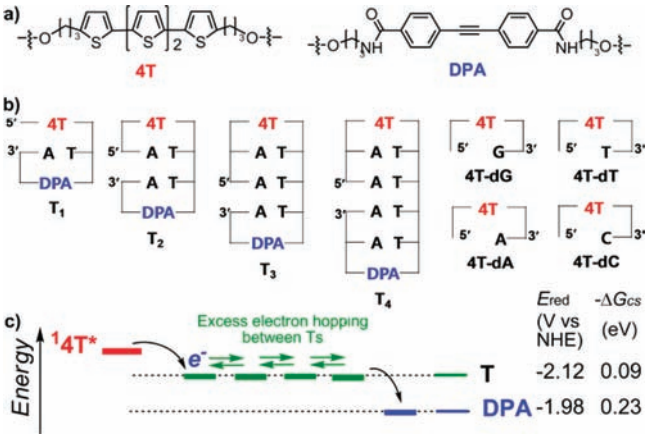

Figure 1. Molecular structures and EET by T-hopping mechanism. (a) Molecular structures of 4T and DPA conjugated to DNA; (b) structures of nicked-dumbbell DNA conjugated with 4T and DPA; (c) simplified illustration of EET mechanism in the present DNA systems. The reduction potentials (E_{red}) of thymine and DPA and driving force for the generation of each charge separated states (ΔG_{CS}) are also indicated.

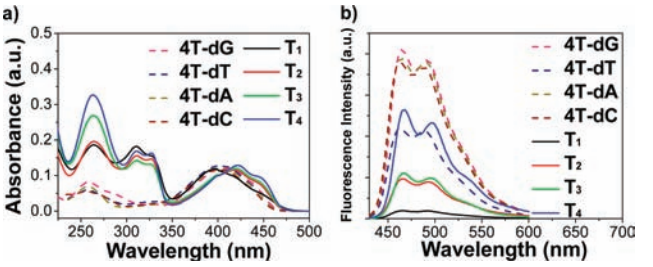

Figure 2. Steady state absorption and fluorescence spectra of nicked-dumbbell DNAs. (a) UV−vis absorption spectra of DNAs in this study in 0.1 M NaCl and 10 mM sodium phosphate, pH 7.0; (b) fluorescence spectra of DNAs in 0.1 M NaCl and 10 mM sodium phosphate, pH 7.0 (λ_{ex} = 415 nm).

spectroscopy. To monitor the EET process within the time window of the present laser flash photolysis apparatus, nicked-dumbbell DNAs were designed to have 1−4 A:T base pairs (<17 Å) between the donor and the acceptor (Figure 1b).

The synthesis of the nicked-dumbbell DNAs was carried out as indicated in the Supporting Information. For the longer DNAs (T_2, T_3, and T_4), formation of a B-type duplex structure under the experimental conditions was indicated by CD and melting temperature (T_m) measurements (Figure S1 and Table S1) as well as by the theoretical calculation of molecular dynamics (MD, Figure S2). T_1 did not show a clear T_m, indicating that a duplex structure is not expected for T_1 due to a shorter DNA length.

In Figure 2a, the steady state absorption spectra of the nicked-dumbbell DNAs were compared to those of reference compounds, in which 4T and a single nucleobase were connected (Figure 1b). It is clear that the nicked-dumbbell DNAs exhibit absorption bands due to 4T and DPA at 422 and 327 nm, respectively, as well as that of nucleobases around 260 nm. It should be noted that the 4T absorption band of the nicked-dumbbell DNAs (T_2, T_3, and T_4) shows a red-shifted peak with a vibrational structure, which is obscure in the reference compounds, indicating that the 4T in this DNA has a planar rigid structure due to conjugation to DNA duplex. The 4T absorption band of T_1 peaked at a similar wavelength as the reference compounds, supporting the absence of the duplex structure. The fluorescence spectra of the DNAs in the present work were obtained by selective excitation of 4T. The fluorescence intensities of 4T-dG, 4T-dA, and 4T-dC are similar to each other, while 4T-dT showed reduced fluorescence intensity (Figure 2b). From the driving force for the charge separation, only T can act as electron acceptor for singlet-excited 4T (^{1}4T*). Thus, the reduced fluorescence intensity of 4T-dT indicates fluorescence quenching by electron transfer to T. The fluorescence spectra of 4T in the nicked-dumbbell DNAs are also shown in Figure 2b. The fluorescence peak positions of 4T in the nicked-dumbbell DNAs are also red-shifted as compared to the reference compounds, in accordance with the absorption peak shift. The reduced fluorescence intensity of the nicked-dumbbell DNAs indicates the photosensitizing electron injection to DNA from ^{1}4T*. It became clear that the fluorescence intensity tended to decrease with a decrease in the number of T between 4T and DPA.

The dynamic process of the nicked-dumbbell DNAs was examined by means of femtosecond laser flash photolysis. In the present study, the sample was excited with a femtosecond laser pulse at 400 nm, which excites 4T selectively. The transient absorption spectra and kinetic traces of ΔO.D. during the laser flash photolysis of T_3 are shown in Figure 3a,b, as a representative case. The broad absorption band with a peak at >700 nm that appeared immediately after the laser excitation was identified to be ^{1}4T*.[14] This band decayed within ∼10 ps after the laser excitation. With the decay of ^{1}4T*, an absorption band of 4T radical cation ($4T^{\bullet+}$) appeared at 675 nm,[15] indicating an electron injection into the adjacent T within ∼10 ps. A transient absorption band assigned to $DPA^{\bullet-}$ appeared at 500 nm[16] with a rising profile over 200 ps (Figure 3). The observation of $4T^{\bullet+}$ and $DPA^{\bullet-}$ indicates the formation of $4T^{\bullet+}$-T_n-$DPA^{\bullet-}$. It is clear that the rising profile observed for $DPA^{\bullet-}$ is the superposition of two rising components. The faster of these rising components can be analyzed using the same rate constant as that for the generation of $4T^{\bullet+}$ and the decay of ^{1}4T* ($k_{cs'}$), indicating that $DPA^{\bullet-}$ is partly generated by single-step charge separation between ^{1}4T* and DPA (k_{ssc} in Figure 4). In contrast, the slow rising component ($k_{arrival}$) has much slower rate than the $4T^{\bullet+}$ rise (Figure 3b). Thus, this slow component is due to reduction of DPA by EET through a consecutive T sequence by hopping of the injected excess electron (i.e., k_{hop} and k_{trap} in Figure 4). This mechanism is supported by the fact that $k_{arrival}$ became slower with an increasing number of intervening T's between 4T and DPA (Figure 3c and Table 1).

In the case of T_4, the longest nicked-dumbbell DNA, the transient absorption spectra showed the initial charge separation between ^{1}4T* and T, but the generation of $DPA^{\bullet-}$ was not observed. The transient absorption at >1 ns showed a peak around 580 nm due to the triplet excited state of 4T (^{3}4T*)[17] (Figure S3d). The formation of ^{3}4T* corresponds to charge recombination between $4T^{\bullet+}$ and $T^{\bullet-}$, generating ^{3}4T* (k_{crT1} in Figure 4). In the present case, the charge recombination is also considered to generate ^{1}4T* (k_{crS1} in Figure 4) as expected from the small driving force for charge separation (−0.09 eV). The latter process is supported by the fact that the decay of ^{1}4T* of T_4 showed two components, and the slower of these decayed with the same time constant as $4T^{\bullet+}$. Furthermore, the regeneration of ^{1}4T* by the charge recombination explains the relatively large fluorescence intensity of the nicked-dumbbell DNAs, despite the efficient excess electron injection process. Therefore, the

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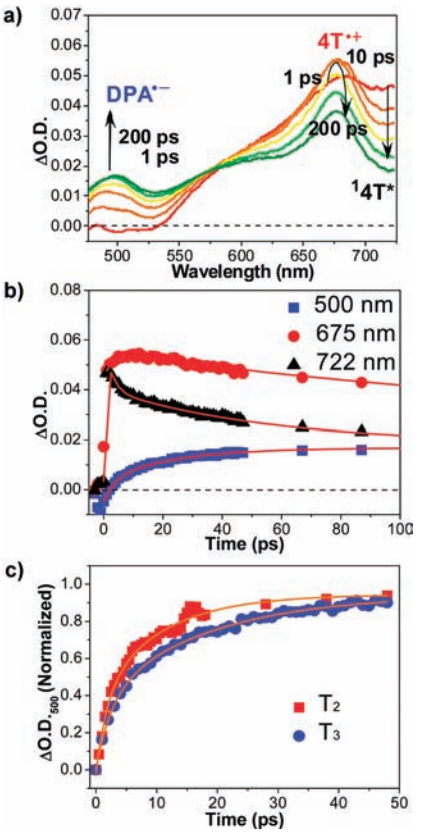

Figure 3. Transient absorption spectra and the kinetic traces during the laser flash photolysis of T_3 upon excitation with 400-nm femtosecond laser pulse. (a) Transient absorption spectra of T_3; 1 ps (red), 10 ps (dark orange), 20 ps (orange), 50 ps (yellow), 100 ps (green), 200 ps (dark green). (b) The kinetic traces of T_3; 500 nm (blue), 675 nm (red), 722 nm (black). (c) The kinetic traces at 500 nm of T_2 and T_3; T_2 (red), T_3 (blue). Orange curves in (b) and (c) are fitted curves.

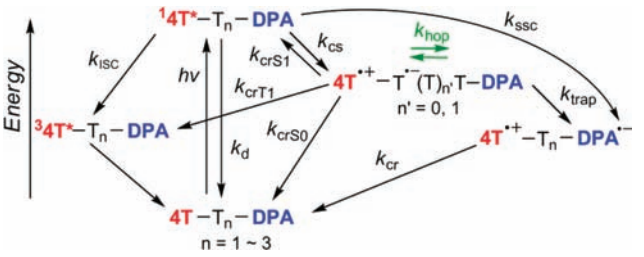

Figure 4. Schematic energy diagram for EET from 4T to DPA. EET by T-hopping after the excess electron injection to T, single-step electron transfer mechanism, recombination processes, and so on are indicated.

insufficient generation of the DPA radical anion in T_4 can be attributed to a fast charge recombination process between $4T^{\bullet+}$ and $T^{\bullet-}$, which generates ^{1}4T* and ^{3}4T* as well as the ground state (k_{crS0} in Figure 4). The fast charge recombination diminishes the possibility of the excess electron arriving at DPA. In the donor-DNA-acceptor systems without these fast deactivation pathways, long-range EET can be expected.

In the case of T_1, the generation of $DPA^{\bullet-}$ was almost simultaneous with that of $4T^{\bullet+}$, both occurring within 1 ps. The faster $k_{cs'}$ rate as compared to the longer DNA can be attributed to the shorter distance between 4T and DPA. The transient

Table 1. Rate Constants of $4T^{\bullet+}$ Generation ($k_{cs'}$), Initial Charge Recombination of $4T^{\bullet+}-T^{\bullet-}$ ($k_{cr'}$), $DPA^{\bullet-}$ Generation ($k_{arrival}$), Charge Recombination of $4T^{\bullet+}-T_n-DPA^{\bullet-}$ (k_{cr}), and Single Electron Hopping through T's (k_{hop})

conjugate	$k_{cs'}$ $(s^{-1})^{a,b}$	$k_{cr'}$ $(s^{-1})^{c,b}$	$k_{arrival}$ $(s^{-1})^{d,b}$	k_{cr} (s^{-1})	k_{hop} (s^{-1})
T_1	5.6×10^{11}	9.0×10^{10}	—[e]	3.9×10^{9}	—[f]
T_2	2.5×10^{11}	6.6×10^{10}	2.0×10^{10}	2.4×10^{9}	4.1×10^{10}
T_3	2.4×10^{11}	4.9×10^{10}	1.0×10^{10}	1.7×10^{9}	4.7×10^{10}
T_4	1.5×10^{11}	2.8×10^{10}	—[g]	—[g]	—[g]

[a] The $4T^{\bullet+}$ generation rate ($k_{cs'}$) is the sum of k_{cs} and k_{ssc} (Figure 4). [b] Estimation error is less than 10%. [c] $k_{cr'}$ is the sum of k_{crS1}, k_{crT1}, and k_{crS0} (Figure 4). [d] $k_{arrival}$ corresponds to the rate constant of the $DPA^{\bullet-}$ slower rise. [e] Difficult to determine due to large contribution of k_{ssc}. [f] The hopping process is not included. [g] Not observed.

spectrum of T_1 at 1 ps exhibits peaks resembling those of $4T^{\bullet+}$ and $DPA^{\bullet-}$ (Figure S3a), but they are shifted compared to the absorption peaks of other DNAs. This finding suggests a strong interaction between radical ions, such as the exciplex interaction which is probably caused by the flexibility of T_1, as is evident from the absence of a T_m value. Because of the spectral change due to the strong interaction, the $k_{arrival}$ of T_1 could not be obtained.

We also measured the transient absorption spectra of the reference compounds, in which 4T and a single nucleobase were connected (Figure 1). In the transient absorption spectra of 4T-dG and 4T-dA, in which the nucleobases are not electron acceptors, the generation of $4T^{\bullet+}$ was not confirmed, indicating that 4T does not exhibit photoionization under the present experimental condition. Thus, photoionization is not included in the present EET mechanism.

As discussed in an earlier section, the generation of $4T^{\bullet+}$ can be attributed to two pathways, that is, the charge separation between ^{1}4T* and the adjacent T and that between ^{1}4T* and DPA. Therefore, the apparent generation rate of $4T^{\bullet+}$ ($k_{cs'}$) is the sum of these two charge separation rates (i.e., k_{cs} and k_{ssc} in Figure 4). From Table 1, it is clear that the $k_{cs'}$ value becomes smaller with an increase in the number of intervening T's between 4T and DPA. This indicates that the contribution of k_{ssc} tends to decrease with an increase in the distance between 4T and DPA in accordance with the distance dependence expected for charge transfer by the tunneling mechanism. The transient absorption change of T_3 (Figure 3) indicates that there is still an apparent contribution of k_{ssc}, while in the case of T_4, this contribution becomes negligible. This trend is also apparent in the fluorescence intensity indicated in Figure 2b. The fluorescence intensity of T_4 is similar to that of 4T-dT, while it decreases with a decrease in the number of intervening T's. In the case of T_1, the fluorescence intensity is quite low, indicating a large contribution of k_{ssc}.

As indicated earlier in this report, the rate of $DPA^{\bullet-}$ generation by T-hopping became slower with an increase in the number of intervening T's between 4T and DPA. In a one-dimensional random walk model, the observed rate is expected to be proportional to the square of the stepping number. The rate constant of the single electron hopping (k_{hop}) through consecutive T, that is, T-hopping, was determined to be $(4.4 \pm 0.3) \times 10^{10}\ s^{-1}$ from the $k_{arrival}$ values of T_2 and T_3 (Table 1) using the one-dimensional random walk model.[4i,18] To the best of our knowledge, this is the first determination of the k_{hop} value for EET in DNA. As for hole transfer in DNA, we have reported the hole hopping rate through a consecutive A sequence to be $2 \times 10^{10}\ s^{-1}$ from the distance dependence of the generated transient absorption band of the

donor radical cation in a photosensitizing acceptor-DNA-donor system.[4f] Lewis et al. reported G-to-G and A-to-A hole hopping rates to be 4.3×10^9 and 1.2×10^9 s^{-1}, respectively, from the direct observation of the generation rates of donor radical cation in a photosensitizing acceptor-DNA-donor system.[4i] Thus, it was revealed that an excess electron can hop through consecutive T's at a faster rate than that of the hole hopping process.

Charge mobility (μ) is an important characteristic in the molecular wire application of DNA in nanotechnology. The excess electron mobility through consecutive T's is calculated to be 2.0×10^{-3} cm^2 V^{-1} s^{-1}, which is lower than that of discotic liquid crystals ($\sim 10^{-1}$ cm^2 V^{-1} s^{-1}),[19a] but similar to those of organic semiconductors (10^{-3}–10^{-1} cm^2 V^{-1} s^{-1}).[19b−d] This mobility suggests that DNA could be of great use when applied to molecular wire. From a biological viewpoint, it has been indicated that EET in DNA is closely related to DNA repair processes.[3] The fast EET seems to be essential for realizing the efficient repair of DNA lesions. The kinetic parameters of EET in DNA are expected to largely depend on various conditions, such as sequence and environment. The effects of these factors on EET will be clarified in the near future.

In summary, we have directly measured the excess electron hopping rate in a consecutive T sequence in nicked-dumbbell DNAs conjugated with 4T and DPA as a photosensitizing electron donor and acceptor, respectively. The single excess electron hopping rate in a consecutive T sequence was determined to be $(4.4 \pm 0.3) \times 10^{10}$ s^{-1}, which is faster than the hole hopping rates in consecutive A or G sequences in DNA. The mechanism of fast EET is an interesting subject that remains to be clarified. In addition, the determination of a fast EET rate in DNA can be applied to the biomedical fields to help better understand DNA repair processes as well as to development of an efficient DNA nanowire.

■ ASSOCIATED CONTENT

Supporting Information. Experimental section, CD spectra, melting temperature, and optimized structure of DNAs. This material is available free of charge via the Internet at http://pubs.acs.org.

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