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Charge Separation in DNA via Consecutive Adenine Hopping

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Abstract: Charge transfer in DNA is of current interest because of the involvement of charge transfer in oxidative DNA damage and electronic molecular devices. We have investigated the charge separation process via the consecutive adenine (A)-hopping mechanism using laser flash photolysis of DNA conjugated with naphthaldiimide (NDI) as an electron acceptor and phenothiazine (PTZ) as a donor. Upon the 355-nm laser flash excitation of NDI, the charge separation and recombination process between NDI and PTZ was observed. The yields of the charge separation via the consecutive A-hopping were slightly dependent upon the number of A bases between the two chromophores, while the charge recombination rate was strongly dependent upon the distance. The charge-separated state persisted over 300 μs when NDI was separated from PTZ by eight A bases. Furthermore, the rate constant of the A-hopping process was determined to be 2×10^{10} s^{-1} from an analysis of the yield of the charge separation depending on the number of A-hopping steps.

Introduction

There is considerable interest in the development of macromolecular chemical systems forming a long-lived charge-separated state for technological advances in solar energy conversion, molecule-based optoelectronics, and a variety of other applications.[1−4] DNA is particularly well-suited for use as a scaffolding medium because it is a thick and stiff molecule easily modified with various molecules. Therefore, if it is possible to form a long-lived charge-separated state on DNA, DNA can be utilized for applications such as a molecular device.[5−7] However, the charge transfer in DNA has not been studied from the aspect of generating a long-lived charge-separated state.

Thus far, there are many reports of theoretical and experimental studies concerning the charge transfer in DNA.[8−18] These reports showed that the rate of photoinduced electron transfer between a donor and acceptor decreased with increasing distance (superexchange mechanism),[10] while a hole generated in DNA could migrate over long distances (200 Å) via the G-hopping mechanism in which the charge tunnels between guanine (G) bases.[13,19] Lewis et al. reported that the lifetime of the charge-separated state in hairpin DNA conjugated with stilbene increased with a hole shift from the proximal G to distal GG and deazaG.[20,21] However, these hole shifts were slow compared with the charge recombination process. In this respect, it seems to be impossible to efficiently increase the distance between charges.

Recently, DNA hole transfer has been demonstrated to occur by the two different mechanisms: G-hopping (superexchange between G's across the intervening A−T bridge)[13,19,22,23] and A-hopping (hole is carried by the bridge base A as $A^{\bullet+}$).[24,25] As for the kinetics of the A-hopping process, we demonstrated that the A-hopping occurred very rapidly with a small distance dependence due to the multihopping process.[26] For the accomplishment of the long-lived charge-separated state, it is necessary to spatially separate the charges over a long dis-

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tance.[2,27] Therefore, it is desirable to utilize the consecutive A-hopping process, but not the single-step charge transfer (superexchange mechanism), and the G-hopping process, to achieve the long-lived charge-separated state in DNA. Herein, we report the charge separation process via the consecutive A-hopping in hairpin DNA possessing naphthaldiimide (NDI) at the hairpin loop as an electron acceptor and phenothiazine (PTZ) at the 5′ end as an electron donor. By monitoring the formation and decay of the NDI radical anion generated by the charge separation upon the 355-nm flash excitation of the NDI chromophore, we have investigated the dependence of the number of A bases on the consecutive A-hopping and the kinetics of the A-hopping process. The yields of the charge-separated state were slightly dependent upon the number of A bases between two chromophores. In contrast, the charge recombination rates were strongly dependent upon the distance. The charge-separated state persisted over 300 μs when NDI was separated from PTZ by eight A bases. From an analysis of the yield of the charge separation depending on the number of A-hopping steps, the rate constant of the A-hopping process was determined to be 2×10^{10} s^{-1}.

Experimental Section

General Technique. Ground-state UV−vis absorption and fluorescence spectra were measured using a JASCO V-530 double-beam spectrophotometer and a Hitachi 850 spectrofluorometer, respectively.

DNA Synthesis. The hairpin DNA used in this study was synthesized on an Applied Biosystems DNA synthesizer with standard solid-phase techniques and purified on a JASCO HPLC with a reverse-phase C-18 column with an acetonitrile/50 mM ammonium formate gradient. Duplex solutions (20 mM sodium phosphate buffer, pH 7.0) were prepared by mixing equimolar amounts of the desired ODN complements and gradually annealing with cooling from 80 °C to room temperature. DNA conjugated with PTZ at the 5′ end and NDI as a linker were synthesized according to a previous procedure.[28,29]

Measurements of Melting Temperature. Thermal denaturation profiles were obtained with a Jasco V-530 spectrophotometer equipped with a Peltier temperature controller. Absorbance of the ODN sample (4 μM duplex in 20 mM sodium phosphate buffer (pH 7.0)) was monitored at 260 nm (A_{260}) from 10 to 70 °C at a heating rate of 1 °C min^{-1}. The T_m value was determined as the maximum in a plot of $\Delta A_{260}/\Delta T$ versus temperature.

Laser Flash Photolysis Experiments. Nanosecond transient absorption measurements were performed using the LFP technique.[30] The third-harmonic oscillation (355 nm, fwhm of 4 ns, 5 mJ/pulse) from a Q-switched Nd:YAG laser (Continuum, Surelight) was used for the excitation light. A xenon flash lamp (Osram, XBO-450) was focused into the sample solution as the probe light for the transient absorption measurement. Time profiles of the transient absorption in the UV−visible region were measured with a monochromator (Nikon, G250) equipped with a photomultiplier (Hamamatsu Photonics, R928) and digital oscilloscope (Tektronics, TDS-580D).

Synthesis of *N,N′*-Bis-(3-dimethylaminopropyl)-1,4,5,8-naphthaldiimide. *N,N*-Dimethyl-1,3-propanediamine (1.3 g, 12 mmol) was added dropwise over 5 min to a solution of naphthalene-1,4,5,8-tetracarboxylic dianhydride in 500 mL of toluene. The reaction mixture was heated at 145 °C for 5 h. The crude mixture was concentrated on a rotary evaporator, and the residue was recrystallized from ethanol (1.2 g, 70%). ^{1}H NMR ($CDCl_3$): δ 8.76 (s, 4H), 4.27 (t, 4H), 2.45 (t, 4H), 2.24 (s, 12H), 1,93 (m, 4H). ESI MASS (positive ion): *m/e* 437 (M + H).

Synthesis of *N,N′*-Bis-(3-dimethylaminopropyl)-1,4,5,8-naphthaldiimide Dihydrochloride (NDIm). A solution of 1 N HCl−ether (20 mL) was added to a solution of *N,N′*-bis-(3-dimethylaminopropyl)-1,4,5,8-naphthaldiimide (0.49 g, 1.1 mmol) dissolved in 10 mL of CH_2Cl_2. After being stirred for 4 h under an N_2 atmosphere, the precipitates were filtered and recrystallized from ethanol (0.12 g, 21%). ^{1}H NMR ($CDCl_3$): δ 9.7 (br s, 2H), 8.70 (s, 4H), 4.13 (t, 4H), 3.17 (t, 4H), 2.74 (s, 12H), 2.07 (m, 4H). ESI MASS (positive ion): *m/e* 437 (M − HCl_2).

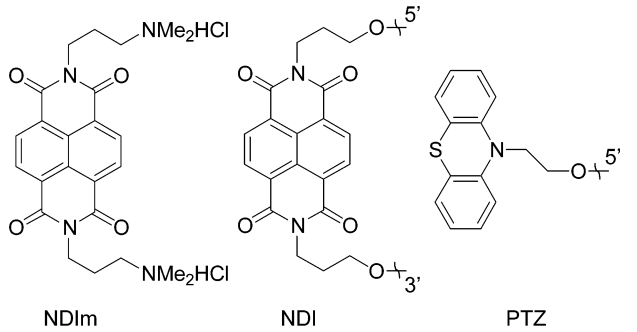

Figure 1. Chemical structures of water-soluble NDI derivative (NDIm), naphthaldiimide (NDI), and phenothiazine (PTZ) conjugated to DNA.

Table 1. Sequence of Hairpin DNA Conjugated with Naphthaldiimide (NDI) and Phenothiazine (PTZ)

DNA	sequence
NP-A4	5′-PTZ-AAAA-NDI-TTTT-3′
NP-A5	5′-PTZ-AAAAA-NDI-TTTTT-3′
NP-A6	5′-PTZ-AAAAAA-NDI-TTTTTT-3′
NP-A7	5′-PTZ-AAAAAAA-NDI-TTTTTTT-3′
NP-A8	5′-PTZ-AAAAAAAA-NDI-TTTTTTTT-3′
NP-AT1	5′-PTZ-ATATA-NDI-TATAT-3′
NP-AT2	5′-PTZ-ATATATA-NDI-TATATAT-3′
NP-G1	5′-PTZ-AGAGA-NDI-TCTCT-3′
NP-G2	5′-PTZ-AAGAA-NDI-TTCTT-3′

Results and Discussion

Properties of Hairpin DNA Conjugated with Naphthaldiimide and Phenothiazine. Hairpin DNA conjugated with naphthaldiimide (NDI) and phenothiazine (PTZ) were prepared via conventional phosphoramidite chemistry according to previous procedures.[28,29] The sequence of the synthetic hairpin DNA (NP-DNA) and chemical structures of NDI and PTZ are shown in Table 1 and Figure 1, respectively. It has been reported that NDI serves as a linker to form a stable hairpin DNA.[28] NP-A*n* ($n = 4-8$) was designed to probe the consecutive A-hopping, and NP-AT*n* and -G*n* were made to examine the influence of the AT repeats and G as a hole trap in the A*n* sequences.

The ground-state absorption and fluorescence spectra for the water-soluble NDI derivative (NDIm) and NDI- and PTZ-conjugated DNA (NP-A5) are shown in Figure 2. The ground-state absorption spectrum for the NP-A5 displayed maxima at wavelengths longer than 320 nm, assigned to the NDI chromophore. Longer wavelength bands of NP-A5 were red-shifted and changed to have a relatively low intensity compared with that of NDIm. Similar spectra were observed for other hairpin DNAs. These spectral changes were previously reported,[31] indicating the weak interaction between the NDI chromophore

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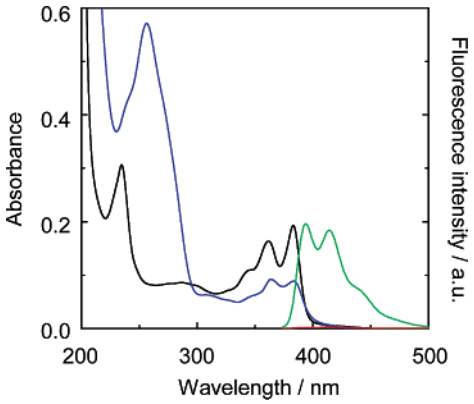


Figure 2. Ground-state absorption and fluorescence spectra of NDIm (black and green) and NP-A5 (blue and red). Absorption and fluorescence spectra were measured in aqueous solution containing 20 mM Na phosphate buffer (pH 7.0), 100 mM NaCl, and 8 μM NP-A5 (strand concentration).

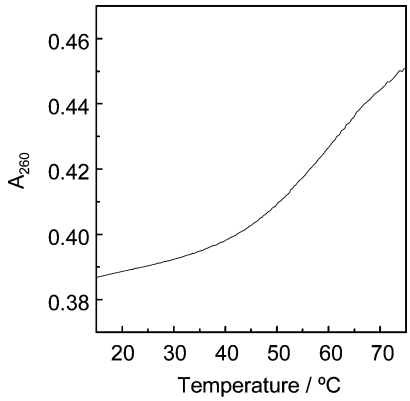


Figure 3. Melting temperature profiles for NP-A5. The melting behavior was determined in the aqueous solution containing 4 μM of NP-A5 (strand concentration), 20 mM Na phosphate buffer (pH 7.0), and 100 mM NaCl. The solution was monitored at 260 nm.

and neighboring nucleobases. No fluorescence of NP-A5 was observed compared to NDIm, suggesting the rapid electron-transfer quenching of NDI in the singlet excited state in accord with the previous report.[28]

The melting curve for NP-A5 shown in Figure 3 gave the melting temperature T_m of 61 °C. The value of T_m was independent of the DNA concentration, indicating the formation of a stable hairpin structure. Other hairpin DNAs showed melting temperatures higher than 45 °C. Furthermore, the CD spectra for all the NDI- and PTZ-conjugated hairpin DNAs showed maxima around 280 and minima around 250 nm, which are characteristic of B-DNA.

Kinetics of Charge Separation and Recombination. The charge separation and recombination processes after the 355-nm laser flash of DNA conjugated with the NDI and PTZ are shown in Scheme 1. Because the reduction potential of NDI in the singlet excited state (^{1}NDI*) is 2.7 V (vs SCE in DMSO), ^{1}NDI* can oxidize all four nucleobases.[32,33] The NDI is adjacent to the A−T base pair, and the oxidation potential of A (E_{ox} = 1.7 V vs SCE in DMSO) is lower than that of T;[32] therefore, it is probable that the electron transfer from ^{1}NDI* to the nearest A occurs immediately after the excitation, resulting in the formation of NDI$^{\bullet-}$ and A$^{\bullet+}$. Accordingly, the charge separation

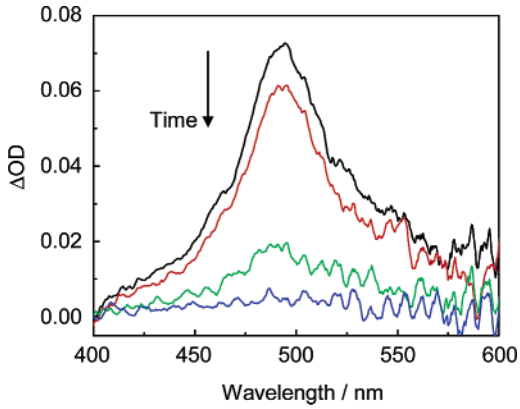
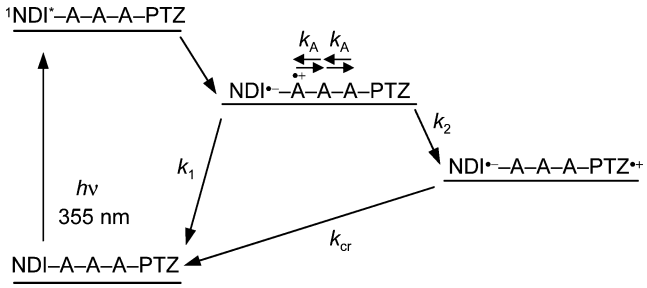


Figure 4. Transient absorption spectra of NP2 obtained at 100 ns, 1, 10, and 100 μs after the 355-nm laser flash excitation in Ar-saturated solution containing 80 μM DNA, 20 mM Na phosphate buffer (pH 7.0), and 100 mM NaCl.

Scheme 1. Kinetic Scheme for the Charge Separation and Charge Recombination in NDI- and PTZ-Conjugated DNA



between NDI and PTZ is considered to occur via the A-hopping process between A's as shown in Scheme 1. In contrast, the charge recombination between NDI and PTZ is expected to occur via the superexchange mechanism.

Charge Separation and Recombination Processes. The charge separation and recombination processes between NDI and PTZ after the 355-nm laser excitation (fwhm of 8 ns, 5 mJ/pulse) were examined by monitoring the formation and decay of the NDI radical anion (NDI$^{\bullet-}$), respectively. In the case of NP-A5, a transient absorption spectrum with a peak at 495 nm was immediately observed after the flash excitation (Figure 4). This transient absorption spectrum was assigned to NDI$^{\bullet-}$ of NDI$^{\bullet-}$-A5−PTZ$^{\bullet+}$, demonstrating that the charge separation process via the A-hopping mechanism occurred very rapidly.[31] The decay of NDI$^{\bullet-}$ with no spectral change indicates the occurrence of the charge recombination. In contrast, no transient absorption spectrum was observed for the hairpin DNA possessing only NDI as a linker, suggesting that the PTZ worked as a strong hole acceptor to inhibit the charge recombination process between NDI$^{\bullet-}$ and A$^{\bullet+}$. Unfortunately, we could not observe the transient absorption of PTZ$^{\bullet+}$ because the molar extinction coefficient of the PTZ$^{\bullet+}$ (1×10^4 M^{-1} cm^{-1} at 520 nm)[34] is small compared with that of NDI$^{\bullet-}$ (1×10^5 M^{-1} cm^{-1} at 495 nm).[31] Therefore, NDI$^{\bullet-}$ in the charge-separated state was only observed in the transient absorption measurement.

The formation and decay of NDI$^{\bullet-}$ for NP-A1, -A3, and -A5 are shown in Figure 5. The quantum yields of the charge separation and rate constants for the charge recombination were determined by analyzing the transient absorption of NDI$^{\bullet-}$

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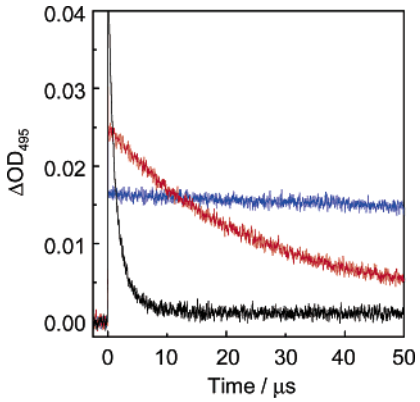

Figure 5. Decay profiles of the transient absorption measured at 495 nm for NP-A4 (black), A6 (red), and A8 (blue).

Table 2. Quantum Yield of Charge Separation (Φ_{cs}) and Rate Constant of Charge Recombination (k_{cr})

DNA	$\Phi_{cs}{}^{a}/10^{-2}$	$k_{cr}{}^{b}/10^{5}$ s^{-1}
NP-A4	2.1	7.5
NP-A5	1.4	1.7
NP-A6	1.0	0.40
NP-A7	0.85	0.12
NP-A8	0.65	0.03
NP-AT1	0.39	2.1
NP-AT2	0.13	0.40
NP-G1	0.37	0.64
NP-G2	0.75	0.66

[a] Determined from the transient absorption of the triplet benzophenone as an actinometer during the 355-nm laser flash photolysis. [b] Obtained from the decay of the transient absorption of NDI$^{\bullet-}$ at 495 nm.

observed after a laser flash (ΔOD_{495}) and the decay profile of NDI$^{\bullet-}$, respectively (Table 2). These quantum yields decreased only slightly with the increasing number of A bases, while the decay rates strongly decreased as the number of A bases increased. The charge recombination rate slowed and occurred in the region of microseconds with the increasing number of A bases. Of special interest, the charge separation state persisted over 300 μs when NDI and PTZ were separated by eight A bases. On the other hand, the charge separation yields dramatically decreased by changing the consecutive A sequence to the AT (NP-AT1 and -AT2) or GC repeat sequence (NP-G1 and -G2). These results would be explained by considering the interstrand A-hopping and hole trapping by G. The interstrand A-hopping is likely to be much slower compared with the intrastrand process because of a decrease in the stacking and intervening hydrogen bonding. A similar trend for the interstrand electron transfer was previously observed.[35,36] In the case of sequences containing G's, it is expected that G serves as a hole trap on the charge shift process because the oxidation potential of G is lower than that of A,[21,33] causing inhibition of the consecutive A-hopping in which a hole migrates to PTZ. Higher charge separation yields for NP-G2 than that for NP-G1 would be attributed to the different location of G. This difference shows that a hole trapped at G for NP-G2 is more distant from the NDI compared to that for NP-G1, causing a slower charge recombination between NDI$^{\bullet-}$ and G$^{\bullet+}$. Hence, the consecutive A sequence is important for the effective A-hopping.

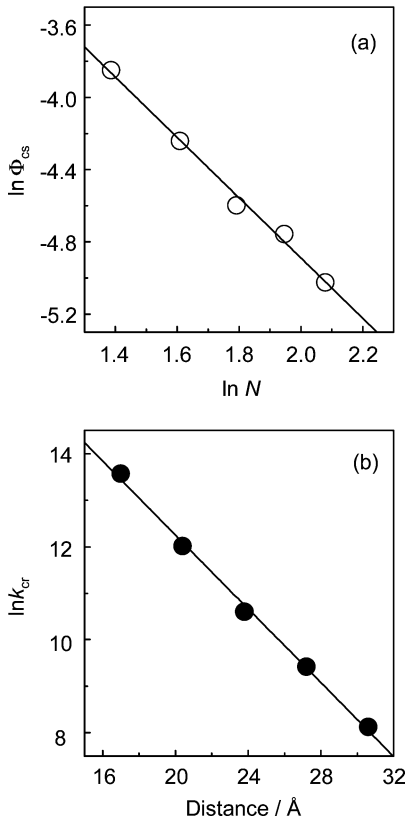

Figure 6. Distance dependence on the charge separation and charge recombination processes. (a) A plot of ln(Φ_{cs}) against the ln(N), where N is the number of hopping steps. (b) A plot of ln k_{cr} against the distance between NDI and PTZ (Δr). Distance of π-stacking was calculated assuming a constant of 3.4 Å^{-1} for the distance between two nucleobases.

Distance Dependence of Charge Separation and Recombination Processes. To elucidate the mechanism of the charge separation and recombination between NDI and PTZ, the distance dependences of these processes were investigated (Figure 6). Assuming that the final charge separation state is accomplished by the process in which a hole generated on the A base migrates to PTZ via the consecutive A-hopping (Scheme 1), the correlation between the charge separation yields (Φ_{cs}) and the number of hopping steps (N) is simply expressed by eq 1:

$$\ln \Phi_{cs} = -\eta \ln (N) \qquad (1)$$

where η is a proportionality factor and N is the number of hopping steps.[25,37,38] In the case of a random walk mechanism, η has a value between 1 and 2. A plot of ln Φ_{cs} versus the ln N gave a straight line and the η-value of 1.7 (Figure 6a), confirming that the charge separation between NDI and PTZ occurred via the random walk process (consecutive A-hoppings) mentioned above. In contrast, the charge recombination between NDI$^{\bullet-}$ and PTZ$^{\bullet+}$ was considered to occur via the superexchange mechanism. In this mechanism, the distance dependence on the charge recombination rate is expressed by eq 2:

$$\ln k_{cr} \propto -\beta \Delta r \qquad (2)$$

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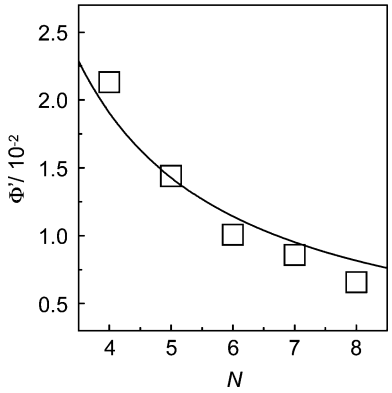

Figure 7. Dependence of quantum yields ratio (Φ′) for the charge separation upon the number of the hopping steps (*N*).

where β is the distance dependence parameter and Δr is the distance between NDI and PTZ. A linear correlation between $\ln k_{cr}$ and the distance (Δr) was obtained to provide the β-value of 0.4 $Å^{-1}$, which is low compared to that for the duplex DNA previously reported (Figure 6b).[10] This might be attributed to the difference in the tunneling energy between the donor or acceptor and bridge states[39,40] or to the structure of the hairpin DNA containing the consecutive A sequence.

The correlation between the rate constants (k_A, k_1, k_2) and charge separation yields is expressed by eq 3:[41]

$$\Phi' = \frac{\Phi_{cs}}{1 - \Phi_{cs}} = \frac{(k_2/k_1)}{1 + (N-1)(k_2/k_A)} \qquad (3)$$

where k_A, k_1, and k_2 are the rate constants of the A-hopping, charge recombination between $NDI^{\bullet-}$ and $PTZ^{\bullet+}$, and the hole shift from adjacent $A^{\bullet+}$ to PTZ, respectively. The electron-transfer process from ^{1}NDI* to nucleobases and charge recombination between the nucleobase radical cation and NDI radical anion were previously reported by Lewis and co-workers, demonstrating that the charge separation and recombination rates between NDI and the A−T pair were 7.3×10^{12} s^{-1} and 2.5×10^{11} s^{-1}, respectively.[28] The rate constants for the A-hopping process were obtained by fitting Φ_{cs} depending on the hopping number (N) to eq 3 using the k_1 value of 2.5×10^{11} s^{-1} to provide the k_A of 2×10^{10} s^{-1} (Figure 7). The rate constant of the A-hopping process (k_A) is much larger than that of hopping from G to GG across one A base (5×10^6 s^{-1}).[20] This difference is attributed to the direct stacking between the A bases for the A-hopping presented in this study.

Conclusions

In the present study, we have demonstrated the formation of the charge-separated state between NDI and PTZ in DNA by utilizing the consecutive A sequence as a bridge. The mechanisms of the charge separation and recombination processes between NDI and PTZ were investigated by monitoring the formation and decay of the transient absorption of $NDI^{\bullet-}$. The transient absorption of $NDI^{\bullet-}$ was observed immediately after the 355-nm flash excitation of the NDI chromophore, demonstrating the occurrence of the charge separation within 5 ns. The yields of the charge separation between NDI and PTZ via the A-hopping process were slightly dependent upon the number of A bases between two chromophores, while the charge recombination rate was strongly dependent upon the distance. The charge-separated state persisted for over 300 μs when NDI was separated from PTZ by eight A bases. Furthermore, the rate constant of the A-hopping was determined to be 2×10^{10} s^{-1} by analyzing the obtained charge separation yields. The charge separation yield was approximately 2%, which was low due to the rapid charge recombination between $NDI^{\bullet-}$ and adjacent $A^{\bullet+}$. However, a high efficiency of the final charge-separated state in DNA may be achieved by replacing NDI with suitable acceptor molecules (M) which slow the initial charge recombination between $M^{\bullet-}$ and $A^{\bullet+}$.

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