DNA Devices

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High-Yield Generation of a Long-Lived Charge-Separated State in Diphenylacetylene-Modified DNA**

*Tadao Takada, Kiyohiko Kawai, Mamoru Fujitsuka, and Tetsuro Majima**

The development of macromolecular chemical systems that are capable of generating a long-lived charge-separated state is of particular interest for technological advances in solar-energy conversion and molecular devices.[1] DNA is a particularly important and promising molecule that can be used as a molecular scaffold for nanostructures and nanotechnology.[2] In addition, there is interesting potential for the use of DNA as a molecular wire as a result of the efficient charge-transport properties through the DNA π stack.[3] DNA-based electrochemical sensors to detect target DNA, protein analytes, and single nucleotide polymorphism have been developed by Barton and co-workers.[4] Recently, Okamoto, Saito, and co-workers reported the photochemical response of functionalized DNA on an electrochemical surface and its diagnostic application for the detection of mismatches.[5] However, the efficient generation of the photocurrent has not yet been achieved because of a rapid charge-recombination process in the charge-separated state after photoirradiation.[6] This process limits the application of DNA for photoelectrochemical devices. In this context, it is necessary to establish a system for the high-yield generation of the charge-separated state in DNA.

Generally, to generate a long-lived charge-separated state, the charge recombination must be slowed down by spatially separating positive and negative charges.[7] Previously, we showed that the rapid hole hopping over consecutive adenine (A) bases can be useful to generate the charge-separated state in DNA.[8,9] However, the yield is not sufficiently high as a result of the initial charge-recombination process within the contact ion pair. As predicted from electron-transfer theory, the rates of charge recombination between the electron donor and acceptor are dependent upon the energetics and, in particularly, the driving force of the process.[10] Lewis, Wasielewski, and co-workers reported on the electron-transfer process between diphenylacetylene (DPA) and DNA in which the charge-recombination process between the DPA radical anion and a neighboring A radical cation was quite slow ($7\times10^{8}\,\mathrm{s}^{-1}$) because the back-electron transfer was deep within the Marcus inverted region ($\Delta G_{\mathrm{cr}} = 3.8$ eV, calculated from the reduction potential of DPA ($E_{\mathrm{red}} = -2.1$ V vs SCE) and the oxidation potential of the A base ($E_{\mathrm{ox}} = 1.7$ V vs SCE); SCE = saturated calomel electrode).[11] Thus, a long-lived charge-separated state in DNA is anticipated to be generated in high yield by combining slow charge-recombination properties and rapid hole hopping through consecutive A bases. Herein, we report the high-yield generation of the long-lived charge-separated state in DPA-modified DNA.

The synthesis of DNA modified with DPA was carried out by conventional phosphoramidite chemistry using the DNA synthesizer as previously reported.[12] The chemical structures of DPA and the sequence of the synthetic DNA are shown in Figure 1a and Table 1, respectively. Two types of DPA-modified DNA derivatives were designed; namely, the hairpin (H-A*n*) and end-capped (E-A*n*) structures. Charge separation and the following hole-hopping process are schematically shown in Figure 1b. As mentioned above, DPA in the singlet excited state ($^{1}\mathrm{DPA}^{*}$) is capable of

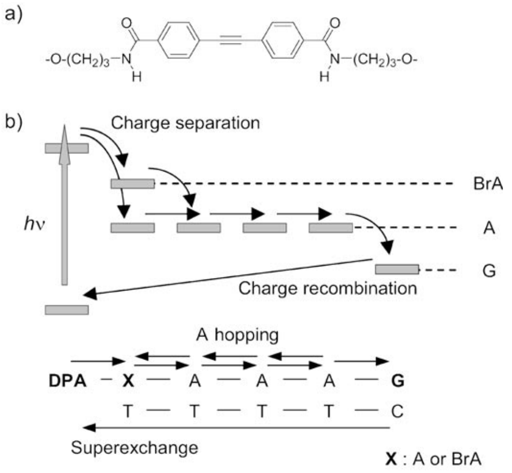

Figure 1. a) Structure of diphenylacetylene (DPA). b) Charge separation and subsequent hole-transfer process through A-base hopping.

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[*] T. Takada, K. Kawai, M. Fujitsuka, Prof. T. Majima
The Institute of Scientific and Industrial Research (SANKEN)
Osaka University
Mihogaoka 8-1, Ibaraki, Osaka 567-0047 (Japan)
Fax: (+81) 6-6879-8499
E-mail: majima@sanken.osaka-u.ac.jp

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Table 1: Sequences of DNA modified with DPA, the yields of charge separation after photoexcitation, and the lifetimes of the charge-separated states.

DNA	Sequence[a]	Yield[b] [%]	τ[b,c] [μs]
H-A3	5′-AAA**G**-AAA-**DPA**-TTT-CTTT-3′	26	0.23 (86%), >50 (14%)
H-A4	5′-AA**G**-AAAA-**DPA**-TTTT-CTT-3′	18	7.6
H-A5	5′-A**G**-AAAAA-**DPA**-TTTTT-CT-3′	16	26
E-A3	5′-**DPA**-AAA-**G**TGTGTGT-3′	15	0.26 (75%), >50 (25%)
E-A4	5′-**DPA**-AAAA-**G**TGTGTGT-3′	13	>50
E-A5	5′-**DPA**-AAAAA-**G**TGTGTGT-3′	11	>50
E-A6	5′-**DPA**-AAAAAA-**G**TGTGTGT-3′	8.4	>50
E-A7	5′-**DPA**-AAAAAAA-**G**TGTGTGT-3′	7.1	>50
E-A8	5′-**DPA**-AAAAAAAA-**G**TGTGTGT-3′	6.2	>50
E-BrA	5′-**DPA**-BrA-AAAAA-**G**TGTGTGT-3′	13	>50

[a] DNA duplexes with hairpin (H-A*n*) and end-capped (E-A*n*) structures. Sequences of single-strand DNA modified with DPA are only shown for the E-A*n* series. [b] Determined by comparing the transient absorption of DPA$^{\bullet-}$ at 490 nm with that of benzophenone, which was used as an actinometer, observed after the laser-pulse excitation. [c] Lifetimes (τ) of charge-separated state were determined by the decay of the transient absorption monitored at 490 nm. Lifetimes that were longer than 50 μs could not be determined owing to the intermolecular charge recombination and the intrinsic decay of DPA$^{\bullet-}$.

oxidizing the A base as well as the guanine (G) base. After the photoexcitation of DPA, charge separation between ^{1}DPA* and A takes place and a hole on the nearest A base can escape from the contact ion pair through A hopping. This provides a long-lived charge-separated state between DPA and the nearest G base (Figure 1b).

The charge-separation and -recombination processes in DPA-modified DNA were characterized by nanosecond time-resolved transient absorption measurements. The transient absorption spectra observed for the DPA-modified DNA (H-A4) upon excitation with a 308 nm laser pulse (FWHM = 50 ns, 8 mJ/pulse) are shown in Figure 2. A strong absorption peak around $\lambda = 500$ nm was observed after photoexcitation and assigned to the DPA radical anion (DPA$^{\bullet-}$). Transient species observed around 500 nm are almost completely quenched by molecular oxygen (see Supporting Information for details about quenching experiments). The quenching experiments confirmed that the transient absorption originated from DPA$^{\bullet-}$ and that the DPA radical cation generated by the two-photon ionization or reductive electron transfer can be excluded. DPA$^{\bullet-}$ was not observed for DNA that does not contain a guanine–cytosine (GC) base pair, indicating that the trapping of a hole at a G site leads to the long-lived charge-separated state. From the intensity of the absorption of DPA$^{\bullet-}$ monitored at $\lambda = 490$ nm, the yield of the charge-separated state was determined to be 18% for this sequence, which is quite high compared with previous results.[8] In earlier studies, we reported that the yields of charge separation for DNA modified with naphthaldiimide ($\Delta G_{cs} = 1.5$ eV) and naphthalimide ($\Delta G_{cs} = 3.0$ eV) were 2.1% and 3.3%, respectively, when these photosensitizers were separated from G by four adenine–thymine (AT) base pairs.[8,13] These results indicate that the yields are correlated with the driving force of the initial charge-recombination process.

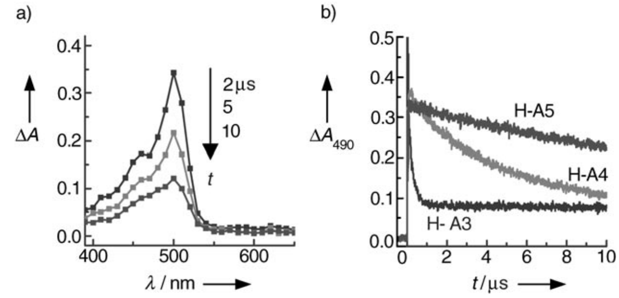

Figure 2. a) Transient absorption spectra for DPA-modified DNA (H-A4) monitored at 2, 5, and 10 μs after the excitation of DPA with a 308 nm laser pulse. b) Decay profiles for H-A3, H-A4, and H-A5 monitored at 490 nm after laser-pulse excitation. Sample solutions contained 20 μM DNA, 20 mM sodium phosphate buffer (pH 7.0), and 100 mM NaCl.

Decay profiles of the charge-separated state for H-A3, H-A4, and H-A5 are shown in Figure 2b. Yields of the charge-separated state and the lifetimes for these DNA duplexes are summarized in Table 1. The strong dependence of the lifetimes for the charge-separated states on the distance demonstrates that the charge recombination between DPA$^{\bullet-}$ and G$^{\bullet+}$ occurred through a superexchange type of mechanism owing to the higher oxidation potential of A relative to that of G. On the other hand, the weak distance dependence of the yields suggests that the long-lived charge-separated states were generated by A hopping. The high yields of the long-lived charge-separated states were also observed for the end-capped structures (E-A*n*). The yields of the charge-separated state obtained for E-A*n* are somewhat lower than those for H-A*n* when the number of A bases between DPA and the nearest G base is the same. This result may be attributed to the structural differences that cause the changes in the initial charge-recombination rate. The long lifetime of the charge-separated state was observed for all E-A*n* except E-A3, because the hole transfer between G bases over the (GT)$_4$ sequence increases with an increase in the distance between the positive and negative charges.[14]

In previous reports, Lewis, Wasielewski, and co-workers demonstrated that hole migration from a contact ion pair cannot occur because of Coulombic interactions.[12] Therefore, there may be a possibility that a hole generated by oxidizing the second A base from DPA migrates to a G base to provide a long-lived charge-separated state. However, on the basis of the superexchange mechanism, the yield of the direct oxidation of the second A base by ^{1}DPA* should be less than 10% because of the strong dependence on distance. Charge-separation yields obtained for H-A3 and H-A4 were higher than 10%, confirming that the hole-escape reaction from the contact ion pair can take place to generate the long-lived charge separated state by A hopping.

To improve the yields of the charge-separated states by changing the oxidation potential of the bridge, an 8-bromo-substituted adenine base (BrA) was incorporated in place of

A at the first position from DPA (E-BrA). As a result of the electron-withdrawing properties of the Br group, BrA shows a higher oxidation potential than A[15] and thus it is expected to facilitate the hole transfer from the contact radical ion pair to the next A base. When the A base nearest to DPA in E-A6 was replaced by BrA (E-BrA), the yield of charge separation was improved by about 50% relative to that of E-A6. This observation suggests that the gradual change in the redox potential over the bridge bases facilitates the hole-transfer reaction from the contact ion pair to the next A base and improves the yield of the charge-separated states.

In conclusion, we have demonstrated the high-yield generation of the long-lived charge-separated state through A-base hopping in DPA-modified DNA. On the basis of the effect of the driving force of the charge-recombination process and the redox gradient of the bridge bases, it was demonstrated that the modulation of the redox properties of the photosensitizer and bridge bases can improve the yield of the long-lived charge-separated state. This observation will be important in the development of DNA-based photoelectrochemical devices.

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