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Distance Dependence of Photoinduced Electron Transfer in DNA

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The DNA helix is a useful molecular material for examining how the π stack mediates electron transfer. In recent years photoinduced electron transfers in DNA were investigated in many systems in which a donor and an acceptor randomly associate with DNA[1–6] or a donor and an acceptor are covalently linked at the terminus of DNA to avoid a multiplicity of the separation distance.[7, 8] The clearest evidence for mediation of electron transfer by the base pairs is the distance dependence; the efficiency of the reaction is represented by the β value. For a DNA–dye mixture, estimations of the β value have already been carried out.[3a,5b] Although a series of determinations of the β value is desirable, the lack of a method for introducing the dye precisely "into" the DNA helix makes it difficult to evaluate the distance dependence clearly. Here we report the distance dependence of electron transfer in a DNA helix using a novel system in which a chromophore is precisely fixed in DNA of defined sequence.

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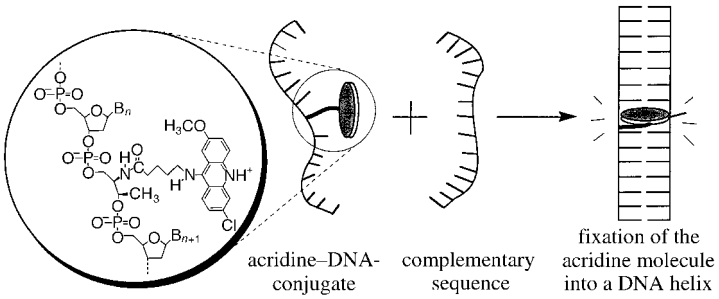
To anchor a chromophore at any desired site of a DNA and to suppress unfavorable thermal fluctuation around the chromophore, we adopted the strategy of introducing 9-amino-6-chloro-2-methoxyacridine (ACMA) at a defined internucleotide site of a DNA[9a, b] (Scheme 1). The thermal



Scheme 1. Schematic representation of the anchoring of ACMA at the desired site in a DNA helix.

stability of the helix and the fluorescence quantum yields from ACMA strongly depend on the chain length between the dye and the DNA as well as on the presence of a nucleobase at the opposite side of the acridine ring.[9c] A tetramethylene linker (Scheme 1) and adenosine at the opposite side of the ACMA unit are most suitable for fixing ACMA into a DNA helix. ACMA provides the strongest emission in the modified DNA, and the whole DNA structure shows particular thermal stability.[9c] The structure in which ACMA is intercalated between neighboring base pairs and the opposite adenosine is pushed out of the helix (extrahelical conformation) was confirmed with 2D-NMR spectroscopy.[10]

Using the corresponding acridine-phosphoramidite[9b] in a DNA synthesizer, we prepared the ACMA – DNA conjugate **I**, which consists of only adenosine and thymidine nucleotides, as well as conjugates **II** – **VIII**, which have a sequence similar to that of **I** and contain guanosine in the 5′ or 3′ directions at different distances (Table 1). To maintain the binding geometry between ACMA and the nucleobases, both sides of ACMA were fixed in purine bases (adenine or guanine). The absorption spectra of ACMA and the wavelengths of the fluorescence maxima (see below) were unchanged for a series of ACMA – DNA conjugates. Hence, the energy level of the ACMA units was identical for all ACMA – DNA conjugates.

We measured the fluorescence spectra of the ACMA units in duplexes **I** – **VIII** to investigate electron transfer through the DNA π stack under conditions in which all DNA molecules are sufficiently stable (0 °C).[9c] The fluorescence quantum yields of these duplexes are listed in Table 1, and the fluorescence spectra of **I** – **IV** are shown in Figure 1. Duplex **I**

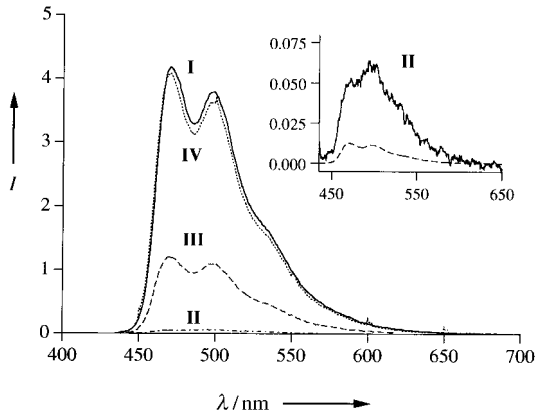


Figure 1. Fluorescence spectra of the ACMA – DNA conjugates **I** – **IV** (intensity *I* in arbitrary units). Inset: Enlarged section of the fluorescence spectrum of **II** (solid line). It can be divided into the SAS (dashed line) of the ACMA firmly fixed in a DNA helix and the nonintercalated (extrahelical) ACMA (see text and ref. [9c]).

Table 1. Fluorescence quantum yields Φ of the ACMA – DNA conjugates **I** – **VIII** and rates of electron transfer from guanine to an excited ACMA in a DNA helix.

Entry	Sample[a]	Direction (distance [Å])[b]	Φ[c]	k_{et} [s^{-1}][d]
I	5′-ATAATAA[Acr]AATTAAT-3′ 3′-TATTATT A TTAATTA-5′	–	0.655	–
II	5′-ATAATAA**G**[Acr]AATTAAT-3′ 3′-TATTATTC A TTAATTA-5′	5′ (3.4)	0.011 (0.002)[e]	1.4×10^{10}[e]
III	5′-ATAATAA**G**A[Acr]AATTAAT-3′ 3′-TATTATTCT A TTAATTA-5′	5′ (6.8)	0.195	1.0×10^{8}
IV	5′-ATAATAA**G**AA[Acr]AATTAAT-3′ 3′-TATTATTCTT A TTAATTA-5′	5′ (10.2)	0.622	2.3×10^{6}
V	5′-ATAATAA[Acr]**G**AATTAAT-3′ 3′-TATTATT A CTTAATTA-5′	3′ (3.4)	0.015 (0.003)[e]	9.5×10^{9}[e]
VI	5′-ATAATAA[Acr]A**G**AATTAAT-3′ 3′-TATTATT A TCTTAATTA-5′	3′ (6.8)	0.307	5.0×10^{7}
VII	5′-ATAATAA[Acr]AA**G**AATTAAT-3′ 3′-TATTATT A TTCTTAATTA-5′	3′ (10.2)	0.647	5.4×10^{5}
VIII	5′-ATAATAA**G**A[Acr]A**G**AATTAAT-3′ 3′-TATTATTCT A TCTTAATTA-5′	3′,5′ (6.8)	0.139	1.6×10^{8}

[a] Sample concentrations: 2.5 μM in 10 mM phosphate buffer (pH 7.2) with 150 mM NaCl. The samples were slowly annealed from 60 °C and kept overnight in the dark. [Acr] stands for the artificial base-free site connecting to ACMA through a tetramethylene linker (see Scheme 1). [b] Under the assumption that the distance between the base pairs is 3.4 Å (see ref. [24]). [c] Measured at 0 °C; excitation wavelength 427 nm. [d] Determined with Equation 2 (see text). [e] Calculated using only the emission from ACMA strictly fixed in a DNA helix (see text and inset of Figure 1).

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showed strong emission bands at 475 and 500 nm, which are attributed to the species-associated spectrum (SAS) of ACMA and reflect its rigid microenvironment.[9c, 11] Indeed, the decay in intensity was monoexponential with a lifetime of 22.8 ns, as measured by single-photon counting.[12] These emission bands cannot be seen for free ACMA in water or for any other ACMA – DNA conjugates;[9c] fast relaxation of the environment around the excited ACMA only gave an emission band at 500 nm.[9c, 11] These results indicate that the ACMA was precisely fixed with unique conformation in a DNA helix, and that the origin of electron transfer can be evaluated without fail.

Since the fluorescence of an ACMA unit is not quenched by a d(AT) base pair,[9c, 13, 14] **I** acts as an "inert matrix" for the photoexcited ACMA. On the other hand, guanine can quench the ACMA fluorescence,[13, 14] and this mechanism is assigned as an electron transfer [Eq. (1)]. It is impossible for an energy

$$[\mathrm{Acr}]^{+}\cdots \mathrm{dG} \xrightarrow{h\nu} [\mathrm{Acr}]^{+*}\cdots \mathrm{dG} \xrightarrow{k_{et}} [\mathrm{Acr}]\cdots \mathrm{dG}^{+} \quad (1)$$

transfer to occur because of the lack of spectral overlap; nucleobases can absorb at $\lambda < 300$ nm. It is clear from electrochemical,[15] theoretical,[16a] and chemical aspects[16b, c] that guanine is the most readily oxidizable residue.

In general, when two dyes (e. g. donor and acceptor) intercalate into a DNA helix, at least two base pairs must exist between them. Furthermore, the loading of the two chromophores in this short distance is sufficient to cause local disruption of the DNA structure of a rod-shape.[17] However, since guanine is used as an electron donor in the present study, there is no such limitation. The fluorescence intensity of duplexes **II** – **VII** clearly decreased as a function of the distance between ACMA and guanine (see Table 1 and Figure 1). For **II** and **V**, in which guanine is adjacent to ACMA, the fluorescence was strongly suppressed to about 2 % of that for **I**. The fluorescence spectra of **II** and **V**, however, showed incomplete SAS of ACMA (inset of Figure 1). These spectra contain the emission from unfixed ACMA, presumably because a very small portion of ACMA can be in an extrahelical conformation.[9c, 18] Although it is rather small, the SAS can be clearly seen.

Since ACMA and guanine are connected through many bonds (alkyl chain, amide bond, and phosphate), it is difficult to imagine that the strong quenching is due to electron transfer through these long bonds.[19, 20] Therefore, it is rational to consider that direct electron transfer occurs through the π stack between ACMA and guanine.[21] The rates of intramolecular electron transfer were evaluated with Equation (2).

$$k_{et} = \frac{1}{\tau_0}\left(\frac{\Phi_0}{\Phi} - 1\right) \quad (2)$$

Here, τ_0 is the excited-state lifetime in the absence of the quencher guanine (that is, for **I**), and Φ_0 and Φ are the fluorescence quantum yields of the ACMA – DNA conjugates in the absence (**I**)[12] or presence of guanine, respectively (**II** – **VIII**; see Table 1). The rates of electron transfer for **II** and **V** were calculated from the quantum yields of the SAS. The rates of electron transfer decrease with increasing distance between ACMA and guanine (see Figure 2). The slopes of the

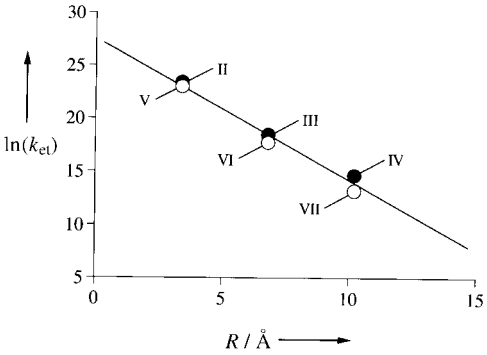

Figure 2. Correlation between the rate of electron transfer k_{et} and the separation distance R in a DNA helix for 5′ (●) and 3′ directions (○). The solid line represents the least-squares fit for the data points.

lines for the 5′ and 3′ directions are very similar, which indicates that the electronic coupling of these directions is practically identical.[26] It is noteworthy that the summation of the rates of electron transfer for **III** and **VI**, in which ACMA and guanine are separated with one d(AT) base pair, is $1.64 \times 10^8\ s^{-1}$. This value is almost identical to that of **VIII**, in which guanines exist in both sides of the ACMA with a separation of one d(AT) base pair. This result is consistent with selective intercalation of ACMA into the target position,[9c] and it can be concluded that the intercalation modes of ACMA – DNA conjugates are not perturbed by changes in base sequence near the ACMA unit.

The most common expression for the distance dependence of the rates of electron transfer can be derived from Equation (3).[19, 22] Here β stands for the effectiveness of the

$$k_{et} = A\, e^{-\beta R} \quad (3)$$

intervening base pairs between the coupling donor and acceptor, and R for the separation between them. When R is set equal to the distance along a B-DNA helix (i. e., 3.4 Å per base stacking;[17] see Figure 2), fitting the electron transfer data to Equation (3) gave a preexponential factor A of 1.20×10^{12} and a β value of 1.42 $Å^{-1}$. These values are comparable with those of protein matrices[19, 22, 23] and show that the π stack in DNA is a moderate mediator and not a special material for electron transfer. The β value is strikingly close to that recently predicted by theoretical calculations,[24] although the results of theoretical calculations are still in disagreement.[25] However, the β value for our system is larger than for electron transfer in other dye – DNA systems: 0.91 and 0.86 $Å^{-1}$ for transfer from photoexcited ethidium or acridine orange, respectively, to *N*,*N*′-dimethyl-2,7-diazapyrenium (DAP);[3a] 0.73 $Å^{-1}$ from Cu^{+} to oxidized ethidium.[5b] We account for the differences in these rates of electron transfer with the following: The donors of the systems are in an excited or high-energy state and are therefore better coupled to the corresponding high-energy bridging state in DNA.[26, 27] The electron transfer studied here occurs from the ground-state guanine with lower energy. This "hole transfer" is not well effectuated due to the high energy of the low-lying unoccupied orbital or LUMO of DNA that works as the transferring path. In fact, the reverse electron transfer for charge recombination from reduced DAP to oxidized ethidium gives

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$\beta = 1.49$ Å^{-1}.[3a] This value is practically identical to that observed in the present study. However, our data is quite different from that of Murphy et al. ($\beta = 0.2$ Å^{-1}),[8a] although the same mediator was used. This large discrepancy could not be explained with the above description.

In conclusion, we measured the long-range electron transfer through a DNA helix and its distance dependence by introducing a dye precisely into a DNA helix. Since these modified DNA are readily prepared by a DNA synthesizer, it is easy to introduce the second or third dyes into the DNA structure and to change the base sequence. We are now in the position to use this system to delineate the reorganization energy, the reverse electron transfer, and the effect of base stacking[16] in a DNA π frame.

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[12] **I**: $\tau = (22.8 \pm 0.1)$ ns (100%), $\chi^2 = 1.21$; **II**: 78 ps (86%); **III**: 5.55 ns (100%); **IV**: 22.6 ns (100%); **V**: 73 ps (91%); **VI** 9.84 ns (100%); **VII**: 22.3 ns (100%); **VIII**: 4.05 ns (100%). The measurements in Table 1 were carried out under the same conditions. We will report further detailed data for **II** – **VIII** in a forthcoming paper.
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Overcoming a Longstanding Challenge: X-Ray Structure of a $[Co_2(CO)_6]$-Complexed Propargyl Cation**

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The ability of mono- and polynuclear transition metal clusters to dramatically enhance the stability of neighboring carbocationic centers is well documented.[1–3] NMR spectroscopy has been widely used to structurally characterize homo- and heteronuclear metal complexes;[4] on the contrary, X-ray crystallography has been used to a lesser extent because of the thermal lability and low crystallinity of organometallic cations. Chronologically, ferrocenyl-[5] and bis(tricarbonylcyclobutadienyliron)-stabilized[6] methyl cations were characterized first, followed by a variety of organometallic species[7–11] with tetrahedral (or quasi tetrahedral) metal cores (Mo_2C_2,[7] $MoCoC_2$,[7a, 8, 11] W_2C_2,[9] and $CoFeC_2$[11]). The synthesis and structure of the propargyl cation stabilized by the $[Co_2(CO)_6]$ cluster have been thoroughly investigated.[12] NMR studies[13–15] revealed two modes of fluxionality, a low-energy *antara*-facial motion of the cationic center between metal atoms, and a high-energy rotation around the bond between the cationic center and the cluster (apical C – C

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