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Laser Flash Photolysis on Electron Transfer Reactions between 1,8-Dihydroxyanthraquinone with Adenine and Cytosine

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Electron transfer (ET) reactions between 1,8-dihydroxyanthraquinone (DHAQ) and two DNA bases, adenine (A) and cytosine (C), have been investigated in CH_3CN/H_2O solution with nanosecond time-resolved laser flash photolysis. After irradiation at 355 nm, the triplet DHAQ is produced via intersystem crossing and reacts with two nucleobases. ET processes for both reactions have been definitely identified, in which two bases play a significant role of electron donor. Based on the measured decay dynamics of various intermediates and the corresponding quenching rates, an initial ET process followed by a secondary proton-transfer reaction is suggested for both the overall reactions. By plotting the observed quenching rate against the concentration of two DNA bases, the bimolecular quenching rate constants are determined as 9.0×10^8 L/(mol·s) for the ^{3}DHAQ*+C reaction and 3.3×10^8 L/(mol·s) for the ^{3}DHAQ*+A reaction, respectively.

Key words: Electron transfer, Proton transfer, 1,8-dihydroxyanthraquinone, Laser flash photolysis, Adenine, Cytosine

I. INTRODUCTION

Electron transfer (ET) process is one of the most significant reactions in biochemical system. Under photoirradiation, the electron-rich nucleobases in DNA are usually primary targets of the excited photosensitizers, which can cause damage of DNA [1−3]. In the past several decades, ET from DNA bases to photosensitizer has attracted extensive interest.

As a common photosensitizer, quinone plays important roles in aerobic respiration and energy-producing photosynthesis. It can participate in transport of electrons in cell membrane as a high efficient electron donor. Numerous photochemical investigations have been performed on the related ET process between nucleobases and various quinones [3−5]. 2-methyl 1,4-naphtoquinone (MQ) and 9,10-anthraquinone (AQ) are two typical photosensitizers. Basu and co-workers performed a series of measurements on the ET and hydrogen abstraction (HA) reactions of these two photoexcited quinones with DNA bases [6−9]. Absorptions of various intermediates including radical pairs and radical cations were identified in transition absorption spectra. Through comparing absorption intensities of intermediates, ET from nucleobases to two quinones has been confirmed. Moreover, ET to MQ from A, C, thymine (T) and uracil (U) shows a consistent behavior with the oxidation-reduction potential (E_{ox}) order as usually expected as that an electron is more favorably transferred from purine than pyrimidine [9]. However, reactivity of these DNA bases to AQ did not follow this sequence. Difference in structural dimension is suggested to cause the alteration. In addition, an external magnetic field effect (MFE) was applied to clarify the radical pairs and cations [6]. Recently, ET and HA reactions between another quinone, tetrachloroquinone (TCBQ), and two pyrimidines (T and U) were investigated respectively [10].

Different from the quinones mentioned above, 1,8-dihydroxyanthraquinone (DHAQ) has a special characteristic of photoexcited intramolecular proton transfer [11, 12]. In the steady-state fluorescence measurement, duel fluorescence emissions were observed and attributed to two dynamic equilibrium structure, normal structure (N) and tautomeric proton-transferred state (T) [11]. The proton-transfer process occurs in a time scale of several tens of femtoseconds [11]. Pan *et al.* investigated the ET and HA reactions between triplet DHAQ and several anilines, *e.g.* triphenylamine (TPA), *N*,*N*-dimethylaniline (DMA), 3,5,*N*,*N*-tetramethylaniline (TMA), dimethyl-p-toluidine (DMT) and 4-dimethylaminobenzoic acid (DMABA) [13]. The quenching rates of triplet DHAQ by these anilines were found close to diffusion-controlled rate limit.

Very recently, we have performed a laser flash photolysis study on ET reactions between DHAQ and three

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pyrimidines. The dynamic decay measurement clarifies the similar photochemical behaviors of N and T structures of DHAQ when they react with pyrimidines under UV irradiation [14]. As far as we know, there is no investigation on ET and HA reactions between DHAQ and purines. According to the lower E_{ox} value, purines are expected to transfer electron to photoexcited DHAQ with a faster rate than pyrimidines. The ET reaction rates between MQ and bases, *e.g.* A and C, were indeed consistent with their E_{ox} values [9]. However, an opposite conclusion was observed for the reactions between AQ and pyrimidines due to the structural dimension of pyrimidines [9]. Therefore, to check difference of ET efficiencies between DHAQ and purines or pyrimidinesis is one of the major aims of the present investigation, since DHAQ has the bigger conjugated structure and steric hindrance than MQ and AQ. In the present work, we choose adenine and cytosine as typical purine and pyrimidine. By applying the nanosecond time-resolved laser flash photolysis, transition absorption spectra are measured for identification of all intermediates produced in ET and HA process between triplet DHAQ and A (or C). Subsequently, decay curves of various intermediates are recorded and fitted in order to obtain the corresponding reaction rates. Thus, ET and HA processes involved in the title reactions can be clarified respectively.

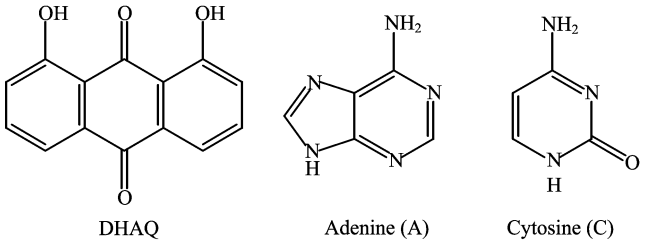
II. EXPERIMENTS

A. Equipment

A 500 W xenon lamp was employed as the analyzing source, while the pulsed excitation light was the third harmonic (355 nm) of a Q-switched Nd:YAG laser (PRO-190, Spectra Physics, repetition rate of 10 Hz). The pulsed duration time was 8 ns and the typical power per pulse of 355 nm light was kept as 6 mJ in experiment. The pulsed laser and xenon light beams crossed at right angle at a flow quartz cuvette with an optical path length of 10 mm. A monochromator equipped with a photomultiplier (CR131, Hamamatsu) was used to analyze the transmission light within a wavelength range of 450−800 nm. The resolution of the present spectral system was 1 nm. A dynamic decay curve of intermediate was averaged by multi-shots to improve the signal-to-noise ratio and recorded with an oscilloscope (TDS3052B, Tektronix). The transient absorption spectra were measured with a multi-shot average mode by scanning the monochromator via a Labview program based on GPIB communication.

B. Materials

1,8-dihydroxyanthraquinone (96%) were purchased from Dr.EhrenstorferGmbH Co. Nucleobases were bought from Sigma-Aldrich Co. and Fluorochem Limited Co., respectively. Both purities of A and C were 99% and used without any purification. Molecular structures of the reagents are shown in Scheme 1. The dominate solvents were acetonitrile of UV spectroscopic grade and triply distilled deionized water. For the mixture solvent, the 9:1 volume ratio of acetonitrile to water was chosen in order to efficiently dissolve all DHAQ and nucleobases, where ratio of water is kept as low as possible to avoid protonation of DHAQ in acidic solvent. In the following experiments, the concentration of DHAQ was kept as 0.5 mmol/L, and those of nucleobases were changed from 1 mmol/L to 5 mmol/L. All the solutions were deoxygenated by purging with high-purity argon (99.99%) for at least 20 min before measurements. The present laser flash photolysis experiments were performed at ambient room temperature (∼25 °C).



Scheme 1 Molecular structures of the reagents.

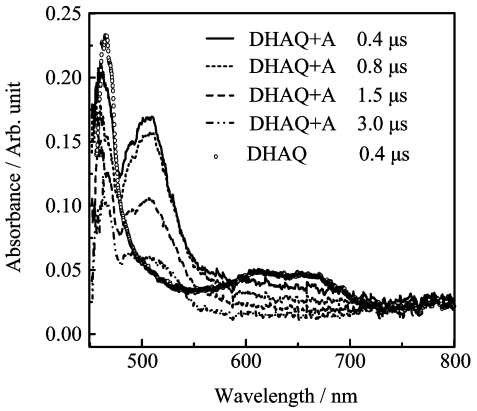


FIG. 1 Transient absorption spectra of DHAQ and A in CH_3CN/H_2O solvent at different time delay after photo-irradiation at 355 nm, where transition absorption spectrum at 0.4 μs delay after irradiation in the absence of bases is exhibited with circle symbols for comparison.

III. RESULTS AND DISCUSSION

A. Photochemical reaction between DHAQ and adenine in CH_3CN/H_2O

Figure 1 shows transient absorption spectra of DHAQ and A (5.0 mmol/L) in CH_3CN/H_2O at different delay times after photo-irradiation in a wavelength range of 450−800 nm. For comparison, that of DHAQ at 0.4 μs

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TABLE I Performance of production of BTX from bio-oil over different catalysts.

Quencher*	465 nm		510 nm	465 nm	
	k_1[a]/10^6s^{-1}	k_2[b]/10^6s^{-1}	k[c]/10^6s^{-1}	k_1[a]/10^6s^{-1}	k_2/10^6s^{-1}
H_2O	1.06±0.03		0.32±0.01	0.96±0.02	
Adenine	3.2±0.2	0.59±0.04	0.86±0.01	3.1±0.4	0.60±0.06[d]
Cytosine	4.6±0.3	0.21±0.01	0.54±0.01	4.6±0.9	0.59±0.04[e]

* Concentration of DHAQ is 0.5 mmol/L and all concentrations of nucleobases are kept as 5.0 mmol/L. k_1 and k_2 represent the rapid and slow quenching rates, respectively.
[a] Carrier is ^{3}DHAQ*.
[b] Carrier is $DHAQ_{+H}$.
[c] Carrier is $DHAQ^-$.
[d] Carrier is $A_{-H}/DHAQ_{+H}$.
[e] Carrier is C_{-H}.

delay time after photolysis in the absence of nucleobase is shown as well. Obviously, a sharp peak at 465 nm and a wide absorption band at ∼650 nm can be clearly observed in both cases, while a new absorption at 510 nm appears once adding adenine. Compared with those in the lack of bases at the same 0.4 μs delay time, both intensities of the 465 and 650 nm bands are reduced a little bit. Thus both bands at 465 and 650 nm are attributed to triplet-triplet absorption of ^{3}DHAQ*, which are quenched by adenine. The assignment can be verified by the additional experiments, in which both absorptions are quenched drastically in the presence of solvated oxygen. Moreover, the new band at 510 nm is expected to correlate to the product of the reaction between ^{3}DHAQ* and adenine.

Due to the low E_{ox}, adenine can play a role of electron donor in its reaction with ^{3}DHAQ* in aqueous solvent as Eq.(1),

$$^3\text{DHAQ}^* + \text{A} \rightarrow \text{DHAQ}^- + \text{A}^+ \qquad (1)$$

thus $DHAQ^-$ and A^+ are produced via electron transfer. Since the major absorption of A^+ is located at 360 nm [4, 8, 9, 15], the new absorption at 510 nm is contributed by $DHAQ^-$, which is generally consistent with the conclusion (∼540 nm) of Pan *et al.*'s experiment [13]. The blue-shift from 540 nm in pure CH_3CN is normally caused by polar interaction of aqueous solvent [16],

According to partial overlap of absorption by ^{3}DHAQ* and $DHAQ^-$ near 465 nm, decay of the absorption at 465 nm may involve complicated kinetics: quenching of ^{3}DHAQ* by adenine, decay of $DHAQ^-$, and/or other unknown decay kinetics. The assumptions can be confirmed by the quenching kinetic measurements. As shown in Fig.2, decay curves of intermediates at 460 and 510 nm present the different quenching rates and production sequences. The absorption intensity at 510 nm is gradually increased to the maximum later than that at 465 nm, indicating that it is indeed produced from the quenching of ^{3}DHAQ*. Thus an electron transfer from ^{3}DHAQ to A definitely occurs,

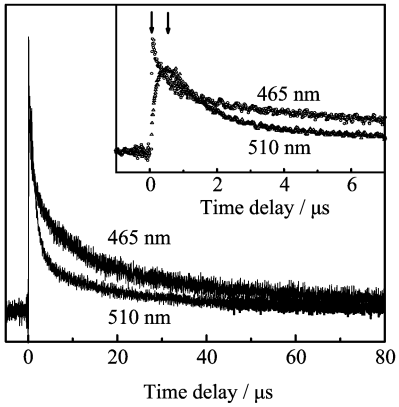

FIG. 2 The dynamic decay curves of reaction intermediates at 465 and 510 nm. The initial decay curves of both absorptions are shown in the insert panel, where the arrows show the delay to reach the maximum of absorption.

in which $DHAQ^-$ and A^+ are produced.

As shown in dynamic curves of Fig.2, the 465 nm absorption shows an initial rapid decay followed by an additional related slow quenching. By fitting the curve at 465 nm with a double exponential function of Eq.(2), the fast (k_1=3.2×10^6 s^{-1}) and slow (k_2=0.59×10^6 s^{-1}) quenching rates are obtained, respectively,

$$I(\lambda) = A_1(\lambda)\exp(-k_1 t) + A_2(\lambda)\exp(-k_2 t) \qquad (2)$$

where k_1 is the quenching rate of ^{3}DHAQ* and the carrier of the slow decay rate k_2 is tentatively expected to be the $DHAQ^-$. Similarly, both quenching rates can also be determined from fitting the decay curve at 650 nm and consistent with the data at 465 nm, which are 3.1×10^6 and 0.60×10^6 s^{-1}, respectively, as shown in Table I. Since the quenching rate of ^{3}DHAQ* is higher than that in the absence of DNA bases, A plays an efficient quencher for electron transfer to ^{3}DHAQ* indeed. It is worth noting that water can also quench ^{3}DHAQ* but the efficiency is much lower than that by A, as shown in Table I. Thus only the quenching by A

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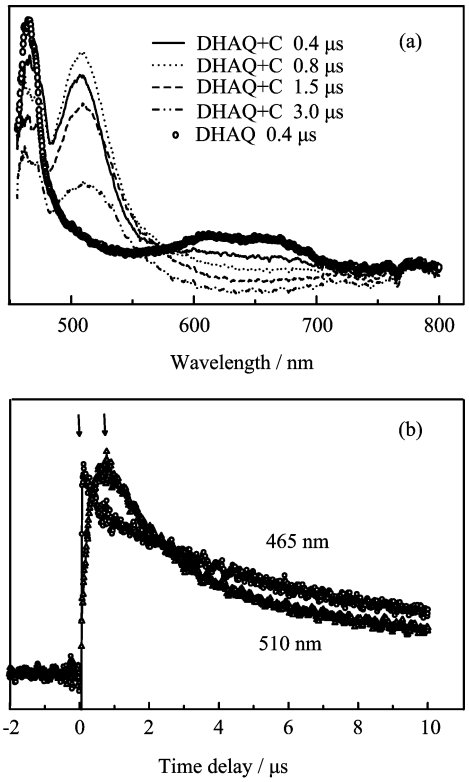

FIG. 3 (a) Transient absorption spectra of DHAQ and C in CH_3CN/H_2O solvent at different time delay after irradiation, where transition absorption spectrum at 0.4 μs delay after irradiation in the absence of bases is exhibited with circle symbols for comparison. (b) The dynamic decay curves of reaction intermediates at 465 and 510 nm are shown respectively.

is taken into account in the bimolecular quenching of ^{3}DHAQ* and A in CH_3CN/H_2O.

In fact, a subsequent proton transfer between $DHAQ^-$ and A^+ may occur in the present reaction system. Thus the slow dynamic mechanisms at 465 and 650 nm probably correspond to decay of the proton-transfer products, $DHAQ_{+H}$ and A_{-H} radicals respectively, as the Eq.(3).

$$DHAQ^- + A^+ \rightarrow DHAQ_{+H} + A_{-H} \quad (3)$$

As only $DHAQ^-$ contributes the absorption at 510 nm, the quenching rate in the above reaction (Eq.(3)) can be determined as 0.86×10^6 s^{-1} by fitting its curve with a pseudo first-order kinetic. The rate is faster than that in the absence of DNA bases as shown in Table I, implying that the proton transfer of Eq.(3) is really efficient.

B. Photochemical reaction between DHAQ with C

Similarly, the electron transfer between ^{3}DHAQ* and C (5.0 mmol/L) has been investigated with laser flash photolysis. The transient absorption spectra of DHAQ and C in CH_3CN/H_2O after photolysis at different time delay are shown in Fig.3(a). Three absorptions can still be found similar to the case of A, and thus the same assignments can be expected. As shown in Fig.3(b), the absorption at 510 nm is rapidly increased with delay time from 0.4 μs to 1.0 μs, and then slowly decreases. The intensities of the other absorptions at 465 and 650 nm are reduced gradually. Therefore, the bands at 465 and 650 nm are mainly attributed to ^{3}DHAQ*, while the strong absorption at 510 nm is coming from $DHAQ^-$.

Specially, absorption of C^+ is located at 480−500 nm in pure CH_3CN [4, 7, 17], and it is expected slightly blue-shifted in polar aqueous solvent. Thus the dynamic process of absorption at 465 nm is probably contaminated by its absorption tail, and a mixed dynamic process including decay of C^+ is initially expected at 465 nm. Moreover, an additional dynamic process similar to the reaction system of DHAQ and A, is also possible for both 465 and 650 nm bands, where an initial electron-transfer process is followed by a secondary proton-transfer reaction as the Eq.(4). $DHAQ_{+H}$ and C_{-H} radicals also have partial contributions in transition absorption spectra of Fig.3.

$$DHAQ^- + C^+ \rightarrow DHAQ_{+H} + C_{-H} \quad (4)$$

As mentioned above, the fast dynamics in decay of the 465 and 650 nm absorptions corresponds to quenching of ^{3}DHAQ*. Consequently, the quenching rate of ^{3}DHAQ* by C can be obtained by fitting these absorption with a double exponential function as the Eq.(2). In fact, at least fitting with triplet exponents has also been tried and the result shows two close slow decay rates, implying that only two main decay mechanisms are involved in the present system. Both the fast rates are determined as 4.6×10^6 s^{-1} at 465 and 650 nm, which is higher than that in the absence of nucleobases. Thus the quenching of ^{3}DHAQ* by C is considerably efficient. In addition, decay rate of $DHAQ^-$ is determined as 0.54×10^6 s^{-1} by fitting the absorption at 510 nm as a pseudo first-order kinetic, which is faster than the fitted slow rate of 0.21×10^6 s^{-1} at 465 nm. Thus the slow decay process observed at 465 nm is impossible to be coming from a proton-transfer of C^+, since both the decay rates of $DHAQ^-$ and C^+ should be close if the decay processes along the pathway of Eq.(4). Compared with k_2 values of 465 and 650 nm in Table I at the existence of A and C, the slow decays of absorptions at 465 and 650 nm are attributed to $DHAQ_{+H}$ radical and A_{-H} (or C_{-H}) radical produced from the proton transfer, respectively. Interestingly, the very near absorption wavelengths of $DHAQ_{+H}$ radical and ^{3}DHAQ* are consistent with the previous observation in reaction system including AQ and MQ [9].

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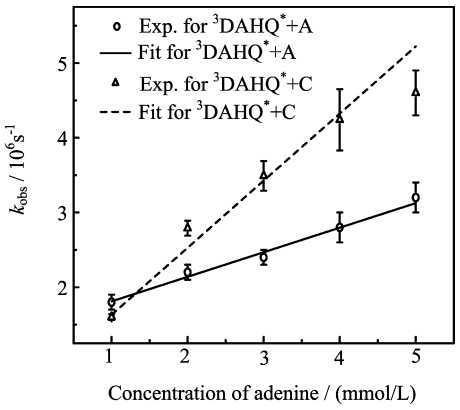

FIG. 4 Plots of the quenching rate $k_{\rm obs}$ of ^{3}DHAQ*at 465 nm *vs.* the concentrations of nucleobases A and C where the linear fittings are shown as well.

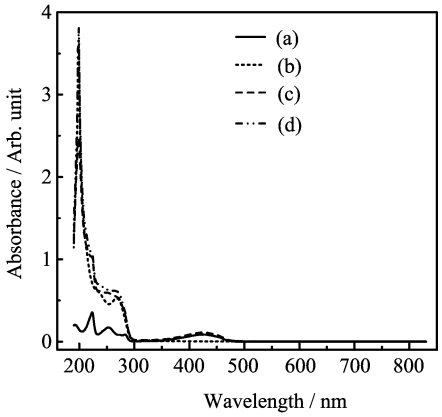

FIG. 5 Steady-state absorption spectra of (a) DHAQ, (b) C, (c) mixed solution of DHAQ and C. The spectrum of (d) is calculated as (a) plus (b) and plotted with a solid line.

C. Quenching rate constants of ^{3}DHAQ* by A and C

When increasing the concentration of nucleobases, the quenching rate of ^{3}DHAQ*is rapidly increased, and the lifetimes of ^{3}DHAQ* are shortened obviously. Based on the spectral assignments above, the quenching rate constant k_q of both ET reactions between ^{3}DHAQ* and these DNA bases are obtained via fitting the decay rate $k_{\rm obs}$ of absorption at 465 nm. Figure 4 shows the linear fitting of $k_{\rm obs}$ against the concentration of bases, A and C, respectively. The good linear correlations are found for both quenching reactions.

From the Eq.(5), the bimolecular quenching rate constant k_q

$$k_{\rm obs} = k_0 + k_q[\text{quencher}] \tag{5}$$

where $k_{\rm obs}$ is determined as the fast quenching rate in dynamic decay of absorption at 465 nm, k_0 and $k_{\rm q}$ are the decay rates of triplet state in the absence and presence of quencher, respectively. For the quenching of ^{3}DHAQ*, the rate constants k_q are determined from the slopes in Fig.4 as 3.3×10^8 L/(mol·s) for A and 9.0×10^8 L/(mol·s) for C, which is much lower than the theoretical diffusion-controlling rate limit in pure CH_3CN (1.94×10^{10} L/(mol·s)). According to steric hindrance between nitrogen heterocycle of bases and DHAQ, the distance between ^{3}DHAQ* and A (or C) is much longer in a solvent cage than that between ^{3}DHAQ* and anilines (*e.g.* TPA, DMA, TMA, DMT, and DMABA) in Pan *et al.*'s experiment [13], which causes ET rate dramatically decreased from diffusion-controlling rate limit.

It is worth emphasizing that quenching rates of ^{3}DHAQ* by C is faster than that by A, indicating that an electron is more favorable to be transferred from C to triplet DHAQ than that from A. It is contrary to their $E_{\rm ox}$ order, $E_{\rm ox}$(A)=1.9 V and $E_{\rm ox}$(C)=2.1 V [18−20]. Two potential factors may cause the contradiction. As indicated in our recent study of the ET efficiencies of three pyrimidines, C, T, and U [14], electron transfer from the $-NH_2$ substitute group is more favored than from the pyrimidine rings [14]. Therefore, DHAQ has an obvious steric hindrance when approaching the $-NH_2$ group of A (or C) due to its large structure of nitrogen heterocycle. In fact, A has much larger heterocycle than C as shown in Scheme 1, and hence more distinct steric hindrance exists to impede DHAQ approaching the $-NH_2$ group of A than that of C. Thus the present experiments show a typical example of influence on ET efficiency by dimensional structure.

Additionally, an unknown chemical reaction has been found between the ground state DHAQ and C when they are mixed in CH_3CN/H_2O solution. Figure 5 shows the steady-state absorption spectra of the mixture solution without any irradiation. The summed spectra of isolated DHAQ and C in CH_3CN/H_2O solution are plotted in Fig.5(d), while that of the mixed DHAQ and C in CH_3CN/H_2O solution is shown in Fig.5(c). Obviously, the absorption of C at ∼200 nm is reduced when mixing with DHAQ, and hence a reaction definitely occurs. It is very similar to the case of tetracyanoethylene (TCNE) and cytosine [21]. As Zhang *et al.* observed, an initial chemical reaction between TCNE and C caused the color of the mixed solution changed, indicating that a ground state complex was produced [21]. Therefore, the photo-induced ET reaction between ^{3}DHAQ* and cytosine is probably contaminated by the concomitant reactions of the complex under irradiation.

IV. CONCLUSION

The photochemical reaction dynamics of DHAQ with two DNA bases, adenine (A) and cytosine (C), has been investigated with a method of nanosecond time-resolved laser flash photolysis. Under 355 nm UV irradiation, transition absorption spectra are measured to clarify all

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intermediates produced in ET and HA process between triplet DHAQ and two nucleobases. Subsequently, dynamic decays of various intermediates are recorded and analyzed to estimate the reaction rates. An initial ET process followed by a secondary proton-transfer reaction is suggested for both the overall reactions. The absorptions at 465 and 650 nm are mainly attributed to ^{3}DHAQ*, while a new strong absorption at 510 nm is produced with adding A or C. The new band is assigned to DHAQ$^-$ anion.

By plotting the observed quenching rate against the concentration of two DNA bases, both bimolecular quenching rate constants k_q are determined as 9.0×10^8 L/(mol·s) for the ^{3}DHAQ*+C reaction and 3.3×10^8 L/(mol·s) for the ^{3}DHAQ*+A reaction, respectively. Moreover, influence of steric hindrance on ET efficiency by dimensional structure is clearly shown by comparing the ET rate constants of the title reaction systems involving A and C.

V. ACKNOWLEDGEMENTS

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