

# Electron transfer reactions between 1,8-dihydroxyanthraquinone and pyrimidines: A laser flash photolysis study



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## ABSTRACT

Electron transfer (ET) and hydrogen abstraction (HA) reactions between a photosensitizer, 1,8-dihydroxyanthraquinone (DHAQ), and three pyrimidines, cytosine (C), thymine (T) and uracil (U), have been investigated with a method of nanosecond time-resolved laser flash photolysis. Under photo-irradiation at 355 nm, both the triplet DHAQ of normal structure and tautomer structure are identified via intersystem crossing (ISC) in pure acetonitrile and  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solvent, and they have the very similar behavior in the reaction with nucleobases. With the aid of a complete spectral assignment, decay dynamics of various intermediates have been measured and discussed. A photo-induced ET process followed a HA reaction is confirmed for the reaction between DHAQ and C, while there is no distinct evidence for ET and HA between  $^3\text{DHAQ}^*$  and T (or U). Interestingly, the quenching rate of triplet DHAQ by three pyrimidines is contrary to the redox potential ( $E_{\text{ox}}$ ) order of these DNA bases. By comparing structural difference of two quinones and the ET efficiency from these pyrimidines to DHAQ with the case of menadione (MQ), we can infinitely demonstrate an alternation in trend in reactivity of these bases caused by substituent group on pyrimidine ring.

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## 1. Introduction

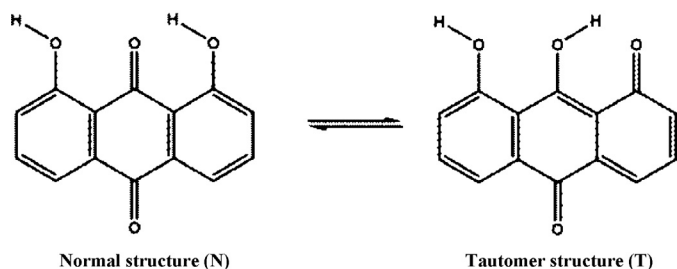
It is well known that electron transfer in the double chain of DNA can induce genetic information error reading and its damage [1–3]. Usually ET is initiated from an oxidation process in presence of oxidizing agents, e.g. photo-irradiation with various photosensitizers [1,4]. In DNA, the electron-rich nucleobases are primary targets of the excited photosensitizers. Thus ET from DNA bases to photosensitizer has attracted extensive interest. Among the nucleobases of guanine (G), adenine (A), cytosine (C), thymine (T) and uracil (U), G has the lowest  $E_{\text{ox}}$  and A is the second, while the  $E_{\text{ox}}$  values of pyrimidines follows a trend of  $\text{T} < \text{C} < \text{U}$  [5,6]. Generally, a lower value of  $E_{\text{ox}}$  of DNA bases supports a more favorable electron transfer. However, substituent group on pyrimidine or purine can affect ET efficiency, as well as the size of conjugated system.

As a common photosensitizer, quinone plays significant roles in aerobic respiration and energy-producing photosynthesis. They can participate in transport of electrons in cell membrane as an efficient electron acceptor. In the past decades, many photochemical investigations have been extensively performed on the related ET process between nucleobases and various quinones [2,7,8]. Photochemical reactions between tetrachloroquinone (TCBQ) and T

and U nucleobases were investigated [9]. Both ET and hydrogen abstraction (HA) were identified respectively in the photochemical system. 2-Methyl 1,4-naphthoquinone or more commonly menadione (MQ) and 9,10-anthraquinone (AQ) are also the popular quinone photosensitizers. Basu and the co-workers performed a series of measurements on their interaction with the DNA bases [10–13]. Radical pairs and radical cations produced from the ET and HA processes were observed. Interestingly, ET to MQ from A, C, T and U shows a consistent behavior with the  $E_{\text{ox}}$  order as usually expected as that an electron is more favorably transferred from purine to MQ than pyrimidine [13]. However, probability of ET from three pyrimidines to AQ did not follow their  $E_{\text{ox}}$  sequence. Therefore, the difference in structural dimension seems able to alter the trend in ET reactivity of DNA bases, as well as substituent group on pyrimidine. In addition, a special external magnetic field effect (MFE) was applied and discussed in interplay between spin dynamics and diffusion dynamics [10].

As a special quinone, 1,8-dihydroxyanthraquinone (DHAQ) is rather unique because an excited state intramolecular proton transfer (ESIPT) exists once being photoexcited as shown in Scheme 1 [14,15]. Dual fluorescence emissions were observed in the steady-state fluorescence measurement, and assigned as contribution from two dynamic equilibrium structure, normal structure (N) and tautomeric proton-transferred state (T) [14,15]. An ultrafast time-resolved fluorescence study suggested that the proton-transfer process occurs in a time scale of several tens of

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**Scheme 1.** Equilibrium of an excited state intramolecular proton transfer of DHAQ.

femtoseconds [14]. The quenching of the lowest triplet DHAQ by 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), were investigated by Pan et al. [16]. Evidences for ET and HA processes were presented, and the quenching rates were found close to diffusion-controlled rate limit and depending in some extent on the charge density of nitrogen atom of anilines.

To our knowledge, there is no investigation on ET and HA between DHAQ and nucleobases. Although only two hydroxyl moieties are added to AQ, DHAQ is expected to show some different photochemical behaviors in ET and HA dynamic processes with DNA bases. The initial dynamic equilibrium between normal structure and tautomer structure may slightly change its electron density of aromatic group, and thus the corresponding ET and HA rates are probably different. In the present work, we focus on the photochemical reaction dynamics of DHAQ with three pyrimidines, C, T and U, with a method of nanosecond time-resolved laser flash photolysis. Transient absorption spectra are measured for identification of all intermediates produced in ET and HA process between triplet DHAQ and nucleobases. Subsequently, decay curves of various intermediates are recorded and fitted in order to obtain the corresponding reaction rates. Thus, ET and HA processes are clarified respectively. By comparing the reaction rates of three pyrimidines, we will draw a conclusion how the substitute group and the conjugated size of pyrimidine affect ET efficiency. Moreover, alteration of the trend in reactivity of three pyrimidines from their  $E_{ox}$  sequence, is explained in a view of structural differences of DHAQ and AQ (or MQ) as well as their electron affinities (EA).

## 2. Experimental

### 2.1. Materials

DHAQ (96%) were purchased from Dr. Ehrenstorfer GmbH Co. Pyrimidines (99%) were bought from Sigma–Aldrich Co. and Fluorochem Limited Co., respectively. All pyrimidines were used without any purification. Molecular structures of the reagents are shown in Scheme 2. The concentration of DHAQ was  $0.5 \times 10^{-3} \text{ mol l}^{-1}$  and that of DNA bases were kept as

$5.0 \times 10^{-3} \text{ mol l}^{-1}$  in all spectral measurements. The dominate solvents were acetonitrile of high performance liquid chromatography reagent and triply distilled deionized water. For the mixture solvent, the 9:1 volume ratio of acetonitrile and water was chosen in order to dissolve both DHAQ and nucleobases efficiently, where ratio of water is kept low to avoid protonation of DHAQ in acidic solvent. All the solutions were deoxygenated by purging with high-purity argon (99.99%) for at least 20 minutes before measurements. The present laser flash photolysis experiments were performed at ambient room temperature ( $\sim 25^\circ \text{C}$ ).

### 2.2. Equipment

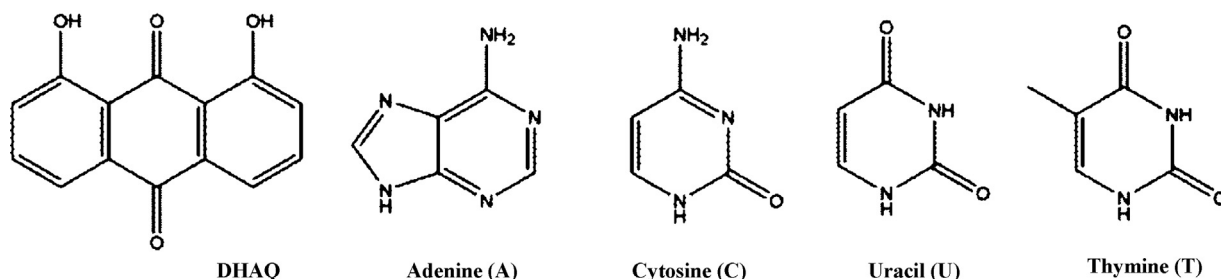
The pulsed excitation light was the third harmonic (355 nm) of a Q-switched Nd:YAG laser (PRO-190, Spectra Physics, repetition rate of 10 Hz). Its pulsed duration time is 8 ns and the typical power per pulse was kept as 4 mJ in experiment. A 500 W Xenon lamp was employed as the analyzing source. The pulsed laser and Xenon light beams perpendicularly passed through a flow quartz cuvette with an optical path length of 10 mm. A monochromator equipped with a photomultiplier (CR 131, Hamamatsu) at the exit slit was used to measure the transmission light after absorption within a wavelength range of 370–800 nm. The spectral resolution of the present system is 1 nm. A dynamic decay curve of intermediate was averaged by 512 shots to improve the signal-to-noise ratio and recorded with an oscilloscope (TDS3052B, Tektronix). During spectral measurements, the transient absorption spectra were recorded with a multi-shot average by scanning the monochromator via a Labview program based on GPIB communication.

## 3. Results and discussion

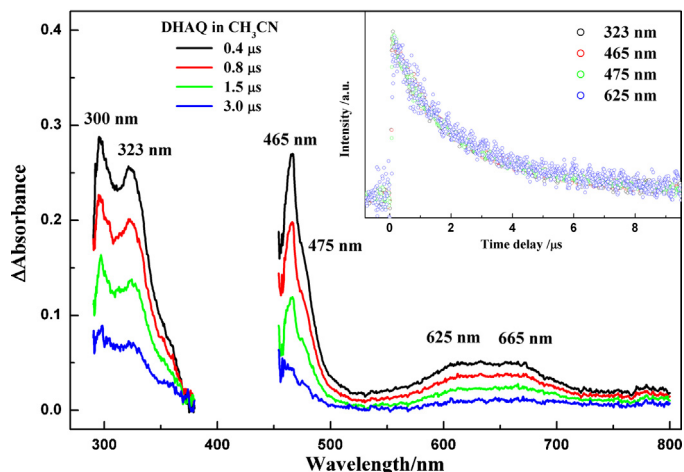
### 3.1. Transient absorption spectra of triplet DHAQ in different solvents

Fig. 1 shows transient absorption spectra of DHAQ in pure acetonitrile at different delay times. The spectral signals in a wavelength range of 370–455 nm are absent due to the strong  $S_1 \leftarrow S_0$  absorption of DHAQ molecule in ground state, and hence no transmission light can be detected. In Fig. 1 three dominate absorption bands at 285–370 nm, 455–500 nm and 580–710 nm, can be distinctly observed. Since only the photosensitizer of DHAQ and the inert solvent of  $\text{CH}_3\text{CN}$  exist in solution, all of three absorptions should be attributed to the unique intermediate,  $^3\text{DHAQ}^*$ , yielded via irradiation and ISC from  $S_1$  to  $T_1$  state. The assignment can be definitely verified by an additional experiment, in which the absorption intensities of all three bands are quenched drastically in the presence of solvated oxygen.

Interestingly, all the absorptions exhibit a doublet-peak profile, e.g. the maximums are located at 300 and 320 nm for the blue band, the 465 and 475 nm peaks are observed for the middle, the 625 and 665 nm maximums are discriminated for the red absorption.



**Scheme 2.** Molecular geometries of DHAQ and four DNA bases.



**Fig. 1.** Transient absorption spectra of DHAQ in pure  $\text{CH}_3\text{CN}$  at different time delay after laser photolysis. The dynamic decay curves of reaction intermediates at 323, 465, 475 and 625 nm are shown respectively in the insert panel as well.

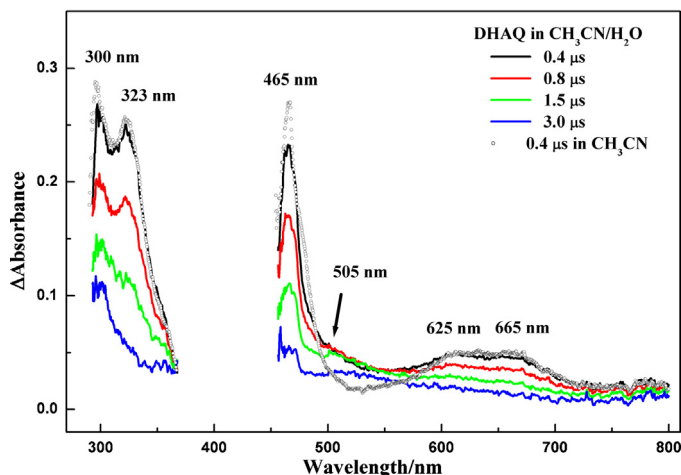
As the previous investigations suggested in Scheme 1 [14,15,17], ESIP would cause a dynamic equilibrium between two structures, normal structure (N) and tautomer structure (T), of the photoexcited DHAQ molecule. Both excited singlet N and T can individually decay to the corresponding triplet states via ISC, which contribute the splitting of each absorption band in Fig. 1. Additionally, the blue absorption component is attributed to triplet–triplet absorption of N, and the red component is contributed by T [14,15].

In order to further verify the spectral assignment, the dynamic decay curves of the transient species at 300, 323, 465, 475, 625 and 665 nm were measured respectively. The typical curves are plotted in the insert panel of Fig. 1 as well. All the quenching rates are obtained by least square fitting of curves with single exponential function and summarized in Table 1, indicating that decay of  $^3\text{DHAQ}^*$  is a pseudo first-order kinetic. Obviously, all the quenching rates are close to  $1 \times 10^6 \text{ s}^{-1}$  in acetonitrile, which generally agrees with the Pan et al.'s experimental data [16]. The faster rate is due to the higher concentration of DHAQ in present experiment than Pan et al.'s measurement. Thus all absorptions in Fig. 1 are definitely originated from the same transient intermediate of  $^3\text{DHAQ}^*$ . Since triplet DHAQ with the structure of N or T has the very close quenching rate, both of them are noted as  $^3\text{DHAQ}^*$  in the photochemical reactions. In the following section, only absorption spectra in a wavelength range of 450–800 nm are shown, since the major intermediates produced in photochemical reactions between  $^3\text{DHAQ}^*$  and electron donors mainly absorb the visible photon.

To investigate the photochemical reaction between DHAQ and nucleobases, the mixed solvent involving water is necessary because the solubility of DNA bases in  $\text{CH}_3\text{CN}$  is too low. Due to the lower electron density of carbonyl group, triplet DHAQ is electrophile in the mixture solution. Thus electron transfer to  $^3\text{DHAQ}^*$  could occur from an electron donor, e.g. nucleobases and water, as shown in Eq. (1).



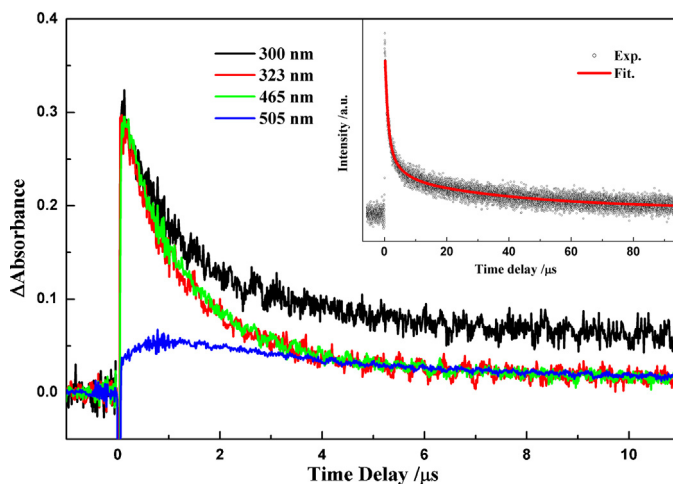
Fig. 2 shows the transient absorption spectra of DHAQ in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  at different time decays. There is negligible wavelength-shift for all the absorptions although the solvent polarity is increased. A complete spectral assignment of Fig. 2 can be confessedly obtained with the aid of those in Fig. 1. Since  $\text{DHAQ}^-$  anion does not absorb the photon at 323 nm, the band is definitely attributed by  $^3\text{DHAQ}^*$ . The triplet DHAQ can also contribute the absorptions at 465 nm, 625 nm and 665 nm. Significantly, a new wide absorption at 505 nm is observed and partially overlaps with



**Fig. 2.** Transient absorption spectra of DHAQ in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solvent at different time delay after laser photolysis at 355 nm, where that of DHAQ in pure  $\text{CH}_3\text{CN}$  at 0.4  $\mu\text{s}$  delay after irradiation is exhibited with a dotted line for comparison.

the original shoulder at 475 nm in Fig. 1, which causes it invisible in Fig. 2.

Compared with Fig. 1, all the absorption intensities are reduced even at the same delay time, implying that  $^3\text{DHAQ}^*$  is quenched by water indeed. Based on Eq. (1),  $\text{DHAQ}^-$  anion is expected as a product of electron transfer and may contribute the new absorption at 505 nm, which is generally consistent with the absorption at 540 nm observed in Pan et al.'s experiment [16]. The blue-shift from 540 nm in pure  $\text{CH}_3\text{CN}$  is normally caused by polar interaction of aqueous solvent [18]. According to partial overlap of absorption by  $^3\text{DHAQ}^*$  and  $\text{DHAQ}^-$  anion, decay kinetics of the absorption at 300 nm may involve two components: quenching of  $^3\text{DHAQ}^*$  by  $\text{H}_2\text{O}$  and decay of  $\text{DHAQ}^-$  anion. The assumptions can be confirmed by a quenching kinetic measurement. As shown in dynamic curves of Fig. 3, both normalized curves of the 323 and 465 nm bands are almost the same, while the 300 nm absorption shows an initial rapid decay followed by an additional related slow quenching. Moreover, the absorption at 505 nm is gradually increased to the maximum far later than the others, indicating that its carrier is the initial quenching product of  $^3\text{DHAQ}^*$  indeed. By fitting the curve at 300 nm with a double exponential function of formula (2), the fast



**Fig. 3.** The dynamic decay curves of reaction intermediates at 300 nm, 323 nm, 465 nm and 505 nm. The experimental and fitted decay curves of absorption at 300 nm are shown in the insert panel.

**Table 1**  
Absorption wavelengths ( $\lambda$ ) and quenching rates ( $k$ ) of intermediates after irradiation of DHAQ in different solvents.

Band	I	II	III	IV	V	VI
CH <sub>3</sub> CN						
$\lambda$ (nm)	300	323	465	475	625	665
$k$ ( $\times 10^6$ s <sup>-1</sup> ) <sup>a</sup>	0.90 $\pm$ 0.07	1.01 $\pm$ 0.07	1.03 $\pm$ 0.06	1.04 $\pm$ 0.05	1.0 $\pm$ 0.3	1.0 $\pm$ 0.3
Carrier	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*
	(N)	(T)	(N)	(T)	(N)	(T)
CH <sub>3</sub> CN/H <sub>2</sub> O						
$\lambda$ (nm)	300	323	465	505	625	665
$k_1$ ( $\times 10^6$ s <sup>-1</sup> )	1.06 $\pm$ 0.08	1.05 $\pm$ 0.04	1.06 $\pm$ 0.03	0.32 $\pm$ 0.01	0.96 $\pm$ 0.02	0.89 $\pm$ 0.03
Carrier 1	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*	DHAQ <sup>-</sup>	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*
$k_2$ ( $\times 10^6$ s <sup>-1</sup> )	0.23 $\pm$ 0.02					
Carrier 2	DHAQ <sup>-</sup>					

<sup>a</sup> The quenching rate of <sup>3</sup>DHAQ\* in CH<sub>3</sub>CN was determined as  $2.0 \times 10^5$  s<sup>-1</sup> at 480 nm in Ref. [16], where the concentration of DHAQ was 0.36 mM.

( $k_1 = 1.06 \times 10^6$  s<sup>-1</sup>) and slow ( $k_2 = 0.23 \times 10^6$  s<sup>-1</sup>) quenching rates are obtained, respectively,

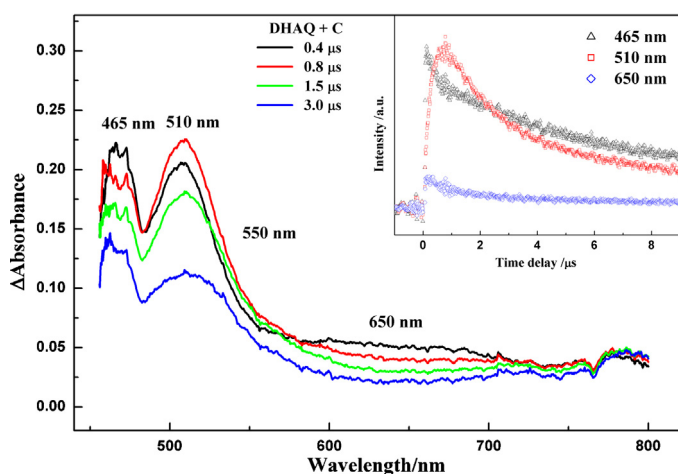
$$I(\lambda) = A_1(\lambda)e^{-k_1 t} + A_2(\lambda)e^{-k_2 t} \quad (2)$$

where  $k_1$  is the quenching rate of <sup>3</sup>DHAQ\* and  $k_2$  is the slow decay rate of DHAQ<sup>-</sup> anion.

In addition, the quenching rate at 505 nm ( $0.32 \times 10^6$  s<sup>-1</sup>) is obtained by fitting as a pseudo first-order kinetic, which is close to the fitted slow decay rate at 300 nm. Therefore it is also attributed by DHAQ<sup>-</sup> anion as we expected. All the obtained quenching rates of the intermediates are listed in Table 1 as well. Obviously, water plays a role of the electron donor in Eq. (1), although the quenching is not very efficient.

### 3.2. Photochemical reaction between triplet DHAQ with cytosine

Due to the lower  $E_{ox}$  than water, nucleobase plays an efficient role of electron donor in its reaction with <sup>3</sup>DHAQ\* in aqueous solvent as Eq. (1). Fig. 4 shows the transient absorption spectra of DHAQ and C in CH<sub>3</sub>CN/H<sub>2</sub>O after irradiation at different time delay. Compared with Fig. 2, no additional absorption is observed. Thus based on the conclusions mentioned above, a complete assignment can be obtained consequently. The bands at 465 nm and 650 nm are mainly attributed to <sup>3</sup>DHAQ\*, while the strong absorption at 510 nm is coming from DHAQ<sup>-</sup> anion. Moreover as shown in the inert panel of Fig. 4, decay curves of intermediates at 465, 510 and 650 nm present the different quenching rates and production sequence. The intensities of the other absorptions at 465 and 650 nm are reduced gradually. The absorption at 510 nm is rapidly



**Fig. 4.** Transient absorption spectra of DHAQ and C in CH<sub>3</sub>CN/H<sub>2</sub>O solvent at different time delay after irradiation. The dynamic decay curves of reaction intermediates at 465 nm, 510 nm and 650 nm are shown respectively in the insert panel.

increased with delay time from 0.4  $\mu$ s to 1.0  $\mu$ s, and then slowly decreases, indicating that it is produced from the quenching of <sup>3</sup>DHAQ\*. Thus an electron transfer from <sup>3</sup>DHAQ to C definitely occurs, in which DHAQ<sup>-</sup> anion and cytosine radical cation (C<sup>+</sup>) are produced.

More complicatedly, absorption of C<sup>+</sup> is located at 480–500 nm in pure CH<sub>3</sub>CN [7,11,19], and it will be 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 mechanism is initially assumed at 465 nm as quenching of <sup>3</sup>DHAQ\* by C and decay of C<sup>+</sup> cation. From fitting of the dynamic curves with a double exponential function as the formula (2), reaction rates between <sup>3</sup>DHAQ\* and C is derived and listed in Table 2. Both quenching rates of triplet DHAQ by C are estimated as  $4.6 \times 10^6$  s<sup>-1</sup> at 465 nm and 650 nm, which is higher than that in the absence of DNA bases. Thus the quenching of <sup>3</sup>DHAQ\* by C is considerably efficient, and C plays a high-efficiency quencher via electron transfer. Interestingly, both the absorptions at 465 nm and 650 nm show an initial rapid decay followed by an additional related slow quenching. The slow quenching rates are determined as  $0.21 \times 10^6$  s<sup>-1</sup> (at 465 nm) and  $0.59 \times 10^6$  s<sup>-1</sup> (at 650 nm) respectively. Since a subsequent proton transfer between DHAQ<sup>-</sup> anion and C<sup>+</sup> cation may occur in the present photochemical reaction system, the slow dynamic mechanisms at 465 nm and 650 nm also probably correspond to decay of the proton-transfer products, DHAQ<sub>+H</sub> and C<sub>-H</sub> radicals respectively, as the following equation.



DHAQ<sub>+H</sub> and C<sub>-H</sub> radicals possibly have contribution for both the bands at 465 nm and 650 nm.

**Table 2**  
Quenching rates ( $\times 10^6$  s<sup>-1</sup>) of intermediates by various electron donors in CH<sub>3</sub>CN/H<sub>2</sub>O.

Quencher <sup>a,b</sup>	H <sub>2</sub> O	C	T	U
465 nm				
$k_1$	1.06 $\pm$ 0.03	4.6 $\pm$ 0.3	1.1 $\pm$ 0.2	1.1 $\pm$ 0.1
Carrier	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*
$k_2$	–	0.21 $\pm$ 0.01	–	–
Carrier		DHAQ <sub>+H</sub>		
510 nm				
$k$	0.32 $\pm$ 0.01 <sup>c</sup>	0.54 $\pm$ 0.01	0.39 $\pm$ 0.01	0.47 $\pm$ 0.01
Carrier	DHAQ <sup>-</sup>	DHAQ <sup>-</sup>	DHAQ <sup>-</sup>	DHAQ <sup>-</sup>
650 nm				
$k_1$	0.96 $\pm$ 0.02	4.6 $\pm$ 0.9	1.1 $\pm$ 0.1	0.99 $\pm$ 0.02
Carrier	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*	<sup>3</sup> DHAQ*
$k_2$	–	0.59 $\pm$ 0.04	–	–
Carrier		C <sub>-H</sub>		

<sup>a</sup> All concentrations of nucleobases are kept as  $5.0 \times 10^{-3}$  mol l<sup>-1</sup>.

<sup>b</sup>  $k_1$  and  $k_2$  correspond to the rapid and slow quenching rates respectively.

<sup>c</sup> The value is determined by fitting the absorption at 505 nm as mentioned in Section 3.1.

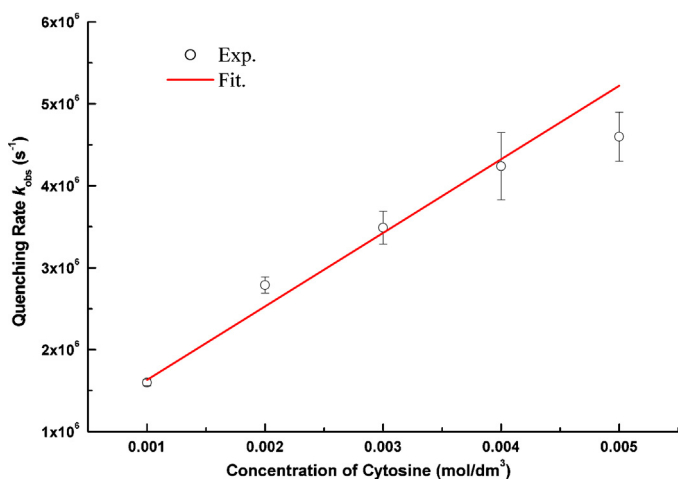


Fig. 5. Plot of the quenching rate  $k_{\text{obs}}$  of  $^3\text{DHAQ}^*$  at 465 nm vs. the concentration of cytosine.

As only  $\text{DHAQ}^-$  anion contributes the absorption at 510 nm, the quenching rate of Eq. (3) can be determined as  $0.54 \times 10^6 \text{ s}^{-1}$  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 2, implying that the proton transfer of Eq. (3) is really efficient. In addition, the decay rate of  $\text{DHAQ}^-$  anion at 510 nm is faster than the derived slow rate of  $0.21 \times 10^6 \text{ s}^{-1}$  (at 465 nm). Thus the slow decay process observed at 465 nm seems unreasonable to mainly come from a proton-transfer of  $\text{C}^+$  cation, since both the decay rates of  $\text{DHAQ}^-$  anion and  $\text{C}^+$  cation should be close as Eq. (3). As suggested in previous experiments [13], the near absorption wavelengths were observed in reaction system including AQ and MQ for the H-added radical and the triplet, e.g.  $\text{AQ}_{\text{+H}}$  (370 nm) and  $^3\text{AQ}^*$  (360 nm),  $\text{MQ}_{\text{+H}}$  (370 nm) and  $^3\text{MQ}^*$  (370 nm). Thus  $\text{DHAQ}_{\text{+H}}$  radical is reasonable to correlate to the slow decays of absorptions at 465 nm, and that at 650 nm is attributed to  $\text{C}_{\text{-H}}$  radical.

Based on the spectral and dynamic assignments above, the quenching rate constant  $k_q$  of reaction between  $^3\text{DHAQ}^*$  and C can be obtained by measuring the decay rate  $k_{\text{obs}}$  of absorption at 465 nm. It is worth noting that water can also quench  $^3\text{DHAQ}^*$  as discussed in Section 3.1, however the efficiency is much lower than that by C. Thus only the quenching by C is taken into account in the bimolecular quenching of  $^3\text{DHAQ}^*$  and C in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ . With the concentration of C increasing, the lifetimes of  $^3\text{DHAQ}^*$  is shortened obviously. As shown in Eq. (4), the bimolecular quenching rate constant  $k_q$  can be derived from plotting  $k_{\text{obs}}$  against the concentration of C.

$$k_{\text{obs}} = k_0 + k_q[\text{quencher}] \quad (4)$$

where  $k_{\text{obs}}$  is determined as the fast quenching rate in dynamic decay of absorption at 465 nm,  $k_0$  and  $k_q$  are the decay rates of triplet state in the absence and presence of quencher, respectively. The rate constant  $k_q$  is determined as  $8.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  from the slope of Fig. 5, which is much lower than the theoretical diffusion-controlling rate limit in pure  $\text{CH}_3\text{CN}$  ( $1.94 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). As Pan et al. observed, the experimental rate constant of  $^3\text{DHAQ}^*$  quenched by anilines was very close to the limit. Therefore, steric hindrance between DHAQ and pyridimine ring is apparent, which causes the distant between  $^3\text{DHAQ}^*$  and C much longer in the solvent cage than that with anilines. Thus the ET rate from pyridimine ring to DHAQ is decreased from diffusion-controlling rate limit. In addition, the lifetime ( $\tau_0$ ) of  $^3\text{DHAQ}^*$  can be determined as  $1.0 \mu\text{s}$  in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  from the intercept of Fig. 5 ( $k_0 = 1/\tau_0$ ).

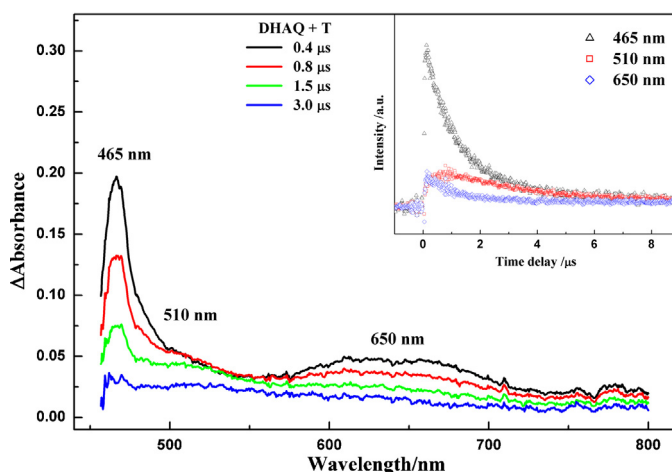


Fig. 6. Transient absorption spectra of DHAQ and T in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solvent at different time delay after photolysis. The dynamic decay curves of reaction intermediates at 465 nm, 510 nm and 650 nm are shown respectively in the insert panel.

### 3.3. Photochemical reactions between triplet DHAQ with thymine and uracil

Figs. 6 and 7 show the transient absorption spectra of DHAQ and T (or U) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  at different decay time after irradiation. Obviously, both of them are very similar to that in Fig. 2, and all the absorptions show negligible wavelength shift and change of intensity. As mentioned above, the 465 nm and 650 nm bands are attributed to  $^3\text{DHAQ}^*$ , while the shoulder absorption at 510 nm is assigned as the contribution of  $\text{DHAQ}^-$  anion.

By fitting the dynamic curves as a pseudo first-order kinetic, the quenching rates of all intermediates can be obtained and summarized in Table 2 as well. Both the quenching rates of  $^3\text{DHAQ}^*$  derived from decay of absorptions at 465 nm and 650 nm are as the same as  $1.1 \times 10^6 \text{ s}^{-1}$  by T, while that in presence of U is  $1.0 \times 10^6 \text{ s}^{-1}$ . Compared with it in the absence of DNA bases, the rates are almost the same and hence the quenching of triplet DHAQ by T or U is not efficient as the electron transfer reaction including C. Interestingly, the decay rates of  $\text{DHAQ}^-$  anion are  $0.39 \times 10^6 \text{ s}^{-1}$  (in the solution of T) and  $0.47 \times 10^6 \text{ s}^{-1}$  (in U), respectively, which are slightly faster than that in the absence of nucleobases. Therefore, a secondary reaction between  $\text{DHAQ}^-$  anion and DNA base cation occurs following the initial electron transfer in the present solution after photolysis. The

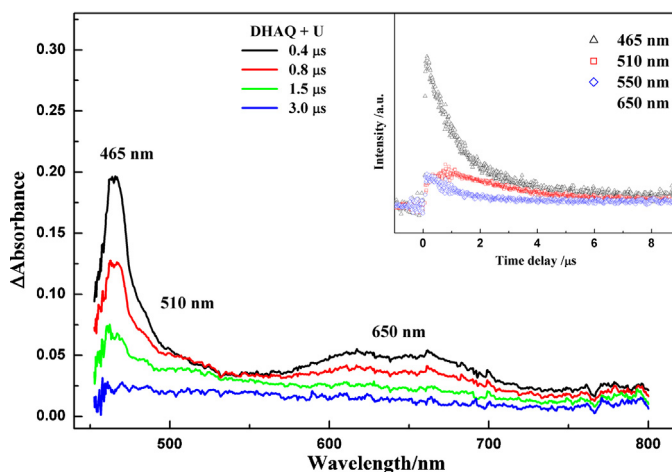


Fig. 7. Transient absorption spectra of DHAQ and U in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solvent at different time delay after photolysis. The dynamic decay curves of reaction intermediates at 465 nm, 510 nm and 650 nm are shown respectively in the insert panel.

proton transfer process responds to decay mechanism of DHAQ<sup>-</sup> anion.

As shown in Scheme 2, three bases of C, U and T have very similar molecular structure. The  $E_{ox}$  values of them are following an order T < C < U [20,21,22], and hence reaction probability of an electron transfer from them to <sup>3</sup>DHAQ\* should be generally in the just opposite sequence. However, the present observation is inconsistent that an electron transfer from C is very efficient but those from T and/or U are too weak to be identified. As shown in Scheme 2, a -NH<sub>2</sub> group is connected to the pyrimidine ring in C while for T and U the second substitute group is also the carbonyl. It is well-known that lone pair of electrons in amino nitrogen can increase electron density of the ring via *p*- $\pi$  conjugation, while the keto oxygen abstracts electrons from the pyrimidine ring and reduces its density [23]. Additionally lone pair of electrons of amino nitrogen is easier to be transferred to electron acceptor [16]. Thus the available electrons provided by C are expected much more than those from T and U. Due to its higher EA, DHAQ can draw any electrons from all possible positions of pyrimidines. Therefore, C shows the better participant ability as electron donor than T and U, and moreover the -NH<sub>2</sub> moiety is more favorable to be transferred than pyrimidine ring. Actually, similar phenomena have been observed in the reaction system of AQ and three pyrimidines [13]. As suggested by Bose and Basu [13], the high EA of electron acceptor, e.g. AQ or DHAQ, can alter the trend in reactivity of these bases from their  $E_{ox}$  sequence. In summary, structural differences and EA values of quinones have a direct influence on their photochemical behavior.

In addition, U and T was found to be a better H donor than C with AQ [13]. However, a direct hydrogen abstraction has not been observed in the present reaction system. Both transient absorption spectra and decay dynamics do not provide any distinct evidences for HA between DHAQ and three pyrimidines. As mentioned above, a secondary HA reaction between DHAQ<sup>-</sup> anion and pyrimidine cation occurs following the initial electron transfer. The overall reaction seems like a HA process via the ET and proton transfer. The difference of HA from pyrimidines to AQ and DHAQ can also be explained from a view of steric hindrance. Two additional hydroxyl moieties can hinder the carbonyl from abstracting hydrogen from a donor. Moreover, the ESIPT dynamic equilibrium can reduce the HA ability of DHAQ in normal structure.

#### 4. Conclusion

ET and HA reactions between DHAQ and three pyrimidines have been investigated with a method of nanosecond time-resolved laser flash photolysis. Under photo-irradiation at 355 nm, transient absorption spectra of DHAQ in pure acetonitrile and CH<sub>3</sub>CN/H<sub>2</sub>O have been recorded at different delay times. A typical double peak splitting is observed for each dominate absorption band, which is attributed to the triplet DHAQ of normal structure and tautomer structure, respectively. The subsequent dynamic measurements indicate the similar photochemical behaviors of N and T structures.

When pyrimidines are added into the solution, ET reactions have been occurred between <sup>3</sup>DHAQ\* and bases. Although transient absorption spectra are similar, the dynamic decays of the intermediates are distinctly changed. In the reaction system involving C, an initial rapid decay followed by an additional related slow quenching has been found for decay dynamics of the absorptions at 465 nm and 650 nm. The corresponding rates are obtained: the faster quenching rate of triplet DHAQ by C are determined as  $4.6 \times 10^6 \text{ s}^{-1}$  while the slow quenching rates are  $0.21 \times 10^6 \text{ s}^{-1}$  (at 465 nm) and  $0.59 \times 10^6 \text{ s}^{-1}$  (at 650 nm) respectively. DHAQ<sub>+H</sub> and C<sub>-H</sub> radicals are suggested to respond for the slow decay dynamics at 465 nm and 650 nm. By plotting the observed quenching rate at 465 nm against the concentration of cytosine, a bimolecular quenching rate

constant  $k_q$  is determined as  $8.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the reaction between <sup>3</sup>DHAQ\* and C.

All the bands show negligible wavelength shift and change of intensity in transition absorption spectra of DHAQ and T (or U) after irradiation at 355 nm. The decay dynamic measurements show that a weak ET process probably happens between triplet DHAQ and T (or U) with the quenching rates of  $1.1 \times 10^6 \text{ s}^{-1}$  by T and  $1.0 \times 10^6 \text{ s}^{-1}$  by U. A secondary proton-transfer reaction between DHAQ<sup>-</sup> anion and DNA base cations are identified as well. However, no distinct evidences are found for direct HA between <sup>3</sup>DHAQ\* and these two bases, which is probably due to steric hindrance of hydroxyl moieties.

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#### References

- [1] C.J. Burrows, J.G. Muller, Oxidative nucleobase modifications leading to strand scission, *Chemical Reviews* 98 (1998) 1109–1151.
- [2] D.T. Breslin, G.B. Schuster, Anthraquinone photoreactions: mechanisms for GG-selective and nonselective cleavage of double-stranded DNA, *Journal of the American Chemical Society* 118 (1996) 2311–2319.
- [3] D. Ly, Y.Z. Kan, B. Armitage, G.B. Schuster, Cleavage of DNA by irradiation of substituted anthraquinones: intercalation promotes electron transfer and efficient reaction at GG steps, *Journal of the American Chemical Society* 118 (1996) 8747–8748.
- [4] S. Steenken, Purine-bases, nucleosides, and nucleotides – aqueous-solution redox chemistry and transformation reactions of their radical cations and e<sup>-</sup> and OH adducts, *Chemical Reviews* 89 (1989) 503–520.
- [5] C.A.M. Seidel, A. Schulz, M.H.M. Sauer, Nucleobase-specific quenching of fluorescent dyes. 1. Nucleobase one-electron redox potentials and their correlation with static and dynamic quenching efficiencies, *The Journal of Physical Chemistry* 100 (1996) 5541–5553.
- [6] S. Steenken, S.V. Jovanovic, How easily oxidizable is DNA? One-electron reduction potentials of adenosine and guanosine radicals in aqueous solution, *Journal of the American Chemical Society* 119 (1997) 617–618.
- [7] J.H. Ma, W.Z. Lin, W.F. Wang, Z.H. Han, S.D. Yao, N.Y. Lin, Triplet state mechanism for electron transfer oxidation of DNA, *Journal of Photochemistry and Photobiology B* 57 (2000) 76–81.
- [8] J.A. Hartley, K. Reszka, J.W. Lown, Photosensitization by antitumor agents. 7. Correlation between anthracenedione-photosensitized DNA damage, NADH oxidation and oxygen consumption following visible-light illumination, *Photochemistry and Photobiology* 48 (1988) 19–25.
- [9] K.H. Liu, L.D. Wu, X.R. Zou, W. Yang, Q. Du, H.M. Su, Photochemical hydrogen abstraction and electron transfer reactions of tetrachlorobenzoquinone with pyrimidine nucleobases, *Chinese Journal of Chemical Physics* 24 (2011) 580–585.
- [10] A. Bose, D. Dey, S. Basu, Interactions of guanine and guanosine hydrates with quinones: a laser flash photolysis and magnetic field effect study, *Journal of Physical Chemistry A* 112 (2008) 4914–4920.
- [11] A. Bose, S. Basu, Medium-dependent interactions of quinones with cytosine and cytidine: a laser flash photolysis study with magnetic field effect, *Biophysical Chemistry* 140 (2009) 62–68.
- [12] A.B.N. Chowdhury, S. Basu, Role of sugar in controlling reaction pattern: a comparative study with adenine and 2'-deoxyadenosine, *Journal of Photochemistry and Photobiology A* 201 (2009) 197–202.
- [13] A. Bose, S. Basu, Interaction of quinones with three pyrimidine bases: a laser flash photolysis study, *Journal of Luminescence* 129 (2009) 1385–1389.
- [14] S.Y. Arzhantsev, S. Takeuchi, T. Tahara, Ultrafast excited-state proton transfer dynamics of 1,8-dihydroxyanthraquinone (chrysin) studied by femtosecond time-resolved fluorescence spectroscopy, *Chemical Physics Letters* 330 (2000) 83–90.
- [15] F.V.R. Neuwahl, L. Bussotti, R. Righini, G. Buntinx, Ultrafast proton transfer in the S-1 state of 1-chloroacetylaminanthraquinone, *Physical Chemistry Chemical Physics* 3 (2001) 1277–1283.
- [16] Y. Pan, Y.H. Gao, L. Yan, H. Pan, J.F. Chen, S.Q. Yu, Reactivity of aromatic amines with triplet 1,8-dihydroxyanthraquinone: a laser flash photolysis study, *Spectrochimica Acta Part A* 66 (2007) 63–67.
- [17] M.H. Vanbenthem, G.D. Gillispie, Intramolecular hydrogen-bonding. 4. Dual fluorescence and excited-state proton-transfer in 1,5-dihydroxyanthraquinone, *The Journal of Physical Chemistry* 88 (1984) 2954–2960.
- [18] G.C. Ferreira, C.C. Schmitt, M.G. Neumann, Dependence of the thioxanthone triplet-triplet absorption spectrum with solvent polarity and aromatic ring substitution, *Journal of the Brazilian Chemical Society* 17 (2006) 905–909.

- [19] R.F. Anderson, S.S. Shinde, A. Maroz, Cytosine-gated hole creation and transfer in DNA in aqueous solution, *Journal of the American Chemical Society* 128 (2006) 15966–15967.
- [20] S.V. Jovanovic, M.G. Simic, One-electron redox potentials of purines and pyrimidines, *The Journal of Physical Chemistry* 90 (1986) 974–978.
- [21] C.E. Crespo-Hernandez, R. Arce, Y. Ishikawa, L. Gorb, J. Leszczynski, D.M. Close, Ab initio ionization energy thresholds of DNA and RNA bases in gas phase and in aqueous solution, *Journal of Physical Chemistry A* 108 (2004) 6373–6377.
- [22] P.U. Civcir, A theoretical study of tautomerism of cytosine, thymine, uracil and their 1-methyl analogues in the gas and aqueous phases using AM1 and PM3, *Journal of Molecular Structure: THEOCHEM* 532 (2000) 157–169.
- [23] X.Y. Zhang, S. Jin, Y.F. Ming, M.G. Fan, Z.R. Lian, S.D. Yao, N.Y. Lin, Electron-transfer reactions between nucleic-acid bases and tetracyanoethylene in acetonitrile, *Journal of Photochemistry and Photobiology A* 85 (1995) 85–88.