Interactions of Guanine and Guanosine Hydrates with Quinones: A Laser Flash Photolysis and Magnetic Field Effect Study

Adity Bose, Debarati Dey, and Samita Basu*

Chemical Sciences Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata −700 064, India

Received: December 18, 2007; Revised Manuscript Received: February 27, 2008; In Final Form: February 28, 2008

Laser flash photolysis and an external magnetic field have been used to study the interaction of two quinone molecules, namely, 9,10-anthraquinone (AQ) and 2-methyl 1,4-naphthoquinone, commonly known as menadione (MQ), with one of the DNA bases, guanine (G) and its nucleoside guanosine hydrate (dG). In organic homogeneous medium, it has been observed that G undergoes a predominant hydrogen (H) abstraction reaction with both the quinones while dG supports photoinduced electron transfer (PET) along with H abstraction. On the other hand, in SDS medium, G supports PET with AQ but not with MQ. However, behavior of dG remains unperturbed toward AQ and MQ with the change in medium. All of these observations have been explained on the basis of stabilization of radical ion pair and difference in size of the quinones, which can affect the distance of approach among the interacting molecules.

1. Introduction

Quinones are ubiquitous in nature. They play central roles in aerobic respiration and energy-yielding photosynthesis. Their function is closely related to their redox potentials, which enable them to participate in the transport of electrons within the cell membrane. In addition, exogenous quinones are used as antibiotics and antitumor agents in medicine[1] and hold promise as radiosensitizers in the treatment of cancer.[2] These compounds probably either interfere with the complex respiration chain at the cellular level or lead to the liberation of toxic free radicals, which can subsequently attack cellular components, including DNA.[3] Photoinduced electron transfer from DNA has already been established to be an important reaction, which is also responsible for DNA damage. Quinones being efficient electron acceptors can serve a good purpose as anticancer agents. Many works have been done on quinone−DNA interaction.[4–6] In this work, we have studied a single DNA base guanine (G) and its corresponding nucleoside guanosine hydrate (dG) with two quinone molecules 9,10-anthraquinone (AQ) and 2-methyl 1,4-naphthoquinone or more commonly menadione (MQ). In our study, we have found that quinones have interacted with the base mainly by two mechanisms, hydrogen (H) abstraction and photoinduced electron transfer.

H abstraction and electron transfer reactions involve the formation of radical pairs and radical ion pairs and in general can be affected by an external magnetic field (MF).[7–11] Magnetic field effect (MFE) is basically the interplay between spin dynamics and diffusion dynamics. By diffusion, the radical ion pairs can separate to an optimum distance where the exchange interaction J becomes almost zero. In this situation, the electron−nuclear hyperfine coupling induces efficient mixing between the triplet ($T_{\pm}$, T_0) and the singlet states. The application of an external magnetic field removes the degeneracy of the triplet states and reduces intersystem crossing (ISC) thus resulting in an increase in the population of the initial spin state. So the MFE is very much sensitive to the distance between the participating radical ions because the hyperfine induced spin flipping depends on J, which in turn has exponential distance dependence. When the radical ion pairs are in contact, the S-T splitting caused by J is much stronger than the hyperfine coupling energies so that spin evolution cannot occur by this mechanism. On the other hand, if the separation between radical ions becomes too large, MFE could not be observed because the geminate characteristics of the initial radical ion pair gets lost although J becomes sufficiently small to induce efficient S-T conversion. Therefore, the requirement of an optimum separation, where both spin flipping and geminate recombination are feasible, becomes a very crucial factor in controlling the MFE. The distance dependence of MFE has been demonstrated earlier in a detailed and quantitative manner by several workers.[11–13] In this work, we have attempted to investigate this aspect by studying the MFE on photoinduced electron transfer between two quinone molecules, AQ and MQ with G and dG in two entirely contrasting media, an organic homogeneous one composed of acetonitrile/water (ACN/ H_20, 9:1, v/v) and a heterogeneous micellar medium of Sodium Dodecyl Sulfate (SDS) in water. The mobility of the participating molecules is expected to be different in these media, which has a direct bearing on their mutual distance of approach during reaction. The MFE has been used as a tool to probe the electron transfer reactions between quinones and DNA bases by identifying the transients formed during their interactions. Quinones and DNA bases mainly interact by means of electron transfer and H abstraction resulting in the formation of radical pairs and radical ion pairs.[6,14,15] MFE can be suitably utilized only in those reactions where radical pairs/radical ion pairs are formed.[7–11] The novelty of MFE lies in the proper detection of the transients formed during interactions among different molecules which in turn, predicts the exact mode of the reaction.

For proper utilization of electron transfer, the photogenerated ions should be prevented from subsequent rapid recombination, a prevalent event in homogeneous media. Organized assemblies such as micelles can prolong the lifetime of charge-transfer states and thus increase the efficiency of charge separation by partitioning of the reactants and/or products.[16] These microhet-

* Corresponding author. Phone: +91-33-2337-5345. Fax: +91-33-2337-4637. E-mail: samita.basu@saha.ac.in.

10.1021/jp711846n CCC: $40.75
Published on Web 05/08/2008

erogeneous systems provide a fundamental understanding of how electron transfer dynamics is influenced by restricted system geometry. Our observations have revealed a remarkable change in reaction pattern on moving from homogeneous to heterogeneous SDS medium.

Reaction Scheme and the Spin Dependent Phenomenon. The reaction scheme of the present system is as follows:

$$Q \xrightarrow{h\nu} {}^1Q^* \xrightarrow{ISC} {}^3Q^* \quad (1)$$

$${}^3Q^* + RH\ (SDS) \rightarrow {}^3(QH^{\bullet\bullet}R) \quad (H\ abstraction) \quad (2)$$

$${}^3(QH^{\bullet\bullet}R) \underset{MF}{\overset{HFI}{\leftrightarrow}} {}^1(QH^{\bullet\bullet}R) \quad (3)$$

$${}^3(QH^{\bullet\bullet}R) \rightarrow QH^{\bullet} + R^{\bullet} \quad (escape\ product) \quad (4)$$

$${}^1(QH^{\bullet\bullet}R) \rightarrow QH{-}R \quad (cage\ product) \quad (5)$$

$${}^3Q^* + D \rightarrow {}^3(Q^{\bullet-}D^{\bullet+}) \quad (electron\ transfer) \quad (6)$$

$${}^3(Q^{\bullet-}D^{\bullet+}) \underset{MF}{\overset{HFI}{\leftrightarrow}} {}^1(Q^{\bullet-}D^{\bullet+}) \quad (7)$$

$${}^3(Q^{\bullet-}D^{\bullet+}) \rightarrow Q^{\bullet-} + D^{\bullet+} \quad (escape\ product) \quad (8)$$

The following steps of reactions are for hydrogen abstraction in case of G/dG with quinones:

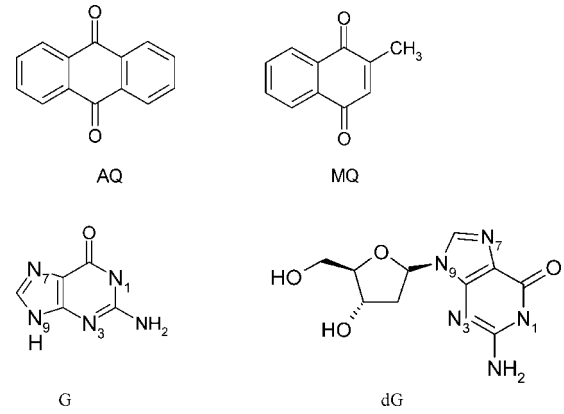
$${}^3Q^* + D \rightarrow {}^3[QH^{\bullet\bullet}D(-H)] \quad (H\ abstraction) \quad (9)$$

$${}^3[QH^{\bullet\bullet}D(-H)] \underset{MF}{\overset{HFI}{\leftrightarrow}} {}^1[QH^{\bullet\bullet}D(-H)] \quad (10)$$

Here, Q represents quinone molecules and D represents base molecules (G/dG). The excited triplet state of quinone, $^3Q^*$, is produced via the excited singlet state through ISC. It abstracts a hydrogen atom from a SDS (RH) molecule (or any suitable H donor) to produce a spin-correlated radical pair in the triplet state, $^3(QH^{\bullet\bullet}R)$, which consists of a semiquinone and a dehydrogenated SDS radical. The ISC from the triplet pair $^3(QH^{\bullet\bullet}R)$ to the singlet pair $^1(QH^{\bullet\bullet}R)$ and the escape of component radicals producing free radicals take place competitively. The singlet geminate radical pairs disappear due to cage reaction and the triplet radical pairs diffuse out of the micelle. Similar phenomena occur during electron transfer.

In this work, we have utilized MFE in the study of electron transfer and H abstraction between quinones and G, and dG individually. Interestingly, although both G and dG have been observed to undergo H abstraction with both the quinones in both media, dG alone has supported electron transfer with MQ. Our observation is an apparent contradiction to the reports of many researchers who have asserted G to be the most easily oxidizable base within a DNA molecule.[4,5,17] Now it is well-established that water plays an important role in the stabilization of biomolecular systems and that the hydrogen bonding capability of water is essential in the interactions between water and biomolecules, such as DNA, RNA, and proteins.[18] Barnett et al. reported the necessity of hydrating water molecules in the charge transport in DNA.[19] Since it is established that G is the most easily oxidizable base among DNA components, a direct role of G/dG in the charge transport is evident. Thus, the apparent contradictory observation has been attributed to the absence of hydration in G because of its low solubility in pure aqueous medium.[20] In our system, because of differential solubility of G and dG in water their distribution in the media will be different too. In this work we have given an experimental proof of the significance of water molecules in the reactions of G and dG. Observations in case of AQ with the same bases have been slightly different. AQ favors electron transfer with G also; however, that is in SDS and not in homogeneous medium. So we believe, reaction pathway depends primarily on the stabilization of transients, which depends on the surrounding media. Moreover, the difference in the reaction pattern of AQ and MQ has been attributed to their size difference, hence to a different distance of approach toward base molecules, which results in switching on and off of a particular reaction. MFE has played a crucial role in the detection of these factors, which determine the reaction path to be taken by the molecules.

CHART 1: Structures of Compounds



2. Experimental Section

2.1. Materials. Menadione (MQ), guanine (G), guanosine hydrate (dG), and sodium dodecyl sulfate (SDS) were purchased from Sigma. 9,10-anthraquinone (AQ) was obtained from Aldrich and was recrystallized from ethanol. UV spectroscopy grade acetonitrile (ACN) was obtained from Spectrochem and used without further purification. Water used for preparation of solutions was triply distilled. All micellar solutions were made by sonication. Chemical structures of the compounds used in this work are shown in Chart 1.

2.2. Spectral Methods. The excitation light was the third harmonic (355 nm) of a Nd:YAG laser (DCR-11, Spectra Physics) with a duration of 8 ns. The analyzing light was from a 250 W xenon lamp. The laser and analyzing light beams, crossed at right angles, passed through a quartz cell with a 1 cm^2 cross section. A monochromator equipped with an IP28 photomultiplier was used to analyze transient absorption (Applied Photophysics). The signals from the photomultiplier were displayed and recorded as a function of time on a Tektronix 500 MHz (1Gs/s sampling rate) oscilloscope. Each data point was obtained with multitimes average to improve the signal-to-noise ratio. The transient absorption were obtained from a series of oscilloscope traces measured with the same solution in a point-by-point manner with respect to the wavelength using the software Origin 5.0. The samples were deaerated by passing pure argon gas for 20 min prior to each experiment. No degradation of the samples was observed during the experiments. The strength of the direct current magnetic field used was 0.08 T.

3. Results and Discussion

Figure 1 shows the transient absorption spectra of pure MQ (0.4 mM) and MQ with G (1 mM) in ACN/H_2O. The transient

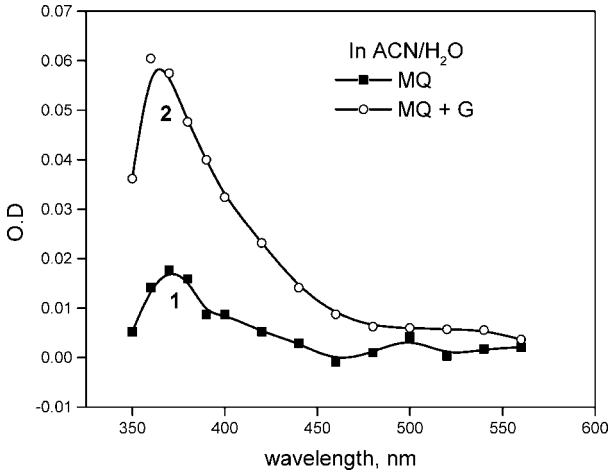


Figure 1. Transient absorption spectra of (1) MQ (0.4 mM) (■), (2) MQ (0.4 mM)-G (1.0 mM) (○) at 1.0 μs time delay after laser pulse with excitation wavelength 355 nm in ACN/H_2O (9:1, v/v).

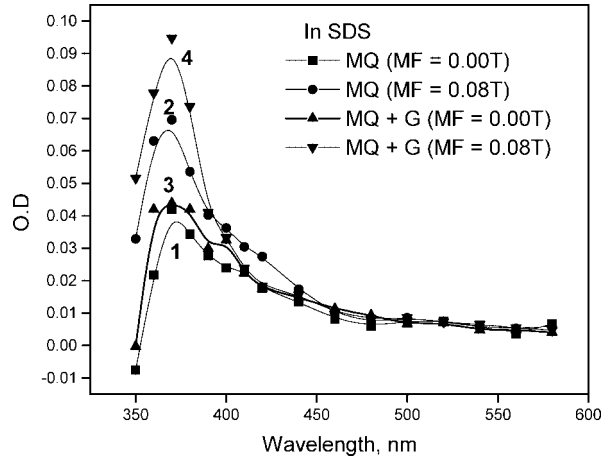


Figure 2. Transient absorption spectra of MQ (0.4 mM) (1) in the absence (■) and (2) presence of magnetic field (•), MQ (0.4 mM)-G (1.0 mM) in (3) the absence (▲) and (4) presence (▼) of magnetic field at a delay of 1.0 μs in SDS micelles.

absorption of MQ reveals a peak at 370 nm, which is associated to its triplet−triplet absorption.[21] On addition of G, the peak at 370 nm region increases. Increased peak height on addition of nucleobases points toward the formation of new species. We have reported earlier that the 370−380 nm and the 480 nm regions are characteristic of the radical anion, $MQ^{\bullet-}$, formed through electron transfer from a base, which acts as an electron donor. Further support of electron transfer comes from a simultaneous observation of radical cation from the base. Earlier reports suggest guanyl radical cation to absorb around 400 and 480 nm.[17,20,22] In case of G, the 370 nm region shows an increased peak height but the region above 480 nm possesses almost no hump, thus, canceling every possibility of existence of radical ion pairs formed through electron transfer between MQ and G. The only possibility with G is that of H abstraction from its potent donor sites as $MQH^{\bullet}$ has been reported to absorb around 370 nm.[21] So, G seems to participate only in H abstraction, and the probability of electron transfer from G to MQ is almost negligible in ACN/ H_2O.

Figure 2 shows the transient absorption spectra obtained on irradiating MQ (0.4 mM) separately and with the base G (1 mM) in 5% SDS medium. The spectra obtained both in the absence and presence of an external magnetic field are depicted in the figure. MQ alone exhibits a peak around 370 nm with a

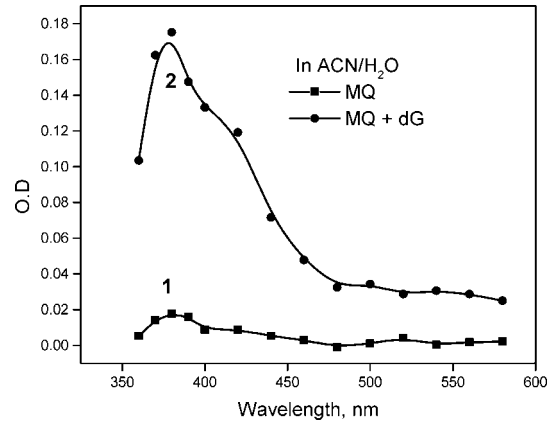


Figure 3. Transient absorption spectra of (1) MQ (0.4 mM) (■), (2) MQ (0.4 mM)-dG (1.0 mM) (•) at 1.0 μs time delay after laser pulse with excitation wavelength 355 nm in ACN/H_2O (9:1, v/v).

shoulder around 400 nm. The peak and the shoulder have been assigned to $MQH^{\bullet}$ formed upon $H^{\bullet}$ abstraction by quinone from a SDS molecule. In the presence of MF, both the peak and the shoulder intensify. This clearly proves that these regions depict the formation of some radicals. Increase in peak intensity on addition of MF provides twofold information: first, an existence of spin correlated geminate radical pair/radical ion pair and second, a triplet state mechanism during electron transfer/H abstraction. The spectra obtained on addition of G to MQ exhibits almost similar peaks but with an increased intensity compared with MQ alone. The increased peak height has been attributed to a higher concentration of $MQH^{\bullet}$ in the presence of G. On the other hand, there is almost no change in the nature of the spectrum beyond 480 nm. Radical ion pairs ($MQ^{\bullet-}$ and $G^{\bullet+}$) are reported to absorb around 400 and 480 nm[17,20–22] respectively. Now $MQH^{\bullet}$ absorbs at 370 nm with a hump at 400 nm, but the region around 480 nm is not affected. Radical ion pairs, if present, will absorb at 480 nm. Also, the presence of two species ($MQH^{\bullet}$ and $MQ^{\bullet-}$) will lead to a broad absorption around 380 nm, whereas a single species $MQH^{\bullet}$ will give a sharper peak at 370 nm. Absence of the 480 nm peak in Figure 2 nullifies the possibility of existence of any radical ion pairs. Hence, G is found to support only H abstraction and almost no electron transfer even in micellar medium.

$$^3MQ^* + G \rightarrow {}^3[MQH^{\bullet\bullet}G(-H)] \qquad \text{(H abstraction)}$$

$$^3[MQH^{\bullet\bullet}G(-H)] \overset{\text{HFI}}{\underset{\text{MF}}{\leftrightarrow}} {}^1[MQH^{\bullet\bullet}G(-H)]$$

Now earlier works have reported on a facile electron transfer from G in DNA to other photosensitizers/electron acceptors[18,22–26] in aqueous solution. But in our experiments, in both organic and micellar media, we have failed to notice any appreciable electron transfer from G to MQ. Now G is seen to be very sparingly soluble in pure neutral water,[20] so in both ACN/H_2O and micelles, it must be reluctant to be associated with the aqueous part. In order to get a clear picture, we have performed our experiments again with the nucleoside dG, that is, guanine with a covalently linked sugar moiety. The reason of our choice is based on the solubility factor, as dG is appreciably soluble in pure water.

Figure 3 shows the transient absorption spectra of pure MQ (0.4 mM) and MQ with dG (1 mM) in ACN/H_2O. Addition of dG has produced a broad absorption maximum around 380 nm with an appreciable hump around the 480 nm region. Now $MQ^{\bullet-}$ has been assigned a peak at 380 nm and a hump around 500

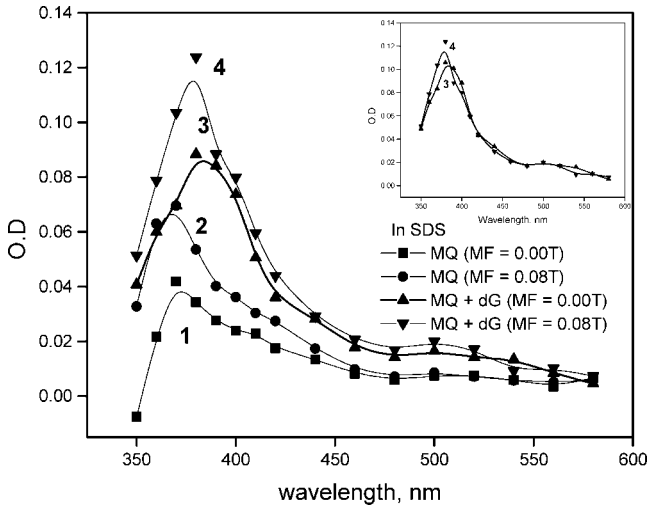


Figure 4. Transient absorption spectra of MQ (0.4 mM) (1) in the absence (■) and (2) presence of magnetic field (•), MQ (0.4 mM)-dG (1.0 mM) in the (3) absence (▲) and (4) presence (▼) of magnetic field at a delay of 1.0 μs in SDS micelles. Inset: Normalized figure of curve 3, in the absence of magnetic field (▲) and curve 4, in presence of magnetic field (▼) with MQ (0.4 mM)-dG (1.0 mM).

nm while $MQH^{\bullet}$ has been assigned a 370 nm maximum. Radical cations ($dG^{\bullet+}$) have been reported to possess a 480 nm hump.[22] So it is evident that dG undergoes electron transfer with MQ in homogeneous ACN/H_2O medium. Figure 4 shows the transient absorption spectra obtained on irradiating MQ (0.4 mM) separately and with the base dG (1 mM) in 5% SDS medium. Addition of dG generates a spectra in marked contrast to the one obtained from G. This spectrum (curve 3) shows a broad maximum around 400 nm. The region above 480 nm also exhibits a hump, which is due to the radical anion of MQ. The inset to Figure 4 reveals a properly scaled up (normalized) figure where curve 3 has been lifted so that the regions from 450−600 nm superimpose with that of curve 4. The regions from 350−450 nm of both curves do not superimpose. This proves that there exists more than one species, since in every probability, two different types of species will behave differently in the presence of a magnetic field. So existence of radical ion pairs is confirmed; hence, a facile electron transfer from dG to MQ is evident in SDS also. A possibility of H atom transfer from dG to MQ cannot be neglected too. First, the semiquinone $MQH^{\bullet}$ also absorbs very close to that of $MQ^{\bullet-}$, and second, the G moiety present in dG has already shown to be an efficient participant in H atom abstraction. Now according to Ravanat et al. and Ghosh et al., guanosine radical cation formed upon electron transfer undergoes a fast deprotonation at neutral pH,[23–25] and the resulting species will be a neutral guanosine radical. So existence of this neutral species in our system cannot be overlooked. However, in our experiment, we are unable to identify separately the neutral $dG^{\bullet}$ because its absorbance around 510 nm[17] maybe masked by the absorbance by the other radical ion pairs mentioned above. Moreover, its existence also confirms a simultaneous participation of dG in electron transfer and H abstraction. Semiquinone formation is possible by the uptaking of either proton or H atom from bases by the quinone molecules. Thus, it is found that addition of a mere sugar unit to the purine base G has resulted in a complete change in the chemistry of the base.

$$^3MQ^* + dG \rightarrow {}^3[MQH^{\bullet\bullet}dG(-H)] \qquad \text{(H abstraction)}$$

$$^3[MQH^{\bullet\bullet}dG(-H)] \overset{HFI}{\underset{MF}{\leftrightarrow}} {}^1[MQH^{\bullet\bullet}dG(-H)]$$

$$^3MQ^* + dG \rightarrow {}^3(MQ^{\bullet-}dG^{\bullet+}) \qquad \text{(electron transfer)}$$

$$^3(MQ^{\bullet-}dG^{\bullet+}) \overset{HFI}{\underset{MF}{\leftrightarrow}} {}^1(MQ^{\bullet-}dG^{\bullet+})$$

$$^3(MQ^{\bullet-}dG^{\bullet+}) \rightarrow MQ^{\bullet-} + dG^{\bullet+} \qquad \text{(escape product)}$$

Magnetic Field Effect (MFE): In the presence of an external MF, the decay of the transient at 370 nm becomes slower (Figure 5), accompanied by an enhanced absorption in the spectrum (Figure 2 and Figure 4). The formation of a spin correlated radical pair ($^3MQH^{\bullet\bullet}R$) (reaction 2) explains this MFE (reaction 3). It is noteworthy that the nature of the decay profiles (at 370 nm) of $MQH^{\bullet}$ is different in the presence of G and dG, particularly in the presence of a field. Decay curves 2 and 4 of Figure 5 are almost equivalent while the same in Figure 6 reveals slight differences. This implies that the radical pairs formed with G and dG are also different. G has produced $MQH^{\bullet}$ while dG generated both $MQH^{\bullet}$ and $MQ^{\bullet-}$. Decay curve 2 is only due to field effect of $MQH^{\bullet}$ in both Figure 5 and Figure 6. Decay curve 4 is the resultant field effect on transients formed from G and dG. So comparison of both curve 2 and curve 4 will reveal existence of different species as evident in our case.

In the presence of an external magnetic field, the decay of the radical pair is expected to be biexponential, that is, the following equation is obeyed for the change in absorbance $A(t)$

$$A(t) = I_f \exp(-k_f t) + I_s \exp(-k_s t)$$

where k_f and k_s are the respective rate constants for the fast and slow components of the decay profiles. The fast components

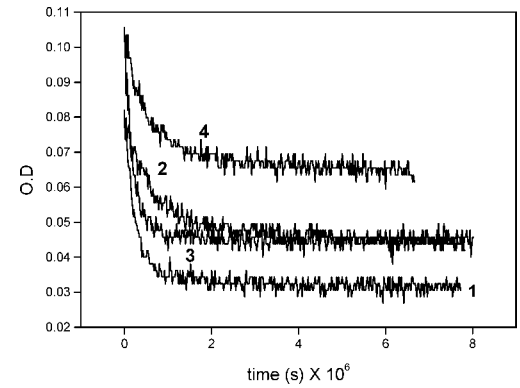


Figure 5. Normalized OD traces at 370 nm obtained by laser flash photolysis (λ = 355 nm) of MQ (0.4 mM) in SDS in the (1) absence and (2) presence of magnetic field and MQ (0.4 mM) and G (1.0 mM) in the (3) absence and (4) presence of magnetic field.

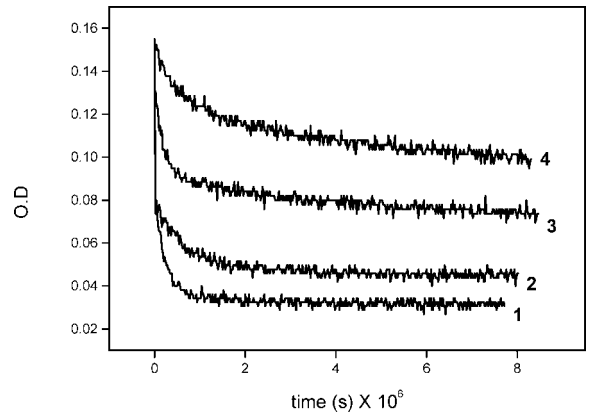


Figure 6. Normalized OD traces at 370 nm obtained by laser flash photolysis (λ = 355 nm) of MQ (0.4 mM) in SDS in the (1) absence and (2) presence of magnetic field and MQ (0.4 mM) and dG (1.0 mM) in the (3) absence and (4) presence of magnetic field.

TABLE 1: Variation of Decay Rate Constant (k_f) and Relative Radical Escape Yield (Y) with Magnetic Field for Aqueous Micellar Solution (SDS) of MQ and the Bases

base	magnetic field (Tesla)	decay rate constant (k_f) $(s)^{-1}$	Y
no base	0.00	4.31×10^6 ($\pm$0.02)	1.00[a]
	0.08	1.70×10^6 ($\pm$0.01)	1.64
G	0.00	1.62×10^6 ($\pm$0.03)	1.00[a]
	0.08	1.13×10^6 ($\pm$0.05)	1.63
dG	0.00	5.30×10^6 ($\pm$0.01)	1.00[a]
	0.08	2.22×10^6 ($\pm$0.02)	1.40

[a] Arbitrarily taken.

of this equation correspond to the radical pair decay in the micellar cage, while the slower one is due to the reaction of the escaped radicals. The k_f values obtained by biexponential fitting of the decay profiles are listed in Table 1. The yields of the radical ions in the bulk of the solvent maybe obtained from the ratio of the absorption due to the free radical ions to that of the initial absorption immediately after the pulse. The relative escape yields after 5 μs are also presented in Table 1. It is observed that, with increasing field, the decay rate decreases and correspondingly the escape yield increases. This implies that the radical ion pairs are generated in triplet spin state. Upon application of MF, the conversion of the triplet radical ion pair to the singlet radical ion pair is retarded, and consequently, the decay rates decrease and escape yield increases.

Photoinduced electron transfer involves the consideration of ionization energy (IE) of the DNA base molecules.[27–29] The factors, which are important to provide an accurate description of DNA ionization energy in aqueous solution, include solvation by water molecules also. The solvent can control the stabilization component of the IE with respect to two distinct types of solute−solvent interactions. These are the specific short-range hydrogen bonding interactions and the long-range solvent polarization interactions.[30] Both H bonding and solvent polarization are basically dipole−dipole interactions.[31] In the former case, an explicit interaction with a limited number of solvent−water molecules could influence the IE by the reorientation of the solvent−water dipoles in the stabilization process of the radical cation−anion pair formed. In the latter case, the solvent polarization interactions could also have a significant effect on the solvation and stabilization of the radical ion pairs. Hernandez et al. have shown that there is a significant role of bulk water solvation in lowering the IE of bases.[32] Thus, absence of hydration in G will evidently raise its IE over the much-hydrated dG. This is expected to result in a better electron transfer from dG than G. The radical ion pairs formed upon electron transfer from dG are appreciably stabilized in aqueous medium, but on the other hand, with G being associated with the hydrophobic region, radical ion pairs formed, if any, will be destabilized and a chance of formation of recombination product will be higher. Thus, probability of electron transfer from G is expected to be much lower than that from dG. This points to an effective role of hydration in determining the mode of reaction of the DNA bases. Now electron transfer from nucleobases depends primarily on their redox potential values. So a role of hydration on redox values is expected too. Langmaier et al. have made a significant contribution in this field. They have investigated the origin of difference between the one-electron redox potentials of G and those of dG.[33] They have shown that IE of dG is lesser than that of G generally ($G = 7.31$ energy/eV and dG = 7.18 energy/eV).[32] But the easy oxidation of G, observed often, stems from the high difference in hydration energy between the radical species of G/dG and the parent molecules. Hydration energy

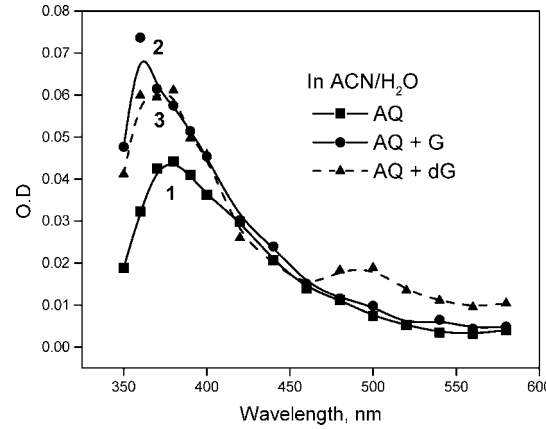


Figure 7. Transient absorption spectra of (1) AQ (0.4 mM) (■), (2) AQ (0.4 mM)-G (1.0 mM) (•), and (3) AQ (0.4 mM)-dG (1.0 mM) (▲) at 1.0 μs time delay after laser pulse with excitation wavelength 355 nm in ACN/H_2O (9:1, v/v).

plays a critical role in rendering G the most easily oxidizable base. So this fact supports our observation, since G fails to be hydrated in our system, so the hydration energy factor is not significant. Thus, dG will be preferably oxidized over G, hence electron transfer, which is basically one-electron oxidation, is favored in dG and not in G.

Now G and dG differ with respect to size, so an involvement of steric factor in determining the reaction course can also be important. To gain further insight into the distance dependence of the quinone−DNA base interaction, we have performed similar experiments with AQ, differing from MQ with respect to steric bulk by possessing an extra phenyl moiety. This modulates the distance of separation of the donor group of G/dG and the two quinone moieties as observed in the following experiments.

Figure 7 displays the transient absorption spectra obtained on irradiating AQ (0.4 mM) alone and in the presence of 1 mM of G and dG in the ACN/H_2O (9:1, v/v) medium. AQ alone exhibits a peak at 360 nm, which we have earlier assigned to its triplet−triplet absorption.[34] Addition of G has resulted in a much increased peak height around 370 nm. The region around 480 nm does not exhibit any appreciable change on addition of G to AQ. We have earlier reported $AQH^•$ to absorb around 370 nm and $AQ^{•-}$ to absorb at 380−400 nm with a second peak at 540 nm.[34] The absence of any peak around 540 nm reduces the possibility of existence of $AQ^{•-}$, hence a possibility of electron transfer with G. So the strong absorbance around 370 nm can only be logically associated to $AQH^•$. Thus, G behaves similarly with both quinones by transferring the H atom predominantly with a low probability of electron transfer in ACN/H_2O. In the case of dG, a peak around 500 nm is observed with a maximum at 380 nm pointing toward a facile electron transfer from dG to AQ. The presence of both the $AQ^{•-}$ and the guanyl radical cation results in peaks at 380 and 500 nm regions. In this context, it is necessary to mention that, in AQ, the 500 nm region exhibits a clear peak while in the case of MQ (Figure 3) an increased absorbance is present without any appreciable hump. This has been attributed to a better photoinduced electron transfer in the case of AQ than in MQ. Can this be associated to the size difference among the quinones? AQ, rather than MQ, possesses an extra phenyl ring; so in a homogeneous medium, because of the random distribution of molecules, MQ can come much closer to dG than AQ. Now a closer approach encourages H bonding between the quinone moieties with hydrogens of dG, which ultimately results in a predominant H abstraction. Photoinduced

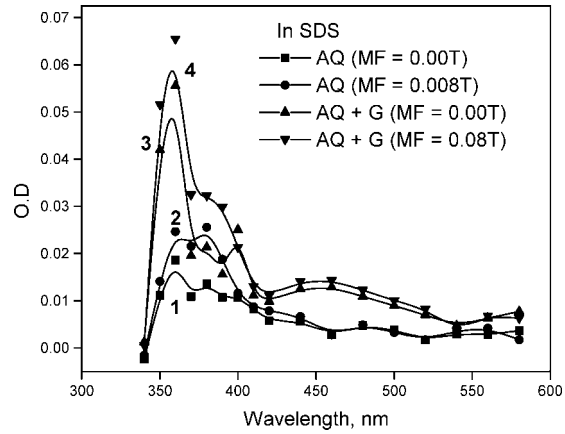


Figure 8. Transient absorption spectra of AQ (0.1 mM) (1) in the absence (■) and (2) presence of magnetic field (•), AQ (0.1 mM)-G (1.0 mM) in the (3) absence (▲) and (4) presence of magnetic field (▼) at a delay of 1.0 μs in SDS micelles.

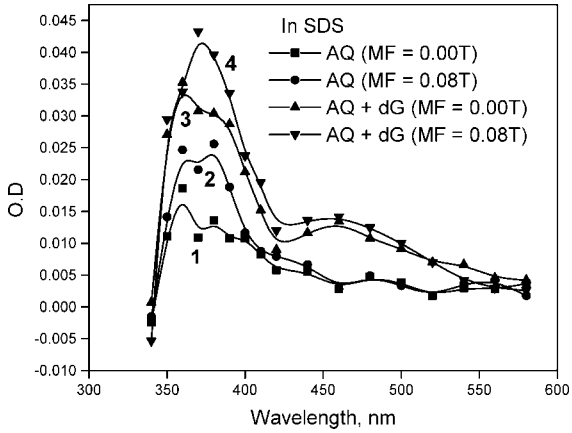


Figure 9. Transient absorption spectra of AQ (0.1 mM) (1) in the absence (■) and (2) presence of magnetic field (•), AQ (0.1 mM)-dG (1.0 mM) in the (3) absence (▲) and (4) presence of magnetic field (▼) at a delay of 1.0 μs in SDS micelles.

electron transfer occurs only with those dG molecules, which are at a distance from MQ and are not H bonded. The bulkier AQ remains almost always at such a distance from the bases, which cannot support H bonding. So in the case of AQ, perhaps the probability of electron transfer increases while H abstraction gets a backseat.[21] For a better understanding, we have repeated our experiments in 10% SDS medium, where the random distribution of molecules has been avoided.

Figure 8 reveals the transient absorption spectra obtained on laser flash of AQ alone (0.1 mM) and in the presence of G (1 mM) in 10% SDS medium. AQ alone presents peaks at 360 and 380 nm, which are associated to the corresponding semiquinone, $AQH^{\bullet}$ formation (curve 1). On addition of G, there is a sharp increase around the 370 nm region. Application of MF produces an appreciable effect denoting the formation of a spin-correlated geminate ion pair in SDS. Now interestingly, the region above 480 nm possesses a hump, with some MFE, which is not present in MQ at all. These regions are the signatures of formation of radical ion pairs, so the occurrence of an electron transfer from G to AQ in the micellar medium is depicted in this figure. Figure 9 reveals the transient absorption spectra obtained on laser flash of AQ alone (0.1 mM) and in the presence of dG (1 mM) in 10% SDS medium. Addition of dG has resulted in an appreciable increase in peaks around the 380 and 400 nm regions with sufficient MFE. Hence, the existence of spin correlated geminate radical pair/radical ion pair is denoted, pointing toward a facile electron transfer and H abstraction from dG to AQ. The existence of a neutral guanosine radical, as previously mentioned, is also possible. The region between 450−500 nm possesses a hump again, with MFE pointing toward the existence of radical ion pairs formed through electron transfer and H abstraction in the triplet state.

TABLE 2: Variation of Decay Rate Constant (k_f) and Relative Radical Escape Yield (Y) with Magnetic Field for Aqueous Micellar Solution (SDS) of AQ and the Bases

base	magnetic field (Tesla)	decay rate constant (k_f) (s^{-1})	Y
no base	0.00	3.01×10^6 (±0.02)	1.00[a]
	0.08	1.52×10^6 (±0.01)	1.67
G	0.00	4.10×10^6 (±0.03)	1.00[a]
	0.08	1.02×10^6 (±0.05)	1.76
dG	0.00	4.41×10^6 (±0.01)	1.00[a]
	0.08	2.13×10^6 (±0.02)	1.46

[a] Arbitrarily taken.

$$^3AQ^* + G \rightarrow {}^3[AQH^{\bullet}G(-H)] \qquad \text{(H abstraction)}$$

$$^3[AQH^{\bullet}G(-H)] \overset{HFI}{\underset{MF}{\leftrightarrow}} {}^1[AQH^{\bullet}G(-H)]$$

$$^3AQ^* + dG \xrightarrow[HFI]{} {}^3[AQH^{\bullet}dG(-H)]$$

$$^3[AQH^{\bullet}dG(-H)] \overset{}{\underset{MF}{\leftrightarrow}} {}^1[AQH^{\bullet}dG(-H)]$$

$$^3AQ^* + G/dG \rightarrow {}^3(AQ^{\bullet-}G^{\bullet+}/dG^{\bullet+})$$

(electron transfer in SDS)

$$^3(AQ^{\bullet-}G^{\bullet+}/dG^{\bullet+}) \overset{HFI}{\underset{MF}{\leftrightarrow}} {}^1(AQ^{\bullet-}G^{\bullet+}/dG^{\bullet+})$$

$$^3(AQ^{\bullet-}G^{\bullet+}/dG^{\bullet+}) \rightarrow AQ^{\bullet-} + G^{\bullet+}/dG^{\bullet+}$$

(escape product)

Table 2 shows the k_f values obtained by biexponential fitting of decay curves of AQ with G and dG and the corresponding escape yield values. Similar to that with MQ, with increasing field, the decay rate decreases and the escape yield increases pointing toward a triplet state reaction.

Therefore, on comparison with MQ, we find that, in the hydrophobic micellar medium, AQ is seen to favor electron transfer to a small extent with G. Behavior of dG with MQ and AQ remains almost the same. Thus, an increase in the bulkness within the acceptor molecule quinone, micellar medium has exhibited electron transfer with G, which was not detectable in homogeneous medium. G is sparingly soluble in aqueous medium, but it is appreciably soluble in micellar medium. So it is evident, in micellar medium, G prefers the hydrophobic core to the bulk water region. Tanimoto et al. has suggested a complete micellization of AQ based on its hydrophobic character.[35,36] So both quinones will remain entrapped in the hydrophobic core along with G while dG remains suspended in the aqueous region because of its high water solubility.

Now for electron transfer to occur, the stability of radical ion pairs is mandatory. In homogeneous organic medium, since radical ion pairs from G and quinones are formed in the hydrophobic zone, stabilization of the radical cation and anion is not appreciated, since these radical ion pairs fail to be solvated; hence, probability of electron transfer from G is not encouraged. Radical ion pairs, if formed at all, will immediately recombine to give starting materials. But micellar medium possesses an additional virtue; it entraps the chemical species

such that a random encounter between them is reduced. Hence, recombination reaction, which has been the ultimate fate of the radical ion pairs, if formed at all, from G and quinones in homogeneous medium, is very much slowed down in a micellar cage. Thus, increased lifetime of the radical ion pair within micelle is responsible for the observation of some electron transfer with G in micellar medium. But still, one point remains to be answered. MQ does not exhibit electron transfer in micellar medium with G. The above discussion of radical ion pair stability in micelle is equally applicable to it. To answer this question, a closer look into the structures of the molecules is necessary. AQ is bulkier than MQ on account of an extra phenyl ring. So MQ can come much closer to the G molecule than AQ. G can form a potential H bond with the quinone moiety of MQ which will bring the two molecules in a favorable orientation such that the H atom formed from G on laser flash will be abstracted by the MQ resulting in the formation of $MQH^{\bullet}$. Thus, we find the probability of H abstraction is very high with MQ. In this situation, if some electron transfer occurs, it faces strong competition with the dominant H abstraction channel. So observation of significant electron transfer with MQ becomes difficult. An intervening phenyl moiety in AQ inhibits the closer approach to the bases, which offsets the formation of a H bond. Hence, probability of H abstraction decreases. So the predominant mode of reaction with AQ and the two bases remains electron transfer in SDS. In the case of dG, the situation with both the quinones remains almost same. The dG being suspended in the aqueous region and the distance of separation with both MQ and AQ, entrapped in the hydrophobic micellar core, remains almost the same. So MQ and AQ exhibit similar behavior with dG in SDS, being photoinduced electron transfer predominantly.

Conclusion

This work reveals the behavior of two quinones, MQ and AQ, with the DNA base G and its nucleoside dG. G has been found to support only H abstraction with MQ while dG has undergone photoinduced electron transfer also. Failure of G to promote electron transfer can be attributed to the failure in the stabilization of radical ion pairs in an organic environment due to its low solubility in aqueous medium. However, a striking difference has been shown by AQ in SDS medium with G. Here, electron transfer is found to be possible. A stabilization of transients by virtue of entrapment in hydrophobic core of micellar medium is responsible for it. Although MQ seemed to fulfill the above requirement, still electron transfer is not observed. So a second requirement has been found to be the controlling factor and that is the distance of separation between reactants. Smaller MQ can come much closer to G, which seems to favor a predominant H abstraction reaction. In AQ, the quinone moieties being flanked on both sides by bulky phenyl groups, probability of H bonding with base molecules decreases because of the increased distance of separation, and the probability of electron transfer increases since it can occur from a distance greater than H bonding. But in smaller MQ, a bulky phenyl group is replaced by a small methyl group, so closer approach of the base is not hindered. So a better H bonding occurs with MQ. Thus, electron transfer seems to face a strong competition with H bonding and, in effect, becomes negligible in MQ. So our work reveals two most vital requirements of electron transfer and H abstraction: first, the stabilization of resulting transients in reaction media and second, the distance among participating molecules.

Acknowledgment. We sincerely thank Mrs. Chitra Raha and Mr. Tapan Pyne for their kind assistance and technical support.

References and Notes

(1) Hartley, J.A. ; Reszka, K.; Lown, J. W. *Photochem. Photobiol.* **1988**, *48*, 19.
(2) Infante, G. A.; Gonzalez, P.; Cruz, D.; Correa, J.; Myers, J. A.; Ahmad, M. F.; Whitter, W. L.; Santos, A.; Neta, P. *Radiat. Res.* **1982**, 92–307.
(3) Powis, P. *Free Radi. Biol. Med.* **1989**, *6*, 63.
(4) Kawai, K.; Majima, T. *J. Photochem. Photobiol., C: Photochem. Rev.* **2002**, *3*, 53.
(5) Ma, J.; Lin, W.; Wang, W.; Han, Z.; Yao, S.; Lin, N. *J. Photochem. Photobiol., B: Bio.* **2000**, *57*, 76.
(6) Breslin, D. T.; Schuster, G. B. *J. Am. Chem. Soc.* **1996**, *118*, 2311.
(7) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.
(8) Bhattacharya, K.; Chowdhury, M. *Chem. Rev.* **1993**, *93*, 507.
(9) *Dynamic Spin Chemistry magnetic controls and spin dynamics of chemical reactions*; Nagakura, S.; Hayashi, H.; Azumi, T., Eds.; Kodansha Ltd.: Tokyo, 1998.
(10) Gould, I. R.; Turro, N. J. ; Zimmt, N. B. ; *Adv. Phys. Org. Chem., Vol. 20*, Academic Press: London, 1980.
(11) Tanimoto, Y., Fujiwara, Y. *Handbook of Photochem. Photobiol. Vol 1; Inorganic Chenistry*, Nalwa, H. S., Ed.; American Scientific Publishers: Stevenson Ranch, CA, 2003.
(12) Staerk, H.; Weller, A.; Triechel, R.; Kuhnle, W. *Chem. Phys. Lett.* **1985**, *118*, 19.
(13) Weller, A.; Staerk, H.; Triechel, R. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 271–332.
(14) Gasper, S. M.; Schuster, G. B. *J. Am. Chem. Soc.* **1997**, *119*, 12762.
(15) Sengupta, T.; Choudhury, S. D.; Basu, S. *J. Am. Chem. Soc.* **2004**, *126*, 10589.
(16) Fox, M. A.; Dewar, J. S.; Dunitz, J. D.; Hafner, K.; Ito, S.; Lehn, J. M. ; Neidenzu, K.; Raymond, K. N.; Rees, C. W.; Vogtle, F. In *Topics in Current Chemistry*; Springler-Verlag: Heidelberg, Germany, 1991, *Vol. 59.*
(17) Kobayashi, K.; Tagawa, S. *J. Am. Chem. Soc.* **2003**, *125*, 10213.
(18) Tsukamoto, T.; Ishikawa, Y.; Vilkas, M. J.; Natsume, T.; Dedachi, K.; Kurita, N. *Chem. Phys. Lett.* **2006**, *429*, 563.
(19) Barnett, R. N.; Cleveland, C. L.; Landman, U.; Boone, E.; Kanvah, S.; Schuster, G. B. *J. Phys. Chem. A* **2003**, *107*, 3525.
(20) Song, Q. H.; Yao, S. D.; Li, H. C.; Zuo, Z. H.; Zhang, J. S.; Lin, N. Y. *J. Photochem. Photobiol. A: Chem.* **1996**, *95*, 223.
(21) Bose, A.; Dey, D.; Basu, S. *J. Photochem. Photobiol. A: Chem.* **2007**, *186*, 130.
(22) Ma, J.; Lin, W.; Wang, W.; Han, Z.; Yao, S.; Lin, N. *J. Photochem. Photobiol. B: Biol.* **2000**, *57*, 76.
(23) Ghosh, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **2006**, *128*, 4172.
(24) Ravanat, J. L.; Saint-Pierre, C.; Cadet, J. *J. Am. Chem. Soc.* **2003**, *125*, 2030.
(25) Anderson, R. F.; Shinde, S. S.; Maroz, A. *J. Am. Chem. Soc.* **2006**, *128*, 15966.
(26) Pan, J. X.; Han, Z. H.; Miao, J. L.; Yao, S. D.; Lin, N. Y.; Zhu, D. Y. *Biophys. Chem.* **2001**, *91*, 105.
(27) Schumm, S.; Prevost, M.; Garcia-Fresnadillo, D.; Lentzen, O.; Moucheron, C.; Kirsch-De Mesmaeker, A. *J. Phys. Chem. B* **2002**, *106*, 2763.
(28) Orlov, V. M.; Smirnov, A. N.; Varshavsky, Ya. M. *Tetrahedron Lett.* **1976**, *17*, 4377.
(29) Hush, N. S.; Cheung, A. S. *Chem. Phys. Lett.* **1975**, *34*, 11.
(30) Gorb, L.; Leszcynski, J. *J. Am. Chem. Soc.* **1998**, *120*, 5024.
(31) *Inorganic Chemistry: Principles of structure and reactivity*, 4th ed; Huheey, J. E.; Keiter, E. A.; Keiter, R. L., Eds.; Addison-Wesley Publishing Company: New York, 2000; p 300.
(32) Crespo-Hernandez, C. E.; Arce, R.; Ishikawa, Y.; Gorb, L.; Leszczynski, J.; Close, D. M. *J. Phys. Chem. A* **2004**, *108*, 6373.
(33) Langmaier, J.; Samec, Z.; Samcova, E.; Hobza, P.; Reha, D. *J. Phys. Chem. B* **2004**, *108*, 15896.
(34) Chowdhury, A.; Basu, S. *J. Lumin.* **2006**, *121*, 113.
(35) Tanimoto, Y.; Udagawa, H.; Itoh, M. *Phys. Chem.,* **1983**, *87*, 724.
(36) Tanimoto, Y.; Shimizu, K.; Itoh, M. *J. Am. Chem. Soc.* **1984**, *106*, 7257.

JP711846N