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Functional Polyelectrolytes as Novel Media for Light-Induced Electron Transfer

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ABSTRACT: Functional polyelectrolytes consisting of charged segments and hydrophobic photoactive groups were demonstrated to critically control the rate and directions of photoredox reactions. Photosensitized reduction of methylviologen (MV^{2+}) and a zwitterionic viologen (SPV) was investigated by using an amphiphilic polyanion (APh) containing phenanthryl residues (Ph) (photoactive groups) and sulfonate groups or a corresponding polycation (QPh) having quaternized ammonium groups. The aggregates of Ph in the aqueous solutions of these polymers provide hydrophobic microdomains that are confined to an electric potential field of the electrolyte segments. A Coulombic attraction of MV^{2+} by a negatively charged interface of APh, which reflected in a ground-state CT interaction between Ph and MV^{2+}, highly disfavored the yield of the transient $MV^{+\cdot}$ in a laser photolysis. In contrast, the highest transient yield of $MV^{+\cdot}$ was encountered in the QPh–MV^{2+} system, in which the ground-state interaction is prohibited due to a Coulombic repulsion. The back-reaction in this system was significantly slowed ($k_b = 3.2 \times 10^8$ M^{-1} s^{-1}) due to the potential barrier of QPh against $MV^{+\cdot}$. The most effective retardation of the back-reaction was achieved in the APh–SPV system ($k_b = 8.7 \times 10^7$ M^{-1} s^{-1}), where the photoproduct, $SPV^{-\cdot}$, is strongly repelled by the negatively charged interface of APh, although the transient yield of the reduced viologen radicals was not so high as that in the QPh–MV^{2+} system.

Introduction

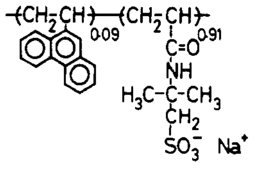
A key factor for the efficient conversion of light energy is to prevent the transient photoproducts from undergoing the thermodynamically favored back-reaction, which remains yet to be solved. It is believed that the media or microenvironments where the photoredox process takes place are of prime importance to achieve this goal. For such media considerable attention has been drawn, over the past decade, to organized assemblies[1] consisting of charged interfaces such as micelles,[2] liposomes,[3] and microemulsions.[4] In these systems an interfacial electrostatic potential field plays a decisive role in charge separation by repelling one of the charged photoproducts into the bulk phase. Therefore, the effectiveness of the interfacial media rests on the magnitude of the surface potential and the exact location with respect to the interface, where the forward electron transfer occurs.

Recently, Calvin and co-workers revealed that colloidal silica is one of the most effective interfacial systems.[5] They estimated the surface potential of the SiO_2 particles to be −170 mV as compared to −85 mV for SDS micelles.[5b] Later, Thomas et al. demonstrated the usefulness of porous colloidal SiO_2 particles.[6]

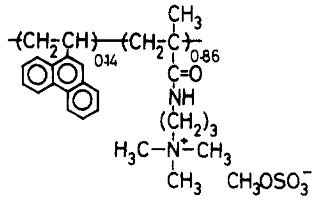
As one type of such organized assemblies, attention was first paid to polyelectrolytes by Meisel and co-workers.[7] Recently, Rabani and co-workers demonstrated that the polyelectrolyte assists with the charge separation by excluding the charged photoproducts from the polymer volume.[8,9] However, the effectiveness appears not to be very high as would be expected from the nature of polyelectrolytes in aqueous solution;[10] i.e., polyelectrolytes as such would have only a weak electric field and no interface.

We have been interested in functional polyelectrolytes because a large variation may potentially be allowed for molecular designing. One can incorporate, for example, charges, photoactive groups, redox centers, etc. into the polymer chain by chemical bonds. These modified polyelectrolytes may be categorized as "functionalized polyelectrolytes" in the sense that part of the polymer directly participates in the events of the light-induced electron-transfer reaction. As the first example of such polyelectrolytes, we have demonstrated that amphiphilic copolymers consisting of charged segments and hydrophobic photoactive groups serve as novel organized assemblies with functionality originating from the microheterogeneous structure in aqueous solutions.[11,12] Recently, we have investigated the photosensitized reduction of the zwitterionic viologen 4,4′-bipyridinium-1,1′-bis(trimethylenesulfonate) (SPV) by the copolymer (APh)[12a] of 9-vinylphenanthrene and sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) containing 9 mol % phenanthryl groups as a photosensitizer.[13] We found that the back-electron-transfer was substantially retarded, which is attributed to an electrostatic repulsion of the photoproduct, $SPV^{-\cdot}$, by the polyanions surrounding the phenanthryl groups. The rate constant for the back-reaction obtained ($k_b = 8.7 \times 10^7$ M^{-1} s^{-1})[13c] is almost comparable to the value reported for the SiO_2 colloidal system ($k_b = 5.7 \times 10^7$ M^{-1} s^{-1}).[5b]

The purpose of the present paper is to report an extended investigation of the electrostatic effect of the amphibhilic polyelectrolytes in the photoredox reaction. The point to be addressed is the promise of these polymers as a new class of organized assemblies.



APh



QPh

Experimental Section

Materials. Preparation of the amphiphilic polyelectrolytes poly(9-vinylphenanthrene-*co*-sodium 2-acrylamido-2-methylpropanesulfonate) (APh)[12] and poly(9-vinylphenanthrene-*co*-(3-methacrylamidopropyl)trimethylammonium methyl sulfate) (QPh)[12c] was reported elsewhere.

The related monomer models sodium 9-phenanthrylmethanesulfonate (AM)[13b] and (2-(3-phenanthrylacetyl)aminoethyl)trimethylammonium methyl sulfate (QM)[12c] were prepared as previously.

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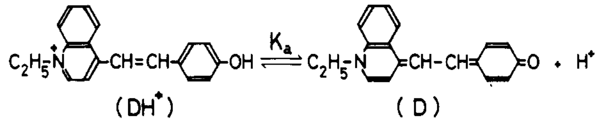
Scheme I



The merocyanine dye 4-[2-(1-ethyl-1,4-dihydroquinolinylidene)ethylidene]cyclohexa-2,5-dienone, was purchased from the Japanese Research Institute for Photosensitizing Dye Co. and used without further purification.

4,4′-Bipyridinium-1,1′-bis(trimethylenesulfonate) (SPV) was prepared according to the method of Brugger et al.[2g]

Measurements. For the estimation of surface potentials the dissociation constant of an acid–base indicator dye was determined by titration using the absorbances of the red (D) and yellow (DH^+) forms of the merocyanine dye (see Scheme I) at various pH values according to the literature.[14] The concentration of the dye was fixed at 1.5×10^{-5} M, and the pH was adjusted with aqueous sodium hydroxide and hydrochloric acid. Absorption spectra were recorded on a Hitachi 142 spectrophotometer.

Laser photolysis was carried out by using a Q-switched ruby laser (NEC SLG-2018) with a temperature-tuning RDA crystal for SHG (80 mJ per flash at 347.1 nm with a pulse width of 20 ns). A monitoring beam from a 150-W xenon arc lamp was set perpendicular to the laser beam. The details of the laser apparatus have been described elsewhere.[15] Sample solutions were placed in a 1-cm quartz cell and were deaerated under vacuum.

Results and Discussion

Surface Potential. In recent articles we have pointed out that the amphiphilic copolymers consisting of electrolyte and polycyclic aromatic segments have a strong tendency to form a microdomain structure as a result of the association of the hydrophobic segments in aqueous solutions.[11,12] The mutual Coulombic repulsion between the segmental electrolyte groups along the polymer chain is competing with the attractive interaction between the hydrophobic groups. As a consequence of the formation of the hydrophobic microdomains, a chain expansion that usually occurs in the common type of polyelectrolytes[10] is highly restricted. In this situation, the loops of the electrolyte segments would be confined to the periphery of the hydrophobic microdomains; thus the amphiphilic polyelectrolytes would provide an interface with a high charge density. In order to evaluate the surface potential of the hydrophobic microdomain of APh, the dissociation constants of an acid–base indicator associated with the interface of the domain were compared with those obtained in an aqueous bulk phase. As an indicator we used a merocyanine dye (an acid–base equilibrium is shown in Scheme I).[14a] The pK_a of a weak electrolyte at a charged surface is known to show a different value from that in an aqueous bulk due to the difference in proton activities. Thus, the pK_a difference, ΔpK_a, can simply be related to the surface potential, ϕ, by applying Boltzmann's law, $\Delta pK_a = -F\phi/2.3RT$, under the assumption that the bulk pK_a is equal to the "intrinsic surface pK_a" (the pK_a value at the same surface except the electric potential is zero),[14] where F is the Faraday constant. Actually, the equilibrium of an indicator associated with a charged interface is also influenced by a local dielectric constant of the interfacial environment, which may be different from that in an aqueous phase.[16] In practice, however, the above assumption is not far from reality as far as one intends to evaluate the surface potential relatively within a series of the analogous type of charged interfaces.[14]

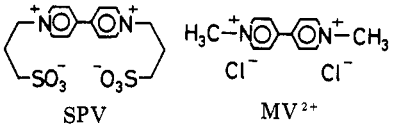
The results are summarized in Table I. In comparing the surface potential of APh with those of the related monomer model (AM) and homopolyelectrolyte (PAMPS), the striking point to make is that only the amphiphilic polyelectrolyte can provide an interfacial electric field as effective as the SDS micelle. The surface potential for the SDS micelle seems to be a little higher than those so far reported (−73 to −129 mV).[14a,b,17] The fact should be taken into consideration that the surface potential value obtained in the present method is sensitive to the location of the dye. As the merocyanine dye is amphiphilic in nature, the indicator may reside in the SDS micelle with the hydrophobic portion of the dye in the interior. Therefore, the value in Table I may reflect the potential of the Stern layer. Although a strict comparison of the surface potential between the APh and SDS micellar systems is not realistic, it may be safe to note that APh provides an interface with a surface potential similar to that of the SDS micelle. A further investigation on the surface potential of the amphiphilic polyelectrolytes is in progress by focusing our attention on the effect of ionic strength.

Table I
pK_a Values of the Merocyanine Dye and Surface Potential Calculated from ΔpK_a

sample/M	pK_a	ΔpK_a[a]	ϕ/mV[b]
Na_2SO_4, 2.5×10^{-2}	8.66		
AM, 3.3×10^{-3}	8.80	−0.14	−8
PAMPS,[c] 2.5×10^{-2}[d]	8.82	−0.16	−10
APh-9, 2.8×10^{-3}[e]	10.8	−2.14	−127
SDS, 7.5×10^{-3}	11.6	−2.94	−174

[a] $\Delta pK_a = pK_a - 8.66$ (pK_a for Na_2SO_4(aq)). [b] Calculated from $\Delta pK_a = -F\phi/2.3RT$. [c] Homopolymer of AMPS. [d] Residual concentration. [e] Residual concentration of phenanthryl group.

Back-Electron-Transfer. Previously, we investigated the light-induced electron-transfer reactions from the excited phenanthryl groups (Ph) in the amphiphilic polyelectrolytes to methylviologen (MV^{2+}) or the neutral, zwitterionic viologen, SPV, with an emphasis on the electrostatic effect on the back-electron-transfer process.[13] Our experiments led us to a remarkable finding that in the APh–SPV system the back-reaction is substantially slowed ($k_b = 8.7 \times 10^7$ M^{-1} s^{-1})[13c], as compared to the diffusion-controlled limiting value ($\sim 7 \times 10^9$ M^{-1} s^{-1}).[18]



SPV MV^{2+}

It is of interest to compare the relative effectiveness of the amphiphilic polyelectrolytes and conventional electrolyte homopolymers. Recently, Rabani and co-workers studied the effect of polybrene (a positively charged polyelectrolyte) and sodium poly(vinyl sulfate) on separating the ionic photoproducts in the $Ru(bpy)_2(CN)_2$–$Fe(CN)_6{}^{3-}$ system[8] and the $Ru(bpy)_3{}^{2+}$–p-disulfonated benzylviologen system,[9] respectively. The rate constants for the back-reaction were reported to be $k_b = 4 \times 10^9$ M^{-1} s^{-1} for the former[8] and $k_b = 2.3 \times 10^9$ M^{-} s^{-1} for the latter system.[9] In the absence of the polyelectrolytes the back-reaction was reported to occur at the diffusion-controlled limiting rate in both cases. It is pointed out that the amphiphilic polyelectrolytes have a much stronger retardation effect on the back-reaction, which, we believe, originates from the presence of the charged interface.

To further probe into this remarkable effect of the highly attractive or repulsive surface potential of the hydrophobic microdomains of APh and the corresponding amphiphilic polycation (QPh), laser photolysis experiments were performed on the various systems including these polymers and the viologens as electron acceptors. Figure 1 shows an example of the decay curves for the viologen radicals generated upon laser excitation of the QPh–SPV system. The decay of the viologen radical anion, $SPV^{-\cdot}$,

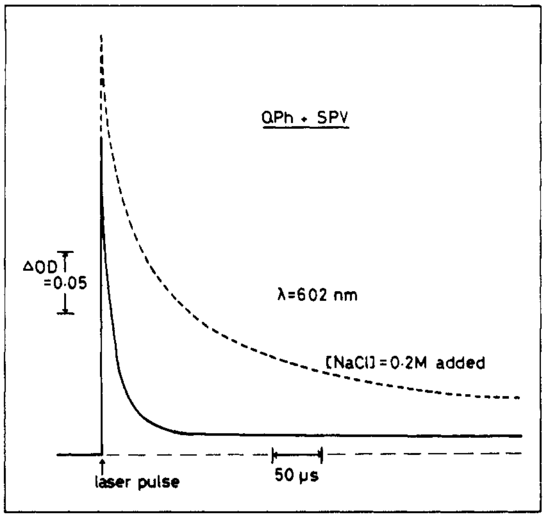
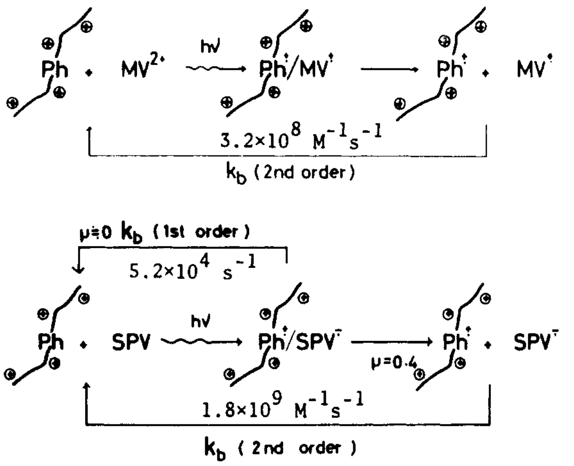


Figure 1. Transient absorption decay of SPV$^{-\cdot}$ followed at 602 nm for the QPh–SPV system: [Ph(residue)] = 2.5 × 10^{-3} M, [SPV] = 1.0 × 10^{-2} M.

Scheme II



was followed at 602 nm in the microsecond time region. It is improtant to note that relatively rapid back-reaction occurs in this system. Analysis of the decay curve reveals that it obeys simple first-order kinetics (k_b = 5.2 × 10^4 s^{-1}). Upon addition of 0.2 M NaCl a dramatic change in the pattern of the decay curve was observed; the back-reaction was considerably slowed and the decay kinetics changed completely to a second-order reaction with the rate constant of k_b = 1.8 × 10^9 M^{-1} s^{-1}. These facts suggest that the photoreduced acceptor, SPV$^{-\cdot}$, cannot escape from the positively charged interface due to electrostatic binding, and hence the back-electron-transfer, as pictured in Scheme II, occurs by a first-order process in the bound state. Since the addition of the inorganic salt interferes with the electrostatic association of SPV$^{-\cdot}$ with the interface, SPV$^{-\cdot}$ can undergo diffusional escape to free ions in the bulk phase. Accordingly, the back-reaction occurs according to a bimolecular process. As for the QPh–MV^{2+} system, the kinetic evaluation of the decay curve of MV$^{+\cdot}$ in the laser photolysis yielded a rate constant of k_b = 3.2 × 10^8 M^{-1} s^{-1} (Scheme II), indicating, as expected from the result for the APh–SPV system,[13c] that the back-reaction is considerably retarded owing to the high electrostatic barrier in the periphery of the hydrophobic microdomains of QPh. As pictured in Scheme III, the change of the order of the back-reaction was also observed for the APh–MV^{2+} system. The negative charge of the interface of APh strongly restricts the escape of the radical cation, MV$^{+\cdot}$, from the surface of the hydrophobic microdomain, leading to a rapid first-order back-reaction (k_b = 1.7 × 10^4 s^{-1}). Upon addition of the salt, the switch-over of the decay kinetics was also observed as in the QPh–SPV system. The reaction order of the k_b reflects whether the ionic photoproducts are bound to the interface or free in the bulk phase.

Scheme III

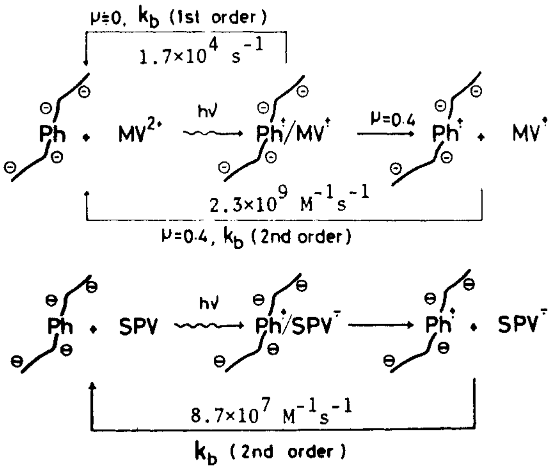
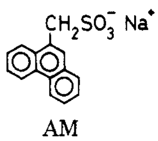


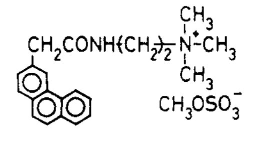
Table II
Rate Constants for the Back-Electron-Transfer (k_b) for Related Monomer Models

monomer model	k_b for SPV	k_b for MV^{2+}
QM	9.6 × 10^9 M^{-1} s^{-1}	8.6 × 10^9 M^{-1} s^{-1}
AM	2.8 × 10^9 M^{-1} s^{-1}	1.8 × 10^4 s^{-1}

The k_b was also determined by laser photolysis for the related monomer model systems for comparison. As given in Table II, QM, the monomer model for QPh, showed a



AM



QM

rapid reverse electron transfer occurring at a bimolecular rate constant close to the diffusion-controlled limit[18] with either MV^{2+} or SPV. This is in marked contrast to the behavior of QPh and a clear indication that a single charge is far from sufficient to cause any electrostatic effect on the photoredox process. In this context, we had expected that AM, the monomer model for APh, would have shown more or less the same behavior as QM. However, the magnitude of k_b (2.8 × 10^9 M^{-1} s^{-1}) for the AM–SPV system was found to be a little lower than the diffusion-controlled limiting value. Furthermore, in the AM–MV^{2+} system, the decay of the photoproduct, MV$^{+\cdot}$, following a laser pulse obeyed a first-order rate law. The decay mechanism in this system appears to be the same as that of the APh system. Presumably, this rather peculiar observation is attributed to the nature of AM, which has a tendency to form aggregates in an aqueous solution as evidenced in a previous work.[13b] As a result of aggregation, AM may act as a "polyanion", leading to a similar kinetic feature as the APh system. However, it should be noted again that the surface potential of AM is about the same as that of PAMPS (homopolyelectrolyte) and much lower than that of APh (Table I). With SPV as an acceptor, this difference in the surface potential is reflected in the effectiveness on the retardation of the back-reaction; i.e., k_b

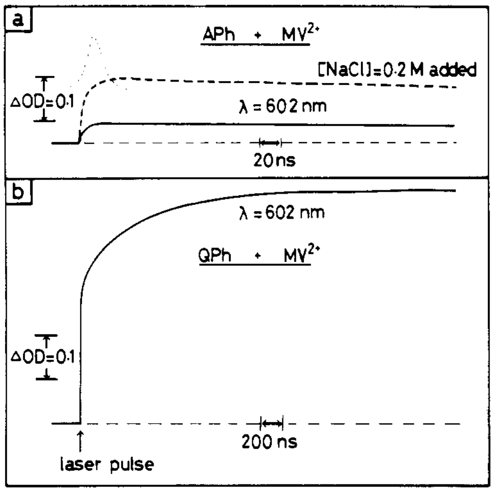


Figure 2. Transient absorption changes of $MV^{+\cdot}$ produced by the 347.1-nm laser pulse: (a) APh–MV^{2+} system; (b) QPh–MV^{2+} system. [Ph(residue)] = 2.5×10^{-3} M, [MV^{2+}] = 1.0×10^{-2} M. The dotted line shows the profile of the laser pulse.

Table III
Effect of Ground-State CT Complexation on the Fluorescence Quenching and the Light-Induced Formation of MV^{+}.

sample	[NaCl] added/M	$A_{390\ nm}$[a] (ground state)	$k_q \times 10^{-9}$[b]/ ($M^{-1}\ s^{-1}$)	$A_{602\ nm}$[c] (after pulse)
APh	0	0.86	380[e]	<0.02
APh	0.2	0.63	146[e]	0.12
AM	0	1.59	31	0.02
Ph/SDS[d]	0	1.06	40	<0.01
QPh	0	0	0.53	0.78
QPh	0.2	<0.05	1.7	0.45
QM	0	0.36	7.3	0.38

[a] Absorbance of the CT band at 390 nm; [Ph(residue)] = 2.5 mM, [MV^{2+}] = 1 mM. [b] Apparent second-order rate constant of fluorescence quenching (cited from ref 13b). [c] Maximum transient absorbance of $MV^{+\cdot}$ at 602 nm after a laser pulse; [Ph(residue)] = 2.5 mM, [MV^{2+}] = 1 mM. [d] Phenanthrene solubilized in SDS micelle; [phenanthrene] = 2.5 mM, [SDS] = 50 mM. [e] These values are orders of magnitude larger than the diffusion-controlled limiting value because a static mechanism is involved.[13b]

= $2.8 \times 10^9\ M^{-1}\ s^{-1}$ (Table II) for the AM system as compared with $k_b = 8.7 \times 10^7\ M^{-1}\ s^{-1}$ (Scheme III) for the APh system. With MV^{2+}, on the other hand, the photoreduced radical cation, $MV^{+\cdot}$, may be stabilized even by a lower potential field of the AM system (Table I) to such an extent that the back-reaction occurs predominantly before undergoing diffusional escape to a free ion. This may be a plausible explanation for the similarity of the k_b values for the AM–MV^{2+} and the APh–MV^{2+} system.

Forward Electron Transfer. In order to gain insight into the forward electron-transfer process, we further performed laser photolysis experiments at nanosecond time scales. In the APh–MV^{2+} system, the rapid growth of $MV^{+\cdot}$ as shown in Figure 2a as well as the extremely efficient fluorescence quenching[19] (Table III) indicates that the forward electron transfer occurs solely from the singlet excited state of Ph. It is important to note that the yield of $MV^{+\cdot}$ is extremely low in this system despite the fact that APh is subjected to a multicycle excitation in a laser shot due to the rapid fluorescence quenching by MV^{2+}. As also shown in Figure 2a, the addition of 0.2 M NaCl increased the yield of $MV^{+\cdot}$ by about 3 times whereas the fluorescence quenching was a little diminished (Table III).

In striking contrast, a distinctive feature of the QPh–MV^{2+} system is that, as is evident in Figure 2b, the buildup of $MV^{+\cdot}$ reaches a considerably higher level, although the fluorescence quenching of QPh is far less effective than that of APh (see Table III). Apparently, the time course of the growth of $MV^{+\cdot}$ after the laser pulse consists of two distinctive components, i.e., an initial sharp rise followed by a slow buildup in about 2 μs. The initial rapid process seems to be complete within the duration time of the laser pulse, resulting in about half the total transient yield of $MV^{+\cdot}$. Presumably, this process involves the forward reaction from the singlet excited Ph. The subsequent slow growth of $MV^{+\cdot}$ suggests a bimolecular reaction between the triplet excited states of Ph ($^3Ph^*$) and MV^{2+}. In fact, the electron transfer via $^3Ph^*$ is considered to be possible on the basis of an estimate of the oxidation potential of $^3Ph^*$ (−1.17 V vs. SCE)[13b] that is sufficiently negative to reduce MV^{2+} (half-wave reduction potential is −0.68 V vs. SCE).[13b] The quantum yield of $MV^{+\cdot}$ production in the QPh–MV^{2+} system was roughly estimated to be ca. 0.1 from the transient yield of $MV^{+\cdot}$, the incident photon number of the laser beam, and the absorbance of the sample solution at 347.1 nm.[20]

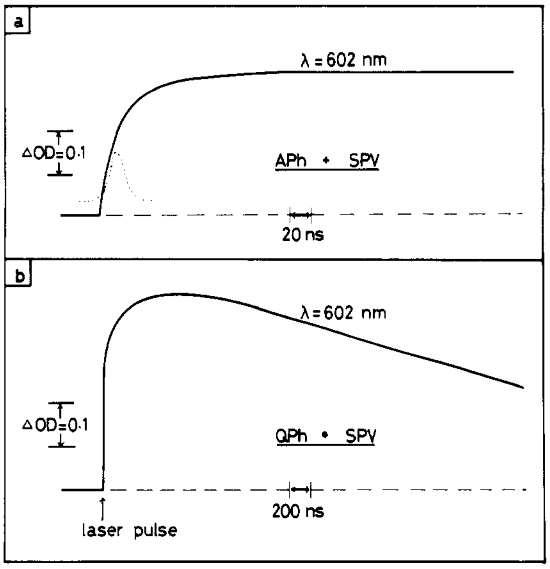


Figure 3. Transient absorption changes of $SPV^{-\cdot}$ produced by the 347.1-nm laser pulse: (a) APh–SPV system; (b) QPh–SPV system. [Ph(residue)] = 2.5×10^{-3} M, [SPV] = 1.0×10^{-2} M. The dotted line shows the profile of the laser pulse.

Figure 3a shows the growth of $SPV^{-\cdot}$ after the laser pulse for the APh–SPV system. It appears that $SPV^{-\cdot}$ is predominantly (over 80% of the total transients) produced from a singlet-state reaction. It is noted that the transient yield of the reduced viologen is about half that in the QPh–MV^{2+} system.

In the system QPh–SPV, an appreciable amount of $SPV^{-\cdot}$ seems to be formed via a triplet reaction (Figure 3b) as in the case for the QPh–MV^{2+} system. The decay of $SPV^{-\cdot}$ is already discernible on the time scale of Figure 3b after passing through the maximum absorbance due to the rapid back-reaction occurring in the bound state (Scheme II).

Effect of Ground-State Interaction. From the results described in the previous section it is concluded that the effectiveness of the fluorescence quenching does not parallel the yield of the transient photoproducts; the less effective the fluorescence quenching, the higher the transient yield of the photoproducts. This is explicable in terms of the adverse effect of the ground-state interaction of Ph and the viologens. In a previous report we discussed that the electrostatic effect is reflected in the ground-state CT interaction between Ph and the viologens.[13b] Figure 4 exhibits the CT band at 390 nm obtained on the solutions used for the laser photolysis experiments. The APh–MV^{2+}

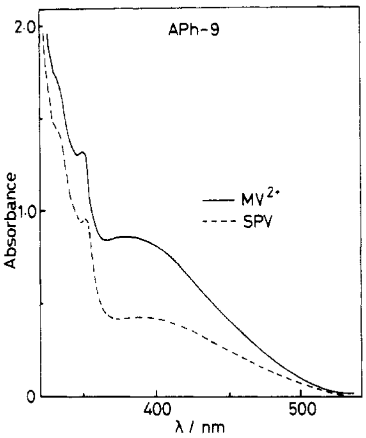


Figure 4. Absorption bands due to ground-state CT complexes between the phenanthryl group of APh and viologens for the solutions used for the laser photolysis experiments shown in Figures 2a and 3a.

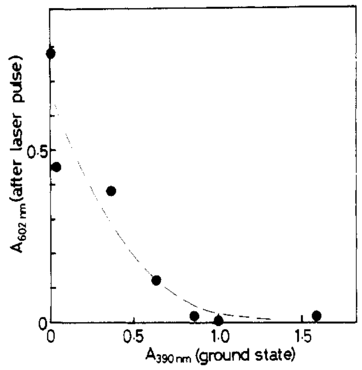
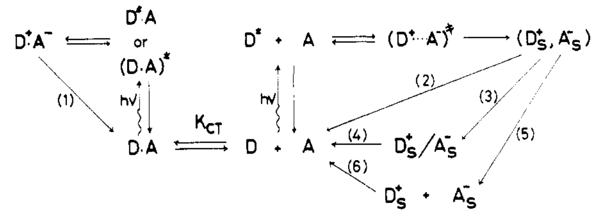


Figure 5. Relationship between the maximum transient absorbances at 602 nm due to $MV^{+}\cdot$ in the laser photolysis and the absorbances due to the ground-state CT bands.

system showed a higher intensity in the CT band than the APh–SPV system obviously due to an electrostatic attraction of MV^{2+} by APh. In Table III the absorbances of these CT bands measured for the various systems containing MV^{2+} as an electron acceptor are summarized. As previously discussed, depending on whether the electrostatic effect is attractive or repulsive, a drastic difference in the complex formation is entailed. The repulsive positive charges in QPh severely prevented the cationic acceptor from access to the phenanthryl groups at a distance close enough to form the CT complex. In Table III the constants for the fluorescence quenching determined in a previous work[13b] are also included. As a measure of the transient yield of the photoreduced viologens, the maximum values of the transient absorbance at 602 nm reached after the laser pulse are listed. It is important to point out that the transient yield of the viologen radicals sharply decreases as the ground-state interaction increases. This relationship is depicted in Figure 5, in which all the values in Table III are plotted. Obviously the ground-state complexation strikingly disfavors the yield of the photoredox products, although it strongly favors the fluorescence quenching that involves a static mechanism.[13b]

A similar effect was reported recently for a system involving charged metalloporphyrins and MV^{2+}. Negatively charged metalloporphyrins, such as zinc tetrakis(*p*-sulfonatophenyl)porphyrin, are known to form ground-state CT complexes with MV^{2+} in aqueous solution as a result of electrostatic attraction between the donor and the acceptor.[21] Despite effective quenching of the excited porphyrins in these system, the yield of the reduced acceptor, $MV^{+}\cdot$, is reported to be extremely low.[21] In contrast, irradiation of a positively charged metalloporphyrin, zinc tetrakis(4-*N*-methylpyridyl)porphyrin, in the presence of MV^{2+} leads to a high yield of $MV^{+}\cdot$, although apparently the quenching process seemed to be much less effective.[21] In the latter case the ground-state complexation seems to be disfavored due to a Coulombic repulsion.

Scheme IV



From the viewpoint of designing an artificial system for conversion and storage of light energy, the question has been asked in the past decade as to whether the ground-state interaction favors or disfavors the yield of photoproducts. Those results reported so far, including the results in the present study, may suggest that such an adverse effect of the complexation on the yield may generally be applied to photoredox systems. However, there is a recent paper which reports the ground-state complexation having a positive effect on the yield of $MV^{+}\cdot$ in the system containing palladium *meso*-tetraphenylporphyrin trisulfonate as a sensitizer.[22]

Scheme IV describes simple kinetic schemes for the photoredox system including ground-state complexation. The electron transfer within the complex may be imagined as an intramolecular process in which excited energy would dissipate by almost simultaneous back-reaction (pathway 1). Thus, the complexation can simply be regarded as causing a decrease in the number of molecules capable of a net electron transfer. In the scheme, (D_s^{+},A_s^{-}) represents a solvent-separated ion pair in a geminate state which, in ordinary cases, either dissipates (pathway 2) or dissociates to yield free ions, D_s^{+} and A_s^{-}. In the absence of subsequent redox reaction branches, the bimolecular decay (pathway 6) is the predominant event in the fate of these free ions. In the systems of APh–MV^{2+} and QPh–SPV, however, the solvent-separated ion pair would not dissociate to free ions but instead would result in the interfacially bound state, D_s^{+}/A_s^{-}, in which the photoreduced products cannot escape from the charged interfacial area due to a strong Coulombic attraction. The first-order back-reactions we observed in these systems are obviously ascribable to the reverse electron transfer in this bound state (pathway 4). This is a new type of back-reaction process that seems to be entirely unique to the microenvironmental system of the functional polyelectrolytes. The solvent-separated ion pair may be either stabilized or destabilized by the interfacial electric field, depending on the sign of the charges. In the latter case, pathway 5 is likely to be facilitated, and the free ions are thus stabilized against the back-reaction (pathway 6). This may be the critical effect that the interfacial microenvironments of the functional polyelectrolytes may have on charge separation.

The results of this study provide useful information for further designing the functional polyelectrolyte, aiming at more effective interfacial assemblies for the light-induced electron-transfer processes.

In conclusion, functional polyelectrolytes consisting of charged segments and phenanthryl groups were demonstrated to serve as novel interfacial microenvironments that critically control the rate and direction and hence the yield of photoredox reactions in the presence of viologens as electron acceptors. The effective retardation of back-electron transfer was achieved in the system where the sign of the charge of the photoreduced viologens is the same as that of the polyions, whereas the opposite combination of the charges facilitate in turn the back-reaction that occurs by a first-order process. The ground-state CT complexation of the phenanthryl groups with methylviologen, which is facilitated by electrostatic attraction between the polyanions and methylviologens, extremely disfavored the yield of photoproducts. These results are of value for further design of functional polyelectrolytes.

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