Photoinduced Electron Transfer to Methylviologen from Zinc(II) Tetraphenylporphyrin Compartmentalized in Unimer Micelles of Amphiphilic Polyelectrolytes

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ABSTRACT: Zinc(II) tetraphenylporphyrin (ZnTPP) moieties are covalently attached to amphiphilic sodium polysulfonates carrying about 60 mol % of lauryl (LA), 2-(naphthyl)methyl (Naph), or cyclododecyl (CD) groups. The ZnTPP moieties are compartmentalized within the hydrophobic clusters in aqueous solution. The charge transfer complexation of the compartmentalized ZnTPP moieties with methylviologen (MV^{2+}) is completely suppressed. The electron transfer (ET) from the singlet excited state of the ZnTPP chromophore to MV^{2+} in the compartmentalized system is 2 orders of magnitude slower than that in a reference copolymer system having no hydrophobic groups. The apparent second-order rate constants for the ET from the triplet excited state of the ZnTPP chromophore to MV^{2+} are almost equal in all the polymer systems. The accumulation of $ZnTPP^{+\bullet}$ was observed as a result of the compartmentalization. The Naph and CD groups are more effective in the accumulation of $ZnTPP^{+\bullet}$ than is the LA group. $ZnTPP^{+\bullet}$ persisted over a period of milliseconds in the terpolymer systems containing the Naph and CD groups.

Introduction

Porphyrins and metalloporphyrins play important roles as functional groups in a wide variety of biological systems.[1,2] In these biological functional systems, metalloporphyrins are situated in inner sites of proteins with specific alignment and orientation.

Photoinduced electron transfer (ET) to methylviologen (MV^{2+}) from various water-soluble tetraphenylporphyrin (ZnTPP) derivatives[3−7] have been studied as a model of an artificial photosynthesis due to the fact that the reduction of water to hydrogen by photogenerated methylviologen cation radical ($MV^{+\bullet}$) is thermodynamically possible. However, for the reduction of water by the photogenerated $MV^{+\bullet}$, catalysts have to be added to the reaction system to overcome the overpotential involved in the water reduction.[6,7] In addition, sacrificial donors, such as ethylenediaminetetraacetic acid (EDTA),[5−7] are necessary to prevent fast back ET from $MV^{+\bullet}$ to the cation radicals of ZnTPP derivatives. Electrostatic interactions between water-soluble ZnTPP derivatives and the acceptor are an important factor to control the photoinduced ET. Both forward and backward ET are very fast in systems of anionic ZnTPP derivatives, such as zinc(II) tetrasulfonylphenylporphyrin ($ZnTSPP^{4-}$), with MV^{2+} due to electrostatic attraction[5] between the donor and the acceptor. However, they are very slow in a cationic ZnTPP derivative system such as a zinc(II) tetrapyridylmethylporphyrin ($ZnTMPyP^{4+}$) system due to electrostatic repulsion.[5] In fact, the formation of the porphyrin cation radical and/or $MV^{+\bullet}$ has been detected only in cationic ZnTPP systems[4,5] despite that the forward ET is slow.

We have shown that photophysics and photochemistry of some chromophores can be greatly modified if they are incorporated into self-organized microphases of some amphiphilic polyelectrolytes in aqueous media.[8−24] Amphiphilic copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (AMPS) and methacrylamides carrying bulky hydrophobic side-chain groups adopt unimolecular micelles (unimer) due to intramolecular hydrophobic self-association of the side-chain hydrophobic groups.[10−14] The unimer micelles consist of hydrophobic clusters in which the hydrophobic side-chain groups are so tightly packed that their molecular motions are highly restricted. Thus, the hydrophobic clusters provide highly constraining microenvironments for chromophores incorporated into the clusters.[15,16]

If a small amount of polycyclic aromatic chromophore is covalently incorporated into the amphiphilic AMPS copolymers bearing bulky hydrophobic groups, such as lauryl (LA), cyclododecyl (CD), and 2-naphthylmethyl (Naph) groups, the chromophore moieties are compartmentalized in the hydrophobic clusters in aqueous media.[8−16] We previously reported that photophysics and photochemistry of the compartmentalized chromophores, such as phenanthrene[17] and pyrene,[18] were very different from those in homogeneous solution. For example, fast ET occurs from the compartmentalized photoexcited aromatic chromophores to MV^{2+} electrostatically bound in the charged outer layer of the hydrophobic clusters, while back ET is considerably slowed, and thus effective charge separation is achieved.[17,18]

In our recent studies using ZnTPP as a chromophore, we recognized the unusual photophysical[19−22] and photochemical[23] behavior of the compartmentalized ZnTPP moieties. In a previous paper, we reported photoinduced electron transfer from the compartmentalized ZnTPP to an onium salt, phenylmethylphenacylsulfonium *p*-toluenesulfonate (PMPS), as the self-destructive electron acceptor.[23] Charge transfer (CT) complexation between the ZnTPP moiety and PMPS which was electrostatically concentrated on the surface of the unimer micelles and ET from the singlet excited state (S_1) of ZnTPP to PMPS were completely prevented because the ZnTPP and PMPS species were separated inside and outside of the unimer micelle, respectively.

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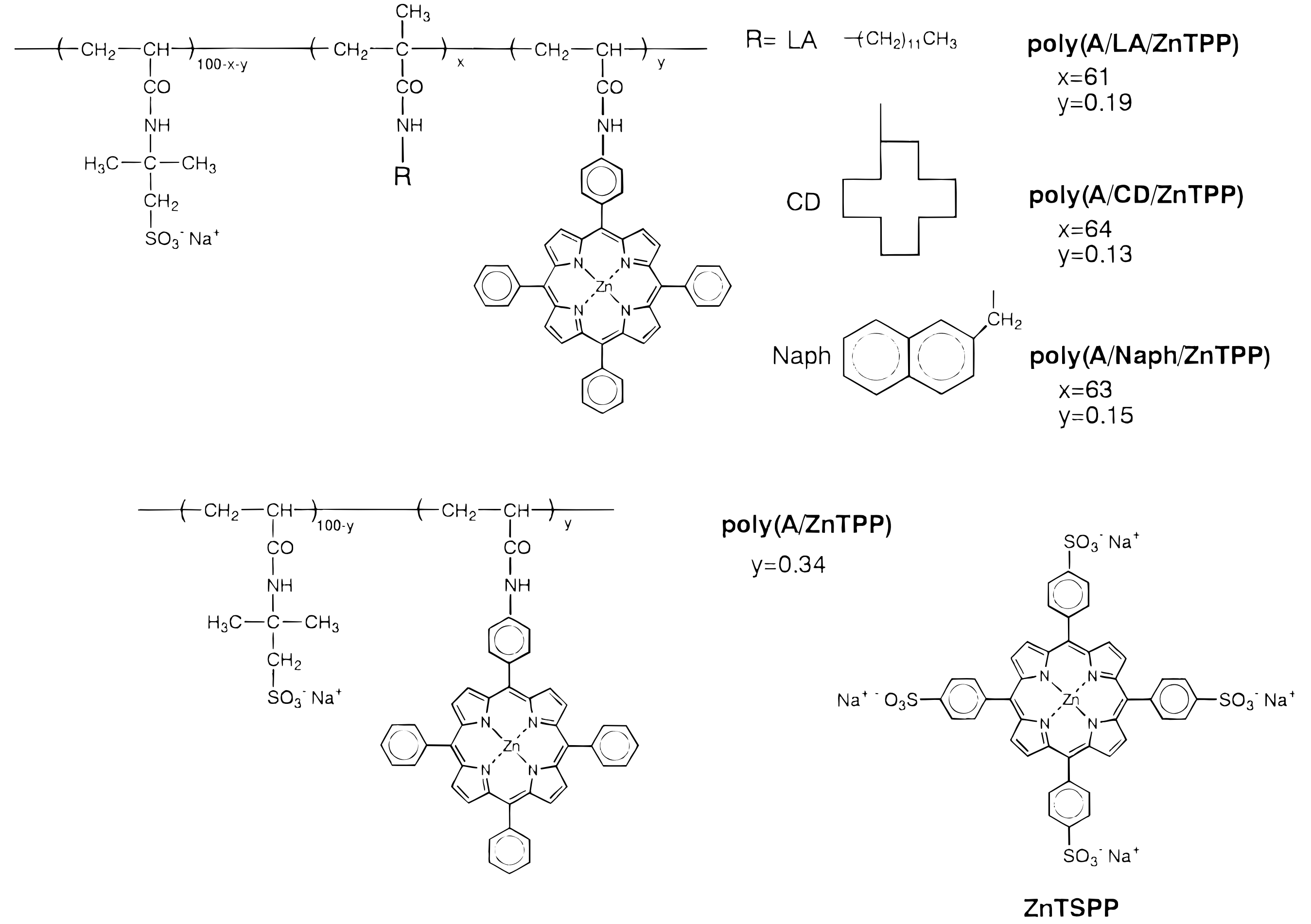
Chart 1



However, ET from the triplet excited state (T_1) of ZnTPP to PMPS occurred to generate porphyrin cation radicals ($ZnTPP^{+\bullet}$) in the hydrophobic microdomain of the unimer micelle. Since the ZnTPP chromophores were protected from the bulk aqueous phase, subsequent reaction between the resulting $ZnTPP^{+\bullet}$ and phenacyl radical from PMPS was prevented. Thus, the resulting $ZnTPP^{+\bullet}$ was efficiently accumulated under steady-state irradiation of visible light.

In the present studies, we conducted photoinduced ET to MV^{2+}, a reversible acceptor, in place of PMPS with the compartmentalized ZnTPP moieties in the LA, CD, or Naph cluster.

Experimental Section

Polymers. The terpolymer of 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS) with 61 mol % *N*-laurylmethacrylamide (LAMAm) and 0.19 mol % 5-[4-(acrylamido)phenyl]-10,15,20-triphenylporphyrinatozinc(II) (ZnAATPP), the terpolymer of AMPS with 64 mol % of *N*-cyclododecylmethacrylamide (CDMAm) and 0.13 mol % ZnAATPP, and the terpolymer of AMPS with 63 mol % of *N*-[(2-naphthyl)methyl]-methacrylamide (2-NaphMAm) and 0.15 mol % of ZnAATPP were prepared as reported previously.[19] For example, in a glass ampule containing 10 mL of *N*,*N*-dimethylformamide, 1.04 g (5.00 mmol) of AMPS, 1.01 g (10.0 mmol) of triethylamine, 1.13 g (5.00 mmol) of 2-NaphMAm, 7.48 mg (10 μmol) of ZnAATPP, and 4.12 mg (25 μmol) of 2,2′-azobis(2-methylpropionitrile) (AIBN) were dissolved in order as listed. The solution was outgassed on a vacuum line by six freeze−pump−thaw cycles and then sealed. Radical polymerization was conducted at 60 °C for 24 h. The reaction mixture was poured into 150 mL of ether to precipitate the resulting terpolymer. The terpolymer was purified by reprecipitating from methanol into a large excess of ether twice and then dissolved in dilute aqueous NaOH whose pH was adjusted to 13. Triethylamine was evaporated by heating the aqueous solution at 90 °C for 30 min with vigorous agitation followed by extraction with *n*-hexane three times. After evaporating the remaining *n*-hexane by heating, the aqueous solution was dialyzed against dilute aqueous NaOH at pH 10 for 1 week. The polymer was recovered by freeze-drying. The conversion was 18.3% (0.4 g) on the basis of the total monomers. The reference copolymer of AMPS and 0.34 mol % ZnAATPP was synthesized as reported previously.[19] The terpolymers containing the LAMAm, CDMAm, or 2-NaphMAm unit and the reference copolymer are abbreviated as poly(A/LA/ZnTPP), poly(A/CD/ZnTPP), poly(A/Naph/ZnTPP), and poly(A/ZnTPP), respectively (Chart 1). The contents of the ZnAATPP unit in these polymers were determined by UV−visible absorption spectroscopy.[19]

Other Materials. Tetrakis(4-sulfonatophenyl)porphyrinatozinc(II) (ZnTSPP) was prepared according to the literature[7] (Chart 1). Methylviologen (MV^{2+}) (Tokyo Kasei Co.) was purified by recrystallization from ethanol. Water was doubly distilled.

Measurements. Absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer at room temperature. Concentrations of the ZnTPP residues in aqueous solutions were adjusted to 2 μM.

Fluorescence spectra were recorded on a Shimadzu RF-5000 spectrofluorophotometer at room temperature. Concentrations of the ZnTPP residues in aqueous solutions were adjusted to 2 μM. The excitation wavelength for the sample solutions was 563 nm.

Laser photolysis was performed by using a Q-switched Nd:YAG laser (Quantaray DCR-2) operated at second harmonics (532 nm). The details of the laser apparatus have been reported elsewhere.[24] A Toshiba KL-48 band-pass (480 nm) and a Toshiba Y-48 cutoff (480 nm) filters were placed between a 150 W xenon arc lamp (analyzing beam) and a sample cell for the measurement of the decay profiles of the $T_n \leftarrow T_1$ absorption of the ZnTPP residue at 480 nm. A Toshiba Y-43 cutoff filter (430 nm) was used in a manner similar to the measurement of time-resolved transient absorption spectra. Concentrations of 10 and 100 μM of the ZnTPP residues in aqueous solution were used for the measurements of the decay profiles at 480 nm and of the time-resolved transient absorption spectra, respectively. The solutions were deaerated by bubbling with argon for 30 min prior to the measurements.

The concentrations of $ZnTPP^{+\bullet}$ were estimated from the time-resolved transient absorption spectra by using eq 7 as follows. In the laser photolysis, a transient absorbance change (OD) at a given time and wavelength is given by

$$\mathrm{OD} = \epsilon_{\mathrm{T}}[\mathrm{T}_1] + \epsilon_{\mathrm{ZnTPP}^{+\bullet}}[\mathrm{ZnTPP}^{+\bullet}] + \epsilon_{\mathrm{MV}^{+\bullet}}[\mathrm{MV}^{+\bullet}] - \epsilon_{\mathrm{S}_0}\{[\mathrm{S}_0]_0 - [\mathrm{S}_0]\} \quad (1)$$

where ϵ_{T}, $\epsilon_{\mathrm{ZnTPP}^{+\bullet}}$, $\epsilon_{\mathrm{MV}^{+\bullet}}$, and ϵ_{S_0} are the extinction coefficients of the lowest triplet excited state of the ZnTPP moiety (T_1), $ZnTPP^{+\bullet}$, $MV^{+\bullet}$, and the ground state of the ZnTPP moiety (S_0) at a given wavelength, respectively. [T_1], [$ZnTPP^{+\bullet}$], [$MV^{+\bullet}$], and [S_0] are the concentrations of T_1, $ZnTPP^{+\bullet}$, $MV^{+\bullet}$, and S_0 at a given time, respectively. $[S_0]_0$ (=100 μM) is the initial concentration of S_0 given by

$$[\mathrm{S}_0]_0 = [\mathrm{T}_1] + [\mathrm{ZnTPP}^{+\bullet}] + [\mathrm{S}_0] \quad (2)$$

If we assume

$$[\mathrm{ZnTPP}^{+\bullet}] = [\mathrm{MV}^{+\bullet}] \quad (3)$$

then we obtain

$$\mathrm{OD} = (\epsilon_{\mathrm{T}} - \epsilon_{\mathrm{S}_0})[\mathrm{T}_1] + (\epsilon_{\mathrm{ZnTPP}^{+\bullet}} + \epsilon_{\mathrm{MV}^{+\bullet}} - \epsilon_{\mathrm{S}_0})[\mathrm{ZnTPP}^{+\bullet}] \quad (4)$$

Absorbance of T_1 (OD_T) is

$$\mathrm{OD}_{\mathrm{T}} = (\epsilon_{\mathrm{T}} - \epsilon_{\mathrm{S}_0})[\mathrm{T}_1] \quad (5)$$

Thus, OD is given by

$$\mathrm{OD} = \mathrm{OD}_{\mathrm{T}} + (\epsilon_{\mathrm{ZnTPP}^{+\bullet}} + \epsilon_{\mathrm{MV}^{+\bullet}} - \epsilon_{\mathrm{S}_0})[\mathrm{ZnTPP}^{+\bullet}] \quad (6)$$

Since OD_T at 650 nm is nearly equal to that at 800 nm,[19]

$$\mathrm{OD}_{650} - \mathrm{OD}_{800} \cong \{(\epsilon_{\mathrm{ZnTPP}^{+\bullet}} + \epsilon_{\mathrm{MV}^{+\bullet}} - \epsilon_{\mathrm{S}_0})_{650} - (\epsilon_{\mathrm{ZnTPP}^{+\bullet}} + \epsilon_{\mathrm{MV}^{+\bullet}} - \epsilon_{\mathrm{S}_0})_{800}\}[\mathrm{ZnTPP}^{+\bullet}] \quad (7)$$

The values of $\epsilon_{\mathrm{ZnTPP}^{+\bullet}}$ and $\epsilon_{\mathrm{MV}^{+\bullet}}$ were approximately estimated from spectra reported in the literature to be 10 000[25] and 7700[26] M^{-1} cm^{-1} at 650 nm, and also to be 2100[25] M^{-1} cm^{-1} and practically zero[4] at 800 nm, respectively. The values of ϵ_{S_0} at 650 and 800 nm were determined to be 1000 and 300 M^{-1} cm^{-1}, respectively.[19]

Results and Discussion

As re reported previously,[19-23] the ZnTPP units are compartmentalized within the hydrophobic microdomains in the unimer micelles formed by the terpolymers in aqueous solution and the chromophores are protected from bulk aqueous phase. Since the amounts of the ZnTPP units loaded on the terpolymers are very small (0.1−0.2 mol %), each ZnTPP unit is independently encapsulated in the hydrophobic microdomain and is prohibited from encountering others. In the reference copolymer, on the other hand, the ZnTPP moieties are exposed to the aqueous phase.

Absorption spectra of ZnTSPP, poly(A/ZnTPP), and poly(A/LA/ZnTPP) in the region of the Soret band in the absence and presence of MV^{2+} in aqueous solution are shown in Figure 1. In the ZnTSPP and poly(A/ZnTPP) systems, the peaks shifted to longer wavelength with an increase in the concentration of MV^{2+}. The poly(A/ZnTPP) system exhibits the red-shift at lower MV^{2+} concentrations than ZnTSPP does because MV^{2+} is electrostatically concentrated on the polymer chain. The charge transfer (CT) formation constants (K_{CT}) for ZnTSPP and poly(A/ZnTPP) estimated from these spectral data by use of the Nash's plot[27] are listed in Table 1. The K_{CT} value for poly(A/ZnTPP) is 1 order of magnitude larger than that for ZnTSPP.

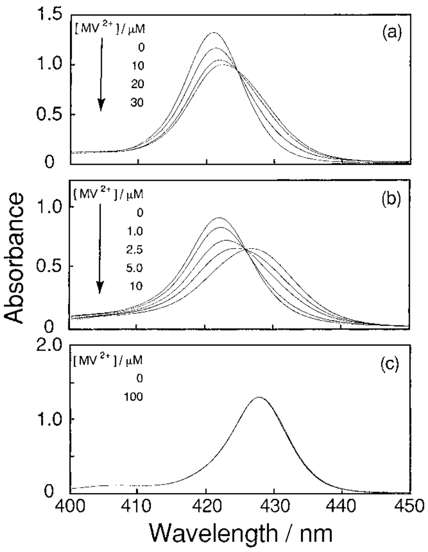


Figure 1. Soret absorption bands for (a) ZnTSPP, (b) poly(A/ZnTPP), and (c) poly(A/LA/ZnTPP) in the presence of varying amounts of MV^{2+} in aqueous solution. The residual concentration of the porphyrin moieties is 2 μM.

Table 1. Formation Constant for the CT Complex (K_{CT}), Stern−Volmer Constant for Fluorescence Quenching (K_{SV}), and Apparent Second-Order Rate Constant for Electron Transfer from Triplet Excited ZnTPP to MV^{2+} in Aqueous Solution ($k_{q,T}$)

sample	K_{CT}/M^{-1}	K_{SV}/M^{-1} ($k_{q,S}/M^{-1}$ s^{-1})[a]	$k_{q,T}/M^{-1}$ s^{-1}
ZnTSPP	2.5×10^4	3.2×10^4 [b] (1.9×10^{13})	8.2×10^9
poly(A/ZnTPP)	2.3×10^5	3.4×10^5 [b] (2.0×10^{14})	2.2×10^9
poly(A/LA/ZnTPP)	*c*	4.8×10^3 (2.8×10^{12})	2.2×10^9
poly(A/Naph/ZnTPP)	*c*	4.8×10^3 (2.8×10^{12})	7.4×10^8
poly(A/CD/ZnTPP)	*c*	2.1×10^3 (1.2×10^{12})	1.8×10^9

[a] The apparent $k_{q,S}$ values were estimated from eq 8 by using the lifetime of singlet excited state of ZnTSPP (1.7 ns).[31] [b] The apparent Stern−Volmer constant was estimated from eq 12. [c] No CT interaction.

In contrast, in the poly(A/LA/ZnTPP) system (Figure 1c), no such changes in spectral profile occurred, although the concentration of added MV^{2+} was higher than those in the ZnTSPP and poly(A/ZnTPP) systems. The other terpolymer systems showed the same results as the poly(A/LA/ZnTPP) system. These results are the same as the previous study using phenylmethylphenacylsulfonium *p*-toluenesulfonate (PMPS) as an electron acceptor[23] and indicate that the CT complexation between the ZnTPP moiety and MV^{2+} was completely prevented due to the protection of the ZnTPP moiety in the hydrophobic cluster, although MV^{2+} species are concentrated on the anionic surface of the unimer micelle.

Electron transfer quenching of the singlet excited state (S_1) of the ZnTPP moiety (^{1}ZnTPP*) is known to occur in homogeneous solution in the presence of MV^{2+} as an acceptor.[5] Apparent second-order rate constants for the ET from ^{1}ZnTPP* to MV^{2+} ($k_{q,S}$) were estimated by a fluorescence quenching experiment with the use of the Stern−Volmer equation:[28]

$$I_0/I = 1 + K_{SV}[Q] \qquad K_{SV} = k_{q,S}\tau_0 \tag{8}$$

where I_0 and I are the fluorescence intensities in the absence and presence of the quencher, respectively, K_{SV} is the Stern−Volmer constant, [Q] is the concentration of the quencher, and τ_0 is the lifetime of S_1 in the absence of the quencher. When CT complexes exist in the system, static quenching of fluorescence occurs. Then, the Stern−Volmer equation can be modified[29,30] as

$$I_0/I = (1 + K_{SV}[Q])(1 + K_{CT}[Q]) \tag{9}$$

$$= 1 + (K_{CT} + K_{SV})[Q] + K_{CT}K_{SV}[Q]^2 \tag{10}$$

if

$$[Q] \ll (1/K_{SV}) + (1/K_{CT}) \tag{11}$$

then

$$I_0/I \cong 1 + K'_{SV}[Q] \tag{12}$$

where K'_{SV} ($=K_{CT} + K_{SV}$) is the apparent Stern−Volmer constant.

The fluorescence spectra for ZnTSPP, poly(A/ZnTPP), and poly(A/CD/ZnTPP) in the absence and presence of MV^{2+} in aqueous solution are shown in Figure 2. Fluorescence quenching was observed in all the systems containing poly(A/LA/ZnTPP) and poly(A/Naph/ZnTPP), although no fluorescence quenching was observed with the same terpolymer systems in our previous study using PMPS.[23] Stern−Volmer plots are shown in Figure 3 and the K_{SV} (K'_{SV}) values estimated from slopes of the plots are listed in Table 1. The K'_{SV} values for ZnTSPP and poly(A/ZnTPP) in the MV^{2+} system are 20 and 4.5 times larger than that in the PMPS system,[23] respectively. This may be due to a difference in the electrostatic attraction and/or reactivities, such as energy gap (exothermicity), reorganization energy, and electronic matrix element, with these acceptors.

The K'_{SV} value for poly(A/ZnTPP) is larger than that for ZnTSPP because MV^{2+} is electrostatically concentrated on the polymer chain, similar to the previous study with PMPS.[23] The K'_{SV} values for poly(A/ZnTPP) and ZnTSPP are almost equal to the K_{CT} values. This suggests that most of the fluorescence quenching occurs by way of the CT complexation. On the other hand, the K_{SV} values for all the terpolymers were 2 orders of magnitude smaller than that for the reference copolymer. Since no CT complexes exist in the terpolymer systems, the fluorescence quenching can only occur by ET from the compartmentalized ^{1}ZnTPP* to MV^{2+}.

For a rough estimation of apparent $k_{q,S}$ by using eq 8, we used a literature value of the lifetime of S_1 of ZnTSPP in aqueous solution (τ_0 = 1.7 ns).[31] These results are listed in Table 1. The ET processes in all the present systems are likely to be static in nature because of electrostatic interactions between MV^{2+} and each polymer or ZnTSPP. In fact, the apparent $k_{q,S}$ values were much larger than a diffusion-limiting rate constant (10^9−10^{10} M^{-1} s^{-1}).[28,32]

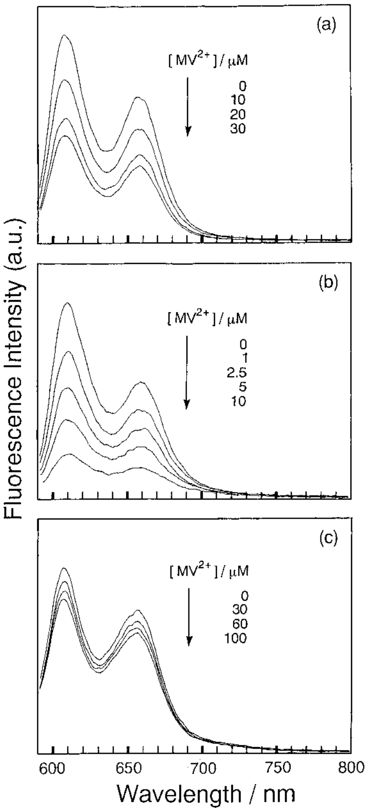


Figure 2. Fluorescence spectra of (a) ZnTSPP, (b) poly(A/ZnTPP), and (c) poly(A/CD/ZnTPP) in the presence of varying concentrations of MV^{2+} in aqueous solution. The residual concentration of the porphyrin moieties is 2 μM. The excitation wavelength is 563 nm.

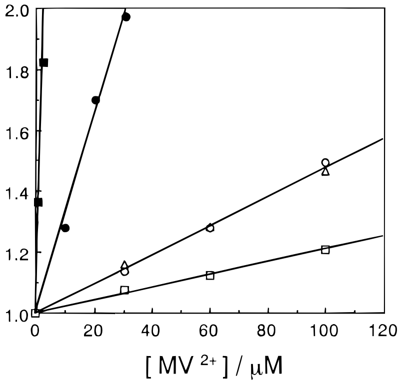


Figure 3. Stern−Volmer plots for the ZnTPP fluorescence quenching by MV^{2+} in aqueous solution: (●) ZnTSPP, (■) poly(A/ZnTPP), (△) poly(A/LA/ZnTPP), (○) poly(A/Naph/ZnTPP), (□) poly(A/CD/ZnTPP).

The order of the K_{SV} values for the hydrophobes in the terpolymers is lauryl ≅ naphthyl > cyclododecyl groups. This reflects differences in the extents of the chromophore protection brought about by the hydrophobic groups. A similar tendency was observed in the fluorescence quenching of pyrene with a titanium(I) ion in our previous work with the CD- and LA-containing terpolymers, pyrene compartmentalized in the corresponding terpolymers.[11]

Time-resolved transient absorption spectra in a millisecond time domain for the terpolymers and the reference copolymer in aqueous solution were previously measured by laser photolysis, and the observed transient spectra were assigned to the triplet−triplet (T−

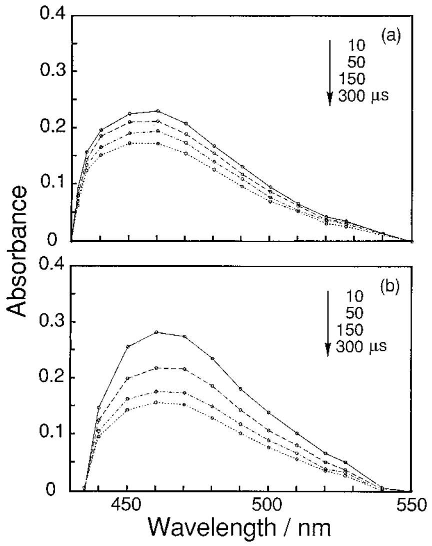


Figure 4. Time-resolved transient absorption spectra for poly(A/ZnTPP) and poly(A/CD/ZnTPP) in the presence of MV^{2+} in aqueous solution: (a) poly(A/ZnTPP) with 10 μM of MV^{2+}; (b) poly(A/CD/ZnTPP) with 30 μM of MV^{2+}. The residual concentration of the porphyrin moieties is 10 μM.

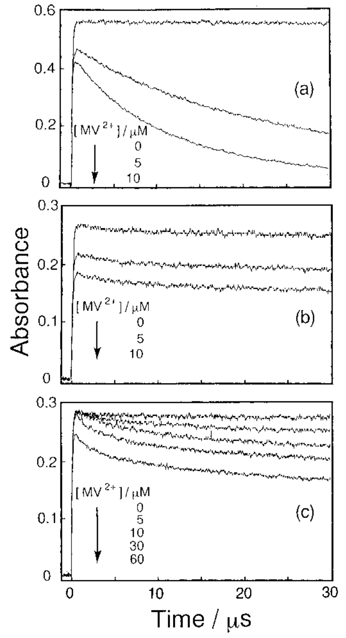


Figure 5. Decay profiles of transient absorption monitored at 480 nm for (a) ZnTSPP, (b) poly(A/ZnTPP), and (c) poly(A/CD/ZnTPP) in the presence of varying concentrations of MV^{2+} in aqueous solution. The residual concentration of the porphyrin moieties is 10 μM.

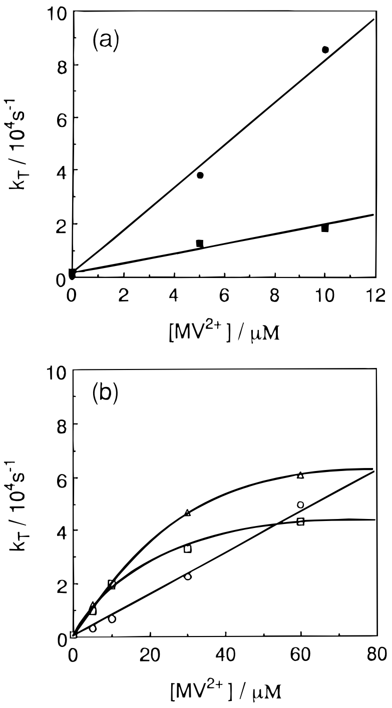


Figure 6. Pseudo-first-order decay constant for the triplet quenching as a function of the concentration of MV^{2+}: (a) (●) ZnTSPP, (■) poly(A/ZnTPP); (b) (△) poly(A/LA/ZnTPP), (○) poly(A/Naph/ZnTPP), (□) poly(A/CD/ZnTPP).

T) absorption of the ZnTPP moieties.[19] Figure 4 shows time-resolved transient absorption spectra for poly(A/ZnTPP) and poly(A/CD/ZnTPP) in the presence of MV^{2+} in aqueous solution. These spectral profiles are similar to those of T−T absorption of the ZnTPP moieties.[19] However, the decays of the absorbances are much faster than that in the absence of MV^{2+}, indicating that ET occurs from T_1 of the ZnTPP moiety (^{3}ZnTPP*) to MV^{2+}. Figure 5 shows the decay profiles for ZnTSPP, poly(A/ZnTPP), and poly(A/CD/ZnTPP) monitored at 480 nm in the presence of varying concentrations of MV^{2+}. The maximum absorbances, which were monitored immediately after laser excitation, decrease with increasing the concentration of MV^{2+}. This may be due to ET from ^{1}ZnTPP*, which occurs in competition with intersystem crossing. To estimate the apparent second-order rate constant ($k_{q,T}$) for ET from ^{3}ZnTPP* to MV^{2+}, pseudo-first-order decay constants (k_T) estimated from the initial slopes of the first-order plots of the decay profiles in Figure 5 are plotted as a function of the concentration of MV^{2+} (Figure 6). The triplet quenching in poly(A/ZnTPP) is less efficient than that in ZnTSPP, as compared in Figure 6a. In poly(A/ZnTPP) some ZnTPP species are close to MV^{2+} and therefore ^{1}ZnTPP* is quenched statically, while some ZnTPP species separated from MV^{2+} can undergo intersystem crossing and ^{3}ZnTPP* is quenched dynamically because the lifetime of ^{3}ZnTPP* is much longer than that of ^{1}ZnTPP*. In the poly(A/LA/ZnTPP) and poly(A/CD/ZnTPP) systems, the plot of k_T against the concentration of MV^{2+} shows a downward curvature similar to that in our previous study with PMPS,[23] indicating that the T_1 quenching becomes less effective as the quenching proceeds (Figure 6b). Namely, the ZnTPP species are buried inside the hydrophobic microdomains with different extents of protection; some ZnTPP species existing near the surface in the microdomain can undergo triplet ET to MV^{2+} located on the surface of the unimer micelle, while some ZnTPP species buried deep in the hydrophobic microdomain cannot participate in the ET event.[23] On the other hand, the plot of k_T against the concentration of MV^{2+} shows a linear line in the poly(A/Naph/ZnTPP) system. We have no clear explanation for this particular observation, but a feasible explanation might be a unique effect of the π-electron cloud in the cluster of the naphthyl moieties mediating the ET from ^{3}ZnTPP* to MV^{2+}. Values of $k_{q,T}$ estimated from the slopes or the initial slopes of the plots in Figure 6 are listed in Table 1. In the terpolymer systems, the magnitude of $k_{q,T}$ values is in the order naphthyl < cyclododecyl < lauryl systems. This order is different from the order for the K_{SV} values. The initial fast quenching in the region of low concentration of MV^{2+} may occur with some ZnTPP species existing near the surface in the microdomain. It should be noted that the k_T values at

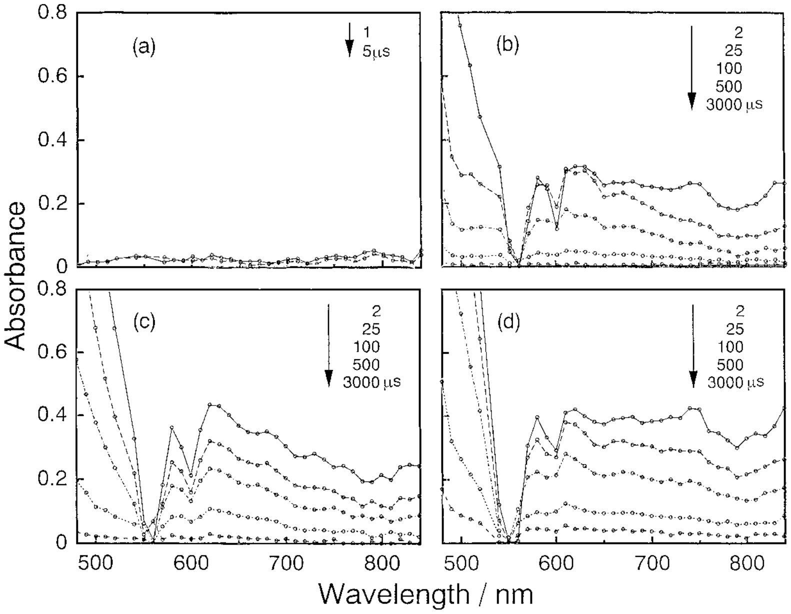


Figure 7. Time-resolved transient absorption spectra of (a) poly(A/ZnTPP), (b) poly(A/LA/ZnTPP), (c) poly(A/Naph/ZnTPP), and (d) poly(A/CD/ZnTPP) in the presence of 5 mM of MV^{2+} in aqueous solution. The residual concentration of the porphyrin moieties is 100 μM.

$[MV^{2+}] = 60\ \mu M$ is in the order cyclododecyl < naphthyl < lauryl groups. This order agrees with the order for K_{SV} values.

Time-resolved transient absorption spectra for the reference copolymer and the terpolymers in the presence of an excess amount of MV^{2+} in aqueous solution are shown in Figure 7. In the copolymer system, absorbances are very weak in the microsecond time region, indicating that $ZnTPP^{+\bullet}$ and $MV^{+\bullet}$ accumulate little although photoexcited ZnTPP species is mostly quenched by MV^{2+}. On the other hand, in the terpolymer systems absorbances persisted for a few miliseconds. However, the spectral profiles are different for each terpolymer. Spectral band profiles appear to change with time because of differences in the relative ratios of $ZnTPP^{+\bullet}$, $MV^{+\bullet}$, and $^3ZnTPP^*$ in the sample solutions after the laser excitation. To estimate the concentration of $ZnTPP^{+\bullet}$ for all the terpolymer systems, the decay profiles at 650 and 800 nm were chosen (Figure 8) because the transient absorbance of $^3ZnTPP^*$ at 650 nm is nearly equal to that at 800 nm. At 1 ms or longer times after laser excitation, only very small absorbances were observed in the poly(A/LA/ZnTPP) system, while significant absorbances were observed in both the poly(A/Naph/ZnTPP) and poly(A/CD/ZnTPP) systems. Figure 9 shows the decay profiles of $ZnTPP^{+\bullet}$ moieties estimated from eq 7. The maximum of the transient concentration of $ZnTPP^{+\bullet}$ in the poly(A/LA/ZnTPP) system was 9.6 μM, which corresponds to 9.6% of the initial concentration of the ZnTPP residue, while those in the poly(A/Naph/ZnTPP) and poly(A/CD/ZnTPP) systems were 11 and 5.6%, respectively. In the poly(A/LA/ZnTPP) system, $ZnTPP^{+\bullet}$ completely decayed 1.5 ms after laser excitation, while in the poly(A/Naph/ZnTPP) and poly(A/CD/ZnTPP) systems, significant amounts of $ZnTPP^{+\bullet}$ remained at 3 ms. It should be noted that, in the latter systems, no significant decays of $ZnTPP^{+\bullet}$ were observed after 1 ms. This reflects the difference in the extents of the chromophore protection by the hydrophobic groups.

It can be seen from Figure 9 that back ET from $MV^{+\bullet}$ to $ZnTPP^{+\bullet}$ is suppressed, owing to the compartmentalization of the ZnTPP moiety. These results are qualitatively consistent with our previous studies using phenanthrene[17] and pyrene[18] as chromophores. Such accumulations of the photoproducts in these systems may be qualitatively explained in a similar manner as the previous studies;[17,18] the charge escapes via an electron exchange between $MV^{+\bullet}$ and MV^{2+} bound side-by-side on the surface of the unimer micelle.[17,33] Free energy gaps ($-\Delta G_0$) for the forward ET from $^1ZnTPP^*$ to MV^{2+} and from $^3ZnTPP^*$ to MV^{2+} are 0.65 and 0.19 eV,[1,6] respectively, and for the back ET is 1.40 eV,[1,6] if the redox potential of the compartmentalized ZnTPP moiety is equal to that of free ZnTPP species. Therefore,

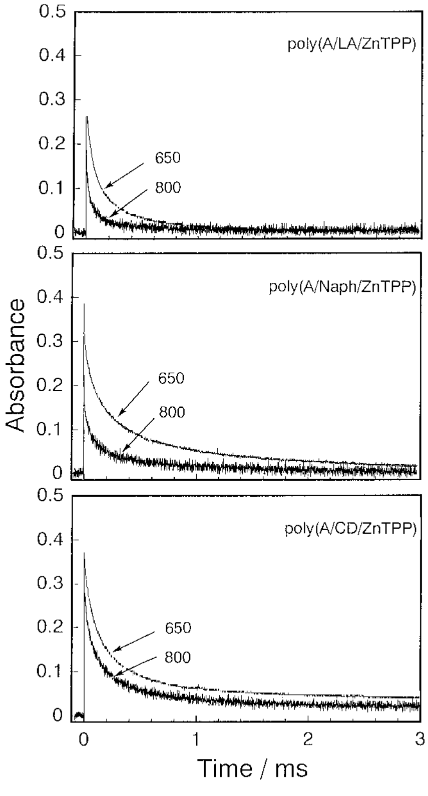


Figure 8. Decay profiles of terpolymer systems monitored at 650 and 800 nm shown in Figure 7.

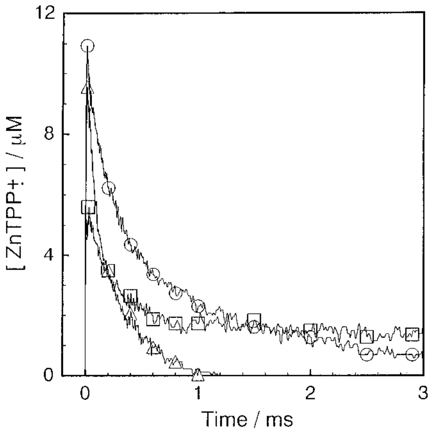


Figure 9. Decay profiles of ZnTPP$^{+\bullet}$ moieties estimated from eq 7: (△) poly(A/LA/ZnTPP), (○) poly(A/Naph/ZnTPP), (□) poly(A/CD/ZnTPP).

back ET in the singlet-ion pairs may be comparable to or faster than forward ET. The back ET in the triplet-ion pairs should be slower than that in the singlet-ion pairs because the back ET in the triplet-ion pair is spin-forbidden. Therefore, the charge escape from the singlet-ion pairs may be difficult to occur, whereas that from the triplet-ion pairs may occur easily. Hence, the back ET can be slowed.

Conclusions

The CT complexation is completely suppressed by the compartmentalization of the ZnTPP moieties in the terpolymers. The ET from ^{1}ZnTPP* to MV^{2+} for the compartmentalized systems is 2 orders of magnitude slower than that for the reference copolymer system because of the steric protection of the compartmentalized ZnTPP by the hydrophobic clusters. The apparent rate constants of the ET from ^{3}ZnTPP* to MV^{2+} ($k_{q,T}$) for the terpolymer systems are almost equal to that for the reference copolymer but are smaller than that for ZnTSPP. The accumulation of ZnTPP$^{+\bullet}$ was observed as a result of the compartmentalization. The naphthyl and cyclododecyl groups are more effective to accumulate ZnTPP$^{+\bullet}$, which persisted over a few milliseconds.

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