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New Quasi-solid Materials as a Medium for Photochemical Reactions

Kazuhisa Suzuki,[†] Hidenobu Shiroishi,[†] Mikio Hoshino,[‡] and Masao Kaneko*,[†]

Faculty of Science, Ibaraki University, 2-1-1 Bunkyo, Mito 310-8512, Japan, and The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako 351-0198, Japan

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Polysaccharide quasi-solids containing a large excess of water were proposed as a new medium for photochemical reactions. Photochemical reaction was studied by the electron-transfer quenching of photoexcited tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) by methyl viologen (MV^{2+}) or propyl viologen sulfonate (PVS^0). The maximum wavelengths of the visible absorption and emission spectra of $Ru(bpy)_3^{2+}$ were 452 and 627 nm, respectively, in both agarose and κ-carrageenan quasi-solids, similar to those in an aqueous solution. Photoinduced electron transfer from the photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} took place by a dynamic mechanism in a 2 wt % agarose/water quasi-solid, the same as in pure water, but occurred by both the dynamic and static mechanisms in a 2 wt % κ-carrageenan/water quasi-solid in high MV^{2+} concentration regions ($[MV^{2+}] > 1$ mM). Since κ-carrageenan contains anionic sulfonate groups, the cationic Ru^{2+} complex and MV^{2+} were supposed to be bound electrostatically near the main chain, so that the static electron transfer would take place. On the contrary, photoinduced electron transfer from the $Ru(bpy)_3^{2+}$ to PVS^0 took place by a dynamic mechanism even in the κ-carrageenan quasi-solid because of the neutral acceptor. The electron transfer in the κ-carrageenan was analyzed with a mechanism involving both the dynamic and static electron transfer by assuming a multistep incorporation of the MV^{2+} into the static quenching sphere around the Ru complex. The electron-transfer rate constants from the photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} were 4.7×10^8 M^{-1} s^{-1} in the agarose quasi-solid and 2.1×10^9 M^{-1} s^{-1} for the dynamic part in the κ-carrageenan quasi-solid. The latter value is approximately 1 order of magnitude as large as that in a homogeneous aqueous solution. Thus, the tight and elastic quasi-solid can in principle work as a medium like liquid water. However, the nanoscale heterostructured main chain can provide a kind of molecular surface where interaction of the reactants controls the mechanism and kinetics, as shown in the κ-carrageenan case.

Introduction

Photochemical reactions have mainly been investigated in solutions where most of the reactions take place by a dynamic mechanism. Photochemical reactions have also been studied in a solid where the diffusion of reactants can hardly take place, so that the reactions occur by a static mechanism.[1−6] Electron transfer from a photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} in a dry solid matrix was first reported by one of the present authors by adsorbing the compounds on a cellulose sheet,[7] and the mechanism of such electron transfer in a dry polymer solid phase has later been established to be a static one in which the reaction components do not move at all for the electron transfer to occur.[8] If chemical reactions can take place in a solid state the same as in a liquid, this will lead to new and wide applications such as chemical reactors, microreactors, electrochemical/photochemical sensors, microanalysis, combinatorial chemistry, laboratories on chips, and so forth. Tight and stable quasi-solid samples containing a large amount of water are easily prepared from polysaccharide. It has been reported that polysaccharides form double helical structures which get entangled with each other to form nanoscale three dimensional networks containing excess liquid. We have found that electrochemical and photochemical reactions can take place in such quasi-solids containing a large excess of water the same as in an aqueous solution.[9] As for the polysaccharides, agarose[10] and κ-carrageenan[11−13] (Figure 1) were used. Carrageenan is a sulfonated polysaccharide extracted from red seaweed. It is classified into three types as kappa (κ-), iota (ι-), and lambda (λ-) carrageenans according to the number (one, two, or three) of sulfonate groups per repeating unit of the disaccharide structure, respectively. When considering the series of carrageenan $\lambda \rightarrow \iota \rightarrow \kappa$, the gelation properties increase in this order and the solution viscosity decreases. Since κ-type carrageenan has the maximum gelation power, it was used in the present study as an anionic polysaccharide in addition to the neutral agarose.

Tris(2,2′-bipyridine)ruthenium(II) complex ($Ru(bpy)_3^{2+}$) has been widely employed as a photosensitizer in a variety of electron-transfer reactions.[14−17] It is well-known that the phosphorescence of $Ru(bpy)_3^{2+}$ is quenched by electron transfer to an acceptor such as methyl viologen (MV^{2+}).[7,8,18−23]

In the present paper we propose the polysaccharide quasi-solids as a new medium for photochemical reactions. We have investigated the photoinduced electron transfer from $Ru(bpy)_3^{2+}$ to MV^{2+} or propyl viologen sulfonate (PVS^0) (Figure 2) in polysaccharide (agarose, κ-carrageenan) quasi-solids containing a large amount of water, by which fundamental properties of the polysaccharide quasi-solids as a medium for photochemical reactions will be discussed.

Experimental Section

κ-Carrageenan powder was purchased from Wako Pure Chemical Ind. Ltd, agarose powder was purchased from Acros

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* To whom correspondence should be addressed.

[†] Ibaraki University.

[‡] The Institute of Physical and Chemical Research (RIKEN).

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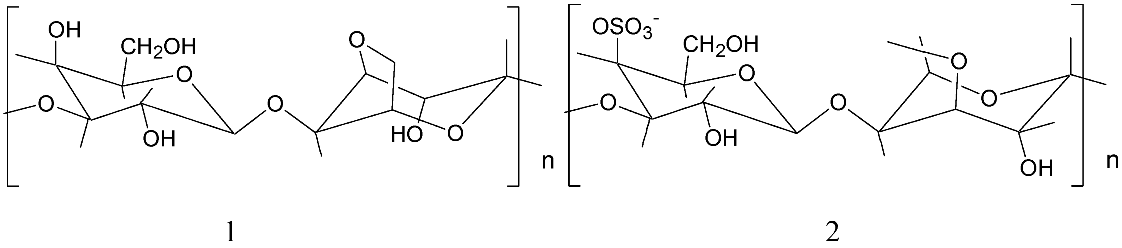

Figure 1. Structures of agarose (1) and *κ*-carrageenan (2).

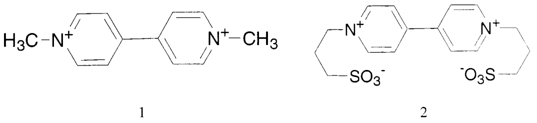

Figure 2. Structures of MV^{2+} (1) and PVS^0 (2).

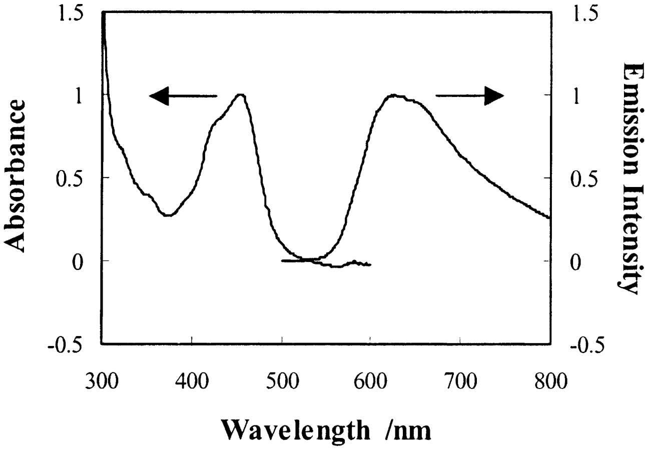

Figure 3. Absorption and corrected emission spectra of $Ru(bpy)_3^{2+}$ in 2 wt % *κ*-carrageenan/water quasi-solid at 298 K.

Organics, and tris(2,2′-bipyridine)ruthenium(II) chloride hexahydrate and methyl viologen dichloride were purchased from Aldrich Co.Ltd. They were used as received. Propyl viologen sulfonate was prepared by keeping a methanol solution of 4,4′-bipyridine (5 mmol) and 1,3-propane sultone (10.5 mmol) at room temperature for 10 h; the resulting white precipitate was collected and washed with acetone and then recrystallized from a ethanol−water (1:1) mixed solution.

Photoinduced electron transfer was investigated in a polysaccharide (*κ*-carrageenan, agarose) quasi-solid containing a large amount of water. A 2 wt % agarose (or *κ*-carrageenan) solution containing 50 μM $Ru(bpy)_3^{2+}Cl_2{\cdot}6H_2O$ was prepared with different MV^{2+} (or PVS^0) concentrations from 0 to 8 mM. The mixture was heated by microwave irradiation (2.45 GHz) to make a homogeneous solution and then cooled to room temperature to prepare a quasi-solid sample containing water in large quantities. The sample is a tight, elastic, and clear quasi-solid. After it was cut into the size ($10 \times 15 \times 2$ mm^3), the film was placed on a precleaned glass slide (10×25 mm^2), fixed at a diagonal position in a quartz cell, and deaerated by introducing wet argon gas for 20 min, for which the wet argon gas was obtained by bubbling Ar gas in water. The sample was fixed at the angle of 60° against excitation light in a quartz cell and irradiated by monochromatic light of wavelength 452 nm from the front surface of the sample.

Visible absorption and emission spectra were measured using a Shimadzu Multispec-1500 spectrophotometer and a Shimadzu RF-5300PC fluorescence spectrophotometer, respectively. Emission decay was measured by a time-correlated single photon counting apparatus (Hitachi-Horiba NAES-550) equipped with a 10-atm nitrogen lamp, for which a UV-30 cut off filter was used at the excitation side and an O-56 cut off filter was set at the monitoring side. Lifetime analysis was computed by the repeated nonlinear least-squares procedure. Laser flash photolysis was carried out under argon by the second harmonic of an Nd:YAG laser, model HY 500 from JK Lasers Ltd. The flash intensity was ∼100 mJ cm^{-2}, and the pulse duration was 20 ns. The decay of the phosphorescence from the photoexcited $Ru(bpy)_3^{2+}$ was monitored at 603 nm, and the formation of methyl viologen cation radical was monitored at 600 nm. All the measurements were carried out under argon at 298 K.

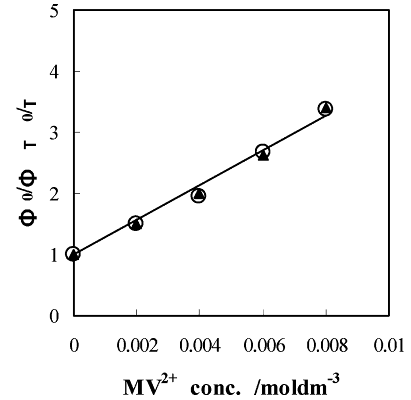

Figure 4. Stern−Volmer plot for the quenching of photoexcited $Ru(bpy)_3^{2+}$ by MV^{2+} in 2 wt % agarose/water quasi-solid under argon at 298 K: (○) Φ_0/Φ; (▲) τ_0/τ.

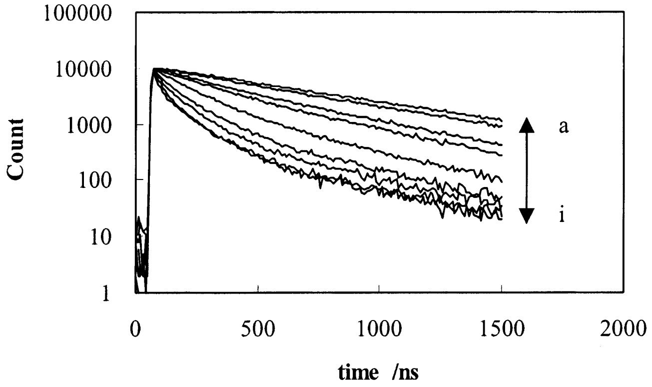

Figure 5. Emission decay curves of $Ru(bpy)_3^{2+}$ at various concentrations of MV^{2+} in 2 wt % *κ*-carrageenan/water quasi-solid under argon at 298 K: (a) $[MV^{2+}] = 0$; (b) 0.1; (c) 0.25; (d) 0.5; (e) 1.0; (f) 2.0; (g) 3.0; (h) 5.0; (i) 8.0 mM.

Results and Discussion

Figure 3 shows visible absorption and corrected emission spectra of 0.05 mM $Ru(bpy)_3^{2+}$ in a 2 wt % *κ*-carrageenan/water quasi-solid ($10 \times 15 \times 2$ mm^3) at room temperature (298 K). The maximum wavelengths of the visible absorption and corrected emission spectra were 452 and 627 nm, respectively, the same as those in an aqueous solution.

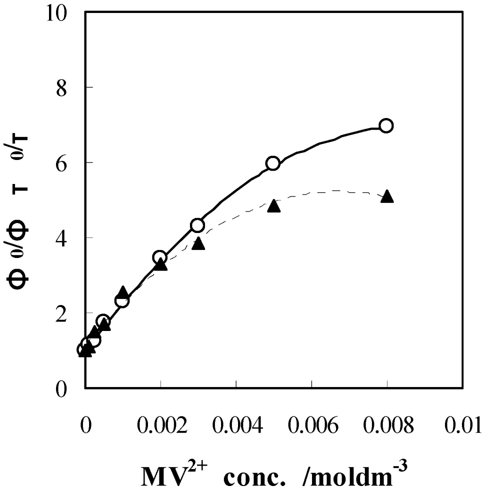

Figure 6. Stern−Volmer plot for the quenching of photoexcited $Ru(bpy)_3^{2+}$ by MV^{2+} in 2 wt % κ-carrageenan/water quasi-solid under argon at 298 K: (○) Φ_0/Φ; (▲) τ_0/τ.

TABLE 1: Emission Lifetime Parameter of $Ru(bpy)_3^{2+}$ at Various Concentrations of MV^{2+} in 2 wt % Agarose/Water Quasi-solid under Argon at 298 K

MV^{2+} conc/mM	lifetime, τ/ns	exponential term, *A*
0	600	0.136
2	402	0.216
4	301	0.249
6	228	0.309
8	176	0.423

TABLE 2: Emission Lifetime Parameter of $Ru(bpy)_3^{2+}$ at Various Concentrations of MV^{2+} in 2 wt % κ-Carrageenan/Water Quasi-solid under Argon at 298 K

	lifetime (ns)			pre-exponential term	
MV^{2+} conc/mM	τ_1	τ_2	τ_{ave}	A_1	A_2
0	584		584	0.198	
0.1	522		522	0.178	
0.25	404	129	389	0.242	0.045
0.5	379	172	346	0.232	0.097
1	268	100	228	0.265	0.222
2	250	86	178	0.211	0.485
3	209	61	151	0.264	0.585
5	166	40	120	0.316	0.757
8	159	35	126	0.337	0.555

TABLE 3: Parameters Obtained by the Stern−Volmer Plot

acceptor	condition	K_1	$k_{q1}/10^6$ s^{-1}	$k_{q2}/10^9$ M^{-1} s^{-1}
MV^{2+}	water[a]			0.33
	agarose[a]			0.47
	κ−carrageenan[b]	20.3	2.28	2.09
PVS^0	water[a]			1.43
	κ−carrageenan[a]			1.46

[a] Analysis by the Stern−Volmer equation (eq 1). [b] Analysis by eq 17.

Photoinduced electron transfer from the photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} or PVS^0 was studied in a polysaccharide quasi-solid containing a large amount of water. The formation of $MV^{\bullet+}$ in a κ-carrageenan quasi-solid was confirmed by the laser flash photolysis. The electron-transfer reaction was mainly studied by the quenching of the phosphorescence from the photoexcited $Ru(bpy)_3^{2+}$ by MV^{2+}. The relative emission yield (Φ_0/Φ) and lifetime (τ_0/τ) ($Ru(bpy)_3^{2+}/MV^{2+}$/agarose) are shown in Figure 4 (Stern−Volmer plots). The Stern−Volmer plots should be linear for a dynamic quenching according to the Stern−Volmer equation (eq 1), and both the plots based on Φ_0/Φ and τ_0/τ versus quencher concentration should fall on the same line,[24−26]

$$\frac{\Phi_0}{\Phi} = \frac{\tau_0}{\tau} = 1 + k_{q2}\tau_0[Q] \tag{1}$$

where Φ_0 and Φ represent the relative emission yield in the absence and the presence of quencher, respectively, τ_0 and τ are emission lifetimes in the absence and the presence of quencher, k_{q2} is the electron-transfer rate constant, and [Q] is the quencher concentration (mol dm^{-3}).

The emission decay curves of the photoexcited $Ru(bpy)_3^{2+}$ at various concentrations of MV^{2+} in the agarose quasi-solid were measured by a time-correlated single photon counting apparatus. The decay curves were expressed by a single-exponential function (eq 2).

$$I(t) = A\exp[-(t/\tau)] \tag{2}$$

The results of lifetime measurements are summarized in Table 1. The emission lifetime of the photoexcited $Ru(bpy)_3^{2+}$ in the 2 wt % agarose quasi-solid was 600 ns in the absence of MV^{2+}, the same as in an aqueous solution.

When MV^{2+} was used as a quencher, the results based on relative emission yield and emission lifetime fitted well with the Stern−Volmer equation in the agarose quasi-solid. It is concluded that the photoinduced electron transfer from the photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} takes place by a dynamic mechanism the same as in an aqueous solution. The electron-transfer rate constant (k_{q2}) from the $Ru(bpy)_3^{2+}$ to MV^{2+} was 4.7×10^8 M^{-1} s^{-1} in the agarose quasi-solid (shown later in Table 3).

Figure 5 shows emission decay curves for photoexcited $Ru(bpy)_3^{2+}$ at various concentrations of MV^{2+} in the κ-carrageenan quasi-solid. In the absence of the MV^{2+}, the decay curve was expressed by a single-exponential function, but in the presence of the MV^{2+} (≥0.25 mM), the decay data could not be fitted to a single-exponential curve. The decay data could be fitted well to a double-exponential curve expressed by[27]

$$I(t) = \sum_{i=1}^{2} A_i \exp[-(t/\tau_i)] \tag{3}$$

where $I(t)$ represents the emission intensity at time t, τ_i the decay time, and A_i the pre-exponential factor. The average lifetime (τ_{ave}) was calculated by[27]

$$\tau_{ave} = \sum_{i=1}^{2} A_i\tau_i^2 \Big/ \sum_{i=1}^{2} A_i\tau_i \tag{4}$$

The results of lifetime measurements are summarized in Table 2. The emission lifetime of the photoexcited $Ru(bpy)_3^{2+}$ in the 2 wt % κ-carrageenan quasi-solid was 584 ns in the absence of MV^{2+}, nearly the same as in an aqueous solution (600 ns). The average lifetime decreased with increasing MV^{2+} concentration.

The relative emission yield and lifetime ($Ru(bpy)_3^{2+}/MV^{2+}$/κ-carrageenan) are shown in Figure 6 (Stern−Volmer plots). In low MV^{2+} concentration regions (≤1 mM), it was indicated that the quenching of the phosphorescence in the κ-carrageenan quasi-solid occurred by a dynamic mechanism because both the plots based on Φ_0/Φ and τ_0/τ fall on the same line. However, both the Φ_0/Φ and the τ_0/τ plots were downwardly deviating in high MV^{2+} concentration regions (>1 mM), with the Φ_0/Φ plots higher than the τ_0/τ plots (Figure 6), showing that the photoinduced electron transfer in the κ-carrageenan quasi-solid

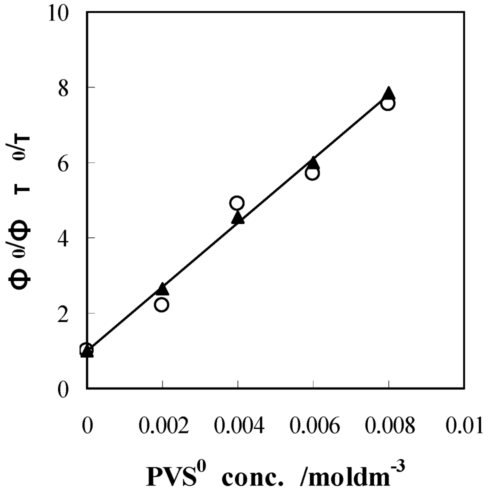

Figure 7. Stern−Volmer plot for the quenching of photoexcited $Ru(bpy)_3^{2+}$ by PVS^0 in 2 wt % κ-carrageenan/water quasi-solid under argon at 298 K: (○) Φ_0/Φ; (▲) τ_0/τ.

involves both dynamic and static mechanisms when the quencher concentration is higher. Although the cationic $Ru(bpy)_3^{2+}$ and MV^{2+} behaved in the agarose quasi-solid almost the same as in an aqueous solution, the electrostatic interaction with sulfonate groups of the κ-carrageenan would become not neglible in high concentration regions because of the equilibrium of the electrostatic binding. The photoinduced electron transfer of the neutral PVS^0 as a quencher occurred by a dynamic mechanism in the κ-carrageenan quasi-solid, as shown in Figure 7, supporting the static mechanism with the cationic MV^{2+}.

The photoinduced electron transfer with both dynamic and static quenchings by MV^{2+} in the κ-carrageenan quasi-solid was analyzed by the quenching model reported previously.[28] The quenching mechanisms were analyzed as follows:

$$\mathrm{P} + \mathrm{Q} \xrightleftharpoons{\mathrm{K_1}} (\mathrm{P}-\mathrm{Q}), \quad K_1 = \frac{[(P-Q)]}{[Q][P]} \tag{5}$$

$$\begin{array}{ll} \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \end{array}$$

$$[\mathrm{P}-(i-1)\,\mathrm{Q}] + \mathrm{Q} \xrightleftharpoons{\mathrm{K_i}} (\mathrm{P}-\mathrm{iQ}), \quad K_i = \frac{[(P-iQ)]}{[Q][P-(i-1)Q]} \tag{6}$$

$$(K_i = K_1 / i) \qquad (i = 1, 2, 3, \ldots)$$

$$\mathrm{P} \xrightarrow{h\nu} {}^*\mathrm{P} \tag{7}$$

$${}^*\mathrm{P} \xrightarrow{k_e} \mathrm{P} + h\nu' \tag{8}$$

$${}^*\mathrm{P} \xrightarrow{k_{nr}} \mathrm{P} \tag{9}$$

$$*\mathrm{P} + \mathrm{Q} \xrightarrow{k_{q2}[Q]} \mathrm{P} + \mathrm{Q} \tag{10}$$

$$(\mathrm{P}-i\mathrm{Q}) \xrightarrow{h\nu} (*\mathrm{P}-i\mathrm{Q}) \tag{11}$$

$$(*\mathrm{P}-i\mathrm{Q}) \xrightarrow{k_e} (\mathrm{P}-i\mathrm{Q}) + h\nu' \tag{12}$$

$$(*\mathrm{P}-i\mathrm{Q}) \xrightarrow{k_{nr}} (\mathrm{P}-i\mathrm{Q}) \tag{13}$$

$$(*\mathrm{P}-i\mathrm{Q}) \xrightarrow{k_{q1}} (\mathrm{P}-i\mathrm{Q}) \tag{14}$$

In these equations, P is probe, Q is the quencher, K_1 is the equilibrium constant of the incorporation of the quencher into the quenching sphere around the Ru complex, k_{q2} is the second-order (dynamic) quenching rate constant, k_{q1} is the first-order (static) quenching rate constant, and k_{nr} and k_e are the rate constants of the nonluminescent and luminescent decay of the excited state of the P, respectively. Equation 5 represents multistep incorporation of MV^{2+} quencher (Q) into the static quenching sphere around the Ru complex (P), and eq 6 is its ith step. The (P−Q) shows P and Q present in a quenching sphere. The excited states of the Ru complex (*P) and (*P−iQ) are created by absorption of irradiation (eqs 7 and 11); the transitions from a photoexcited state to the ground state are represented by the photoluminescence (eqs 8 and 12), radiationless deactivation (eqs 9 and 13), dynamic quenching (eq 10), and static quenching (eq 14).

Assuming that the distribution of the emission probe in the quenching sphere follows the Poisson distribution (for which $K_i = K_1/i$), the probability of existing i quenchers in a quenching sphere P_i is expressed as[28]

$$P_i = \frac{m^i}{i!}\exp(-m)$$

$$(m = K_1[\mathrm{Q}]_t) \tag{15}$$

The total quencher concentration ($[\mathrm{Q}]_t$) is expressed by using the concentration in bulk water ([Q]).

$$[\mathrm{Q}]_t = [\mathrm{Q}](K_1[\mathrm{P}]_t + 1) \tag{16}$$

In this model, the relation between the relative emission intensity (Φ_0/Φ) and the total quencher concentration $[\mathrm{Q}]_t$ was calculated as follows:[29]

$$\frac{\Phi_0}{\Phi} = \frac{(1 + k_{q1}\tau_0)(X + Y[\mathrm{Q}]_t)}{X + Y[\mathrm{Q}]_t + \tau_0(Xk_{q1} - k_{q2}[\mathrm{Q}]_t)\exp(-K_1[\mathrm{Q}]_t/X)} \tag{17}$$

$$\left(X = K_1[\mathrm{P}]_t + 1,\ Y = \tau_0 k_{q2},\ [\mathrm{P}]_t = \sum_{i=0}^{\infty}[(\mathrm{P} - i\mathrm{Q})]\right)$$

The Stern−Volmer plots (Φ_0/Φ) in the κ-carrageenan quasi-solid were analyzed by fitting eq 17 with the software of the quenching mechanism analyzer,[30] and the obtained parameters are shown in Table 3 with the calculated curve shown in Figure 6. The dynamic electron-transfer rate constant (k_{q2}) from the photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} was 2.1×10^9 M^{-1} s^{-1} in the κ-carrageenan quasi-solid (2.6×10^9 M^{-1} s^{-1} by laser flash photolysis), which is approximately 1 order as large as that in an aqueous solution (3.3×10^8 M^{-1} s^{-1}) (1.2×10^8 M^{-1} s^{-1} by laser flash photolysis), probably by a concentration effect of the MV^{2+} in the anionic domain of κ-carrageenan. We had investigated the quenching of photoexcited anionic polymer-pendant $Ru(bpy)_3^{2+}$ by MV^{2+} in water.[31] The dynamic quenching rate constant was larger than that of the monomeric $Ru(bpy)_3^{2+}$ because of the electrostatic effect of the polyanionic domains. This tendency is almost similar to that in the κ-carrageenan quasi-solid. From the ratio of the electron-transfer rate constants between agarose (4.7×10^8 M^{-1} s^{-1}) and κ-carrageenan (2.1×10^9 M^{-1} s^{-1}), it is inferred that the concentration effect by the sulfonate groups of κ-carrageenan is about 4.5.

Conclusions

Polysaccharide quasi-solids containing a large amount of water were proposed as a new medium for photochemical reactions. Photoinduced electron transfer in a polysaccharide (agarose, κ-carrageenan) quasi-solid has been investigated by the electron-transfer quenching of photoexcited $Ru(bpy)_3^{2+}$ by MV^{2+}.

Photoinduced electron transfer from the photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} took place by the dynamic mechanism the same as in an aqueous solution in the agarose quasi-solid.

However, photoinduced electron transfer occurred by both the dynamic and static mechanisms in the anionic κ-carrageenan quasi-solid. The photoinduced electron transfer of neutral PVS^0 as a quencher occurred by a dynamic mechanism even in the κ-carrageenan quasi-solid. The electron transfer in the κ-carrageenan quasi-solid was analyzed with a mechanism involving both the dynamic and static electron transfer by assuming a multistep incorporation of the MV^{2+} into the static quenching sphere around the Ru complex. To conclude, the tight and elastic quasi-solid can in principle work as a medium like liquid water. However, the nanoscale heterostructured main chain can provide a kind of molecular surface where interaction of the reactants controls the mechanism and kinetics, as shown in the κ-carrageenan case.

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Note Added after ASAP Posting. This article was posted ASAP on 6/28/2003. Changes have been made to eqs 7, 8, and 12. The correct version was posted on 7/7/2003.

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