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Quenching of Excited $Ru(bpy)_3^{2+}$ in Nafion Ionomer Solution and in Nafion Membrane

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The behavior of excited $Ru(bpy)_3^{2+}$ with the electron–acceptor quenchers methyl viologen and $C_{60}F_{36}$ in ethanol containing Nafion ionomer and in the water nanochannels of Nafion membrane was investigated by measurement of luminescence quenching. In Nafion ionomer solution, $Ru(bpy)_3^{2+}$ and methyl viologen are adsorbed onto Nafion aggregates, whereas $C_{60}F_{36}$ is held in Nafion aggregates. In the nanochannels of Nafion membrane, $Ru(bpy)_3^{2+}$ and methyl viologen were found to diffuse, even though the diffusion constant was ca. 1/20 of that in bulk ethanol solvent.

Keywords: luminescence quenching; Nafion; proton channel; $Ru(bpy)_3^{2+}$

INTRODUCTION

In light of their potential high efficiency and small size and also their environmental friendliness, the practical application and dissemination of proton exchange membrane fuel are cells (PEMFCs) are eagerly awaited [1]. As the high price and limited supply of platinum (Pt) constitute high barriers to the attainment of this goal, a reduction in the Pt loading of the electrocatalysts is desirable. This requires an improvement in the cell performance per unit mass of Pt. Thus far, we have reported that the cell performance is improved when the fullerene derivatives $C_{60}F_{36}$ and $C_{60}(OH)_{10}$ are added to the Nafion ionomer to produce a membrane electrode assembly (MEA) [2].

The structure of the proton channels in Nafion has been extensively studied. Gierke proposed a regular alternation model of spherical

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clusters channels [3] while Schmidt-Rohr and Chen recently proposed a model of parallel cylindrical nanochannels [4]. In any event, such proton channels, being made up of a Nafion side branch containing a sulfonic group, need to be modified by the addition of fullerene derivatives to enhance the proton transport efficiency.

It is important to elucidate the nature of the microenvironments of the proton channels in the Nafion membrane. The solution properties of Nafion in water or in alcohol may also provide information on the proton channels. Rod-like aggregation particles are found in the Nafion solution due to the hydrophobic interaction of the fluorocarbon backbone. The ionic side chains are located around the surface of the rod, and hence the surface is considered to be a reversed model of the inner wall of the proton channels.

In the present article, we discuss the luminescence quenching reactions of excited tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$, I in Fig. 1) due to electron transfer to methyl viologen (MV^{2+}, II in Fig. 1) or $C_{60}F_{36}$ in solutions containing Nafion ionmer and in Nafion membrane. In the $Ru(bpy)_3^{2+}$–MV^{2+} system, both luminescence probe and the quencher are cationic, and hence they interact with anionic side chain of Nafion. Alternatively the analysis of this quenching process makes clear the microenvironments of the proton channels in Nafion. As for the $Ru(bpy)_3^{2+}$–$C_{60}F_{36}$ system, the investigation of luminescence quenching will provide a certain interpretation for the improved performance of MEA prepared on addition of the fullerene derivatives.

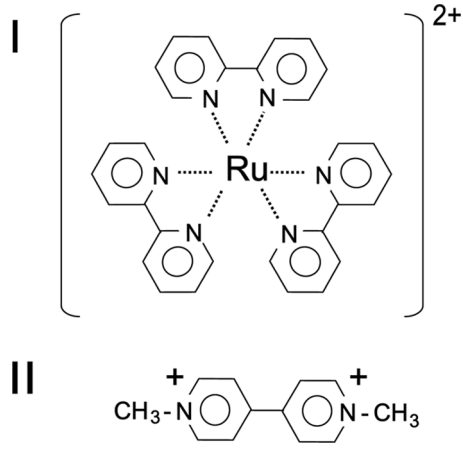

FIGURE 1 Molecular structures of $Ru(bpy)_3^{2+}$ (I) and MV^{2+} (II).

EXPERIMENTAL

$Ru(bpy)_3^{2+}$ and methyl viologen (MV^{2+}) (G. R. Grade, Tokyo Kasei) were used as received. Nafion membrane (Nafion 117, 1.78×10^{-4} m in thickness) and 5 wt% Nafion ionomer solution in a mixture of lower aliphatic alcohols and water were purchased from Du Pont and Sigma-Aldrich, respectively. $C_{60}F_{36}$ was purchased from MTR, Ltd.

The spectra of $Ru(bpy)_3^{2+}$ luminescence were measured with a Perkin Elmer spectrophotofluorometer (LS50B). The mean diameter of Nafion aggregates in ethanol was obtained by dynamic light scattering (DLS) measurements with a particle analyzer (HPP5001, Malvern Instruments, Ltd.) under the assumption that the aggregates were spherical.

The luminescence decay curves were determined by exciting the sample at the wavelength of 455 nm with an LED pulse (fwhm: 1.3 ns) and by observing the decay curve at the wavelength of 596 nm with a fluorescence lifetime spectrometer (1000 U, Horiba Jobin Yvon) shown in Fig. 2.

All solutions for luminescence measurement were deoxygenated by flushing with Ar gas for at least 20 min. To occlude $Ru(bpy)_3^{2+}$ into the

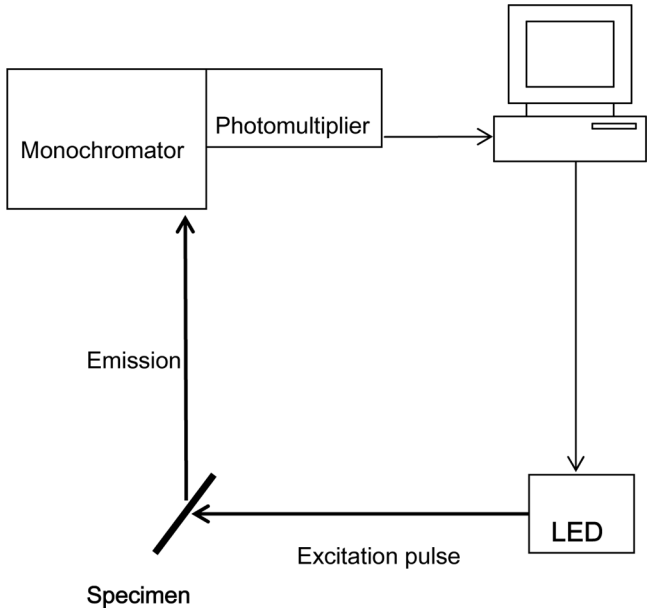

FIGURE 2 Schematics of experimental setup to detect the luminescence decay curves.

Nafion membrane, a $20 \times 20\,mm^2$ section of the membrane (ca. 130 mg) was immersed in an aqueous solution of a weighted quantity of $Ru(bpy)_3^{2+}$ for at least two days. The yellow color of the solution faded, and the membrane turned yellow. The occlusion of MV^{2+} was carried out in a similar manner. All luminescence measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Luminescence Quenching of $Ru(bpy)_3^{2+}$–MV^{2+} System in Nafion Ionomer Solution

The luminescence of $Ru(bpy)_3^{2+}$ is quenched by the electron acceptor MV^{2+} in polar solvents. The quenching route is schematically shown in Fig. 3. The quenching can be described by the Stern–Volmer equation:

$$I_0/I = 1 + K_{SV}[MV^{2+}], \quad (1)$$

where I_0 is the intensity of luminescence in the absence of quencher, I is the intensity in the presence of quencher, and K_{SV} is the Stern–Volmer constant. When this quenching is carried out with a Nafion ionomer solution in ethanol, a characteristic curve with a spike as shown in Fig. 4 is obtained instead of the simple Stern–Volmer straight line. I_0/I shows a peak at $1.5 \times 10^{-4}\,M$ ($1\,M = 1\,mol\ dm^{-3}$) of MV^{2+}, where 95% of the $Ru(bpy)_3^{2+}$ luminescence is quenched, and the luminescence is restored with further addition of the quencher.

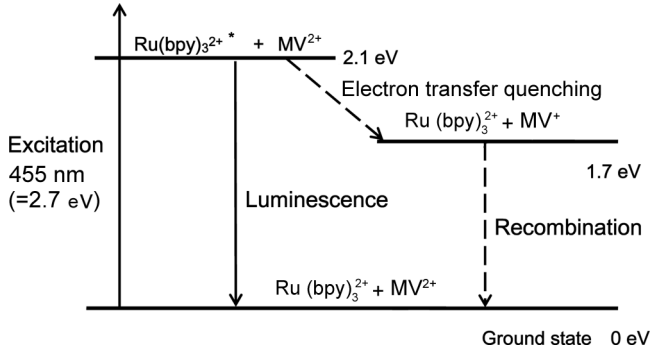

FIGURE 3 Energy level diagram of excited $Ru(bpy)_3^{2+}$ and the quenching process.

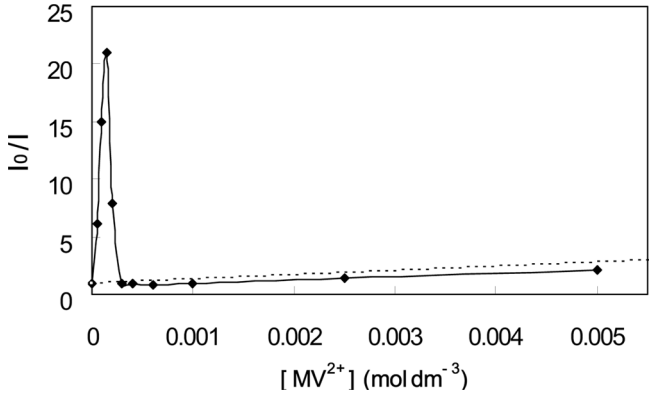

FIGURE 4 (I_0/I)–[Quencher] relation for luminescence quenching of $Ru(bpy)_3^{2+}$–MV^{2+} system in ethanol containing Nafion ionomer. $[Ru(bpy)_3^{2+}] = 6 \times 10^{-5}$ M. [Nafion] $= 3 \times 10^{-4}$ M in sulfonic side chain unit. Dashed line indicates Stern–Volmer plot for quenching by MV^{2+} in ethanol.

When MV^{2+} concentration is higher than 5×10^{-4} M, the quenching is similar to that in bulk solution.

These results can be explained in terms of the limited capacity of the aggregation particles of Nafion to adsorb cations. All $Ru(bpy)_3^{2+}$ cations may be adsorbed onto Nafion aggregates when MV^{2+} concentration is low. Under these conditions, the luminescence is effectively quenched because both $Ru(bpy)_3^{2+}$ and MV^{2+} are concentrated by adsorption onto Nafion aggregates. With increase in the MV^{2+} concentration, all adsorption sites may be occupied by $Ru(bpy)_3^{2+}$ and MV^{2+}. With further increase in MV^{2+}, $Ru(bpy)_3^{2+}$ seems to be expelled into the bulk solution. Eventually, almost all of the $Ru(bpy)_3^{2+}$ ions appear to be removed from the vicinity of the Nafion aggregates, where the concentration of MV^{2+} is very high. The expelled $Ru(bpy)_3^{2+}$ ions undergo simple luminescence quenching of the Stern–Volmer type quite similar to that in bulk solution.

This quenching behavior of excited $Ru(bpy)_3^{2+}$ is similar to that reported in $Ru(bpy)_3^{2+}$–cationic quencher–poly(vinyl sulfate) systems [5,6]. However, the peculiarity of our Nafion system is that the sum of the $Ru(bpy)_3^{2+}$ concentration and MV^{2+} concentration at the (I_0/I) peak is almost equal to the concentration of Nafion ionomer in the sulfonic side chain units. When the luminescence is quenched most effectively, all cationic species are just situated exclusively in anionic side chain positions on rod-like Nafion aggregates. In the case of poly (vinyl sulfate) systems, the sum concentration of [$Ru(bpy)_3^{2+}$] and

$[MV^{2+}]$ at the (I_0/I) peak is ca. 1/10 of the [poly(vinyl sulfate)] in the monomer unit [5]. The distinction can be attributed to the density of the sulfonic group in the molecular assemblies. The density of the sulfonic side chain in Nafion aggregates is lower, and hence bulky cations such as $Ru(bpy)_3^{2+}$ or MV^{2+} can be adsorbed stoichiometrically.

Luminescence Quenching of $Ru(bpy)_3^{2+}$–$C_{60}F_{36}$ System in Nafion Ionomer Solution

Buckminster fullerene (C_{60}) is known as an electron-acceptor quencher [7]. The fullerene derivative $C_{60}F_{36}$ is used to quench the luminescence of excited $Ru(bpy)_3^{2+}$ both in bulk ethanol and in Nafion ionomer solution. As shown in Fig. 5, the quenching in Nafion ionomer solution is depressed to a considerable extent. $C_{60}F_{36}$ is thought to be held in the Nafion aggregates as the fluorocarbon backbone of the Nafion located in the aggregates has an affinity for $C_{60}F_{36}$. As $Ru(bpy)_3^{2+}$ cations are present on the surface of the aggregates, the $C_{60}F_{36}$ in the aggregates cannot quench the luminescence of the excited $Ru(bpy)_3^{2+}$.

The affinity of $C_{60}F_{36}$ for the fluorocarbon backbone of the Nafion aggregates is corroborated by DLS measurement. The drastic increase in the particle size of the Nafion aggregates shown in Fig. 6 is attributed to their incorporation of $C_{60}F_{36}$ atoms. The addition of $C_{60}F_{36}$ to

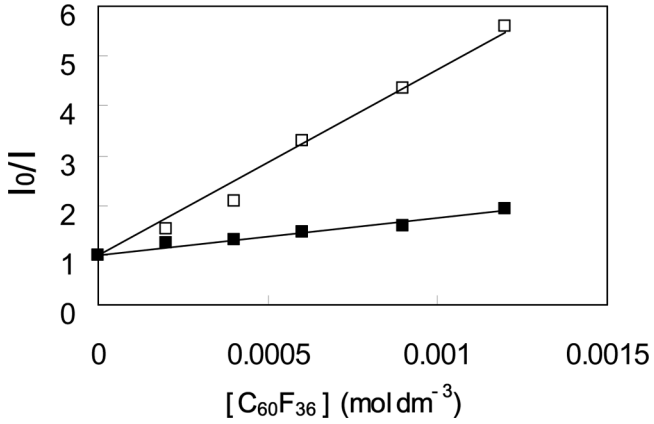

FIGURE 5 (I_0/I)–[quencher] relation for luminescence quenching of $Ru(bpy)_3^{2+}$–$C_{60}F_{36}$ system (1) in ethanol (□) and (2) in ethanol containing Nafion ionomer (■). $[Ru(bpy)_3^{2+}] = 6 \times 10^{-5}$ M. [Nafion] $= 3 \times 10^{-4}$ M in sulfonic side chain unit.

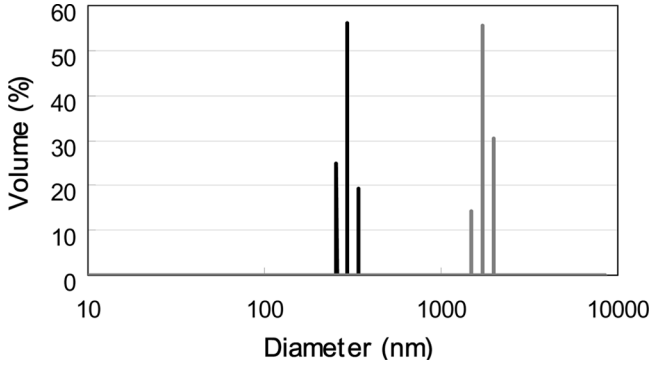

FIGURE 6 Distribution function of particle size for Nafion aggregates in ethanol obtained from DSL measurement. Black bars: Nafion aggregates; Nafion concentration in sulfonic side chain unit: 3×10^{-4} M. Gray bars: Nafion aggregates in ethanol containing 1.5×10^{-4} M $C_{60}F_{36}$.

the Nafion ionomer solution affects the size of the Nafion aggregates. In a similar manner, the fullerene derivatives added to the Nafion ionomer to produce MEA affect the texture of the proton channels in the Nafion. This may provide an appropriate explanation for the high performance of the MEA containing fullerene derivatives.

Luminescence Quenching of $Ru(bpy)_3^{2+}$–MV^{2+} System in Nafion Membrane

When a Nafion membrane is used as a polymer electrolyte for a fuel cell, a supply of water is essential. In humidified channels of which the inner wall consists of sulfonic side chains of Nafion, protons are propagated. To investigate the nature of these proton channels, we examined the luminescence quenching reactions of a $Ru(bpy)_3^{2+}$–MV^{2+} system.

Pieces of Nafion membrane ($2 \times 2 \times 0.0178\,cm^3$, 0.130 mg) were used as specimens. The amount and the concentration of sulfonic acid in the specimens were 1.0×10^{-4} mol and 1.4 M, respectively. After immersion in an aqueous solution containing 3×10^{-7} mol of $Ru(bpy)_3^{2+}$ for two days, all $Ru(bpy)_3^{2+}$ ions were occluded into the membrane. The specimen turned a homogeneous yellow and the concentration of $Ru(bpy)_3^{2+}$ was calculated to be 4.2×10^{-3} M. The luminescence from the excited $Ru(bpy)_3^{2+}$ in the Nafion membrane was similar to that in bulk ethanol or aqueous solution except for a bathochromic shift of ca. 10 nm.

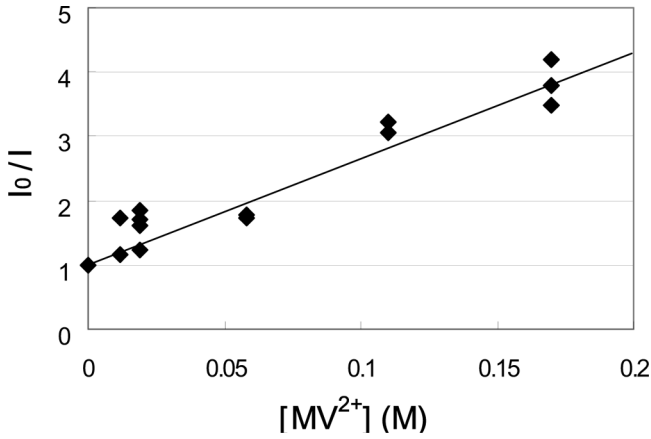

FIGURE 7 (I_0/I)–[MV^{2+}] relation for luminescence quenching of excited $Ru(bpy)_3^{2+}$ in Nafion membrane. [$Ru(bpy)_3^{2+}$] = 4.2×10^{-3} M. [sulfonic side chain] = 1.4 M.

Subsequent immersion for two days in aqueous solutions containing MV^{2+} caused the MV^{2+} ions to be occluded into the membrane also, which resulted in the quenching of $Ru(bpy)_3^{2+}$ luminescence. The (I_0/I)–[quencher] relation, shown in Fig. 7, can be described by the Stern–Volmer Eq. (1). The value of K_{SV} is ca. 18 for this luminescence quenching in the Nafion membrane. As the value of K_{SV} for quenching in bulk ethanol solution is ca. 330, the quenching reaction in the Nafion membrane is relatively suppressed.

The black dots in Fig. 8 show the decay curve of $Ru(bpy)_3^{2+}$ luminescence in Nafion membrane, where $Ru(bpy)_3^{2+}$ ions can be thought of as present both in the vicinity of the sulfonic group and in the free water region of the proton channel. As the luminescence lifetime is influenced by the microenvironment, the resulting decay curve was multi-exponential. The lifetime of $Ru(bpy)_3^{2+}$ luminescence in Nafion membrane is similar in range to that in bulk solvent ($\tau_0 \sim 650$ ns, single-exponential decay).

When 7.9×10^{-6} mol of MV^{2+} is occluded into a Nafion membrane containing $Ru(bpy)_3^{2+}$, the MV^{2+} concentration is 0.11 M, and the occlusion causes the $Ru(bpy)_3^{2+}$ luminescence to decay at a higher rate as shown by the gray dots in Fig. 8. The increase in the luminescence decay rate in the presence of MV^{2+} indicates that $Ru(bpy)_3^{2+}$ and MV^{2+} are diffused throughout the proton channels in the Nafion membrane, showing that they are not fixed at the sulfonic groups in the membrane.

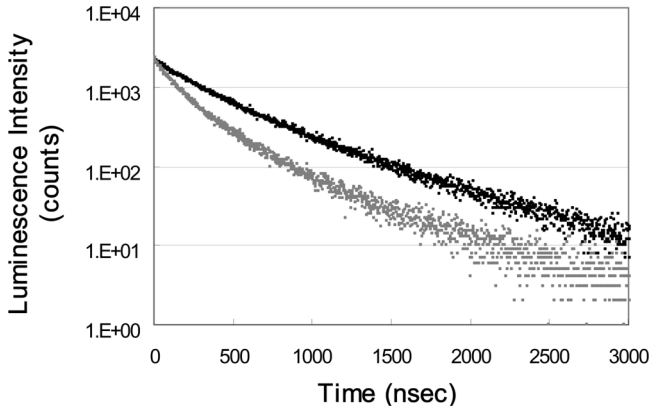

FIGURE 8 Decay curves of $Ru(bpy)_3^{2+}$ luminescence in Nafion membrane. $[Ru(bpy)_3^{2+}] = 4.2 \times 10^{-3}$ M. [sulfonic side chain] = 1.4 M. $[MV^{2+}]$: black dots: 0; gray dots: 0.17 M.

CONCLUDING REMARKS

In the present study, we demonstrated the luminescence quenching behaviors of $Ru(bpy)_3^{2+}$–MV^{2+} and $Ru(bpy)_3^{2+}$–$C_{60}F_{36}$ systems in ethanol-containing Nafion aggregates and of a $Ru(bpy)_3^{2+}$–MV^{2+} system occluded into a Nafion membrane. In the former systems, the (I_0/I) ([quencher] relation showed that $Ru(bpy)_3^{2+}$ and MV^{2+} are adsorbed onto Nafion aggregates, while $C_{60}F_{36}$ is held in Nafion aggregates. In the latter system, $Ru(bpy)_3^{2+}$ and MV^{2+} were shown to diffuse through the proton channels in the Nafion membrane with a diffusion constant ca. 1/20 of that in bulk ethanol solvent. These findings suggest that photochemical measurement with a probe ion $Ru(bpy)_3^{2+}$ might further elucidate the properties of Nafion aggregates in solvent and of proton channels in Nafion membrane.

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