Behaviour of Ru(bpy)$_{3}^{2+}$ on the Surface of Water-Soluble Single-Walled Carbon Nanotubes on Adding Other Cations

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ABSTRACT

Behaviour of excited Ru(bpy)$_{3}^{2+}$ bound to the surface of water-soluble single-walled carbon nanotubes on addition of other cations have been investigated by measuring Ru(bpy)$_{3}^{2+}$ luminescence. In contrast to what was observed with a solution containing rod-like aggregation particles of Nafion, we found that Ru(bpy)$_{3}^{2+}$ has a stronger attraction than that of other cations to the sulfonic groups on the carbon nanotubes. Such a difference is attributed to the unique micro-environmental characteristics of the molecular assemblies.

Keywords: Nanostructures; Single-Walled Carbon Nanotube; Ru(bpy)$_{3}^{2+}$; Luminescence Quenching

1. Introduction

The photochemical properties of tris(2,2’-bipyridine) ruthenium(II) dichloride (Ru(bpy)$_{3}^{2+}$) and related photosensitizers have been subjected to various investigations from the viewpoint of solar energy conversion [1-10]. The electron transfer phenomena of these sensitizers in the excited state have been studied in detail both in bulk and heterogeneous systems [1,4,6-10]. It is important to elucidate the nature of these systems as microenvironments in which the photoinduced electron transfer reaction processes occur.

In a previous study [8,9], we demonstrated luminescence quenching in Ru(bpy)$_{3}^{2+}$-methyl viologen dichloride (MV$^{2+}$) systems in an ethanol containing Nafion ionomer. Rod-like aggregation particles are found in the Nafion ionomer solutions because of the hydrophobic interactions of fluorocarbon backbones. Side chains containing sulfonic groups are located near the surface of the rod [11,12]. In this system, both Ru(bpy)$_{3}^{2+}$ and MV$^{2+}$ are cationic; therefore they interact with the anionic surface of the rod-like aggregation particles. A remarkable enhancement in quenching is observed when both Ru(bpy)$_{3}^{2+}$ and MV$^{2+}$ are adsorbed on the rod-like aggregation particles. The luminescence is restored with further addition of MV$^{2+}$, because Ru(bpy)$_{3}^{2+}$ appears to be released into the bulk solution. The released Ru(bpy)$_{3}^{2+}$ ions undergo simple luminescence quenching in the bulk solution.

We also reported an interaction between Ru(bpy)$_{3}^{2+}$ and a water-soluble single-walled carbon nanotube (SWCNT) [13]. The solubility of the SWCNT in water is secured by poly(m-aminobenzene sulfonic acid) (PABS) covalently bonded to the SWCNT. The molecular weight of the PABS is 400 - 800, which indicates that each PABS molecule contains on an average three sulfonic groups. Cationic Ru(bpy)$_{3}^{2+}$ is adsorbed on each sulfonic group, and the luminescence of Ru(bpy)$_{3}^{2+}$ at the sulfonic group adjacent to the trunk of the SWCNT is quenched by the mechanism of electron transfer to the SWCNT. On the other hand, two-thirds of Ru(bpy)$_{3}^{2+}$ is not quenched, because the SWCNT is remote for electron transfer.

In the present study, we analyze the behaviour of Ru(bpy)$_{3}^{2+}$ on the surface of the water-soluble SWCNTs on adding other cations. The results of these investigations will contribute to the improvement of organic photovoltaic solar cells.

2. Experimental

Ru(bpy)$_{3}^{2+}$ (Tokyo Kasei), MV$^{2+}$ (Tokyo Kasei), sodium chloride and calcium dichloride were used as received. The SWCNT (Cat. No. 639230) was obtained from Sigma-Aldrich Co [14]. The SWCNT (10 mg) was sonicated in 1 dm$^3$ of water for 2 h. The suspension was filtered through a 1-µm-pore-size membrane, and the greenish-grey filtrate was used for the mother liquor to dissolve the luminescent Ru(bpy)$_{3}^{2+}$ and the additives. In the mother liquor, the concentration of the sulfonic group on the surface of the dissolved SWCNT was 7.5 × 10$^{-6}$
mol/dm³.

Luminescence spectra were measured using a fluorescence spectrometer (Perkin Elmer LS50B). All aqueous solutions for the luminescence measurement were de-oxygenized by flushing with Ar gas for 20 min.

3. Results and Discussion

Luminescence spectra of Ru(bpy)³⁺ are shown in Figure 1. The intensity of luminescence from the aqueous solution with the SWCNT ([sulfonic group] = 5 × 10⁻⁶ mol/dm³) is lower than that without the SWCNT. The excitation beam and luminescence in the sample solution are absorbed by the SWCNTs, which reduces the luminescence intensity. In addition, a part of the luminescence of Ru(bpy)³⁺ is quenched by the associated SWCNT. As shown in Figure 1, the concentration of Ru(bpy)³⁺ is 5 × 10⁻⁵ mol/dm³ and all Ru(bpy)³⁺ ions are adsorbed to the sulfonic groups of the SWCNTs. Hence the luminescence intensity is reduced to two-thirds of that already reduced by SWCNT absorption.

As shown in Figure 2, the addition of Na⁺ has no effect on the luminescence intensity of Ru(bpy)³⁺ in a wide range of Na⁺ concentrations. This implies that Ru(bpy)³⁺ is still adsorbed on the sulfonic groups of the SWCNTs even in the presence of high concentration of Na⁺. In case of Ca²⁺, the luminescence intensity of Ru(bpy)³⁺ increases with increasing concentration of the added Ca²⁺. The intensity at 0.001 mol/dm³ of Ca²⁺ is 1.5 times greater than that in the absence of Ca²⁺. At this concentration of Ca²⁺, almost all adsorption sites may be occupied by Ca²⁺ and Ru(bpy)²⁺ ions are released into the bulk solution. Quenching of luminescence from Ru(bpy)³⁺ ions at the sites adjacent to the SWCNT is now cancelled, and the luminescence of the corresponding Ru(bpy)³⁺ is recovered. As the ratio of Ru(bpy)³⁺ adjacent to the SWCNT is one-third of the total, the luminescence intensity increases correspondingly.

In a previous study [8,9], we reported that Ru(bpy)³⁺ ions adsorb onto the sulfonic groups on the rod-like aggregation particles of Nafion and that Ru(bpy)³⁺ is released into the bulk solution by the addition of MV²⁺. In this case, the concentrations of the sulfonic groups and Ru(bpy)³⁺ are 3 × 10⁻⁴ mol/dm³ and 6 × 10⁻⁵ mol/dm³, respectively. When 3 × 10⁻⁴ mol/dm³ of MV²⁺ is added to this solution, luminescence measurements suggest that Ru(bpy)³⁺ ions are mostly released into the bulk solution. For the Nafion aggregation particles, the propensity to adsorb Ru(bpy)³⁺ or MV²⁺ is not distinguished.

In case of the Ru(bpy)³⁺-cation system in the present SWCNT solution, the luminescence intensity could be simulated assuming that there is no selectivity for adsorption between Ru(bpy)³⁺ and the added cation. As is plotted with open circles in Figure 2, the luminescence intensity of Ru(bpy)³⁺ increases with the concentration of the added cation (See Appendix). The intensity at the concentration of 5 × 10⁻⁵ mol/dm³ is simulated to be 1.455 times greater than that in the absence of the cation. In practice, 4 × 10⁻⁴ mol/dm³ of Ca²⁺ releases almost all Ru(bpy)³⁺, thereby increasing the luminescence intensity by a factor of 1.5. The discrepancy between the simulated values and the empirical results with Ca²⁺ and Na⁺ suggests that the adsorption affinity of Ru(bpy)³⁺ for the SWCNT sulfonic groups is much higher than that of Ca²⁺, and that Na⁺ no longer replaces Ru(bpy)³⁺. Moreover, further addition of Ca²⁺ does not influence the luminescence intensity of Ru(bpy)³⁺ because Ca²⁺ is not a quencher for Ru(bpy)³⁺.

Figure 1. Steady-state luminescence spectra of Ru(bpy)³⁺ in water and (b) in water containing SWCNTs. [Ru(bpy)³⁺] = 5 × 10⁻⁶ mol/dm³. [sulfonic group] on SWCNTs = 5 × 10⁻⁶ mol/dm³.

Figure 2. Luminescence intensity versus concentration of the added cation. Added cation: (◆) Na⁺; (●) Ca²⁺. The simulated intensity is plotted with ○ (see text). The luminescence intensity of the solution without added cation is normalized to 100.
MV$^{2+}$ is a well-known electron accepting cation that can quench the luminescence of Ru(bpy)$_3^{2+}$. When both Ru(bpy)$_3^{2+}$ and MV$^{2+}$ are adsorbed onto the sulfonic groups on the rod-like aggregation particles of Nafion, a remarkable enhancement in quenching and a restoration of the luminescence were correlated with the relative concentrations of Ru(bpy)$_3^{2+}$, MV$^{2+}$ and the sulfonic group [8,9]. In the case of the sulfonic groups on the SWCNTs, the luminescence intensity is also influenced by the concentration of MV$^{2+}$, as shown in Figure 3. When the concentration of MV$^{2+}$ is low, a remarkable enhancement in quenching is expected for both Ru(bpy)$_3^{2+}$ and MV$^{2+}$ existing in the vicinity of the SWCNT. However, the dependence of MV$^{2+}$ concentration on the luminescence intensity is, in reality, similar to that of Ca$^{2+}$ in a concentration range up to $5 \times 10^{-5}$ mol/dm$^3$. The electron acceptor MV$^{2+}$ seems unable to quench the luminescence of Ru(bpy)$_3^{2+}$ as is seen with Ca$^{2+}$, which demonstrates no luminescence quenching ability. Each sulfonic group of the PABS covalently attached to the SWCNT seems to be remote from the others, and adsorbed MV$^{2+}$ cannot quench the luminescence of Ru(bpy)$_3^{2+}$ adsorbed on remote sulfonic groups. Figure 3(a) also suggests that the relative adsorption affinity of MV$^{2+}$ for the sulfonic groups seems to be quite similar to that of Ca$^{2+}$.

At a high concentration of MV$^{2+}$, Ru(bpy)$_3^{2+}$ ions are released into the bulk solution. In the bulk solution, the concentration of MV$^{2+}$ is already sufficient to quench the luminescence of Ru(bpy)$_3^{2+}$. The luminescence decreased with an increasing concentration of MV$^{2+}$ as a result of a simple Stern-Volmer type of luminescence quenching (Figure 3(b)).

The low affinity of Na$^+$ ion adsorption onto the sulfonic groups of the SWCNTs, compared with that of Ru(bpy)$_3^{2+}$, can be explained on the basis of the valence. Single-charged cations have a lower attraction to anions than double-charged cations. On the other hand, Ru(bpy)$_3^{2+}$, MV$^{2+}$ and Ca$^{2+}$ have a 2+ valence. Although the affinity of Ru(bpy)$_3^{2+}$ and MV$^{2+}$ to the sulfonic groups on the Nafion aggregate is identical, Ru(bpy)$_3^{2+}$ has a significantly greater affinity to the sulfonic groups on the SWCNTs than MV$^{2+}$ or Ca$^{2+}$. This enhanced attraction between Ru(bpy)$_3^{2+}$ and the sulfonic groups of PABS on the surface of SWCNTs is expected to be assisted by van der Waal’s attractive forces between the benzene nucleus of PABS and the 2,2'-bipyridine ligand of the cationic complex.

4. Concluding Remarks

In the present study, we have observed the luminescence intensity of Ru(bpy)$_3^{2+}$ on the surface of water-soluble SWCNTs on addition of other cations. A comparison with solutions containing the rod-like aggregation particles of Nafion highlights the different micro-environmental characteristics of these molecular assemblies as mediums for photochemical electron transfer reactions. The accumulation of such information would be applicable to the design of high-performance organic photovoltaic solar cells.

REFERENCES


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Appendix

As shown in Figure 1A, each PABS has an average of three sulfonic groups and is covalently bonded to the SWCNT. As the SWCNT is an electron acceptor, the luminescence from excited Ru(bpy)$_2^{3+}$ adsorbed on the sulfonic groups adjacent to the SWCNT (site-A) is quenched [13].

On adding other cations to a solution of Ru(bpy)$_2^{3+}$ ($5 \times 10^{-6}$ mol/dm$^3$) and SWCNTs (the concentration of the sulfonic group is $5 \times 10^{-6}$ mol/dm$^3$), Ru(bpy)$_2^{3+}$ ions adsorbed on the sulfonic group are released into the bulk solution. In the bulk solution, the luminescence from Ru(bpy)$_2^{3+}$ is no longer quenched by the SWCNT. The intensity of the released Ru(bpy)$_2^{3+}$ is 1.5 times greater than that of the adsorbed ions. Details of the simulated luminescence intensity are shown in Table 1A.

Figure 1A. Schematic illustration of the SWCNT. Ca. one PABS is covalently bonded per 11 carbon atoms of the SWCNT.

Table 1A. Simulated luminescence intensity of Ru(bpy)$_2^{3+}$ on adding a solution of cations with a hypothetical sulfonic group affinity identical to that of Ru(bpy)$_2^{3+}$. The concentration of SWCNT-associated sulfonic groups is $5 \times 10^{-6}$ mol/dm$^3$.

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<th>relative amount of Ru(bpy)$_2^{3+}$ released for the bulk solution</th>
<th>relative intensity of the luminescence from Ru(bpy)$_2^{3+}$ adsorbed on the SWCNT</th>
<th>relative intensity of the luminescence from Ru(bpy)$_2^{3+}$ released for the bulk solution</th>
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*: $[\text{Ru(bpy)}_3^{2+}] = 5 \times 10^{-6}$ mol/dm$^3$. Copyright © 2012 SciRes. JSEMAT