

# Behaviour of $\text{Ru}(\text{bpy})_3^{2+}$ on the Surface of Water-Soluble Single-Walled Carbon Nanotubes on Adding Other Cations

Hiroshi Shioyama

National Institute of Advanced Industrial Science and Technology (AIST), Osaka, Japan.  
Email: shioyama.h@aist.go.jp

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## ABSTRACT

Behaviour of excited  $\text{Ru}(\text{bpy})_3^{2+}$  bound to the surface of water-soluble single-walled carbon nanotubes on addition of other cations have been investigated by measuring  $\text{Ru}(\text{bpy})_3^{2+}$  luminescence. In contrast to what was observed with a solution containing rod-like aggregation particles of Nafion, we found that  $\text{Ru}(\text{bpy})_3^{2+}$  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;  $\text{Ru}(\text{bpy})_3^{2+}$ ; Luminescence Quenching

## 1. Introduction

The photochemical properties of tris(2,2'-bipyridine) ruthenium(II) dichloride ( $\text{Ru}(\text{bpy})_3^{2+}$ ) 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  $\text{Ru}(\text{bpy})_3^{2+}$ -methyl viologen dichloride ( $\text{MV}^{2+}$ ) 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  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{MV}^{2+}$  are cationic; therefore they interact with the anionic surface of the rod-like aggregation particles. A remarkable enhancement in quenching is observed when both  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{MV}^{2+}$  are adsorbed on the rod-like aggregation particles. The luminescence is restored with further addition of  $\text{MV}^{2+}$ , because  $\text{Ru}(\text{bpy})_3^{2+}$  appears to be released into the bulk solution. The released  $\text{Ru}(\text{bpy})_3^{2+}$  ions undergo simple luminescence quenching in the bulk solution.

We also reported an interaction between  $\text{Ru}(\text{bpy})_3^{2+}$

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  $\text{Ru}(\text{bpy})_3^{2+}$  is adsorbed on each sulfonic group, and the luminescence of  $\text{Ru}(\text{bpy})_3^{2+}$  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  $\text{Ru}(\text{bpy})_3^{2+}$  is not quenched, because the SWCNT is remote for electron transfer.

In the present study, we analyze the behaviour of  $\text{Ru}(\text{bpy})_3^{2+}$  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

$\text{Ru}(\text{bpy})_3^{2+}$  (Tokyo Kasei),  $\text{MV}^{2+}$  (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<sup>3</sup> of water for 2 h. The suspension was filtered through a 1- $\mu\text{m}$ -pore-size membrane, and the greenish-grey filtrate was used for the mother liquor to dissolve the luminescent  $\text{Ru}(\text{bpy})_3^{2+}$  and the additives. In the mother liquor, the concentration of the sulfonic group on the surface of the dissolved SWCNT was  $7.5 \times 10^{-6}$

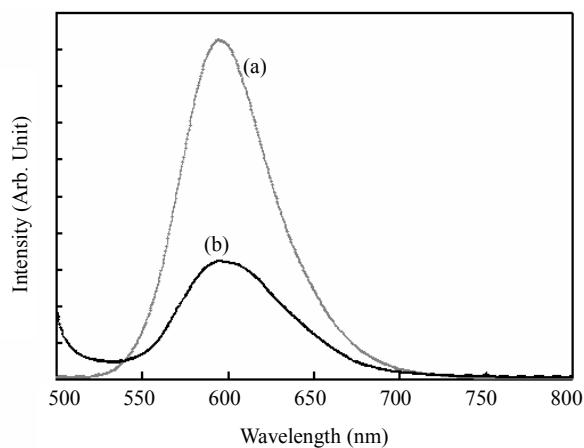
$\text{mol}/\text{dm}^3$ .

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

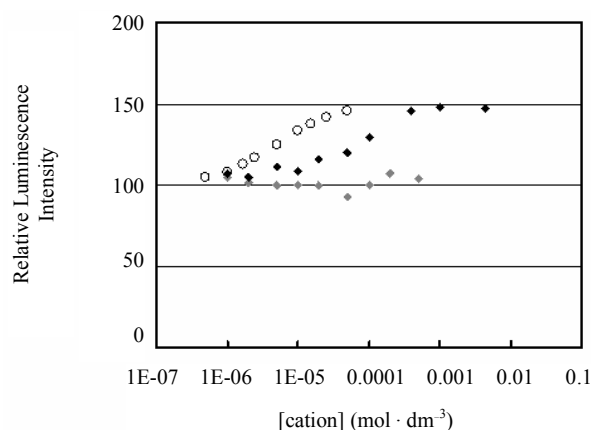
### 3. Results and Discussion

Luminescence spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  are shown in **Figure 1**. The intensity of luminescence from the aqueous solution with the SWCNT ([sulfonic group] =  $5 \times 10^{-6} \text{ mol}/\text{dm}^3$ ) 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  $\text{Ru}(\text{bpy})_3^{2+}$  is quenched by the associated SWCNT. As shown in **Figure 1**, the concentration of  $\text{Ru}(\text{bpy})_3^{2+}$  is  $5 \times 10^{-6} \text{ mol}/\text{dm}^3$  and all  $\text{Ru}(\text{bpy})_3^{2+}$  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  $\text{Na}^+$  has no effect on the luminescence intensity of  $\text{Ru}(\text{bpy})_3^{2+}$  in a wide range of  $\text{Na}^+$  concentrations. This implies that  $\text{Ru}(\text{bpy})_3^{2+}$  is still adsorbed on the sulfonic groups of the SWCNTs even in the presence of high concentration of  $\text{Na}^+$ . In case of  $\text{Ca}^{2+}$ , the luminescence intensity of  $\text{Ru}(\text{bpy})_3^{2+}$  increases with increasing concentration of the added  $\text{Ca}^{2+}$ . The intensity at  $0.001 \text{ mol}/\text{dm}^3$  of  $\text{Ca}^{2+}$  is 1.5 times greater than that in the absence of  $\text{Ca}^{2+}$ . At this concentration of  $\text{Ca}^{2+}$ , almost all adsorption sites may be occupied by  $\text{Ca}^{2+}$  and  $\text{Ru}(\text{bpy})_3^{2+}$  ions are released into the bulk solution. Quenching of luminescence from  $\text{Ru}(\text{bpy})_3^{2+}$  ions at the sites adjacent to the SWCNT is



**Figure 1.** Steady-state luminescence spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  (a) in water and (b) in water containing SWCNTs. [ $\text{Ru}(\text{bpy})_3^{2+}$ ] =  $5 \times 10^{-6} \text{ mol}/\text{dm}^3$ . [sulfonic group] on SWCNTs =  $5 \times 10^{-6} \text{ mol}/\text{dm}^3$ .



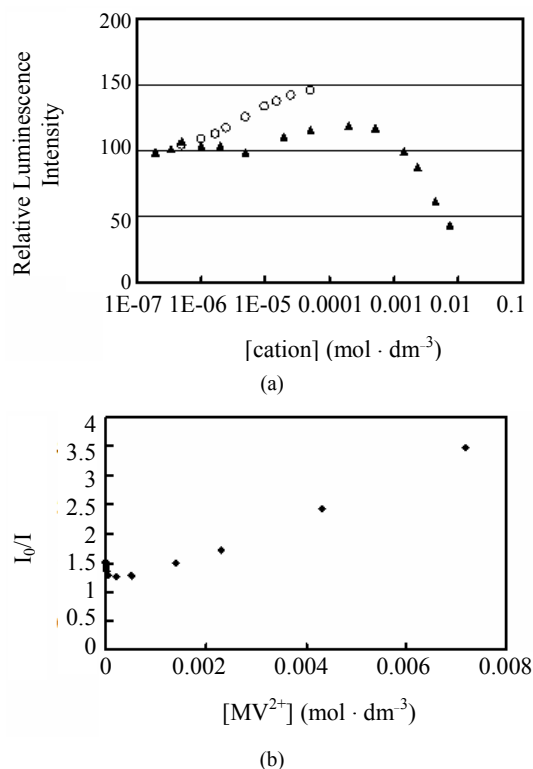
**Figure 2.** Luminescence intensity versus concentration of the added cation. Added cation: (◆)  $\text{Na}^+$ ; (◆)  $\text{Ca}^{2+}$ . The simulated intensity is plotted with ○ (see text). The luminescence intensity of the solution without added cation is normalized to 100.

now cancelled, and the luminescence of the corresponding  $\text{Ru}(\text{bpy})_3^{2+}$  is recovered. As the ratio of  $\text{Ru}(\text{bpy})_3^{2+}$  adjacent to the SWCNT is one-third of the total, the luminescence intensity increases correspondingly.

In a previous study [8,9], we reported that  $\text{Ru}(\text{bpy})_3^{2+}$  ions adsorb onto the sulfonic groups on the rod-like aggregation particles of Nafion and that  $\text{Ru}(\text{bpy})_3^{2+}$  is released into the bulk solution by the addition of  $\text{MV}^{2+}$ . In this case, the concentrations of the sulfonic groups and  $\text{Ru}(\text{bpy})_3^{2+}$  are  $3 \times 10^{-4} \text{ mol}/\text{dm}^3$  and  $6 \times 10^{-5} \text{ mol}/\text{dm}^3$ , respectively. When  $3 \times 10^{-4} \text{ mol}/\text{dm}^3$  of  $\text{MV}^{2+}$  is added to this solution, luminescence measurements suggest that  $\text{Ru}(\text{bpy})_3^{2+}$  ions are mostly released into the bulk solution. For the Nafion aggregation particles, the propensity to adsorb  $\text{Ru}(\text{bpy})_3^{2+}$  or  $\text{MV}^{2+}$  is not distinguished.

In case of the  $\text{Ru}(\text{bpy})_3^{2+}$ -cation system in the present SWCNT solution, the luminescence intensity could be simulated assuming that there is no selectivity for adsorption between  $\text{Ru}(\text{bpy})_3^{2+}$  and the added cation. As is plotted with open circles in **Figure 2**, the luminescence intensity of  $\text{Ru}(\text{bpy})_3^{2+}$  increases with the concentration of the added cation (See Appendix). The intensity at the concentration of  $5 \times 10^{-5} \text{ mol}/\text{dm}^3$  is simulated to be 1.455 times greater than that in the absence of the cation. In practice,  $4 \times 10^{-4} \text{ mol}/\text{dm}^3$  of  $\text{Ca}^{2+}$  releases almost all  $\text{Ru}(\text{bpy})_3^{2+}$ , thereby increasing the luminescence intensity by a factor of 1.5. The discrepancy between the simulated values and the empirical results with  $\text{Ca}^{2+}$  and  $\text{Na}^+$  suggests that the adsorption affinity of  $\text{Ru}(\text{bpy})_3^{2+}$  for the SWCNT sulfonic groups is much higher than that of  $\text{Ca}^{2+}$ , and that  $\text{Na}^+$  no longer replaces  $\text{Ru}(\text{bpy})_3^{2+}$ . Moreover, further addition of  $\text{Ca}^{2+}$  does not influence the luminescence intensity of  $\text{Ru}(\text{bpy})_3^{2+}$  because  $\text{Ca}^{2+}$  is not a quencher for  $\text{Ru}(\text{bpy})_3^{2+}$ .

$\text{MV}^{2+}$  is a well-known electron accepting cation that can quench the luminescence of  $\text{Ru}(\text{bpy})_3^{2+}$ . When both  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{MV}^{2+}$  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  $\text{Ru}(\text{bpy})_3^{2+}$ ,  $\text{MV}^{2+}$  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  $\text{MV}^{2+}$ , as shown in **Figure 3**. When the concentration of  $\text{MV}^{2+}$  is low, a remarkable enhancement in quenching is expected for both  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{MV}^{2+}$  existing in the vicinity of the SWCNT. However, the dependence of  $\text{MV}^{2+}$  concentration on the luminescence intensity is, in reality, similar to that of  $\text{Ca}^{2+}$  in a concentration range up to  $5 \times 10^{-5} \text{ mol/dm}^3$ . The electron acceptor  $\text{MV}^{2+}$  seems unable to quench the luminescence of  $\text{Ru}(\text{bpy})_3^{2+}$  as is seen with  $\text{Ca}^{2+}$ , which



**Figure 3.** (a) Luminescence intensity versus the concentration of added  $\text{MV}^{2+}$  ( $\blacktriangle$ ). The simulated intensity is plotted with  $\circ$  (see text). The luminescence intensity of the solution without  $\text{MV}^{2+}$  is normalized to 100; (b) Stern-Volmer-type plot of Luminescence intensity versus the concentration of added  $\text{MV}^{2+}$  ( $\blacklozenge$ ). A hypothetical luminescence intensity of  $\text{Ru}(\text{bpy})_3^{2+}$  in the absence of  $\text{MV}^{2+}$  is defined as  $I_0$ , where the excitation beam and luminescence in the sample solution are absorbed by the SWCNT, but the luminescence of  $\text{Ru}(\text{bpy})_3^{2+}$  is not quenched by the SWCNT. This hypothetical intensity is indicated as 150 in **Figure 3(a)**.

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  $\text{MV}^{2+}$  cannot quench the luminescence of  $\text{Ru}(\text{bpy})_3^{2+}$  adsorbed on remote sulfonic groups. **Figure 3(a)** also suggests that the relative adsorption affinity of  $\text{MV}^{2+}$  for the sulfonic groups seems to be quite similar to that of  $\text{Ca}^{2+}$ .

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

The low affinity of  $\text{Na}^+$  ion adsorption onto the sulfonic groups of the SWCNTs, compared with that of  $\text{Ru}(\text{bpy})_3^{2+}$ , 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,  $\text{Ru}(\text{bpy})_3^{2+}$ ,  $\text{MV}^{2+}$  and  $\text{Ca}^{2+}$  have a 2+ valence. Although the affinity of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{MV}^{2+}$  to the sulfonic groups on the Nafion aggregate is identical,  $\text{Ru}(\text{bpy})_3^{2+}$  has a significantly greater affinity to the sulfonic groups on the SWCNTs than  $\text{MV}^{2+}$  or  $\text{Ca}^{2+}$ . This enhanced attraction between  $\text{Ru}(\text{bpy})_3^{2+}$  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  $\text{Ru}(\text{bpy})_3^{2+}$  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.

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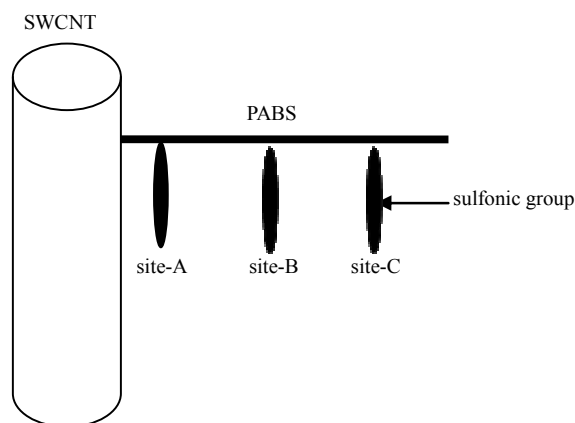
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## Appendix

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  $\text{Ru}(\text{bpy})_3^{2+}$  adsorbed on the sulfonic groups adjacent to the SWCNT (site-A) is quenched [13].

On adding other cations to a solution of  $\text{Ru}(\text{bpy})_3^{2+}$  ( $5 \times 10^{-6} \text{ mol/dm}^3$ ) and SWCNTs (the concentration of the sulfonic group is  $5 \times 10^{-6} \text{ mol/dm}^3$ ),  $\text{Ru}(\text{bpy})_3^{2+}$  ions adsorbed on the sulfonic group are released into the bulk solution. In the bulk solution, the luminescence from  $\text{Ru}(\text{bpy})_3^{2+}$  is no longer quenched by the SWCNT. The intensity of the released  $\text{Ru}(\text{bpy})_3^{2+}$  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  $\text{Ru}(\text{bpy})_3^{2+}$  on adding a solution of cations with a hypothetical sulfonic group affinity identical to that of  $\text{Ru}(\text{bpy})_3^{2+}$ . The concentration of SWCNT-associated sulfonic groups is  $5 \times 10^{-6} \text{ mol/dm}^3$ .

concentration of added cation ( $\text{mol/dm}^3$ )	relative concentration of added cation in comparison with $[\text{Ru}(\text{bpy})_3^{2+}]^*$	relative amount of $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed on the SWCNT	relative amount of $\text{Ru}(\text{bpy})_3^{2+}$ released for the bulk solution	relative intensity of the luminescence from $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed on the SWCNT	relative intensity of the luminescence from $\text{Ru}(\text{bpy})_3^{2+}$ released for the bulk solution	overall luminescence intensity
0	0	1	0	100	0	100
$5 \times 10^{-7}$	1/10	10/11	1/11	$100 \times 10/11 = 90.9$	$100 \times 1/11 \times 1.5 = 13.6$	104.5
$1 \times 10^{-6}$	1/5	5/6	1/6	$100 \times 5/6 = 83.3$	$100 \times 1/6 \times 1.5 = 25$	108.3
$1.67 \times 10^{-6}$	1/3	3/4	1/4	$100 \times 3/4 = 75$	$100 \times 1/4 \times 1.5 = 37.5$	112.5
$2.5 \times 10^{-6}$	1/2	2/3	1/3	$100 \times 2/3 = 66.7$	$100 \times 1/3 \times 1.5 = 50$	116.7
$5 \times 10^{-6}$	1	1/2	1/2	$100 \times 1/2 = 50$	$100 \times 1/2 \times 1.5 = 75$	125
$1 \times 10^{-5}$	2	1/3	2/3	$100 \times 1/3 = 33.3$	$100 \times 2/3 \times 1.5 = 100$	133.3
$1.5 \times 10^{-5}$	3	1/4	3/4	$100 \times 1/4 = 25$	$100 \times 3/4 \times 1.5 = 112.5$	137.5
$2.5 \times 10^{-5}$	5	1/6	5/6	$100 \times 1/6 = 16.7$	$100 \times 5/6 \times 1.5 = 125$	141.7
$5 \times 10^{-5}$	10	1/11	10/11	$100 \times 1/11 = 9.1$	$100 \times 10/11 \times 1.5 = 136.4$	145.5

\*:  $[\text{Ru}(\text{bpy})_3^{2+}] = 5 \times 10^{-6} \text{ mol/dm}^3$ .