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Makoto Ogawa^a, Misako Inagaki^a, Nobuhiro Kodama^{a,b}, Kazuyuki Kuroda^a & Chuzo Kato^a

^a Department of Applied Chemistry, Waseca University, Ohkubo-3, Shinjukuku, Tokyo, 169, Japan

^b TOSOH Corporation, Hayakawa 2743-1, Ayase-shi, Kanagawa, 252, Japan

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Luminescence of Tris(2,2'-bipyridine)ruthenium(II) Incorporated in Mica-Organic Polymer Intercalation Compounds

MAKOTO OGAWA, MISAKO INAGAKI, NOBUHIRO KODAMA*, KAZUYUKI KURODA and CHUZO KATO

Department of Applied Chemistry, Waseda University,
 Ohkubo-3, Shinjuku-ku, Tokyo 169, Japan.

*TOSOH Corporation, Hayakawa 2743-1, Ayase-shi, Kanagawa 252, Japan.

Abstract Luminescence of $\text{Ru}(\text{bpy})_3^{2+}$ incorporated in a swelling mica-poly(vinylpyrrolidone)(PVP) intercalation compound was investigated. In the sterically limited interlayer space of mica, $\text{Ru}(\text{bpy})_3^{2+}$ was forced to be surrounded by PVP in close contact, showing a novel controlled luminescent behavior.

INTRODUCTION

Photochemical reactions on solid surfaces have attracted increasing attention from a practical viewpoint of uses such as solar energy conversion and preparation of thin films. Among possible matrices, layered clay minerals, in particular smectites, provide interesting two dimensional heterogeneous media for photochemical processes. Smectites are 2:1 type layered clay minerals consisting of negatively charged silicate layers and readily exchangeable interlayer cations, (Figure 1) and possess various attractive features such as adsorptive property, large surface area and so on.¹ Studies on physicochemical properties in such ordered matrices have an advantage

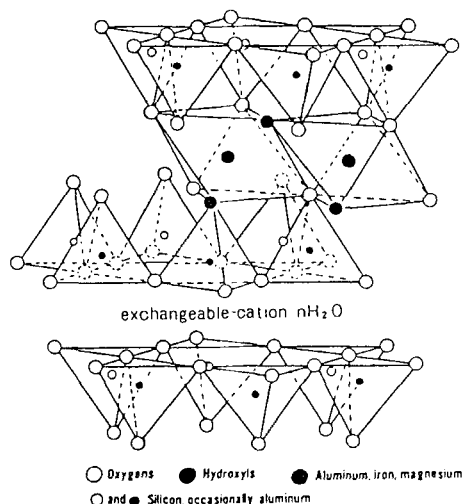


Figure 1. Layered structure of smectites

so that the reaction behavior may be understood in connection with the structure at a molecular level.

$\text{Ru}(\text{bpy})_3^{2+}$ is one of the molecules studied most extensively because of its unique combination of chemical stability, luminescence, and so on.² Photoprocess of $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed on smectites has already been investigated³⁻¹³ and two types of quenching of the excited state of $\text{Ru}(\text{bpy})_3^{2+}$ have been pointed out. One is self quenching due to aggregation of $\text{Ru}(\text{bpy})_3^{2+}$ and the other is quenching by iron which is included in natural smectites. We now report a novel way to control luminescent behavior of $\text{Ru}(\text{bpy})_3^{2+}$ by its intercalation into a swelling mica with poly(vinylpyrrolidone). In order to exclude the effect of iron, an artificial mica, whose properties are similar to smectites, was used. In the system, $\text{Ru}(\text{bpy})_3^{2+}$ was surrounded by PVP in close contact in the sterically limited interlayer space to show a unique luminescent behavior.

EXPERIMENTAL SECTION

A fluor-tetrasilicic mica (Tsm, supplied from Topy Ind.Co.) was used as the host material. $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) was used after recrystallization from deionized water. PVP (Mw=1000, Tokyo Kasei Co.) was used as received. A Tsm-PVP intercalation compound was prepared by the method used for the preparation of a montmorillonite-PVP intercalation compound.¹² $\text{Ru}(\text{bpy})_3^{2+}$ was exchanged for Na ions by a conventional ion exchange method in an aqueous media. A $\text{Ru}(\text{bpy})_3^{2+}$ -Tsm intercalation compound was prepared by a conventional method for comparison.

RESULTS AND DISCUSSION

The basal spacing of the Tsm-PVP intercalation compound was 2.30 nm. The expansion of the interlayer spacing was 1.34 nm, indicating the intercalation and bimolecular coverage of PVP in the interlayer space.¹² After the reaction with $\text{Ru}(\text{bpy})_3^{2+}$, the basal spacing increased.(Table 1) The expansion of the interlayer region varied from 1.39 to 1.68 nm. Since the intercalation of tris(bpy) chelates requires the expansion of the interlayer space by ca. 0.8 nm, we can

Table 1. Basal spacings of the intercalation compounds, amounts of the adsorbed species, and luminescence maxima

Amounts of $\text{Ru}(\text{bpy})_3^{2+}$ (mmol/100g Tsm)	Basal spacing (nm)	Amount of PVP (g/100g Tsm)	*Ratio of PVP to $\text{Ru}(\text{bpy})_3^{2+}$	Luminescence maxima (nm)
Tsm-PVP	2.30	42	-	-
8	2.35	42	48	596
17	2.45	36	19	604
33	2.59	29	8	605
43	2.64	24	5	608

*molar ratio of PVP monomer unit to $\text{Ru}(\text{bpy})_3^{2+}$

conclude that both $\text{Ru}(\text{bpy})_3^{2+}$ and PVP were accommodated in the interlayer space.

The absorption maximum due to the "metal-to-ligand charge transfer" transition of $\text{Ru}(\text{bpy})_3^{2+}$ shifted toward red (<468 nm) upon intercalation into the Tsm-PVP intercalation compound. On the other hand, the luminescence maximum shifted toward blue. These spectroscopic features are different from those of the $\text{Ru}(\text{bpy})_3^{2+}$ -Tsm intercalation compound, indicating that cointercalation of PVP caused the change in the microenvironment of $\text{Ru}(\text{bpy})_3^{2+}$. It is supposed that the polarity and/or rigidity of the surrounding matrices were responsible for the spectral shifts.

More notable point is a possibility to control the wavelength of luminescence maximum by the intercalation into the Tsm-PVP intercalation compound. The luminescence maximum shifted gradually toward lower wavelength region with the decrease in the loading of $\text{Ru}(\text{bpy})_3^{2+}$. Judging from the ratio of PVP monomer units to adsorbed $\text{Ru}(\text{bpy})_3^{2+}$ (Table 1), the dipole density of the surrounding matrices also changed gradually depending on the loading level and has a direct relation to the degree of the blue shift. Thus, the dipole density arisen from PVP is supposed to cause the change in the spectra. By the incorporation of $\text{Ru}(\text{bpy})_3^{2+}$ into the sterically limited space, PVP was forced to surround $\text{Ru}(\text{bpy})_3^{2+}$ in close contact. Consequently, $\text{Ru}(\text{bpy})_3^{2+}$ became more sensitive to the change in the polarity of the surrounding.

Compared to the $\text{Ru}(\text{bpy})_3^{2+}$ -Tsm intercalation compound, the $\text{Ru}(\text{bpy})_3^{2+}$ -Tsm-PVP intercalation compounds gave an intense emission. Additionally, the emission intensity increased with the decrease in the loading. Previous studies on luminescence of $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed on smectites have revealed that $\text{Ru}(\text{bpy})_3^{2+}$ aggregates to cause self-quenching even at a low loading level. In the $\text{Ru}(\text{bpy})_3^{2+}$ -Tsm-PVP intercalation compounds, cointercalated PVP was supposed to isolate $\text{Ru}(\text{bpy})_3^{2+}$ to suppress self-quenching due to aggregation. As mentioned above, the molar ratio of PVP to $\text{Ru}(\text{bpy})_3^{2+}$ increased with the decrease in the loading. Thus, with the increase in the relative amount of PVP, more effective isolation of $\text{Ru}(\text{bpy})_3^{2+}$ was achieved to intensify the luminescence.

Cointercalated PVP played an important role to suppress self-quenching as well as to alter the microenvironment of $\text{Ru}(\text{bpy})_3^{2+}$. Smectite-organic polymer intercalation compounds have advantages such as thermal stability and film forming ability. Further studies on the novel system and on the effects of organic polymers with different polarity are now in progress and will be reported subsequently.

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