Luminescence of Tris(2,2′-bipyridine)ruthenium(II) Cations ([Ru(bpy)$_3$]$^{2+}$) Adsorbed in Mesoporous Silica

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The adsorption of a cationic luminescence probe, tris(2,2′-bipyridine)ruthenium(II) ([Ru(bpy)$_3$]$^{2+}$), into a mesoporous silica was investigated in order to understand the nature of mesoporous silicas as immobilizing media for organic guest species. The adsorption of the probe into the mesoporous silica was conducted by the reaction using a dimethylformamide solution of [Ru(bpy)$_3$]$^{2+}$ chloride. The adsorbed amount of [Ru(bpy)$_3$]$^{2+}$ was controlled by changing the concentration of the solutions. When the samples were dehydrated, the adsorbed [Ru(bpy)$_3$]$^{2+}$ ions aggregated to cause self-quenching of the luminescence. The luminescence was intensified dramatically upon hydration of the samples, indicating that the aggregated [Ru(bpy)$_3$]$^{2+}$ ions were dispersed in the mesopore to suppress the self-quenching.

Introduction

After the discovery of mesoporous silicas prepared by the cooperative organization of surfactant and inorganic species,[1] the synthesis, characterization, and applications of the supramolecular-templated mesostructured materials have been extensively investigated.[2] The possible applications of this class of materials includes adsorbents, catalysis and their supports, and future optoelectronics materials. To functionalize mesoporous silicas, the surface modification of mesoporous silicas, such as the immobilization of catalytically active sites and photo- and electro-active species, has been investigated so far.[2–4] The coprecipitation of functionalized silicas, as well as the postsynthetic treatment of mesoporous silicas, has been utilized for this purpose. The states and the distribution of functional units in the mesopore are worth investigating, because they should significantly affect the physicochemical properties of the resulting functionalized silicas. However, the spatial distribution and the dynamic behavior of the guest species have not been well-documented.

This paper reports the adsorption of tris(2,2′-bipyridine)-ruthenium(II) complex cations ([Ru(bpy)$_3$]$^{2+}$) into a mesoporous silica. The excited-state properties of [Ru(bpy)$_3$]$^{2+}$ have been extensively investigated because of their unique combination of chemical stability, capability of photosensitizing redox reactions, and electrochemical and photophysical properties.[5] Photoprocesses of [Ru(bpy)$_3$]$^{2+}$ in various heterogeneous media have been reported[6,7] in order to probe the physicochemical characteristics of the interfaces to which conventional characterization techniques do not have an access. The luminescence characteristics of the [Ru(bpy)$_3$]$^{2+}$ adsorbed in the mesoporous silica are worth investigating to understand the nature of the mesopore as well as the states of the catalytically active sites on the mesopore. In the present study, we found that [Ru(bpy)$_3$]$^{2+}$ was adsorbed on the mesopore and that the states changed reversibly upon hydration/dehydration. The reversible change in the states of the guest species should be considered for the functions and the applications of the host–guest systems derived from mesoporous silicas.

Experimental Section

A mesoporous silica was prepared from a layered silicate, kanemite (NaHSi$_2$O$_5$·nH$_2$O), and octadecyltrimethylammonium chloride according to the method described previously and hereafter designated as C18-FSM.[8] The formation of the C18-FSM was confirmed by the X-ray diffraction pattern,[9] the transmission electron micrographs,[10] and the nitrogen adsorption/desorption isotherms.[11] The C18-FSM possesses a BET surface area of ca. 1100 m^2·g^{-1} with the average pore diameter of 3.6 nm, as determined from the nitrogen adsorption/desorption isotherms by the Horvath–Kawazoe method.[12] A regular hexagonal arrangement of the mesopore was observed by both TEM and XRD, as reported previously.[8]

Because the pore size is large enough to accommodate the [Ru(bpy)$_3$]$^{2+}$ ion, the adsorption of the [Ru(bpy)$_3$]$^{2+}$ into the C18-FMS was conducted by the reaction between the C18-FSM with a dimethylformamide (DMF) solution of [Ru(bpy)$_3$]$^{2+}$ dichloride hexahydrate at room temperature for 18 h. The resulting solids were collected by centrifugation, washed with DMF and acetone, and dried at 100 °C for 1 day. The amounts of the adsorbed [Ru(bpy)$_3$]$^{2+}$ were determined by the change in the concentration of [Ru(bpy)$_3$]$^{2+}$ in solution before and after the reaction with the the C18-FSM.[13]

Results and Discussion

By the reaction of the C18-FSM with a DMF solution of [Ru(bpy)$_3$]$^{2+}$ chloride, orange solids were obtained. The color
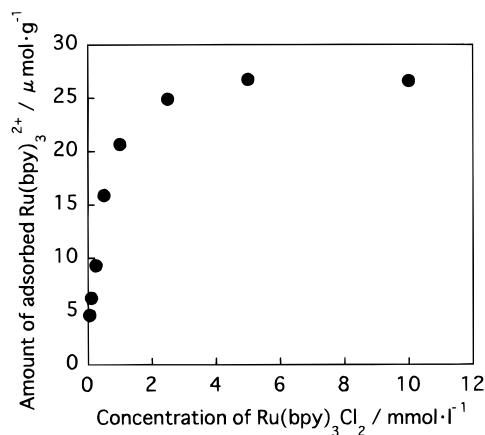
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Tris(2,2′-bipyridine)ruthenium(II) Cations

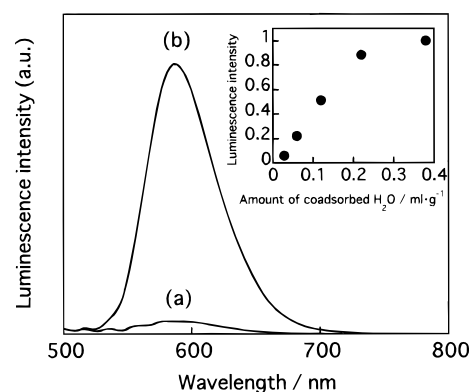*J. Phys. Chem. B, Vol. 104, No. 35, 2000* **8555**

Figure 1. Amounts of the adsorbed $[Ru(bpy)_3]^{2+}$ as a function of the concentration of $[Ru(bpy)_3]^{2+}$ in DMF.
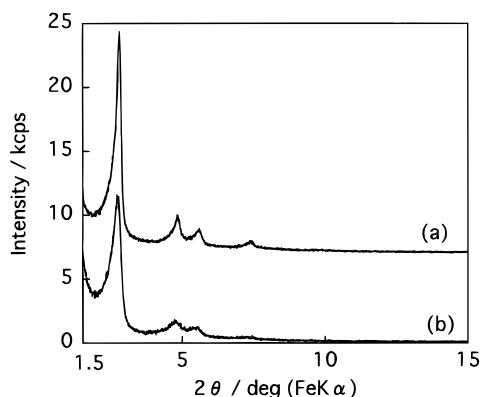
Figure 2. X-ray powder-diffraction patterns of C18-FSM (a) before and (b) after the adsorption of $[Ru(bpy)_3]^{2+}$.

Figure 3. Luminescence spectra of the $[Ru(bpy)_3]^{2+}$-adsorbed C18-FSM (the $[Ru(bpy)_3]^{2+}$ loading of 36 $\mu mol \cdot g^{-1}$) (a) dehydrated and (b) hydrated.

was preserved even after the washing with acetone and DMF, although a certain amount of $[Ru(bpy)_3]^{2+}$ was desorbed. Because no Cl^- was detected in the washed products,[14] $[Ru(bpy)_3]^{2+}$ ions were thought to be adsorbed by a cation-exchange reaction with protons of silanol groups located on the mesopore surfaces. Figure 1 shows the amounts of the adsorbed $[Ru(bpy)_3]^{2+}$ as a function of the probe concentration. With the increase in the concentration, the adsorbed $[Ru(bpy)_3]^{2+}$ amount increased. Repeated reactions utilizing a fresh $[Ru(bpy)_3]^{2+}$ DMF solution of the same concentration led to further adsorption of $[Ru(bpy)_3]^{2+}$. The maximum amount of adsorbed $[Ru(bpy)_3]^{2+}$ was 36 $\mu mol \cdot g^{-1}$.

The X-ray diffraction patterns of the products were almost the same as that of the as-synthesized C18-FSM, showing that the mesostructure did not change during the adsorption of $[Ru(bpy)_3]^{2+}$. The X-ray diffraction pattern of the $[Ru(bpy)_3]^{2+}-$C18-FSM with an adsorbed $[Ru(bpy)_3]^{2+}$ amount of 36 $\mu mol \cdot g^{-1}$ is shown in Figure 2b, along with that of the as-synthesized C18-FSM (Figure 2a) as typical examples. It is worth noting as a merit of the mesoporous silicas that such bulky species as $[Ru(bpy)_3]^{2+}$ can be incorporated into the pore by such a simple adsorption method. The pore volume decreased from 0.82 to 0.65 $mL \cdot g^{-1}$, as revealed by the nitrogen-adsorption isotherms, confirming that the $[Ru(bpy)_3]^{2+}$ adsorbed in the mesopore to reduce the pore volume accessible for nitrogen. Assuming that the $[Ru(bpy)_3]^{2+}$ ions are spherical ions with a diameter of 1.2 nm, we estimated the volume occupied by the adsorbed $[Ru(bpy)_3]^{2+}$ to be 0.02 $mL \cdot g^{-1}$. The observed decrease in the pore volume (0.17 $mL \cdot g^{-1}$) is much larger than that estimated from the adsorbed $[Ru(bpy)_3]^{2+}$. It was thought that the adsorbed $[Ru-$

$(bpy)_3]^{2+}$ aggregate in the cylindrical mesopore suppressed the adsorption of nitrogen into the mesopore.

If one assumes that the $[Ru(bpy)_3]^{2+}$ is arranged in a cylindrical one-dimensional mesopore homogeneously, the mean separation between adjacent $[Ru(bpy)_3]^{2+}$ ions at the $[Ru(bpy)_3]^{2+}$ loading level of 36 $\mu mol \cdot g^{-1}$ is estimated to be ca. 5 nm from the BET surface area (1100 $m^2 \cdot g^{-1}$) of the as-synthesized mesoporous silica. Thus, $[Ru(bpy)_3]^{2+}$ can be adsorbed and distributed molecularly in the mesopore at such a concentration level. It has been reported that there are differentl acidic silanol groups within the mesoporous silica MCM-41, as evidenced by IR spectra as well as by dye-probe experiments.[15,16] The concentration of the silanol groups on the mesopore surface would vary, depending on the synthetic conditions, such as the calcination temperature for surfactant removal. A more quantitative discussion on the amounts of the cationic probes is now underway using mesoporous silicas prepared under different synthetic conditions and surface modifications, as well as other cationic dyes.

In the luminescence spectra of the products,[17] very weak luminescence due to the MLCT transition of the $[Ru(bpy)_3]^{2+}$ was detected, irrespective of the loading amounts. When the samples were stored in a highly humid environment, the luminescence bands were intensified dramatically. The luminescence spectra of the $[Ru(bpy)_3]^{2+}-$C18-FSM with an adsorbed amount of 36 $\mu mol \cdot g^{-1}$ before and after the hydration are shown in Figure 3. The luminescence was weakened when the hydrated samples were dehydrated. The change in the luminescence intensity occurred repeatedly, suggesting that the coadsorbed water molecules alter the state of the adsorbed $[Ru(bpy)_3]^{2+}$.

Judging from these observations, the adsorbed $[Ru(bpy)_3]^{2+}$ aggregated in the mesopore seemed to cause self-quenching when the samples were dehydrated. Upon adsorption of water molecules, the aggregation of $[Ru(bpy)_3]^{2+}$ altered and the $[Ru(bpy)_3]^{2+}$ ions were dispersed to some extent in the mesopore. Consequently, the self-quenching of the adsorbed $[Ru(bpy)_3]^{2+}$ was suppressed to give relatively intense MLCT luminescence, as seen in Figure 3b. The MLCT luminescence intensity increased with the increase in the amount of the adsorbed water molecules, as shown in the Figure 3 inset. It was thought that the interactions between the $[Ru(bpy)_3]^{2+}$ and the surface of the mesopore were weak. Therefore, the state of the adsorbed $[Ru(bpy)_3]^{2+}$ can be varied by the coadsorbing species (water molecules in the present experiment).

For the hydrated products, the MLCT luminescence maxima of the adsorbed $[Ru(bpy)_3]^{2+}$ were observed around 585 nm,
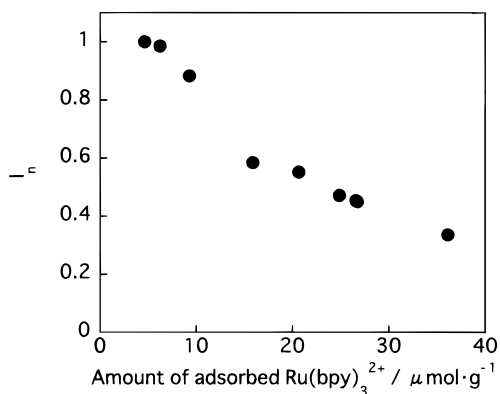
Figure 4. Relationship between the relative luminescence intensity and the $[Ru(bpy)_3]^{2+}$ loading. The relative luminescence intensity was normalized by the $[Ru(bpy)_3]^{2+}$ loading in the samples as expressed in the text.

irrespective of the loading amounts. The luminescence maxima are blue-shifted from that observed for a dilute aqueous solution of $[Ru(bpy)_3]^{2+}$, reflecting possible interactions between the $[Ru(bpy)_3]^{2+}$ and the surface of the mesopore. This observation is consistent with those observed for the $[Ru(bpy)_3]^{2+}$ adsorbed on relevant silicas, such as colloidal silica[18] and sol−gel-derived silica gels.[19]

The relationship between the luminescence intensity and the adsorbed amount of $[Ru(bpy)_3]^{2+}$ is shown in Figure 4. The intensity was normalized by the amount of $[Ru(bpy)_3]^{2+}$ as the equation of $I_n = I_m/m$; where I_n, I_m, and m denote normalized luminescence intensity, observed luminescence intensity, and the adsorbed amount of $[Ru(bpy)_3]^{2+}$, respectively. The deviation from $I_n = 1$ seen in Figure 4 indicates that the possibility of the self-quenching increased at higher $[Ru(bpy)_3]^{2+}$ loading, even at the fully hydrated states. As discussed above, the average distance can be derived from the BET surface area and the adsorbed $[Ru(bpy)_3]^{2+}$ amount. The value was ca. 5 nm, even at the highest loading level (36 $\mu mol \cdot g^{-1}$). The observed variation in the luminescence intensity suggests that the self-quenching occurred to some extent even at very low loading level and in the hydrated states. Because the amounts of the $[Ru(bpy)_3]^{2+}$ are low, self-quenching is less plausible when the adsorbed $[Ru(bpy)_3]^{2+}$ cations distribute homogeneously. It was supposed that the $[Ru(bpy)_3]^{2+}$ cations distribute inhomogeneously in the mesopore and that the variation of the loading level affects the relative contribution of the aggregated (nonluminescent) and isolated (luminescent) species, along with the average distance of the $[Ru(bpy)_3]^{2+}$.

The organization of transition-metal polypyridine complex cations in mesoporous silicas has been reported previously for such applications as catalysts[20,21] and electrodes.[22] Because the states of the adsorbed complexes significantly affect the properties of the resulting host−guest systems, the present observation on the reversible rearrangement of the adsorbed $[Ru(bpy)_3]^{2+}$ brings a new insight on the materials design. Studies

of the states of the guest species on the mesoporous silicas having different surface properties are worth investigating in order to clarify the nature of the mesoporous silicas as the host matrixes. Host−guest systems based on the mesoporous silicas with controlled morphology, which includes films,[23] fibers,[24] aero gels,[25] and hollow and hard sphere,[26] may lead to inorganic−organic hybrid devices with optoelectronic and sensing functions.

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