Relaxation of Photoexcited Tris(2,2′-bipyridine)ruthenium Complex ($[Ru(bpy)_3]^{2+}$) in Mesopores

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Received December 28, 2010
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The excited state relaxation of tris(2,2′-bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) in aluminum containing mesoporous silica was investigated as a function of loading amount and temperature. The concentration dependence of $[Ru(bpy)_3]^{2+}$ on the luminescence intensity suggests that the self-quenching of $[Ru(bpy)_3]^{2+}$ is a dynamic process in the temperature range of 20 to 120 °C.

Mesoporous silica (MPS) is a promising material to host a variety of guest species, due to their well-shaped nanospaces in the size range of 2 to several tens of nm. Taking advantage of the characteristic features of MPSs, dyes or nanoparticles have been incorporated into the mesopores to prepare photofunctional hybrid materials.[1] For constructing host–guest hybrid materials with such functions as catalytic, optical, and electronic, the spatial distribution and mobility of functional units in solid matrices are key issues.[1–3]

We have been interested in the states of tris(2,2′-bipyridine)-ruthenium complex ($[Ru(bpy)_3]^{2+}$)[4] in the mesopores because the excited state properties of the complex change reflecting the environment.[5–8] In this study, luminescence of $[Ru(bpy)_3]^{2+}$ in aluminum containing mesoporous silica (Al-MPS) was investigated in the temperature range of −196 to 120 °C to investigate the relaxation processes. The states of the immobilized functional units in mesopores are not well understood due to the lack of information. Therefore, the intermolecular reaction between the adsorbed species in the mesopores is worth investigating. Since the relaxation of the excited state is significantly affected by the temperature, the luminescence of the adsorbed species as a function of temperature is an interesting topic. However, as far as we know, there are only reports on the states of the adsorbed dyes at different temperature.[9,10] Accordingly the relaxation of $[Ru(bpy)_3]^{2+}$ on MPS is investigated.

Al-MPS was hydrothermally synthesized by a method described by Mokaya[11] from fumed silica, aluminum tri(*iso*-propoxide) (ATIP), dodecyltrimethylammonium bromide (C_{12}TAB), trimethylammonium hydroxide (TMAOH), and water at the molar ratio of 1:0.02:0.25:0.2:40 (SiO_2:ATIP:C_{12}TAB:TMAOH:H_2O). Deionized water, TMAOH, and C_{12}TAB were mixed with magnetic stirring at 35 °C. Fumed silica and ATIP were added to the mixtures at 1 h, and then further stirred for 1 h at the same temperature. The mixtures were aged for 20 h, after that they were allowed to react at 150 °C for 48 h. After washing with deionized water until bromide free and drying under reduced pressure, the samples were calcined in air at 550 °C for 8 h. The adsorption of $[Ru(bpy)_3]^{2+}$ into Al-MPS was conducted by the reaction between Al-MPS with ethanol solutions of $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (2.5 μ L^{-1}–0.5 mmol L^{-1}) at room temperature for 1 day, subsequently washed with ethanol and dried under reduced pressure. The pores of the samples were thought to be filled with water at 20 °C, judging from the TG-DTA curves. Luminescence spectra of the powder samples in the temperature range of −196 to 120 °C were recorded on a Hitachi F-4500 fluorescence spectrometer equipped with a cryostat DN-1704 (Oxford Instruments Co., Ltd.). The air inside the cryostat chamber was displaced by nitrogen before cooling measurement.

Al-MPS with the pore size of 2.2 nm and the cation-exchange capacity of 0.18 mmol g^{-1}, which was generated by the Al introduction, was used (Table 1). $[Ru(bpy)_3]^{2+}$ was adsorbed on Al-MPS from ethanol solutions to give orange-colored powders. The adsorbed $[Ru(bpy)_3]^{2+}$ amounts used in the present study were 2.9, 76, and 130 mmol L^{-1} (Table 2). All the emission spectra of the samples excited at 450 nm showed a photoluminescence at around 600 nm ascribable to the phosphorescence of $[Ru(bpy)_3]^{2+}$ (Figure 1). The luminescence maxima were shifted toward longer wavelength (585–600 nm) with the increase of the loading amount of $[Ru(bpy)_3]^{2+}$.[12,13] This indicates that the intermolecular interactions between the adjacent complex became dominant with the increase in loading. In order to compare the luminescence efficiency with the loading amount, the integrated area of emission was normalized by the amount of the complex (the integrated area of emission in the range of 520–750 nm was divided by the adsorbed amount of $[Ru(bpy)_3]^{2+}$).

By the displacement of the air in the sample chamber with nitrogen, the luminescence of $[Ru(bpy)_3]^{2+}$ adsorbed on Al-MPS intensified, indicating that oxygen quenches the excited state of $[Ru(bpy)_3]^{2+}$ (Figure 1 and Table 3).

Table 1. Characteristics of Al-MPS

	BET surface area /m^2 g^{-1}	BJH pore size /nm	Pore volume[a] /mL g^{-1}	Amount of Brønsted acidic site[b] /mmol g^{-1}
Al-MPS	780	2.2	0.43	0.18

a) Calculated from BET surface area and BJH pore size (=BET surface area × BJH pore size/4). b) Determined by ammonia temperature programmed desorption measurement.

Table 2. Characteristics of $[Ru(bpy)_3]^{2+}$ Adsorbed Al-MPSs

	Amount of adsorbed $[Ru(bpy)_3]^{2+}$		Average distance between adjacent $[Ru(bpy)_3]^{2+}$[b] /nm
	/μmol g^{-1}	/mmol L^{-1} [a]	
Al-MPS	1.3	2.9	150
	33	76	5.7
	57	130	3.3

a) Calculated from adsorbed amount of $[Ru(bpy)_3]^{2+}$ and pore volume listed on Table 1. b) Calculated from adsorbed amount of $[Ru(bpy)_3]^{2+}$, BET surface area, and BJH pore size (=BET surface area/(BJH pore size × π × amount of adsorbed $[Ru(bpy)_3]^{2+}$(mol g^{-1}) × N_A), N_A is Avogadro's constant).

Published on the web May 21, 2011; doi:10.1246/bcsj.20100364

The luminescence spectra of $[Ru(bpy)_3]^{2+}$ adsorbed Al-MPS in the temperature range of −196 to 120 °C under nitrogen are shown in Figure 2 (data obtained during heating are shown); where the data were obtained for the samples with the concentrations of $[Ru(bpy)_3]^{2+}$ of 2.9, 76, and 130 mmol L^{-1}. The spectra did not change between cooling and heating processes, meaning that the states of adsorbed $[Ru(bpy)_3]^{2+}$ depend on the temperature. All the emission spectra of the samples in the examined temperature range showed emission at around 600 nm ascribable to the phosphorescence of $[Ru(bpy)_3]^{2+}$. The luminescence maxima shifted toward shorter wavelength (from 610 to 565 nm) at lower temperature. In the spectra of $[Ru(bpy)_3]^{2+}$(2.9 mmol L^{-1}) adsorbed Al-MPS, an emission band around 620 nm appeared below −50 °C (Figures 2A and 3A). Similar phenomena have been reported for the spectra of $[Ru(bpy)_3]^{2+}$ in glycerol solution;[14] the shift of the emission maxima and the appearance of the band at 620 nm, which is attributed to low lying ^{3}MLCT transition, at lower temperature are caused by the inhibition of the solvent (water) rearrangement around the excited complex possibly because the phase transition of the coadsorbed water in the mesopore. The freezing point depression of water in the mesoporous silica (MCM-41) with the pore diameter of 2.2 nm (ca. 50 °C) was reported, though the surface acidity is not considered.[15] On the other hand, the spectra of the $[Ru(bpy)_3]^{2+}$ adsorbed Al-MPS with high loading (76 and 130 mmol L^{-1}) did not show the emission at around 620 nm in the examined temperature range, while the intensity showed the maximum value at ca. −50 °C (Figures 2B and 2C and Figures 3B and 3C). A possible reason is the aggregation of $[Ru(bpy)_3]^{2+}$

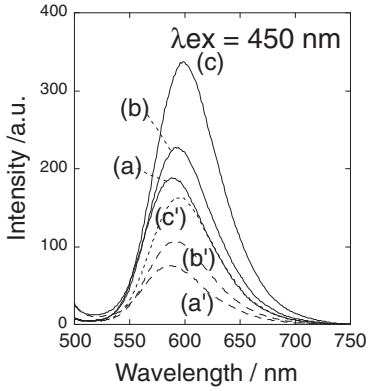

Figure 1. Luminescence spectra of $[Ru(bpy)_3]^{2+}$ adsorbed on Al-MPS before (dotted line) and after (solid line) the displacement of the air with nitrogen; the concentration of $[Ru(bpy)_3]^{2+}$ are 2.9 (a), (a′); 76 (b), (b′); and 130 mmol L^{-1} (c), (c′).

Table 3. Relative Emission Intensity of $[Ru(bpy)_3]^{2+}$ Adsorbed Al-MPSs at Low Loading Level (2.9 mmol L^{-1}) as a Function of Temperature

Atmosphere	Temperature/°C	Relative emission intensity[a)]
Air	20	1.0
Nitrogen	20	2.4
Nitrogen	70	1.0
Nitrogen	100	0.67
Nitrogen	120	0.51

a) Calculated from the integrated area of emission in the range of 520–750 nm divided by the value at 20 °C under air.

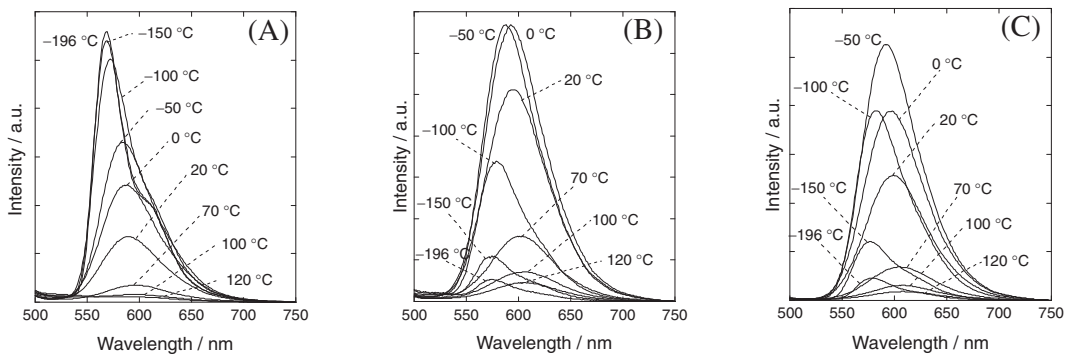

Figure 2. Luminescence spectra of $[Ru(bpy)_3]^{2+}$ adsorbed on Al-MPS during heating (−196 to 120 °C); 2.9 (A), 76 (B), and 130 mmol L^{-1} (C). The excitation wavelength is 450 nm.

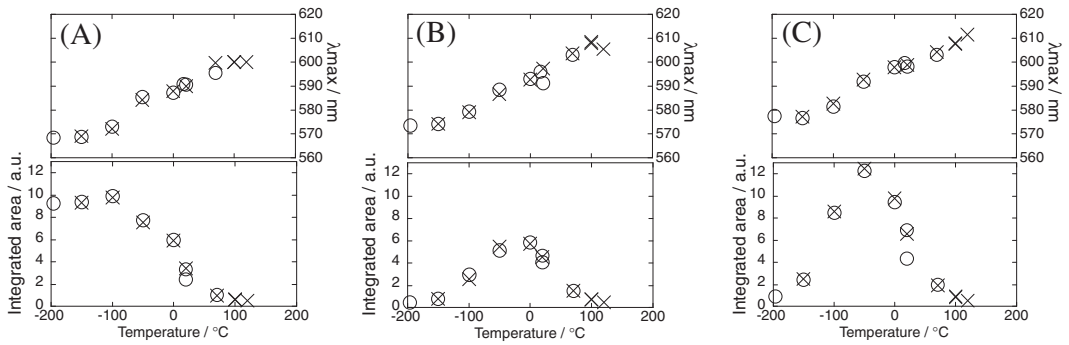

Figure 3. Integrated area of emission (the integrated area of emission in the range of 520–750 nm was divided by the adsorbed amount of $[Ru(bpy)_3]^{2+}$) and the luminescence maxima of $[Ru(bpy)_3]^{2+}$ adsorbed on Al-MPS as a function of temperature: 2.9 (A), 76 (B), and 130 mmol L^{-1} (C): cooling process (circle) and heating process (cross).

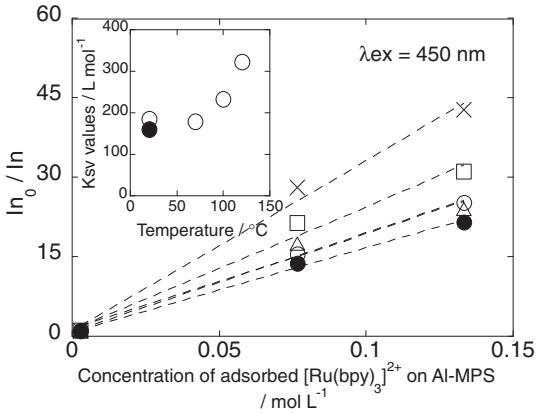

Figure 4. Quasi Stern–Volmer (SV) plots of $[Ru(bpy)_3]^{2+}$ adsorbed on Al-MPS in the temperature range of 20 to 120 °C; 20 °C under air (filled circle) and 20 (open circle), 70 (triangle), 100 (square), and 120 °C under nitrogen (cross). The inset shows the relationship between the temperature and K_{sv} values: under air (filled circle) and under nitrogen (open circle).

during the freezing or melting of water; the intermolecular interactions between the complexes are dominant at lower temperature, causing the relaxation of the excited-state $[Ru(bpy)_3]^{2+}$. When the adsorbed amount of $[Ru(bpy)_3]^{2+}$ is high (76 or 130 mmol L^{-1}), the freezing and melting behavior of the coadsorbed water will be more complex. In addition, the luminescence intensity of $[Ru(bpy)_3]^{2+}$ (2.9 mmol L^{-1}) adsorbed Al-MPS pretreated by heating at 80 °C for 3 h under reduced pressure also shows the maximum value at ca. −50 °C (Supporting Information (SI) 1 and 2). This supports the above idea. Further investigation such as ^{1}H NMR or neutron scattering as a function of temperature or the introduction of other molecules (such as ionic solution) into pore is useful to access this.[16]

Concentration quenching of adsorbed $[Ru(bpy)_3]^{2+}$ in Al-MPS at 20 °C under air and in the temperature range of 20 to 120 °C under nitrogen was examined (Figure 4 and Table 3). Both under air and under nitrogen at 20 °C, quasi SV plots show linear regressions. The displacement of air in the sample chamber with nitrogen provides the increased gradient of the regression line, K_{sv} value. This indicates that the distance between adjacent $[Ru(bpy)_3]^{2+}$ in the mesopore was controlled even under nitrogen atmosphere and the inhibition of oxygen quenching leads longer luminescence lifetime of $[Ru(bpy)_3]^{2+}$, causing the increase of the self-quenching efficiency (K_{sv} value). In the temperature range of 20 to 120 °C under nitrogen, the quasi SV plots also show linear relationships. The gradient of SV plot (K_{sv} value) increases at higher temperature, indicating that dynamic quenching (diffusion-controlled reaction) is dominant in this temperature range. On the other hand, below 0 °C, the SV plots do not show linear relation, showing upward convex plots (SI3). Possible reasons for this phenomenon could be the following. In the temperature range of −50 to 20 °C, the mobility of $[Ru(bpy)_3]^{2+}$ is restricted to the extent that dynamic quenching is inhibited, and the distance between adjacent $[Ru(bpy)_3]^{2+}$ is not sufficiently short to cause static quenching, showing upward convex plots even at high loading (130 mmol L^{-1}; the average distance between adjacent $[Ru(bpy)_3]^{2+}$ is ca. 3.3 nm, listed on Table 2).

For MPS which can host a large amount of $[Ru(bpy)_3]^{2+}$ (>130 mmol L^{-1}), the distance between adjacent $[Ru(bpy)_3]^{2+}$ is shorter (<3 nm), it is expected that the static quenching is dominant at lower temperature, showing downward convex SV plots. For MPS that shows stronger interaction with $[Ru(bpy)_3]^{2+}$ (for example, SPh-MPS[8]), it is expected that $[Ru(bpy)_3]^{2+}$ is less mobile, causing the self-quenching efficiency (K_{sv} value) to increase moderately at higher temperature. For MPS with bigger pore size (>2.2 nm), where the diffusion of $[Ru(bpy)_3]^{2+}$ is easier, it is expected that the self-quenching efficiency (K_{sv} value) increases more strongly at higher temperature. The effect of the loading amount of $[Ru(bpy)_3]^{2+}$, the host–guest interactions and the nanopore size on the quenching rates and process as a function of temperature is worth further investigation.

The photoluminescence of $[Ru(bpy)_3]^{2+}$ on Al-MPS (BJH pore size is 2.2 nm) was examined in the temperature range of −196 to 120 °C. The quasi SV plots in the temperature range of 20 to 120 °C showed a linear relationship and the quenching efficiencies (K_{sv} value) increase at higher temperature, suggesting that the self-quenching is a dynamic process.

This work was partially supported by a Grant-in-Aid for G-COE research, Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. Waseda University also supported us financially as a special research project (No. 2009B-370).

Supporting Information

Luminescence spectra of $[Ru(bpy)_3]^{2+}$ adsorbed on Al-MPS after dehydration in the temperature range of −196 to 120 °C, integrated area of emission and the luminescence maxima of $[Ru(bpy)_3]^{2+}$ adsorbed on Al-MPS after dehydration as a function of temperature, quasi Stern–Volmer plots of $[Ru(bpy)_3]^{2+}$ adsorbed on Al-MPS under nitrogen in the temperature range of −50 to 20 °C. These materials are available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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