Surface modification of Mesoporous Silica to Control the States of Tris(2,2′-bipyridine)ruthenium(II) Cations

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The adsorption and immobilization of tris(2,2′-bipyridine)-ruthenium(II) ($[Ru(bpy)_3]^{2+}$) in mesoporous silicas (C18-FSM) modified by the introduction of aluminum as well as sulfonic acid groups were investigated. The complex was immobilized by the cooperative effects of electrostatic interactions between $[Ru(bpy)_3]^{2+}$ cation and sulfonic acid group and the interactions with the phenyl rings of the mesopore surface and the bipyridine rings.

The immobilization of guest species into porous inorganic solids has extensively been investigated to construct functional inorganic-organic supramolecular materials. Mesoporous silicas prepared by supramolecular templating methods possess various attractive features such as well-defined and controllable pore sizes, large surface area, and reactive surfaces for the guest organization.[1] Although the spatial distribution of photo- and electro-functional units as well as their mobility are the factors to control the properties of the resulting hybrid materials, they are yet to be investigated.

Recently, we have utilized a luminescence probe, tris(2,2′-bipyridine)ruthenium(II) complex cation (abbreviated as $[Ru(bpy)_3]^{2+}$),[2] for the study on a mesoporous silica.[3] The luminescence intensity of $[Ru(bpy)_3]^{2+}$ adsorbed onto mesoporous silica changed dramatically and reversibly upon hydration/dehydration, indicating that the adsorbed $[Ru(bpy)_3]^{2+}$ cations aggregate to cause self-quenching in the dehydrated state while those are dispersed molecularly in the hydrated state. Here we report the effects of surface engineering of mesoporous silicas by the introduction of aluminum as well as sulfonic acid groups on the states of adsorbed $[Ru(bpy)_3]^{2+}$. The incorporation of Al[4] and sulfonic acid group[5–8] into mesoporous silicas generates active sites for adsorption, ion exchange and catalytic reactions. We have found that these surface modifications significantly and differently affect the states of $[Ru(bpy)_3]^{2+}$.

Mesoporous silica was prepared from a layered silicate, kanemite according to the method described previously and hereafter designated as C18-FSM.[9] Surface modification of C18-FSM was conducted by the two procedures reported for silica gels.[10] C18-FSM was modified by the reaction with 3-mercaptopropyl(dimethoxy)methylsilane followed by the oxidation of the thiol groups with aqueous H_2O_2 to sulfonic acid.(The product was designated as C18-FSM-C3S.) Another modification was carried out by the reaction of C18-FSM with 2-phenylethyl(dichloro)methylsilane and subsequent sulfonation with chlorosulfonic acid.(C18-FSM-PhS) Aluminum containing mesoporous silica (Al/Si = 0.054) was synthesized by the method described previously[11] and designated as Al-C18-FSM. The isomorphous substitution of Si with Al resulted in the generation of acidic site. The BJH pore size was determined as summarized in Table 1. Though the pore sizes of the modified materials were slightly smaller than the unmodified one, they were still large enough to accommodate $[Ru(bpy)_3]^{2+}$.

Table 1. BJH pore size and maximum amount of adsorbed $[Ru(bpy)_3]^{2+}$

	BJH pore size /nm	Maximum amount of adsorbed $[Ru(bpy)_3]^{2+}$ [a]
C18-FSM	3.3	0.036
Al-C18-FSM	3.1	0.090
C18-FSM-C3S	2.9	0.25
C18-FSM-PhS	2.8	0.61

a: mmol/g of SiO_2.

The adsorption of $[Ru(bpy)_3]^{2+}$ into the mesoporous silicas was conducted from dimethylformamide (DMF) solution as described previously.[3] The surface modification led the substantial increase in the amount of adsorbed $[Ru(bpy)_3]^{2+}$. The amounts of the adsorbed $[Ru(bpy)_3]^{2+}$ are close to the cation exchange capacities determined by titration with NaOH, indicating that $[Ru(bpy)_3]^{2+}$ adsorbed by electrostatic interactions with negatively charged sites formed by the surface modifications.

In the photoluminescence spectra of the dehydrated products (the adsorbed $[Ru(bpy)_3]^{2+}$ amount was set at a constant value of 0.05 mmol/g) (Figure 1), very weak luminescence due to the MLCT transition of $[Ru(bpy)_3]^{2+}$ was detected for the Al-C18-FSM and C18-FSM-C3S, while intense luminescence was observed for the C18-FSM-PhS. The luminescence bands were intensified dramatically when Al-C18-FSM and C18-FSM-C3S were hydrated and the luminescence intensity became almost the same as reported for C18-FSM.[2] These observations indicate that the self-quenching caused by the aggregation of the adsorbed $[Ru(bpy)_3]^{2+}$ occurred in dehydrated Al-C18-FSM and C18-FSM-C3S.

On the other hand, $[Ru(bpy)_3]^{2+}$ ions were dispersed effectively in the mesopore of C18-FSM-PhS even in the dehydrated state. The interactions between $[Ru(bpy)_3]^{2+}$ and the mesopore surface of C18-FSM-PhS are so strong that $[Ru(bpy)_3]^{2+}$ is fixed even in the dehydrated state and the redistribution of adsorbed $[Ru(bpy)_3]^{2+}$ is less plausible. Considering the difference between C18-FSM-C3S and C18-FSM-PhS systems, the difference between alkyl and phenyl groups must be concerned with the states of $[Ru(bpy)_3]^{2+}$. The

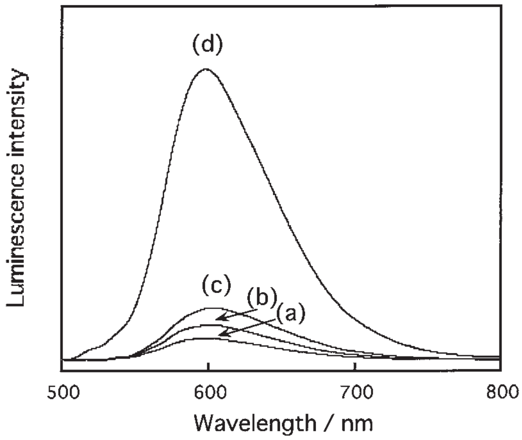

Figure 1. Luminescence spectra of the $[Ru(bpy)_3]^{2+}$ adsorbed on mesoporous silicas; (a) C18-FSM, (b) C18-Al-FSM, (c) C18-FSM-C3S and (d) C18-FSM-PhS. The adsorbed $[Ru(bpy)_3]^{2+}$ amount was adjusted to 0.05 mmol/g.

interactions of $[Ru(bpy)_3]^{2+}$ with the phenyl rings of hosts have been reported for $[Ru(bpy)_3]^{2+}$-zirconium phosphate sulfophenyl-phosphonate intercalation compounds.[12] Note that cooperative effects of electrostatic interactions and the attractions between phenyl group and bipyridine rings of the complex are so effective to control the states of the adsorbed species.

In summary, the sulfonic groups attached to the phenyl groups covalently bound to the mesopore surface are effective to immobilize $[Ru(bpy)_3]^{2+}$ probably through cooperative effects of electrostatic and aromatic interactions.

References

1 A. Stein, B. J. Melde, and R. C. Schroden, *Adv. Mater.*, **12**, 1403 (2000).
2 K. Kalyanasundaram, "Photochemistry of Polypyridine and Porphyrin Complexes," Academic Press, London (1992).
3 a) M. Ogawa, T. Nakamura, J. Mori, and K. Kuroda, *J. Phys. Chem. B.* **104**, 8554 (2000). b) M. Ogawa, K. Kuroda, and T. Nakamura, *Microporous Mesoporous Mater.*, **48**, 159 (2001).
4 A. Tuel, *Microporous Mesoporous Mater.*, **27**, 151 (1999).
5 M. H. Lim, C. F. Blanford, and A. Stein, *Chem. Mater.*, **10**, 467 (1998).
6 D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka, and G. D. Stucky, *Chem. Mater.*, **12**, 2448 (2000).
7 I. Diaz, C. Marquez-Alvarez, F. Mohino, J. Perez-Pariente, and E. Sastre, *J. Catal.*, **193**, 283 (2000).
8 W. D. Bossaert, D. E. De Vos, W. M. Van Rhijn, J. Bullen, P. J. Grobet, and P. A. Jacobs, *J. Catal.*, **182**, 156 (1999).
9 S. Inagaki, A. Kawai, N. Suzuki, Y. Fukushima, and K. Kuroda, *Bull. Chem. Soc. Jpn.*, **69**, 1449 (1996).
10 R. D. Bradley and W. T. Ford, *J. Org. Chem.* **54**, 5437 (1989).
11 S. Inagaki, Y. Yamada, and Y. Fukushima, *Stud. Surf. Sci. Catal.*, **105**, 109 (1997).
12 J. L. Colón, C. Y. Yang, A. Clearfield, and C. R. Martin, *J. Phys. Chem.*, **92**, 5777 (1998).