

## Metal Ion Sensing by Luminescence from an Ion-exchange Adduct of Clay and Cationic Cyclometalated Iridium(III) Complex

Hisako Sato,<sup>1,2</sup> Kenji Tamura,<sup>3</sup> Masahiro Taniguchi,<sup>4</sup> and Akihiko Yamagishi\*<sup>5</sup>

<sup>1</sup>Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033

<sup>2</sup>PRESTO, Japan Science and Technology Agency, Tokyo

<sup>3</sup>National Institute for Materials Science, Tsukuba 305-0044

<sup>4</sup>Kanazawa Institute University, Kanazawa

<sup>5</sup>Ochanomizu University, Tokyo 112-8610

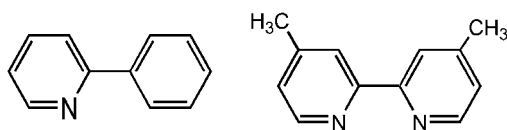
(Received September 18, 2008; CL-080899; E-mail: yamagishi.akihiko@ocha.ac.jp)

A cationic iridium(III) complex,  $[\text{Ir}(\text{ppy})_2\text{dmbpy}]^+$  (ppy = 2-phenylpyridine and dmbpy = 4,4'-dimethylbipyridine), was adsorbed by colloiddally dispersed montmorillonite clay. The emission quantum yield ( $\Phi$ ) decreased from 0.06 to 0.01 on adsorption, while  $\Phi$  recovered to ca. 0.12 by adding alkali or alkaline earth metal ions to the concentration of ca.  $2 \times 10^{-2}$  or  $2 \times 10^{-5}$  M, respectively.

Clay is an environmental-friendly ubiquitous material. We have studied clay-metal complex interactions with a focus on chiral recognition.<sup>1</sup> So far ion-exchange adducts have proven to be an efficient adsorbent to achieve optical resolution, chiral sensing, and stereoselective energy transfer.<sup>1-3</sup> In these attempts, various properties relevant to metal complexes are utilized to follow the adsorption processes. Among them, emission spectra often provide a key to monitoring the delicate change of adsorption structures. In most previous works, polypyridyl  $\text{Ru}^{\text{II}}$  complexes have been applied as an emitting species such as  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy = 2,2'-bipyridine) and  $[\text{Ru}(\text{phen})_3]^{2+}$  (phen = 1.10-phenanthroline).<sup>4,5</sup>

Recently cyclometalated iridium(III) complexes have demonstrated highly luminescent properties. The lifetime of excited triplet states is sufficiently long (ca. 1  $\mu\text{s}$ ) and the quantum yield attains a value as high as 10–100%.<sup>6-9</sup> The complexes are used for photodiodes and oxygen sensors.<sup>8</sup> There has been reported however, no attempt of applying iridium(III) complexes to clay systems. The highly emitting properties of the complexes would be helpful to reveal the details of their interactions with clay and solvent molecules. The present work reports the role of clay as an adsorbent in the luminescent behavior of a cationic cyclometalated iridium(III) complex.

An iridium(III) complex,  $[\text{Ir}(\text{ppy})_2\text{dmbpy}]\text{PF}_6$  (ppy = 2-phenylpyridine and dmbpy = 4,4'-dimethylbipyridine; Scheme 1), was synthesized according to the reported method.<sup>8,9</sup> The compound was identified by mass spectrum, <sup>1</sup>H NMR and UV spectrum.<sup>10</sup> Sodium montmorillonite (Kunipia-P, Kunimine Ind. Co.;  $(\text{Na}_{0.49}\text{Mg}_{0.14})(\text{Si}_{7.70}\text{Al}_{0.30})(\text{Al}_{3.12}\text{Mg}_{0.68}\text{Fe}_{0.19})\text{O}_{20}(\text{OH})_4$ ) was used as a clay material. Its cation-exchange capacity



**Scheme 1.** Structures of the ligands used: ppy (left) and dmbpy (right).

**Table 1.** The luminescence quantum yield ( $\Phi$ ) of  $[\text{Ir}(\text{ppy})_2\text{dmbpy}]\text{PF}_6$  in various solvents<sup>a</sup>

Solvent ( $\lambda_{\text{max}}$ /nm)	$\Phi$ (degassed)
$\text{CHCl}_3$ (556 nm)	0.69
THF (559 nm)	0.47
$\text{CH}_3\text{CN}$ (558 nm)	0.35
$\text{CH}_3\text{OH}$ (557 nm)	0.34
$\text{H}_2\text{O}$ (559 nm)	0.056

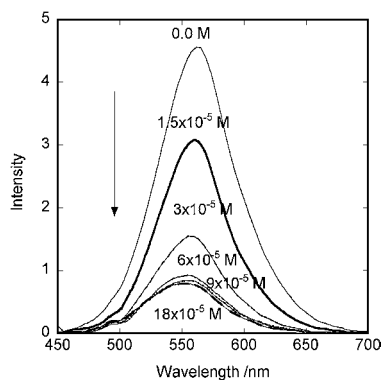
<sup>a</sup>The wavelength of excitation ( $\lambda_{\text{ex}}$ ) was 430 nm. The quantum yield was determined relative to the  $\Phi$  value of  $[\text{Ru}(\text{bpy})_3]^{2+}$  in air-equilibrated water ( $\Phi = 0.028$ ).<sup>5</sup>

(CEC), which represents the maximum amount of ion-exchanged cations, is stated to be 1.15 meq  $\text{g}^{-1}$ . Adsorption was carried out by mixing a solution of the iridium(III) complex with a clay suspension within 10 milliseconds by means of a stopped-flow apparatus (Unisoku Co., Ltd.). This procedure realized the uniform adsorption of the metal complexes over clay particles particularly at low loading.<sup>11</sup>

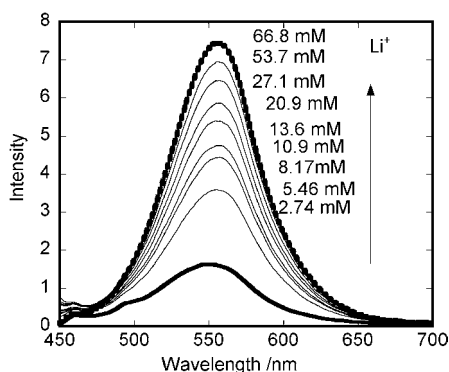
Table 1 shows the results of the luminescence quantum yield ( $\Phi$ ) of  $[\text{Ir}(\text{ppy})_2\text{dmbpy}]\text{PF}_6$  in various solvents under the degassed condition.  $\Phi$  attained a value as high as 0.7–0.5 in aprotic solvents ( $\text{CHCl}_3$  and THF), while it decreased to 0.3–0.06 in protic solvents ( $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$ ). The situation contrasted with polypyridyl  $\text{Ru}^{\text{II}}$  complexes whose quantum yield depends little on the kind of a solvent (e.g.,  $[\text{Ru}(\text{bpy})_3]^{2+}$ :  $\Phi = 0.055$  ( $\text{H}_2\text{O}$ ), 0.062 ( $\text{CH}_3\text{CN}$ )).<sup>6</sup>

Figure 1 shows the luminescence spectrum of an aqueous dispersion containing  $[\text{Ir}(\text{ppy})_2\text{dmbpy}]^+$  and various amounts of clay under degassed conditions.  $\Phi$  decreased from 0.06 to 0.01 with the increase of added clay. The main cause for the decrease of  $\Phi$  might be the quenching of  $\text{Fe}^{\text{III}}$  ions in the octahedral sheet of a clay layer. The introduction of air had little effect on  $\Phi$ .

When LiCl was added under air to an aqueous dispersion of the iridium(III) complex and the sufficient amount of clay,  $\Phi$  was found to increase from 0.01 to ca. 0.12 with the increase of LiCl from 3 to 67 mM (Figure 2). It should be noted that the saturated value of  $\Phi$  exceeded the original value in a degassed aqueous solution ( $\Phi = 0.056$ ). No dissociation of  $[\text{Ir}(\text{ppy})_2\text{dmbpy}]^+$  from clay particles took place at  $[\text{LiCl}] = 80$  mM. This was confirmed by the fact that no metal complex was left in the supernatant solution after centrifuging out clay particles from the sample dispersion. Nearly the same curve was obtained on addition of other alkali metal ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$ ) (Figure 3). The effect of metal ions was more



**Figure 1.** Luminescence spectra of an aqueous dispersion containing  $[\text{Ir}(\text{ppy})_2\text{dmbpy}]^+$  ( $6.5 \times 10^{-6} \text{ M}$ ) and various amounts of clay. The concentration of clay was expressed in terms of CEC ( $\lambda_{\text{ex}} = 430 \text{ nm}$ ). The maximum loading of  $\text{Ir}^{\text{III}}$  complex was 5.4% with respect to the CEC of clay. The small peak around 500 nm was due to the Raman scattering by water.

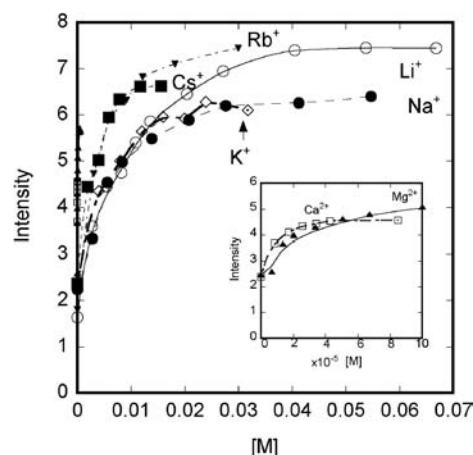


**Figure 2.** Luminescence spectra of an aqueous dispersion containing clay ( $1.5 \times 10^{-4} \text{ M}$ ) and  $[\text{Ir}(\text{ppy})_2\text{dmbpy}]^+$  ( $6.5 \times 10^{-6} \text{ M}$ ) in the presence of various amounts of  $\text{LiCl}$ . The excitation wavelength was 430 nm.

prominent for divalent metal ions. In the case of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , for example, the increase of  $\Phi$  up to 0.10 attained at a concentration as low as  $10^{-5} \text{ M}$  (the inset of Figure 3).

The adsorbed iridium(III) complexes experienced quenching action partly by  $\text{Fe}^{\text{III}}$  ions and partly by water molecules. The effect of metal ions on the recovery of luminescence indicated that bound metal ions diminished the quenching ability of water molecules. It was suggested that the adsorption of metal ions hydrated water molecules on the clay surface. Such hydration might deprive water molecules of quenching ability towards the iridium(III) complexes. If that is the case, the effect is thought to be critically dependent on the charge of the metal ion, because the hydration is stronger for metal ions of higher valence. The fact that alkaline earth metal ions were more effective than alkali metal ions was in accord with this view.

It should be emphasized that the influence of metal ions as observed here appeared at concentrations as low as  $10^{-5} \text{ M}$ .



**Figure 3.** The intensity of luminescence at 560 nm as a function of added metal ions for the aqueous dispersion of clay ( $1.5 \times 10^{-4} \text{ M}$ ) and  $[\text{Ir}(\text{ppy})_2\text{dmbpy}]^+$  ( $6.5 \times 10^{-6} \text{ M}$ ). The inset is the enlarged figure for divalent metal ions ( $\lambda_{\text{ex}} = 430 \text{ nm}$ ).

No work has ever revealed such hydration effects by metal ions at such a low concentration. Highly emitting properties of the present iridium(III) complex enabled us to detect the effect under such extreme conditions. From a practical point of view, the present finding may open the possibility of developing the sensing of metal ions by use of the emission from a clay–metal complex adduct.

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## References and Notes

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