doi:10.1246/cl.2011.63
Published on the web December 2, 2010

Enantioselective Sensing by Luminescence from Cyclometalated Iridium(III) Complexes Adsorbed on a Colloidal Saponite Clay

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Emission from a cationic cyclometalated iridium(III) complex, Δ- or Λ-[Ir(ppy)$_2$(dmbpy)]$^+$ (Hppy: 2-phenylpyridine and dmbpy: 4,4′-dimethyl-2,2′-bipyridine), adsorbed on a colloidal saponite clay was quenched stereoselectively by chiral [Ru(acac)$_3$] (acac: acetylacetonato) in a solution at the overall selectivity factor of $K_{\mathrm{SVo}}(\Delta\text{–}\Delta \text{ or } \Lambda\text{–}\Lambda)/K_{\mathrm{SVo}}(\Delta\text{–}\Lambda) = 1.84$ in favor of the pseudo-enantiomeric pair between the emitter and the quencher.

Enantioselective luminescence quenching is a dynamic recognition phenomenon.[1] The discrimination of chirality is accomplished within the short lifetime of an excited molecule.[2–4] One approach for enhancing chiral selectivity is to fix an emitting species on macromolecules such as proteins and DNA.[5] Macromolecules may assist the emitter to orient preferably for the stereoselective attack by a quencher.

In recent years, extensive attention has been paid to highly luminescent cyclometalated iridium(III) complexes.[6–10] The lifetime of an excited triplet state is sufficiently long (ca. 1 µs), and the quantum yield attains a value as high as 0.1–1.0.[6] Iridium(III) complexes are applied to photoresponsive molecular devices such as photodiodes and oxygen sensors.[6] As far as our literature survey has shown, however, no work has been reported on the enantioselective luminescence quenching of cyclometalated iridium(III) complexes. If the emitting properties of the Ir(III) complexes are connected with their chiral structures, it may open a possibility for luminescent chiral sensing.

In the present communication, we used a clay mineral as a host to fix the orientation of an iridium(III) complex toward a quencher. Smectite clay is a layered material ubiquitous in nature.[11–14] One layer consists of an octahedral alumina or magnesia sheet sandwiched by two tetrahedral phyllosilicate sheets. It is negatively charged due to isomorphous replacement by lower valent cations. Cationic species are adsorbed either within the interlayer spaces or on an external surface. Adsorbed species can take a uniform orientation under the steric control of two-dimensional silicate networks.[11] Due to these characteristics, clay–chiral metal complex adducts have been utilized as an adsorbent for chiral recognition processes such as optical resolution, chiral sensing, and stereoselective energy transfer.[11] The present work is an attempt of combining the unique adsorption properties of a clay with the highly luminescent capability of iridium(III) complexes.

A cationic iridium(III) complex, [Ir(ppy)$_2$(dmbpy)]PF$_6$ (Hppy: 2-phenylpyridine and dmbpy: 4,4′-dimethyl-2,2′-bipyridine), was synthesized according to a reported method.[8] The compound was identified by mass spectrum, ^{1}H NMR spectrum, and UV spectrum.[9a] The optical resolution of this compound was attempted by using several resolving agents such as antimonyl tartrate, dibenzoyltataric acid, and chiral tris(oxalato)chromium(III) or by chromatographic resolution on chiral packing materials.[10] All of these attempts failed to achieve enantiomeric separation to a measurable degree. The only successful method was to use an ion-exchange adduct of a clay and chiral [Ru(phen)$_3$]$^{2+}$ (phen: 1,10-phenanthroline) as a resolving agent.[13b] A racemic mixture of Ir(III) complex was dissolved in methanol and mixed with the adduct of either Δ- or Λ-[Ru(phen)$_3$]$^{2+}$/synthetic hectorite. After being stirred for 12 h, the dispersion was centrifuged. When the filtrate was analyzed by circular dichroism (CD), it was found that Δ- and Λ-[Ir(ppy)$_2$(dmbpy)]$^+$ remained in the supernatants as an enantiomer less strongly adsorbed by Δ- or Λ-[Ru(phen)$_3$]$^{2+}$/synthetic hectorite, respectively. Repeating the above procedure several times, the apparent Δε of enantiomeric Ir(III) complex in the supernatant attained a constant value. The CD spectra are shown in Figure 1. By comparing those with those reported for enantiomeric [Ir(ppy)$_3$],[10] it was concluded that the optical purity of resolved [Ir(ppy)$_2$(dmbpy)]$^+$ was as high as 90%.

Synthetic saponite (Kunimine Ind. Co.; (Na$_{0.77}$)[(Si$_{7.20}$Al$_{0.80}$)(Al$_{0.03}$Mg$_{5.97}$)]O$_{20}$(OH)$_4$) was used as a clay material. Its cation-exchange capacity (CEC), which represents the maximum amount of ion-exchanged cations, is stated to be 0.75 mequiv g^{-1}. Adsorption was carried out by mixing a solution of the iridium(III) complex with a clay suspension within 10 ms by means of a stopped-flow apparatus (Unisoku Co., Ltd.). This procedure guaranteed the uniform adsorption of the metal complexes over clay particles particularly even at low loading.[13]

The luminescence quantum yield (*Φ*) of [Ir(ppy)$_2$(dmbpy)]PF$_6$ was measured in various solvents under deaerated con-

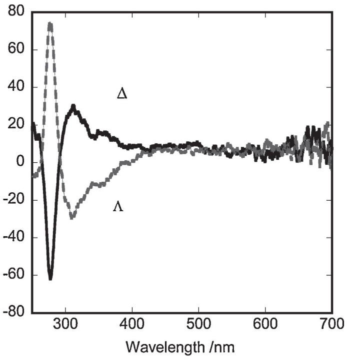

Figure 1. The circular dichroism spectra of Δ- and Λ-[Ir(ppy)$_2$(dmbpy)]PF$_6$ dissolved in methanol.

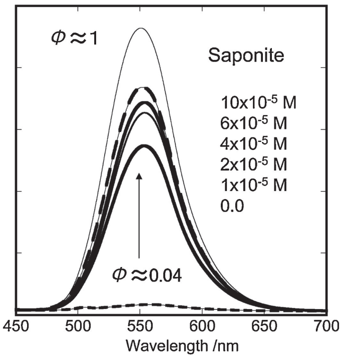

Figure 2. The effect of synthetic saponite on the luminescence spectra of $[Ir(ppy)_2(dmbpy)]PF_6$ under air. The excitation wavelength was 430 nm. The lowest dotted curve was an emission spectrum in the absence of clay. A medium was 3:1 (v/v) H_2O/CH_3OH, [Ir(III) complex] $= 1.0 \times 10^{-5}$ M and [clay] $= 0$–1.0×10^{-4} M. The small shoulder at 500 nm without clay might arise from the Raman scattering of water.

Table 1. The lifetime of $[Ir(ppy)_2(dmbpy)]$ in various conditions

Species	Condition	Lifetime/ns[a]
Ir complex in $CHCl_3$	air-saturated	106
	deaerated	420
Ir complex in 3:1 (v/v)	air-saturated	69.2
H_2O/CH_3OH	deaerated	75.8
Ir complex/saponite in	air-saturated	243, 540[b]
3:1 (v/v) H_2O/CH_3OH	deaerated	531

[a]Excitation wavelength: 337 nm. [b]The decay curve was simulated by two components.

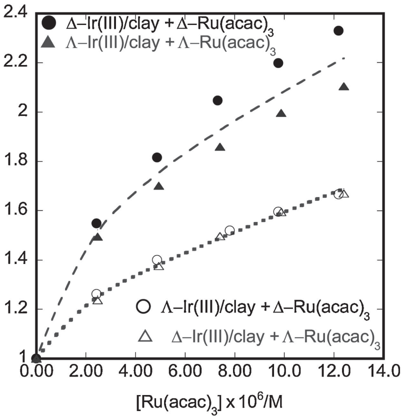

Figure 3. The Stern–Volmer plots for the quenching of $[Ir(ppy)_2(dmbpy)]^+$ by $[Ru(acac)_3]$ in the presence of synthetic saponite. The broken and dotted curves were the calculated results according to eq 1. [Ir(III) complex] $= 1.2 \times 10^{-6}$–1.5×10^{-6} M and [clay] $= 2.0 \times 10^{-4}$ M.

ditions. The wavelength of excitation (λ_{ex}) was 430 nm. The quantum yield was determined relative to the Φ of $[Ru(bpy)_3]^{2+}$ in air-equilibrated water (0.028).[15] Φ attained a high value in aprotic solvents (0.70 ($CHCl_3$) and 0.75 (THF)), while it decreased in protic solvents (0.49 (CH_3OH) and 0.04 (H_2O)). This contrasted with the polypyridyl–Ru(II) complexes whose quantum yield depends little on the kind of solvent (e.g., $[Ru(bpy)_3]^{2+}$, 0.055 (H_2O) and 0.062 (CH_3CN)).[2]

Figure 2 shows the luminescence spectra of an aqueous dispersion containing $[Ir(ppy)_2(dmbpy)]PF_6$ and various amounts of a clay under air. Φ increased from 0.04 to ca. 1.0 with the increase of an added clay even in an aqueous medium. The main cause for the increase of Φ might lie in the elimination of water molecules in the vicinity of the Ir(III) complexes located on a clay surface. The structural fixation of a dmbpy ligand in the iridium(III) complex could be another factor. The introduction of air had little effect on Φ. Thus clay provided such a site protected from quenching by oxygen molecules. A similar effect on the luminescence intensity of the iridium(III) complexes was observed when they were adsorbed by other kinds of macromolecules such as DNA (Supporting Information).[19] The emission intensity continued to increase even after addition of an equivalent amount of clay and attained the maximum value around [clay]/[Ir(III)] = 10. This might reflect that the adsorbed complexes were in an isolated state, being free from self-quenching among them. The cross-sectional area of Ir(III) complex was estimated to be 0.9 nm^2. No contact among the adsorbed metal complexes took place at this loading level (10%).

The effect of clay on the transient behavior of excited Ir(III) complexes was studied by lifetime measurement under various conditions (Supporting Information).[19] Table 1 summarizes the decay lifetime of emission when a colloidal dispersion of a clay and Ir(III) complexes was excited at 337 nm under various conditions. Under air, the decay profile was composed of at least two components. This suggested that there were more than two kinds of adsorption states. For example, a part of the complexes were in the interlayer space, and the other on the external surface of a clay. If this was the case, the latter state was more easily quenched by oxygen molecules in correspondence to the shorter component of lifetime. Under argon atmosphere, the decay profile for a clay dispersion changed to a single exponential curve whose lifetime was nearly equal to the longer component under air. This was reasonable since the Ir(III) complexes on an external surface were no more quenched by oxygen molecules.

The highly emitting properties of the Ir(III) complex bound by clay prompted us to investigate the possibility of stereoselective energy transfer. For that purpose, a tris(β-diketonato)-ruthenium(III), $[Ru(acac)_3]$, was chosen as a chiral quencher.[13a] The emission intensity at 650 nm was compared between two systems, clay/Δ-Ir(III)/Δ-$[Ru(acac)_3]$ (pseudo-enantiomeric combination) and clay/Δ-Ir(III)/Λ-$[Ru(acac)_3]$ (pseudo-racemic combination), in 3:1 (v/v) water–methanol. In both cases, the intensity of emission decreased on adding $[Ru(acac)_3]$, indicating that Ru(III) complex acted as a quencher in these systems.[19]

The quenching effect was analyzed in terms of Stern–Volmer plots (Figure 3). From the figure, it is apparent that luminescence quenching was more efficient for the clay/Δ-Ir(III)/Δ-$[Ru(acac)_3]$ system than for the clay/Δ-Ir(III)/Λ-$[Ru(acac)_3]$ over the whole concentration range. The plots showed the tendency of leveling off at higher concentration of the quenchers. The curves were fitted by the two-site model as given by eq 1.[16] The parameters are summarized in Supporting Information.[19]

$$\frac{I_0}{I} = \left[\frac{f_1}{1 + K_{\mathrm{SV1}} P_0} + \frac{f_2}{1 + K_{\mathrm{SV2}} P_0}\right]^{-1}$$
$$f_1 + f_2 = 1$$
$$K_{\mathrm{SV}}{}^0 = f_1 x K_{\mathrm{SV1}} + f_2 x K_{\mathrm{SV2}} \qquad (1)$$

in which I_0, I, f_1, f_2, P_0, K_{SV1}, and K_{SV2} denote the emission intensities in the absence of and in the presence of a quencher, the fractions of processes 1 and 2, the concentration of a quencher, and the Stern–Volmer constants for the processes 1 and 2, respectively. $K_{\mathrm{SV}}{}^0$ is the overall Stern–Volmer constant.

In order to confirm the existence of stereoselectivity, we performed the same experiments for the opposite emitter/quencher combinations or the clay/Λ-Ir(III)/Λ-[Ru(acac)$_3$] (pseudo-enantiomeric combination) and the clay/Λ-Ir(III)/Δ-[Ru(acac)$_3$] (pseudo-racemic combination). From the $K_{\mathrm{SV}}{}^0$ obtained from eq 1, the overall selectivity factor, which is defined to be the ratio of $K_{\mathrm{SV}}{}^0(\Delta\text{–}\Delta$ or $\Lambda\text{–}\Lambda)/K_{\mathrm{SV}}{}^0(\Delta\text{–}\Lambda)$, was obtained to be 1.84 in favor of the pseudo-enantiomeric combination.

Assuming that the quenching took place by way of an encounter-controlled quenching process, K_{SV} is expressed by $k_{\mathrm{d}}\tau$, in which k_{d} is the diffusion rate constant and τ the lifetime of excited state. Inserting $K_{\mathrm{SV}} = 8.98$ (or 9.58) $\times 10^5\,\mathrm{M}^{-1}$ for the enantiomeric (or racemic) combination, and $\tau = 540\,\mathrm{ns}$, k_{d} is calculated to be 1.66 (or 1.78) $\times 10^{12}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. These k_{f} values are both nearly two-orders higher than the diffusion constants estimated for [Ru(acac)$_3$].[17] Thus the quenching reaction was not a simple collisional process, but it might involve the process of molecular association on a clay surface.

It was added that no stereoselectivity was detected in methanol for the same emitter/quencher pairs. Thus the fixation of the iridium(III) complex on a clay surface was concluded to be a crucial step for chiral recognition. The energy levels of HOMO and LUMO orbitals of [Ir(ppy)$_2$(dmbpy)]$^+$ were calculated as described in Supporting Information.[18,19] The results explained the electronic absorption and emission spectra of this complex.[19]

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