Efficient Energy Transfer of Cationic Iridium(III) Complexes on the Surface of a Colloidal Clay

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ABSTRACT: Energy transfer was investigated by co-adsorbing blue and red emitting cationic iridium(III) complexes, $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ ($\text{dfppyH} = 2\text{-(4',6'-difluorophenyl)pyridine}$, $\text{L} = 4,4'\text{-dimethyl-2,2'-bipyridine}$) and $[\text{Ir}(\text{piq})_2\text{L}]^+$ ($\text{piqH} = 1\text{-phenyisoquinoline}$), respectively, onto the colloidal particles of a synthetic saponite in 1:3 (v/v) methanol/water. Firstly the blue emitter was adsorbed at 25 % loading of the cation-exchange capacity (CEC) of the clay. Thereafter $[\text{Ir}(\text{piq})_2\text{L}]\text{ClO}_4$ was added from 0.4 % to 8 % loading. Under the irradiation of the suspension at 430 nm, the initial emission peak at 500 nm due to the blue emitter decreased with the

1 simultaneous increase of the emission peak at 590 nm due to the red emitter. The emission was
2 mostly due to the latter at its highest loading (8 %). The results indicated that energy transfer
3 took place from the excited blue emitter to the red one efficiently. The life-time of the excited
4 blue emitter was measured in the presence of the red emitter. The stationary and transient
5 emission results were analyzed on the basis of the Förster-type energy transfer mechanism. The
6 accumulation of the reactants on clay particle was essential to the present type of energy transfer,
7 since no energy transfer occurred in the absence of a clay in the similar concentration ranges.

1. Introduction

Luminescent energy transfer is the dynamic process that occurs via the excited state of a donor molecule (Calzagerri, 2012; McLaurin, et al., 2013; Verma and Ghosh, 2012). The process plays a critical role in artificial and natural photochemical processes such as photosynthesis, photo-sensitized molecular transformation and solar cells (Gust, 2009; Hasobe, 2013; Hoertz and Mallouk, 2005). An effort has been focused on controlling the alignment and relative orientation of donor and acceptor molecules in order to attain high efficiency and selectivity (Flamigni et al., 2008; Kaschak et al., 1999; Takagi et al., 2013; Takagi et al., 2002). In biological systems, for example, optimization is achieved by fixing these molecules in the membranes or in the inner cavities of enzymes (Hasobe, 2013). In artificial systems, varieties of organic and inorganic materials have been employed as a host (Takagi, 2013).

Among the inorganic hosts, a clay mineral is characterized by its two-dimensional layered structure (Shirasaki et al., 2010). Cationic species are intercalated in the narrow galleries between aluminosilicate layers (Bujádk et al., 2010; Dey et al., 2013; Fujii et al., 2011; Hussain et al., 2010; Ishida et al., 2011; Ishida et al., 2012; Ishida et al., 2013; Kuroda et al., 2010; Ogawa and

1 Kuroda, 1995; Olvero, et al., 2014; Rao et al., 2011; Rao et al., 2013; Sasai et al. 2009; Sato et al.,
2 2005; Sato and Yamagishi, 2007; Wang et al., 2012; Yamagishi and Sato, 2012) . There have
3 been several attempts in determining energy transfer systems on clay surfaces to enhance the
4 efficiency of energy transfer. For example, cationic pyridylporphyrines exhibited energy transfer
5 whose efficiency depended on the surface density on a clay surface (Ishida, 2011). The inter- and
6 intra-layer energy transfer processes were observed to occur when organic donors and acceptors
7 were intercalated within the interlayer spaces of a clay (Ishida et al., 2011; Ishida et al., 2013;
8 Sasai, et al., 2009).

9 In recent years, an extensive attention has been paid to cyclometalated iridium complexes
10 due to high emitting properties (Brulatti et al., 2012; Lowry and Bernhard, 2006; Mochizuki et
11 al.,2013; Morimoto et al. 2012; Nakamaru,1982; Sato et al., 2009; Sato et al., 2010; Sato et al.,
12 2011a; Sato et al., 2011b; Sato et al., 2014; Shi et al., 2011; Tamayo et al., 2005; Tordera et al.,
13 2012; Ulbricht, et al., 2009; Waki et al., 2011). The lifetime of excited triplet states is long and
14 the quantum yield attains a value as high as 10 ~ 100 %. Thus it is interesting to couple the
15 emitting properties of iridium(III) complexes with the unique character of a clay as a host. For
16 example, when a cationic iridium(III) complex, $[\text{Ir}(\text{ppy})_2\text{L}]^+$ (ppyH = 2-phenylpyridine and L =
17 4,4'-dimethylbipyridine), was adsorbed by a colloiddally dispersed synthetic saponite, the
18 quantum yield of emission increased remarkably. Moreover stereoselectivity appeared when
19 chiral $[\text{Ir}(\text{ppy})_2\text{L}]^+$ was quenched by chiral $[\text{Ru}(\text{acac})_3]$ (acac = acetylacetonato) (Sato et al.,
20 2011b). Since no such stereoselectivity appeared for the same pair in a homogeneous medium,
21 the clay played a role of not only enhancing emission yield, but also assisting molecular
22 discrimination.

In the present work, we employed synthetic sodium saponite to fix two kinds of iridium(III) complexes. The used complexes were $[\text{Ir}(\text{dfppy})\text{L}]\text{ClO}_4$ and $[\text{Ir}(\text{piq})\text{L}]\text{ClO}_4$ ($\text{dfppyH} = 2\text{-(4',6'-difluorophenyl)pyridine}$ and $\text{piqH} = 1\text{-phenyisoquinoline}$) as blue and red emitters, respectively. Energy transfer from the blue to the red emitters was investigated by measuring stationary emission spectra and the life-time of emission when they were co-adsorbed by a colloidal clay particle.

2. Experimental

Materials: Cationic iridium(III) complexes, $[\text{Ir}(\text{dfppy})_2\text{L}]\text{ClO}_4$ and $[\text{Ir}(\text{piq})_2\text{L}]\text{ClO}_4$, were synthesized according to the reported method (Lowry and Bernhard, 2006). The compounds were identified by mass spectra, $^1\text{H-NMR}$ and UV spectra (Supporting Information).

Synthetic sodium saponite (Kunimine Ind. Co. Japan) with the elemental composition of $[(\text{Na}_{0.25}\text{Mg}_{0.07})(\text{Mg}_{2.98}\text{Al}_{0.01})(\text{Si}_{3.6}\text{Al}_{0.4})\text{O}_{10}(\text{OH})_2]$ (denoted by SAP) was used as the clay material. Its cation-exchange capacity (CEC), which represents the maximum amount of ion-exchanged cations, is stated to be 0.80 meq g^{-1} . Adsorption was carried out by mixing a solution of the iridium(III) complex with a clay dispersion under vigorous stirring in order to achieve the uniform distribution of an adsorbate over clay particles particularly at low loading.

Electronic absorption and stationary emission measurements: UV-visible electronic spectra were recorded with a U-2810 spectrophotometer (Hitachi, Japan). Emission spectra were measured with a FP-6200 fluorophotometer (JASCO, Japan). The temperature dependence of the emission spectrum was recorded with a fluorometer FP-6500 (JASCO, Japan) equipped with a temperature-changing cell holder Unispeks (UNISOKU, Japan).

Measurements of emission lifetime: The lifetime of emission was measured with a TSP-1000M-PL-ES (UNISOKU, Japan) at room temperature under air. The instrument was equipped with a pulse YAG laser at 355 nm. The emission decay curves were averaged for 130 transient signals. The curves were simulated in terms of multi-exponential decays.

3. Results and Discussion

Spectroscopic properties of iridium(III) complexes: The electronic absorption spectra of the perchlorate salts of iridium(III) complexes dissolved in a 1:3 (v/v) methanol/water medium are shown in Figure S1 (the supporting information). The bands around 400 ~ 300 nm were assigned to the LMCT for all complexes. It was located at the longer wavelength region for [Ir(piq)₂L]⁺ than for [Ir(dfppy)₂L]⁺ due to the delocalization of π -electrons in the naphthyl group of the former complex. The bands around 300 ~ 250 nm were assigned to the π - π^* transitions localized in the ligands.

Figures 1(a) and (b) show the emission spectra of methanol solutions of [Ir(dfppy)₂L]ClO₄ and [Ir(piq)₂L]ClO₄, respectively. The maximum wavelength ($\lambda_{\max}$) of the emission was 512 nm and 590 nm for [Ir(dfppy)₂L]⁺ (blue emitter) and [Ir(piq)₂L]⁺ (red emitter), respectively. The quantum yield (Φ) of the emission was determined in various solvents by use of [Ru(bpy)₃]Cl₂ in air-equilibrated water as a standard. The wavelength of excitation (λ_{ex}) was 430 nm. Φ was calculated according to eq. (1):

$$\Phi = \Phi_{st} \left(\frac{A_{st}}{A} \right) \left(\frac{D}{D_{st}} \right) \left(\frac{n^2}{n_{st}^2} \right) \quad (1),$$

where Φ is quantum yield for an iridium(III) complex, A absorbance at 430 nm, D an irradiated area, n refractive index. The subscript st means the standard value for [Ru(bpy)₃]²⁺ ($\Phi_{st} = 0.028$)

(Nakamaru, 1982). According to the results in Table 1, Φ attained a high value in aprotic solvents (0.33 and 0.04 (CH_2Cl_2)), respectively, while it was low in protonic solvents (0.13 and 0.02(CH_3OH)) for $[\text{Ir}(\text{dfppy})_2\text{L}]\text{ClO}_4$ and $[\text{Ir}(\text{piq})_2\text{L}]\text{ClO}_4$, respectively. Solvation through hydrogen bonding in protonic media might result in non-radiative energy dissipation through the vibrational modes of solvent molecules.

Figure 1. Emission spectra of iridium(III) complexes in methanol: (A) $[\text{Ir}(\text{dfppy})_2\text{L}]\text{ClO}_4$, (a) 6.3×10^{-6} M, (b) 9.3×10^{-6} M, (c) 1.5×10^{-5} M and (d) 2.9×10^{-5} M ; (B) $[\text{Ir}(\text{piq})_2\text{L}]\text{ClO}_4$, (a) 9.4×10^{-7} M, (b) 1.9×10^{-6} M, (c) 2.8×10^{-6} M and (d) 3.7×10^{-6} M.

Table 1. Quantum yield of emission in various solvents

Solvent	refractive index	$[\text{Ir}(\text{dfppy})_2\text{L}]\text{ClO}_4$	$[\text{Ir}(\text{piq})_2\text{L}]\text{ClO}_4$
Methanol	1.33	0.13	0.02
Acetone	1.45	0.10	0.02
Acetonitrile	1.42	0.11	0.02
Dichloromethane	1.35	0.33	0.04

Chloroform	1.34	0.19	0.03
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Effects of SAP on the emission properties: Figures 2 shows the emission spectrum of a 1:3 (v/v) methanol/water dispersion containing SAP and an iridium(III) complex. The concentration of SAP was changed from 2.0×10^{-6} M to 6.2×10^{-5} M in terms of cation-exchange capacity (CEC). This corresponded to the change of the loading of each iridium(III) complex from 75 % to 1.5 %. The wavelength of excitation (λ_{ex}) was 430 nm. In the case of $[\text{Ir}(\text{dfppy})_2\text{L}]^+$, the maximum wavelength was shifted from 512 nm to 500 nm on adding SAP accompanied with the increase of Φ from 0.3 to c.a.1.0. In case of $[\text{Ir}(\text{piq})_2\text{L}]^+$, Φ increased from 0.04 to 0.06 with little change of the emission peak position when SAP was added.

Figure 2. The effect of SAP on the emission spectra: (A) $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ (1.8×10^{-6} M) and (B) $[\text{Ir}(\text{piq})_2\text{L}]^+$ (9.4×10^{-7} M) in 1:3 (v/v) methanol/water. The concentration of SAP in terms of cation-exchange capacity was: (A) (a) no SAP, (b): 2.0×10^{-6} M, (c) 3.7×10^{-6} M, (d) 2.5×10^{-5} M and (e) 6.2×10^{-5} M; (B) (a) no SAP, (b) 6.2×10^{-6} M, (c) 1.2×10^{-5} M, (d) 2.5×10^{-5} M and (e) 6.2×10^{-5} M.

Stationary measurements on energy transfer: The energy transfer from a donor ($[\text{Ir}(\text{dfppy})_2\text{L}]^+$) to an acceptor ($[\text{Ir}(\text{piq})_2\text{L}]^+$) was studied in the presence of 3.7×10^{-6} M of SAP in 1:3 (v/v) methanol/water. Firstly $[\text{Ir}(\text{dfppy})_2\text{L}](\text{ClO}_4)$ was added at a concentration of 9.3×10^{-7} M (or 25 % loading). Thereafter $[\text{Ir}(\text{piq})_2\text{L}]\text{ClO}_4$ was added from 1.6×10^{-8} M to 3.1×10^{-7} M, which corresponded to the loading from 0.4 % to 8 %. As shown in Figure 3, the initial emission peak at 500 nm due to excited $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ (denoted as $[\text{Ir}(\text{dfppy})_2\text{L}]^{+*}$) decreased with the simultaneous increase of the emission peak at 590 nm due to $[\text{Ir}(\text{piq})_2\text{L}]^{+*}$. At the highest loading of $[\text{Ir}(\text{piq})_2\text{L}]^+$ (8 %), the emission was mostly due to $[\text{Ir}(\text{piq})_2\text{L}]^{+*}$. The results indicated that energy transfer occurred efficiently from $[\text{Ir}(\text{dfppy})_2\text{L}]^{+*}$ to $[\text{Ir}(\text{piq})_2\text{L}]^+$ on a clay surface. The process was visualized by the luminescent color change from blue to red on adding $[\text{Ir}(\text{piq})_2\text{L}]\text{ClO}_4$ as shown in Figure S2 (the supporting information).

For comparison, similar experiments were performed in the absence of SAP. The emission spectra are shown in Figure S3, when $[\text{Ir}(\text{piq})_2\text{L}]\text{ClO}_4$ was added from 1.6×10^{-8} M to 3.1×10^{-7} M to a 1:3 (v/v) methanol/water solution containing 9.3×10^{-7} M of $[\text{Ir}(\text{dfppy})_2\text{L}]\text{ClO}_4$. The intensity of the peak at 500 nm due to $[\text{Ir}(\text{dfppy})_2\text{L}]^{+*}$ changed little and the increase of the emission peak at 590 nm was negligible. The results indicated that energy transfer occurred to a negligible extent in the absence of SAP. The accumulation of the donor and acceptor molecules on the same clay particles was thought to be the main factor to enhance the efficiency of energy transfer at concentrations as low as 10^{-6} M.

In order to investigate the influence of loading on the efficiency of energy transfer, the amount of SAP in a 1:3 (v/v) methanol/water dispersion was changed from 1.2×10^{-6} M to 6.2×10^{-5} M under the constant concentration of $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ (9.3×10^{-7} M). This corresponded to the change of the loading of $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ from 75 % to 1.5 %. To a dispersion containing the

constant concentrations of SAP and $[\text{Ir}(\text{dfppy})_2\text{L}]^+$, $[\text{Ir}(\text{piq})_2\text{L}]^+$ was added from 1.6×10^{-8} M to 3.1×10^{-7} M. The change of the emission spectrum during this procedure is shown in Figure S4 (the supporting information). When the intensity of the emission peak at 590 nm at the highest concentration of $[\text{Ir}(\text{piq})_2\text{L}]^+$ (or 3.1×10^{-7} M) was noted, it reduced with the increase of the SAP concentration. In other words, the efficiency of energy transfer from $[\text{Ir}(\text{dfppy})_2\text{L}]^{+*}$ to $[\text{Ir}(\text{piq})_2\text{L}]^+$ decreased with the increase of SAP. The results are analyzed later in terms of the change of the intermolecular distance between the emitter and acceptor molecules on a clay surface.

Figure 3. The change of the emission spectra of $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ adsorbed by SAP, when a methanol solution of $[\text{Ir}(\text{piq})_2\text{L}]\text{ClO}_4$ was added. The medium was 1:3 (v/v) methanol/water. The concentration of SAP was 3.7×10^{-6} M (in terms of cation-exchange capacity) and the loading of $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ 25%. (9.3×10^{-7} M) The loading level of added $[\text{Ir}(\text{piq})_2\text{L}]^+$ was (a) 0.0%, (b) 0.4 %, (c) 0.80%, (d) 1.3%, (e) 1.7%, (f) 2.5%, (g) 4.2% and (h) 8.2%. Curve I denotes the emission spectrum of $[\text{Ir}(\text{piq})_2\text{L}]^+$ alone at the loading level of 8.2%.

When the temperature of the sample was varied from 273K to 313K, the two peaks at 500 nm and 590 nm increased by 15 % with little change of their relative ratio (Figure S5) (supporting information). The ratio of the emission intensities at 500 to 590 remained nearly at constant. The results indicated that the present energy transfer involved no thermally activated process.

Analyses of stationary emission spectra on the basis of the Förster-type mechanism:

The results of the stationary emission spectra (Figures 3 and 4) were analyzed on the basis of the Förster-type energy transfer mechanism as shown by eq. (2) (Ishida, 2011):

$$F_{ET}(\nu) = (1 - \eta_{ET} - \phi_{dfppy}) \times F_{dfppy}^0(\nu) + (1 + \frac{1 - 10^{-A_{dfppy}}}{1 - 10^{-A_{piq}}} \eta_{ET}) \times F_{piq}^0(\nu) \quad (2),$$

in which $F_{ET}(\nu)$ is the emission spectrum of a dispersion containing $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ (donor) and $[\text{Ir}(\text{piq})_2\text{L}]^+$ (acceptor) adsorbed by SAP, $F_{dfppy}^0(\nu)$ the emission spectrum of a suspension containing $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ adsorbed by SAP, $F_{piq}^0(\nu)$ the emission spectrum of a suspension containing $[\text{Ir}(\text{piq})_2\text{L}]^+$ adsorbed by SAP, η_{ET} the energy transfer efficiency from the donor to the acceptor, ϕ_{dfppy} the quenching efficiency of the donor and A_{dfppy} (or A_{piq}) the absorbance of the donor (or the acceptor) at 430 nm, respectively. The parameters obtained from the results in Figure 3 were summarized in Table 2. The observed and calculated curves are compared as shown in Figure S5 (the supporting information).

Table 2. Summary of energy transfer parameters obtained from the stationary emission spectra

Parameter	1:3(v/v) CH ₃ OH/ H ₂ O	Synthetic saponite (SAP) (3.7 x 10 ⁻⁶ M)
η_{ET}^*	0	0.52
ϕ_{dfppy}	0.20	0
A_{dfppy}^{**}	2.7x10 ⁻⁵	6.8x10 ⁻⁴
A_{piq}^{**}	3.1x10 ⁻⁴	2.1x10 ⁻⁴

(*) η_{ET} corresponds to the loading of 25 % ([Ir(dfppy)₂L]⁺) and 0.8 % ([Ir(piq)₂L]⁺).

(**) A_{dfppy} and A_{piq} were determined by the separate measurements.

From the results of Figure S4 (the supporting information), energy transfer efficiency (η_{ET}) was plotted as a function of the loading of [Ir(dfppy)₂L]⁺ at the constant ratio of [Ir(dfppy)₂L]⁺ (donor) to [Ir(piq)₂L]⁺ (acceptor). As shown in Figure 4, η_{ET} increased with the increase of the loading or the surface density of the iridium(III) complexes. It might reflect the situations that η_{ET} increased with the shortening of the intermolecular distance for a pair of an emitter and a donor on a clay surface.

Figure 4. The dependence of the efficiency of energy transfer (η_{ET}) on the loading of $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ at the various ratios of $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ to $[\text{Ir}(\text{piq})_2\text{L}]^+$. The concentration of SAP was varied from 1.2×10^{-6} M to 6.2×10^{-5} M in terms of cation-exchange capacity. The concentration of $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ was 9.3×10^{-7} M. The concentration (or the ratio of donor-to-acceptor) of $[\text{Ir}(\text{piq})_2\text{L}]^+$ was (a) 1.6×10^{-8} M (58 : 1), (b) 3.2×10^{-8} M (29 : 1) and (c) 6.3×10^{-8} M (14 : 1), respectively.

Transient measurements on energy transfer processes: The lifetime of emission was measured for a SAP suspension (6.4×10^{-6} M) containing $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ (1.6×10^{-6} M) or $[\text{Ir}(\text{piq})_2\text{L}]^+$ (6.2×10^{-7} M). Emission was monitored at 500 nm or 580 nm, respectively, when the complexes were excited at 355 nm. The decay curves of the emission are shown in Figure S6 (the supporting information). The decay curves were simulated by the sum of two exponential components. As a result, two lifetimes were obtained as $\tau_D(\text{fast}) = 0.39 \mu\text{s}$ and $\tau_D(\text{slow}) = 0.85 \mu\text{s}$ for $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ and $\tau_A(\text{fast}) = 0.15 \mu\text{s}$ and $\tau_A(\text{slow}) = 0.92 \mu\text{s}$ for $[\text{Ir}(\text{piq})_2\text{L}]^+$, respectively.

The lifetime of $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ was measured on a 1:3 (v/v) methanol/water dispersion containing the constant concentrations of SAP (6.4×10^{-6} M), $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ (1.6×10^{-6} M) and the various concentrations of $[\text{Ir}(\text{piq})_2\text{L}]^+$ ($0 \sim 4.1 \times 10^{-7}$ M). The results are summarized in Table 3. Both of $\tau_D(\text{fast})$ and $\tau_D(\text{slow})$ decreased with the increase of the concentration of $[\text{Ir}(\text{piq})_2\text{L}]^+$, indicating that the contribution of energy transfer increased, leading to shortening the lifetime of $[\text{Ir}(\text{dfppy})_2\text{L}]^+*$. The results are analyzed according to the following equation

$$K_{ET} = \frac{1}{\tau} - \frac{1}{\tau_D} \quad (3),$$

in which K_{ET} is the rate of energy transfer from the donor to the acceptor, τ and τ_D the emission life time of the donor in the presence and absence of the acceptor. Assuming that each component of the decay curve represented an independent energy transfer process, the analyzed results are shown in the same table. Notably the rate of energy transfer, K_{ET} , increased non-linearly with the concentration of $[\text{Ir}(\text{piq})_2\text{L}]^+$ (acceptor) for both the slow and fast processes.

Table 3. The lifetime of $[\text{Ir}(\text{dfppy})_2\text{L}]^{+*}$ in a dispersion containing SAP (6.4×10^{-6} M), $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ (1.6×10^{-6} M) and $[\text{Ir}(\text{piq})_2\text{L}]^+$. ($0 \sim 4.2 \times 10^{-7}$ M).

Loading of $[\text{Ir}(\text{piq})_2\text{L}]^+$ %	500 nm $\tau_{D(\text{fast})}$ / μs	500 nm $\tau_{D(\text{slow})}$ / μs			f_1 (fast) [#]	f_2 (slow) [#]	$K_{ET}(\text{fast})$ $1/\mu\text{sec}^{-1}$	$K_{ET}(\text{slow})$ $1/\mu\text{sec}^{-1}$
0	0.39	0.85	-	-	0.024 (1.0)	0.025 (1.0)		
1.6	0.35	0.79	-	-	0.01 (1.0)	0.006 (0.6)	0.32	0.06
3.3	0.28	0.74	-	-	0.007 (1.0)	0.004 (0.57)	1.05	0.17
4.9	0.18	0.61	-	-	0.005 (1.0)	0.004 (0.8)	3.12	0.45
6.5	0.13	0.51	-	-	0.025 (1.0)	0.026 (1.0)	5.38	0.80

#) The relative amplitudes of the slow and first components in the decay signals.

An adsorption model on a clay surface: The above results demonstrated that energy transfer took place efficiently on a clay surface. The present cationic metal complexes were thought to be adsorbed due to the electrostatic interaction with negative charges in a clay layer. For SAP, the surface density of the negative charge on a phyllosilicate sheet is calculated to be 1.56 nm² per one negative charge on the basis of cation-exchange capacity and surface area (750 m²g⁻¹) (Takagi et al. 2002).

The energy transfer from [Ir(dfppy)₂L]⁺* to [Ir(piq)₂L]⁺ was most likely to occur via the Förster-type mechanism. If this was the case, η_{ET} depends on the intermolecular distance (R) for a given pair of a donor and an acceptor as below:

$$\eta_{ET} = 1/(1 + (R/R_c)^6) \quad (4)$$

in which R_c is the critical distance at which the efficiency of energy transfer was 0.5. R_c is a function involving the overlap of the emission spectrum of a donor with the electronic absorption spectrum of an acceptor and the relative orientation of a donor-acceptor pair (Ishida et al., 2011).¹⁸ Since η_{ET} decreases rapidly with the increase of R, it is reasonable to assume that energy transfer occurred **between the nearest pair of [Ir(dfppy)₂L]⁺* to [Ir(piq)₂L]⁺ on a clay surface.**

Each curve of Figure 4 corresponds to the situations that the loading level or surface density of donors and acceptors varied under the constant number of donor-acceptor pairs. Firstly it was attempted to interpret the results on the basis of the simplest model that both [Ir(dfppy)₂L]⁺ and [Ir(piq)₂L]⁺ were adsorbed randomly, achieving a uniform distribution on the surface. No specific interaction was assumed between these iridium(III) complexes. Accordingly the average intermolecular distance between the neighboring molecules depended on the total

loading of these molecules. Let the area occupying one negative charge (1.56 nm^2) be denoted as S_0 . At the loading level of x (< 1), one iridium(III) complex occupies an area of S_0/x . Assuming the area to take a shape of a circle, its radius is $r = (S_0/x)^{0.5}/\pi$. An intermolecular distance (R), which is defined as the distance from the center of one complex to that of the other, is equated to be $R = 2r$.

Scheme 1 shows an example of such a distribution, when $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ (25 % loading) and $[\text{Ir}(\text{piq})_2\text{L}]^+$ (8 % loading) were adsorbed on a phyllosilicate surface (the final state in Figure 3). The shortest intermolecular distance between a donor and an acceptor is estimated to be 2.1 nm in this case. The results of Figure 4 are re-plotted as the logarithm of η_{ET} against the logarithm of the nearest intermolecular distance (R) (Figure 5). As a result, $\ln(\eta_{ET})$ decreased nearly linearly with the increase of $\ln R$. Although these features are in accord with the Förster-type energy transfer as predicted by equation (4) for the case of $(R/R_c) \gg 1$, η_{ET} depended on $(R/R_c)^{-n}$ with $n = 0.5 \sim 1.5$ that is much less than the theoretically predicted value of $n = 6$. In other words, the intermolecular distance did not increase as predicted from the random distribution model, when the surface density of the iridium(III) complexes was lowered. The results indicated that there existed an attractive interaction between the donor and acceptor molecules on a clay surface to form the aggregated domain in which the intermolecular distance would not increase so rapidly on diluting the adsorbed molecules.

Figure 5. The plot of the logarithm of η_{ET} versus the logarithm of the nearest intermolecular distance between $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ and $[\text{Ir}(\text{piq})_2\text{L}]^+$ on the surface of a clay (re-plotted from the results in Figure 4). The nearest intermolecular distance was estimated on the random distribution model.

Figure 6 shows the dependence of K_{ET} on the concentration of $[\text{Ir}(\text{piq})_2\text{L}]^+$ from the lifetime measurements under the constant loading of $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ as obtained from Table 3. Thus it corresponded to the variation of K_{ET} with the increase of the number of donor-acceptor pairs. For both the fast and slow components, K_{ET} increased non-linearly with the concentration of $[\text{Ir}(\text{piq})_2\text{L}]^+$ or it increased in proportion to $\{[\text{Ir}(\text{piq})_2\text{L}]^+\}^n$ ($n = 2.0$ and 1.9 for the fast and slow decays, respectively). In other words, the number of donor-acceptor pairs at the nearest sites increased more than expected from the random distribution model ($n = 1$) at the higher concentration of the acceptors, suggesting the formation of aggregation domains.

The origin of two components in the decay process was unclear. Two components in the decay curves were already seen for $[\text{Ir}(\text{dfppy})_2\text{L}]^{+*}$ in the absence of $[\text{Ir}(\text{piq})_2\text{L}]^+$. Thus it might correspond to the heterogeneous character of surface properties such as the non-uniform distribution of the negative charges in a layer. If this was the case, the slow and fast processes possibly correspond to the energy transfer for the pairs at the long and short nearest distances.

Figure 6. The dependence of K_{ET} on the loading of $[\text{Ir}(\text{piq})_2\text{L}]^+$ according to the results in Table 3.

Scheme 1. The model of adsorption of $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ and $[\text{Ir}(\text{piq})_2\text{L}]^+$ on the phyllosilicate sheet of SAP. The complexes are assumed to be distributed randomly on a surface at 3:1 ratio. According to this scheme, the nearest distance between $[\text{Ir}(\text{dfppy})_2\text{L}]^+$ and $[\text{Ir}(\text{piq})_2\text{L}]^+$ is estimated to be 2.1 nm.

4. Conclusion

Energy transfer took place efficiently between the donor and acceptor molecules on the surface of a colloidal clay particle. The processes were analyzed in terms of the Förster-type mechanism on a two-dimensional surface. The formation of aggregation domains for the donor and acceptor molecules on a surface was suggested to be one of the factors in achieving such efficiency. The initial blue emission due to the donors changed to the red emission due to the acceptors from the visual observation. This demonstrated that a clay mineral was regarded as a medium tuning the color of emission from excited molecules.

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