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Harvesting of Light Energy by Iridium(III) Complexes on a Clay Surface

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Energy transfer was investigated between two types of iridium(III) complexes, $[Ir(dfppy)_2(C_n\text{-bpy})]^+$ (dfppyH = 2-(2',4'-difluorophenyl)pyridine; C_n-bpy = 4,4'-dialkyl-2,2'-bipyridine; dialkyl = dimethyl (C_1), didodecyl (C_{12}), and dinonyldecyl (C_{19})) and $[Ir(piq)_2(C_n\text{-bpy})]^+$ (piqH = 1-phenyisoquinoline) as donor and acceptor, respectively. The complexes were co-adsorbed by colloidally dispersed synthetic saponite. The efficiency of energy transfer (η_{ET}) was obtained from emission spectra at various donor-to-acceptor ratios (D/A) on the basis of the Förster-type energy transfer mechanism. For C_1-bpy, η_{ET} was as high as 0.5 with a D/A of ca. 20. The results implied that the photon energy captured by several donor molecules was collected by a single acceptor molecule (i.e. the harvesting of light energy). Enantioselectivity was observed, which indicates the participation of a contact pair of donor and acceptor molecules. For C_{12}-bpy and C_{19}-bpy, η_{ET} was low and exhibited no enantioselectivity, because their long alkyl chains inhibited close contact between the donor and acceptor molecules.

Introduction

Recently, there has been extensive research to construct an artificial light harvesting system that mimics photosynthetic bio-organisms.[1-13] One approach is to fix a photoresponsive species into the cavities of macromolecular hosts.[14-20] Various types of organic and inorganic materials have been applied as a host material to achieve efficient energy transfer, among which clay minerals are unique in that they can intercalate neutral and ionic species within their two-dimensional interlayer spaces.[21-32]

Cyclometalated iridium(III) complexes have recently attracted attention as a potentially useful photosensitizer with a high quantum yield and long lifetime.[33-39] For example, *fac*-$[Ir(ppy)_3]$ (ppy = 2-phenylpyridine) is reported to have a quantum yield of 0.40 and a lifetime of 1.9 μs when it is dissolved in 2-methyltetrahydrofuran.[39]

We have investigated the energy transfer processes between two cyclometalated iridium(III) complexes with different emission maxima, when they are co-adsorbed in a colloidal dispersion of synthetic saponite. Energy transfer in the system was investigated by measuring the stationary and transient emission spectra.[32] Efficient transfer of photon energy occurred in reactant concentration ranges as low as 10^{-5}–10^{-6} M. The accumulation of donors and acceptors on a clay particle was considered to be a main factor in attaining high efficiency.

In the present work, the process of energy transfer within a clay was studied with a focus on the following two aspects: (i) the possibility of enantioselectivity and (ii) the effect of alkyl chains in the reactant molecules.

According to the Förster-type mechanism,[40] energy transfer efficiency (η_{ET}) for a donor and acceptor pair is expressed as follows:

$$\eta_{ET} = 1/(1 + (R/R_0)^6), \qquad (1)$$

where R denotes the distance between the donor and acceptor molecules, and R_0 is the Förster radius, at which the efficiency of energy transfer takes a value of 0.5.[40] With respect to enantioselectivity, the small perturbation of R caused by the stereochemical interaction may influence η_{ET} to a detectable extent due to its high order dependence on R. Although most of the components in biomolecular species are chiral, the role of molecular chirality has rarely been examined in energy transfer processes.[41,42] With regard to the effect of alkyl chains, it is uncertain whether they simply inhibit direct contact of the donor/acceptor pair or facilitate the arrangement of the donor/acceptor pair in a favourable orientation. Biomolecular systems often carry amphiphilic moieties to assist in molecular aggregation; therefore, such effects would be worthy of investigation.

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To examine these effects, chiral Ir(III) complexes with alkyl chains of various lengths were synthesized. The main concern was to examine how delicately a molecular aggregate should be organized to harvest light energy efficiently, that is, whether delicate manipulation of the donor and acceptor arrangement is required or a simple medium such as clay nanosheets can attain reasonable energy transfer efficiency.

Results and Discussion

Preparation and optical properties of chiral Ir(III) complexes: Chart 1 shows the molecular structures of the Ir(III) complexes used in the present work. $[Ir(dfppy)_2(C_n\text{-bpy})]^+$ (dfppyH = 2-(2',4'-difluorophenyl)pyridine; C_n-bpy = 4,4'-dialkyl-2,2'-bipyridine) and $[Ir(piq)_2(C_n\text{-bpy})]^+$ (piqH = 1-phenyisoquinoline) were used as donor and acceptor molecules, respectively, for Förster-type photon energy transfer. The length of alkyl chains in C_n-bpy was varied as dimethyl (C_1), didodecyl (C_{12}), and dinonyldecyl (C_{19}) groups. These were prepared by reacting a dimer, $[\{Ir(dfppy)Cl\}_2]$ or $[\{Ir(piq)Cl\}_2]$, with C_n-bpy in glycerol and the products were identified from ^{1}H nuclear magnetic resonance (^{1}H NMR) and mass spectroscopy measurements (Supporting Information).

Racemic mixtures of the prepared Ir(III) complexes were eluted on a chiral column. As a result, optical resolution was achieved for C_1-bpy and C_{12}-bpy. However, the C_{19}-bpy complexes were adsorbed onto the column so firmly that no complex was eluted. A typical chromatogram is shown as an example in Supporting Information. Figure 1 shows circular dichroism (CD) spectra for the resolved enantiomers of $[Ir(dfppy)_2(C_1\text{-bpy})](ClO_4)$ and $[Ir(piq)_2(C_1\text{-bpy})](ClO_4)$. Comparing the CD spectra of analogous compounds ($[Ir(ppy)_3]$; ppy = 2-phenylpyridine), the first and second fractions were concluded to contain Δ- and Λ-enantiomers, respectively.[43]

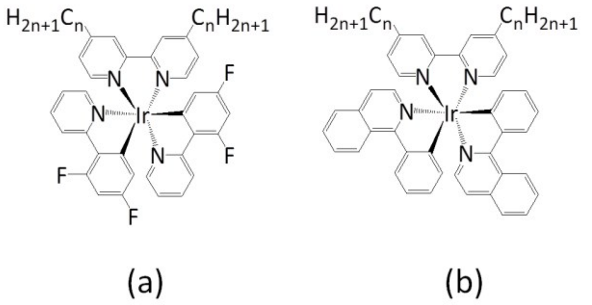

Chart 1. (a) Structures of the Ir(III) complexes, (a) Δ-$[Ir(dfppy)_2(Cn\text{-bpy})]$+ (dfppyH = 2-(4',6'-difluorophenyl)pyridine; Cn-bpy = 4,4'-dialkyl-2,2'-bipyridine) and (b) Δ-$[Ir(piq)_2(Cn\text{-bpy})]^+$ (piqH = 1-phenyisoquinoline) used in this work.

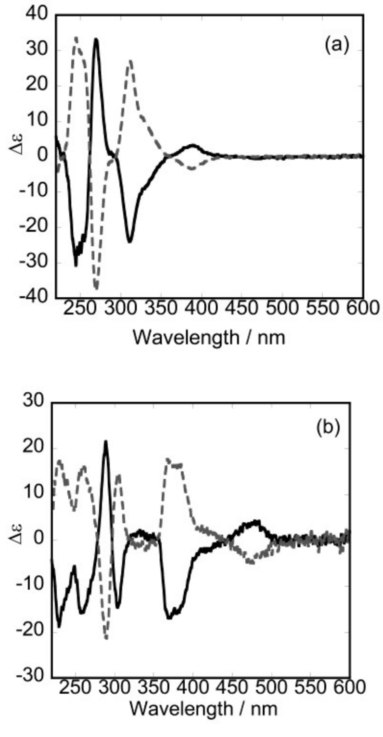

Figure 1. CD spectra for the resolved enantiomers of (a) $[Ir(dfppy)_2(C_1\text{-bpy})]ClO_4$ and (b) $[Ir(piq)_2(C_1\text{-bpy})]ClO_4$ dissolved in methanol. The solid and dotted curves are for the first and second fractions, respectively.

Steady-states emission properties: Synthetic saponite (SAP) was dispersed in a mixture of 4:1 (v/v) water/methanol. The SAP concentration ([SAP]) was adjusted in the range of 3–12×10^{-6} eq L^{-1}, in terms of the cation-exchange capacity (CEC). $[Ir(dfppy)_2(C_n\text{-bpy})](ClO_4)$ (donor) in a methanol solution was added to the suspension under rigorous stirring to a loading level of 15–60% CEC. Thereafter, a methanol solution of $[Ir(piq)_2(C_n\text{-bpy})](ClO_4)$ (acceptor) was added in the same way. The loading of $[Ir(piq)_2(Cn\text{-bpy})]^+$ was varied from 0 to 19% CEC. The emission spectra were measured at various donor-to-acceptor ratios (D/A) at constant concentrations of the donor and SAP. Enantioselectivity was examined by comparing the following four pairs: (a) Δ-donor/Δ-acceptor, (b) Δ-donor/Λ-acceptor, (c) Λ-donor/Δ-acceptor, and (d) Λ-donor/Λ-acceptor. When enantioselectivity was present, there would be a difference in the emission behaviour between the homochiral pairs ((a) and (d)) and the heterochiral pairs ((b) and (c)).

Figure 2 shows the change in the emission spectra for C_1-bpy at [SAP] = 6×10^{-6} eq L^{-1}. An increase of the adsorbed amount of $[Ir(piq)_2(C_1\text{-bpy})]^+$ resulted in a decrease in the intensity of the emission peak at 590 nm due to excited $[Ir(dfppy)_2(C_1\text{-bpy})]^+$ (or simply $[Ir(dfppy)_2(C_1\text{-bpy})]^{+*}$), while the intensity of the emission peak at 600 nm due to $[Ir(piq)_2(C_1\text{-bpy})]^{+*}$

simultaneously increased. At D/A less than 5, the spectrum was close to that of $[Ir(piq)_2(C_1\text{-bpy})]^{+*}$.

As a comparison, $[Ir(dfppy)_2(C_1\text{-bpy})]^+$ and $[Ir(piq)_2(C_1\text{-bpy})]^+$ were adsorbed separately onto SAP. When the two suspensions were mixed, the emission spectrum from the mixture was an overlap of that from each separate suspension. Moreover, no indication of energy transfer was observed in the absence of SAP for the same concentration ranges, which implies that the energy transfer occurs only when both the donor and acceptor molecules are adsorbed on the same clay particles. When a suspension of SAP with co-adsorbed $[Ir(dfppy)_2(C_1\text{-bpy})]^+$ (60% CEC) and $[Ir(piq)_2(C_1\text{-bpy})]^+$ (19% CEC) was centrifuged, no complex was detected in the supernatant. Therefore, no dissociation of an adsorbed complex occurred under the present conditions.

Comparing the results shown in Figure 2, it was deduced that the energy transfer efficiency of the hetero-chiral pair was ca. 2–5% more than that of the homo-chiral pair. The appearance of such stereoselectivity implies that energy transfer proceeded through the involvement of a contact pair of a donor and an acceptor, in which the molecules were able to detect their stereochemical characters.

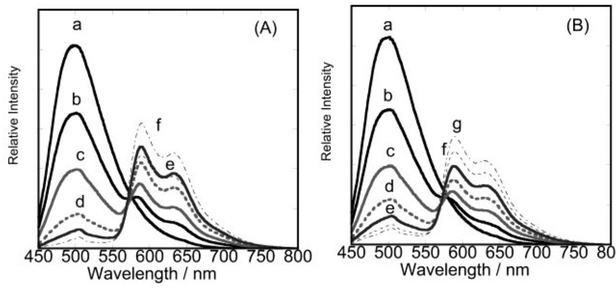

Figure 2. Change of emission spectra for $[Ir(dfppy)_2(C_1\text{-bpy})]^+$ ions adsorbed on SAP by the addition a methanol solution of $[Ir(piq)_2(C_1\text{-bpy})]ClO_4$. The enantiomers used were (A) Δ-$[Ir(dfppy)_2(C_1\text{-bpy})]^+/\Lambda$-$[Ir(piq)_2(C_1\text{-bpy})]^+$ and (B) Δ-$[Ir(dfppy)_2(C_1\text{-bpy})]^+/\Delta$-$[Ir(piq)_2(C_1\text{-bpy})]^+$. The medium was 4:1 (v/v) water/methanol. The concentration of SAP was 6.0×10^{-6} eq L^{-1} in terms of the CEC and the loading of $[Ir(dfppy)_2(C_1\text{-bpy})]^+$ was 30%. The loading of $[Ir(piq)_2(C_1\text{-bpy})]^+$ was (a) 0.0, (b) 0.8, (c) 1.9, (d) 3.7, (e) 5.6, (f) 7.5, and (g) 9.2%, respectively.

Similar experiments were performed at [SAP] = 3×10^{-6} eq L^{-1} and 1.2×10^{-5} eq L^{-1} for the same concentration ranges of donor and acceptor, the results of which are shown in the Supporting Information. The same enantioselectivity was deduced when the concentration of SAP was varied.

To observe the effects of alkyl chains in energy transfer, similar experiments were performed for the pairs of $[Ir(dfppy)_2(C_n\text{-bpy})]^+$ and $[Ir(piq)_2(C_n\text{-bpy})]^+$ (n = 12 and 19), and the results are shown in the Supporting Information. Energy transfer occurred less effectively, so that the emission from $[Ir(dfppy)_2(C_n\text{-bpy})]^{+*}$ remained appreciable, even at a D/A of ca. 2. The results imply that the alkyl chains play the role to inhibit direct contact between the central cores of the donor and acceptor molecules, rather than attract them through hydrophobic interactions. No stereoselectivity was observed for n = 12.

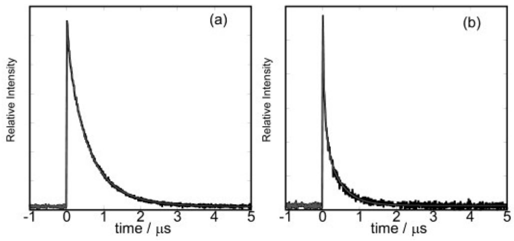

Figure 3. Lifetimes for the emission at 490 nm when a SAP suspension containing Λ-$[Ir(dfppy)_2(C_1\text{-bpy})]^+$ and Δ-$[Ir(piq)(C_1\text{-bpy})]^+$ was irradiated with a light pulse at 355 nm. The medium was 4:1 (v/v) water/methanol. The concentration of SAP was 6.0×10^{-6} eq L^{-1} CEC. (a) Λ-$[Ir(dfppy)_2(C_1\text{-bpy})]^+$ (Loading 30 %) (b) The loadings of Λ-$[Ir(dfppy)_2(C_1\text{-bpy})]^+$ and Δ-$[Ir(piq)_2(C_1\text{-bpy})]^+$ were 30% and 3.0%, respectively.

Analyses of the steady state emission spectra: The stationary emission spectra were analyzed using equation (2), which is derived on the basis of the Förster-type mechanism.[40]

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

Here $F_{ET}(\nu)$ denotes the total emission profile in the wavelength region from 450 to 700 nm. $F_{dfppy}{}^0(\nu)$ and $F_{piq}{}^0(\nu)$ represent the emission spectra of SAP suspensions containing the separate donors and acceptors, respectively. η_{ET} denotes the energy transfer efficiency from the donor* to the acceptor, and ϕ_{dfppy} is the quenching efficiency of the donor. ϕ_{piq} is introduced as an enhancement parameter by the SAP. A_{dfppy} and A_{piq} are the absorbance of the SAP suspensions containing the separate donors and acceptors, respectively, which were obtained by separate measurements. Equation (2) was applied to the observed stationary emission spectra to calculate η_{ET}. The efficiency was as high as 50% at a D/A of ca. 20. Therefore, the photon energy captured by a number of donor molecules was collected by a single acceptor molecule or the harvesting of photon energy was realized on a clay surface. The results of the investigated systems are summarized in Table 1.

Table 1. Summary of the energy transfer efficiency for pairs of donor/acceptor in a colloidal suspension of SAP.

Donor/Acceptor*	SAP/[eq L^{-1}] ×10^{-6}	η_{ET} at D/A = 8–15
Δ-DFPPY-C$_1$/Δ-PIQ-C$_1$	3	0.52
Δ-DFPPY-C$_1$/Λ-PIQ-C$_1$	3	0.57
Λ-DFPPY-C$_1$/Δ-PIQ-C$_1$	3	0.57
Λ-DFPPY-C$_1$/Λ-PIQ-C$_1$	3	0.52
Δ-DFPPY-C$_1$/Δ-PIQ-C$_1$	6	0.80
Δ-DFPPY-C$_1$/Λ-PIQ-C$_1$	6	0.85
Λ-DFPPY-C$_1$/Δ-PIQ-C$_1$	6	0.85
Λ-DFPPY-C$_1$/Λ-PIQ-C$_1$	6	0.81
Δ-DFPPY-C$_1$/Δ-PIQ-C$_1$	12	0.70
Δ-DFPPY-C$_1$/Λ-PIQ-C$_1$	12	0.75
Λ-DFPPY-C$_1$/Δ-PIQ-C$_1$	12	0.65
Λ-DFPPY-C$_1$/Λ-PIQ-C$_1$	12	0.62
Δ-DFPPY-C$_{12}$/Δ-PIQ-C$_{12}$	3	0.08
Δ-DFPPY-C$_{12}$/Λ-PIQ-C$_{12}$	3	0.15
Λ-DFPPY-C$_{12}$/Δ-PIQ-C$_{12}$	3	0.06
Λ-DFPPY-C$_{12}$/Λ-PIQ-C$_{12}$	3	0.10
DFPPY-C$_{19}$/PIQ-C$_{19}$	3	0.10

(*) DFPPY-C$_n$ and PIQ-C$_n$ denote [Ir(dfppy)$_2$(C$_n$-bpy)]$^+$ and [Ir(piq)$_2$(C$_n$-bpy)]$^+$ (n = 1, 12 and 19), respectively.

Dynamic aspects of energy transfer: The decay of emission from a SAP suspension containing Λ-[Ir(dfppy)$_2$(C$_1$-bpy)]$^+$ and Δ-[Ir(piq)$_2$(C$_1$-bpy)]$^+$ was monitored at 490 nm after irradiation of a light pulse at 355 nm. The transient curves shown in Figure 3 were analyzed on the assumption that they were the sum of two exponential components, represented as follows:

$$y = F_{fast}\exp(-t/\tau_{fast}) + F_{slow}\exp(-t/\tau_{slow}) \quad , \quad (3)$$

where τ_{fast} and τ_{slow} denote the fast and slow life times, and F_{fast} and F_{slow} denote the respective pre-exponential factors at 490 nm. The rate of energy transfer (k_{ET}) was obtained from the measured lifetime of Λ-[Ir(dfppy)$_2$(C$_1$-bpy)]$^{+*}$ according to equation (4):

$$k_{ET} = 1/\tau - 1/\tau_D, \quad (4)$$

where τ and τ_D denote the lifetimes of Λ-[Ir(dfppy$_2$(C$_1$-bpy)]$^{+*}$ in the presence and absence of Δ-[Ir(piq)$_2$(C$_1$-bpy)]$^+$, respectively. From the measurements of life time, η_{ET} was obtained according to the following equation:

$$\eta_{ET} = k_{ET}/(k_{NT} + k_{ET}), \quad (5)$$

where k_{NT} is equal to $1/\tau_D$. The decay curve consisted of two components; therefore, the analyses were performed independently for the fast and slow components. Figure 4 shows that η_{ET} increased with the acceptor concentration. The fast components gave higher η_{ET} than the slow components. As for the effect of a SAP amount, η_{ET} decreased with an increase of [SAP] at a constant D/A. Thus, a decrease of the surface densities of reactants resulted in a decrease of the energy transfer efficiency. η_{ET} was higher than 50% at a D/A of ca. 20; therefore, the harvesting of light energy was also confirmed by the transient measurements.

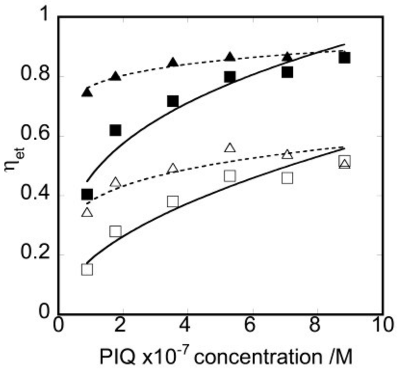

Figure 4. Dependence of η_{ET} on the concentration of [Ir(piq)$_2$(C$_1$-bpy)](ClO$_4$)$_n$ added. The concentration of SAP was 6×10^{-6} M (triangles) and 1.2 x10^{-5} M (squares) CEC and the loadings of [Ir(dfppy)$_2$(C$_1$-bpy)]$^+$ and [Ir(piq)$_2$(C$_1$-bpy)]$^+$ were 30% and 15%. Solid and open symbols represent the fast and slow lifetimes, respectively.

Model for harvesting light energy on a clay surface: According to the Förster-type resonance mechanism, the Förster radius R_0 in equation (1) is expressed in terms of the overlap integral of the spectral profile of the emission from a donor with that of the absorption by an acceptor.[40] R_0 is estimated to be 2.6 nm for the [Ir(dfppy)$_2$(C$_1$-bpy)]$^{+*}$/[Ir(piq)$_2$(C$_1$-bpy)]$^+$ pair and 2.0 nm for the [Ir(dfppy)$_2$(C$_1$-bpy)]$^{+*}$/[Ir(dfppy)$_2$(C$_1$-bpy)]$^+$ pair (Supporting Information).

Under the present experimental conditions, the SAP suspension was stable without coagulation. Thus, it was assumed that the clay was exfoliated into single layers and that the [Ir(dfppy)$_2$(C$_1$-bpy)]$^+$ and [Ir(piq)$_2$(C$_1$-bpy)]$^+$ cationic complexes were both adsorbed on the surface of the clay layers through electrostatic interaction. On the basis of the elemental compositions of SAP (Experimental Section), one negative charge occupies an area of 0.60 nm^2 on a phyllosilicate surface. Such an area occupied by one negative charge is denoted as an adsorption site or simply a site. When two Ir(III) complexes are adsorbed at adjacent sites, they are separated by ca. 0.8 nm. η_{ET} in equation (1) is estimated to be 0.8; therefore, the energy transfer takes place efficiently. When the complexes are adsorbed at sites adjacent to the nearest neighbours, η_{ET} is estimated to be less than 0.1, which contributes little to the energy transfer.

The distribution of donor and acceptor molecules is simulated under the assumption that both are adsorbed randomly at the sites on a surface. Figure 5 shows two examples of distribution when the donor (empty circles) and acceptor (filled circle) are adsorbed at loadings of 25 and 1%, respectively. Among the donors, one excited donor is represented by a filled square. Assuming a random distribution, the possibility that an acceptor molecule is located next to the excited donor is calculated to be 0.013. If energy transfer occurs only for such a direct pair, then η_{ET} is calculated to be 0.010, which is much lower than that observed experimentally (0.45).

One rationale for the observed high efficiency is that the photon energy captured by the initially excited donor migrates among the donors until it reaches a site next to an acceptor. Such migration of energy is possible because both donor/donor and donor/acceptor pairs possess sufficient R_o for energy transfer to occur. Based on this assumption, the distribution shown in the left panel of Figure 5 allows the energy transfer to occur (or "**ET**-case"), while the distribution shown in the right panel of Fig. 5 does not allow energy transfer (or "**NET**-case"). The fractions of "**ET**-cases" were obtained out of 100 randomly generated distributions at various D/A, and the results are shown in Fig. 6. The fraction of "**ET**-cases" was as high as 70% at D/A = 30 and increased with a decrease of D/A. Thus, the observed high efficiency of energy transfer suggests the migration of light energy among the neighbouring donors until it reaches an acceptor. The harvesting of light energy is thus considered to occur on a clay surface by this mechanism.

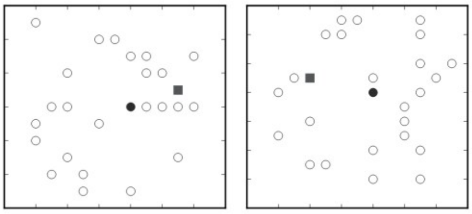

Figure 5. Examples of random distributions of donors (empty circles) and an acceptor molecule (filled square). The excited donor molecule is represented by a filled circle; (left) the excitation energy migrated from an excited donor to an acceptor ("**ET**-case"), and (right) the excitation energy did not reach an acceptor ("**NET**-case").

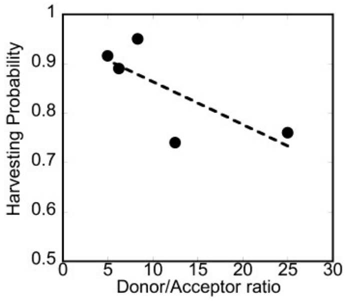

Figure 6. Dependence of the percentage fraction of "**ET**-cases" on D/A. The calculation was made for 100 randomly generated distributions.

Experimental Section

Materials:$[Ir(dfppy)_2Cl]_2$ (dfppyH = 2-(2',4'-difluorophenyl)pyridine) and $[Ir(piq)_2Cl]_2$ (piqH = 1-phenyisoquinoline) were purchased from Furuya Metal Co., Ltd., Japan. The dialkylated 4,4'-bipyridines (C_n-bpy = 4,4'-dialkyl-2,2'-bipyridine; dialkyl = dimethyl (C_1), didodecyl (C_{12}), and dinonyldecyl (C_{19})) were synthesized and characterized as reported previously.[25] The cationic cyclometalated Ir(III) complex $[Ir(dfppy)_2(C_n\text{-bpy})]ClO_4$ was prepared by refluxing $[Ir(dfppy)_2Cl]_2$ with an equal amount of C_n-bpy in glycerol at 180 °C for 6 h. The compound was purified chromatographically by elution on a high performance liquid chromatography (HPLC) column (CAPCELL PAK C18, MG, Shiseido Inc. Ltd., Japan) with 4:1 (v/v) methanol/chloroform as the eluent. Characterization of the product was conducted using ^1H NMR in $CDCl_3$ and mass spectroscopy.[32] Synthetic saponite (SAP; Kunimine Ind. Co.) was used as the adsorbent, of which the elemental composition and cation-exchange capacity (CEC) were stated to be $[(Na_{0.25}Mg_{0.07})(Mg_{2.98}Al_{0.01})(Si_{3.6}Al_{0.4})O_{10}(OH)_2)]$ and 80 meq per 100 g, respectively.[32] The average SAP particle size was reported to be ca. 20 nm.

Optical resolution: The prepared compounds were eluted on a chiral column (CHIRALPACK IA, Daicel, Japan) with acetonitrile containing 0.1% of diethylamine and trifluoroacetic acid as an eluent at a flow rate of 0.5 mL min^{-1}. The elution was monitored at 430 nm.

Instrumentation: ^1H NMR and ^{13}C NMR spectra were recorded with a spectrometer (AVANCE400, Bruker). UV-visible electronic spectra were recorded with UV-vis spectrophotometer (UV-2450, Shimadzu). Emission spectra were measured with a fluorophotometer (RF-5300PC, Shimadzu). Circular dichroism spectra were measured with a polarimeter (J-820, Jasco, Japan). The lifetime of emission was measured with a photoluminescence measurement instrument (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 curve was obtained by averaging 130 pulsed signals. The curves were analyzed under the assumption of multi-exponential decays. Centrifugation of a suspension of SAP with co-adsorbed [Ir(dfppy)$_2$(C$_1$-bpy)]$^+$ (60% CEC) and [Ir(piq)$_2$(C$_1$-bpy)]$^+$ (19% CEC) was performed with a microcentrifuge (RevSpin RS-102, Revsci) at 10000 rpm for 30 min.

Conclusions

For the system where both donors and acceptors were co-adsorbed by clay particles, small but definite enantioselectivity was observed in the energy transfer processes, which indicates the participation of a contact donor/acceptor pair. Energy transfer occurred efficiently with a D/A of ca. 20. A mechanism for the harvesting of photon energy was proposed, in which light energy migrates among donor molecules on a clay surface until it reaches an acceptor molecule. The results represent a benchmark for the construction of systems with efficient light harvesting properties by the use of clay minerals.

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