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Chiral Phosphorescent Probes for Amino Acids: Hybrids of Iridium(III) Complexes with Synthetic Saponite

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An attempt of developing a chiral luminescent probe for amino acids was described. Two types of chiral iridium(III) complexes were synthesized: [Ir(dfppy)$_2$(*R*-pep-bpy)]$^+$ (dfppyH = 2-(2',4'-difluorophenyl)pyridine; *R*-pep-bpy = 4,4'-bis((*R*-1,2-dimethylpropyl)aminocarbonyl-2,2'-bipyridine) and [Ir(piq)$_2$(*R*-pep-bpy)]$^+$ (piqH = 1-phenyisoquinoline) In both complexes, amido groups (*R*-pep-) were attached to 2,2'-bipyridine with an intension of increasing affinity towards an amino acid. The complexes were optically resolved on a chiral column. When the complexes were adsorbed by the colloidal particles of synthetic saponite, they were highly emissive even in a medium containing water. The remarkable quenching of emission was observed for the combination of [Ir(dfppy)$_2$(*R*-pep-bpy)]$^+$ and tryptophan methyl ester. By use of the enantiomeric complexes, the possibility of enantioselective quenching was examined for various amino acid derivatives.

Introduction

Cyclometalated iridium(III) complexes have recently attracted an extensive attention as a potentially useful photosensitizer with high quantum yield and long lifetime.[1-12] There have been reported several attempts of using luminescent iridium(III) complexes within biological systems.[13-24] For example, the patterning of cancer tissue in living cells was performed by use of luminescent Ir(III) complexes.[17] An iridium(III) complex capable of coordinating histidine was used as a selective sensor of histidine residues in proteins. It remains to be clarified yet how the emission behaviours of iridium complexes are affected by interacting with amino acids particularly as to chirality effects.

The present work studied the interaction of chiral iridium(III) complexes with amino acids or their derivatives. Generally an iridium(III) complex reduces its emitting properties in a medium containing water. It was found previously that emission capability recovered when the complexes were adsorbed by a colloidal particle of a clay mineral.[25-29] Based on this fact, we investigated energy transfer by co-adsorbing two iridium(III) complexes with different emitting properties onto a colloidal particle of synthetic saponite.[25] Efficient transfer of photon energy occurred in the concentration range as low as 10^{-6} M. The accumulation of a donor and an acceptor of light energy on the same clay particles was considered to be a main factor to achieve high efficiency.

The present work intended to develop a chiral photo-sensor of amino acids by use of the hybrid of a clay and an iridium(III) complex. Clay minerals are harmless for bioorganisms in spite of their high capability in adsorption. Such a sensor would be useful to detect a target amino acid *in situ* in living cells. Our purpose at the present stage was to study the interaction of iridium(III) complexes with amino acids as a benchmark for their selective sensing.

Results and Discussion

Preparation and optical properties of Ir(III) complexes: Chart 1 shows the molecular structures of Ir(III) complexes used in the present work. [Ir(dfppy)$_2$(*R*-pep-bpy)]$^+$ (dfppyH = 2-(2',4'-difluorophenyl)pyridine; *R*-pep-bpy = 4,4'-bis((*R*-1,2-dimethylpropyl)aminocarbonyl-2,2'-bipyridine; denoted as **Ir-1**) and [Ir(piq)$_2$(*R*-pep-bpy)]$^+$ (piqH = 1-phenyisoquinoline; denoted as **Ir-2**) were used as an emitting molecule. The chiral amido group, *R*-pep-, was attached to 2, 2'-bipyridine in order

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†Electronic Supplementary Information (ESI) available: ^{1}HNMR and mass spectra; Chromatogram for diastereomeric separation; Quenching of Ir-1 and Ir-2 by *RS*-tryptophan methyl ester in methanol; Dynamic Quenching of Ir-1 by *RS*-tryptophan methyl ester in synthetic saponite suspensions; Quenching effects of amino acid methyl esters; Enantiomeric effects of quenching for pairs for *R*- or *S*-tryptophan methyl ester and Δ- or Λ- **Ir-1**; Chromatogram for optical resolution and CD spectra of DNB-al-Me; The transient measurements of the emission from **Ir-1** in the presence of *R*- or *S*-DNB-al-Me; The calculation of quantum yield of emission. See DOI: 10.1039/x0xx00000x

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to enhance affinity towards amino acids through the formation of hydrogen bonding. The molecules were prepared by reacting a dimer, [{Ir(dfppy)Cl}$_2$] or [{Ir(piq)Cl}$_2$], with *R*-pep-bpy in glycerol. The products were identified from ^{1}H-NMR and mass spectroscopy (ESI†).

The diastereomeric mixtures (Δ- and Λ-*R*-isomers) were eluted on a chiral column (Experimental Section). A typical chromatogram is shown in ESI†. Figures 1 and 2 show the UV-vis and circular dichroism (CD) spectra of the separated diastereomers, respectively. 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.[25,30]

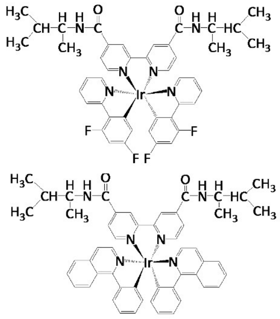

Chart 1. The molecular structures of Ir(III) complexes used in the present work: (upper) [Ir(dfppy)$_2$(*R*-pep-bpy)]+ (denoted as **Ir-1**) and (lower) [Ir(piq)$_2$(*R*-pep-bpy)]$^+$ (denoted as **Ir-2**).

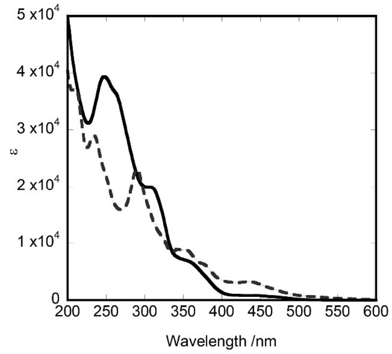

Figure 1. The UV-vis spectra of the perchlorate salts of **Ir-1** (solid) and **Ir-2** (dotted) dissolved in methanol.

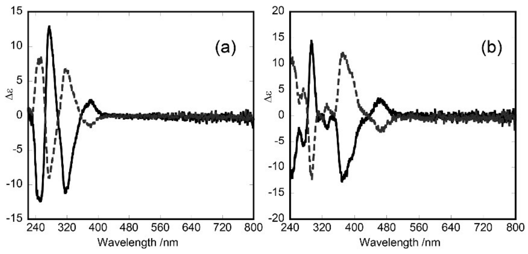

Figure 2. The CD spectra of the perchlorate salts of the diastereomers of (a) **Ir-1** (left) and (b) **Ir-2** (right) dissolved in methanol. The solid and dotted curves are for the Δ- and Λ-isomers, respectively.

Emission properties in solutions: Figures 3(a) and (b) show the emission spectra of **Ir-1** and **Ir-2** in various media, respectively. Both complexes were emissive in chloroform with the quantum yield (denoted as Q.Y.) of 0.35 and 0.02 as shown by curves (I), respectively. The emission was assigned to the transition from the mixed state of ^{3}MLCT and ^{3}LC.[4] Their emission ability decreased in a mixture of 3:1 (v/v) water/methanol to Q. Y. = 0.06 and 0.001 as shown by curves (II), respectively. When synthetic saponite (denoted as SAP) was present at the loading level of c.a. 7 % in the same medium, the emission recovered remarkably up to Q.Y. = 0.21 and 0.01 as shown by curves (III), respectively. The observed enhancement of emission was ascribed to the partial elimination of water molecules around the iridium(III) complexes adsorbed on the surface of synthetic saponite. The displacement of the emission peak towards the shorter wavelength might be caused by the electric field effect arising from the negative charge of a synthetic saponite layer in stabilizing the ground state of an adsorbed Ir(III) molecule.

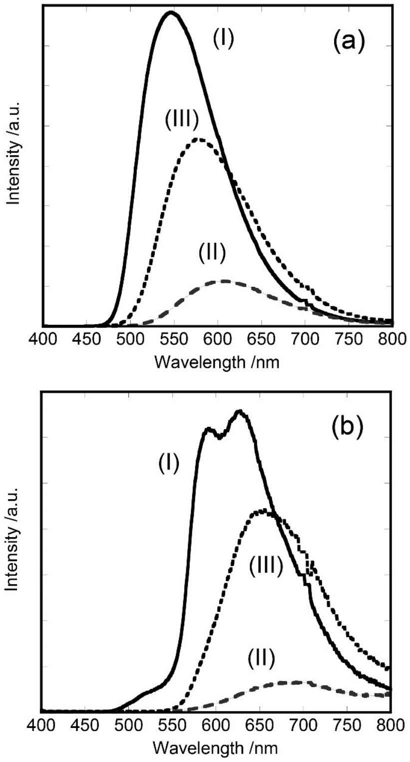

Figure 3. The emission spectra of the perchlorate salts of (a) **Ir-1** (1.8×10^{-5} M) (left) and (b) **Ir-2** (1.5×10^{-5} M) (right). The medium was (I) chloroform, (II) 3:1 (v/v) water/methanol and (III) 3:1 (v/v) water/methanol containing SAP (2.5×10^{-4} eqL^{-1}). The excitation wavelength was 350 nm.

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Effects of amino acids on stationary emission: The effects of amino acids on emission were investigated. SAP was dispersed in a mixture of 3:1 (v/v) water/methanol. The concentration of SAP was adjusted at [SAP] = 2.5×10^{-4} eqL^{-1} in terms of the cation-exchange capacity (CEC). Racemic **Ir-1** or **Ir-2** in a methanol solution was added to the suspension under rigorous stirring to a loading level of ca. 7 % of CEC. Thereafter a methanol solution of amino acid methyl ester (**aa**) was added. The emission spectra were measured at various amounts of **aa**.

Among the investigated **aa**'s, tryptophan methyl ester (denoted as tryp-Me) exhibited remarkable influence on the emission of **Ir-1**. Figures 4(a) and (b) show the change of the emission spectra on adding various amounts of racemic tryptophan methyl ester (denoted as *RS*-tryp-Me) to a dispersion containing SAP/**Ir-1** and SAP/**Ir-2**, respectively. In case of SAP/**Ir-1**, the intensity of emission decreased with the increase of the added amount of *RS*-tryp-Me, while no change of the emission spectrum was observed in case of SAP/**Ir-2**. The results implied that *RS*-tryp-Me acted as a quencher for **Ir-1**, but not for **Ir-2**.

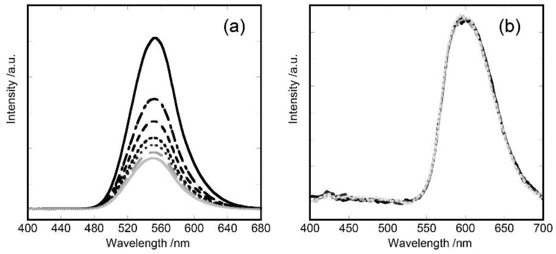

Figure 4. The emission spectra of (a) SAP/**Ir-1** (left) and (b) SAP/**Ir-2** (right) (both 7 % loading) in 3:1 (v/v) water/methanol containing SAP (2.5×10^{-4} eqL^{-1}), respectively. The concentration of added *RS*-tryp-Me is indicated in Figure 5.

The quenching effect in Figure 4 (a) was analysed by plotting I_o/I against [aa] (Stern-Volmer plots) (Figure 5). Here I_o and I are the heights of the emission peak in the absence and presence of *RS*-tryp-Me, respectively. Since the plot was curved, two quenching parameters were introduced in order to reproduce the experimental results according to the expressions below:

$$\frac{I_0}{I}=[\frac{f_1}{1+K_{sv1}C}+\frac{f_2}{1+K_{sv2}C}]^{-1}$$

$$f_1+f_2=1$$

$$K_{svav}=f_1\times K_{sv1}+f_2\times K_{sv2} \qquad (1)$$

In the above equations, K_{SV1} and K_{SV2} are two quenching parameters and f1 and f2 their fractions, respectively. K_{svav} is the average value of the quenching constants, which represents the slope of the Stern-Volmer plot at [*RS*-tryp-Me] = 0 (Fig. 5). K_{SV1} and K_{SV2} were obtained to be 500 and 15000 M^{-1}, leading to 8400 M^{-1} for K_{svav}. The origin for the presence of two quenching paths might be sought in the difference in adsorption states. SAP was exfoliated mostly to a single layer. Some layers, however, might be double or triple layers before complete exfoliation. Accordingly iridium(III) complexes were adsorbed either on an external surface or between the interlayer space of layers. It was expected that quenching efficiency was more rapid for an iridium (III) complex adsorbed on an external surface than for an iridium complex adsorbed between the interlayer spaces. These situations might result in the appearance of two routes for quenching processes. For comparison, the quenching of the same system was investigated in methanol. In such a homogeneous medium, the Stern-Volmer plot was linear, giving a single value for K_{SV} (ESI†). Ksv in methanol was obtained to be 235 M^{-1} that was lower than those of the colloidal clay systems. The above results implied that the adsorption by synthetic saponite resulted in enhancing both the emission intensity and the quenching rate.

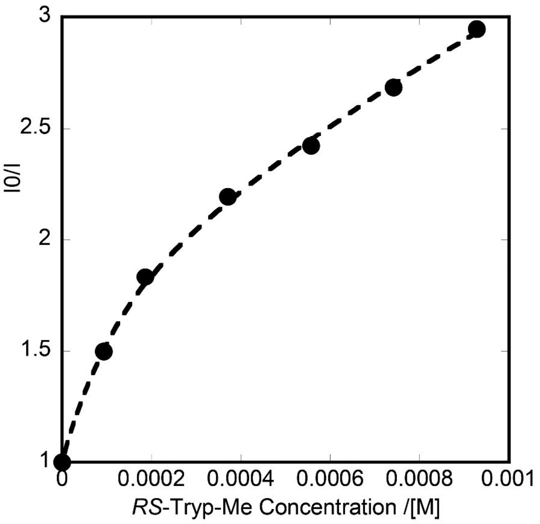

Figure 5. The Stern-Volmer plots for the quenching effect of *RS*-trp-Me on the emission from SAP/**Ir-1:** [**Ir-1**] = 2.0×10^{-5}M and [SAP] = 2.5×10^{-4} eq L^{-1}. The solvent was 3:1 (v/v) water/methanol. The dotted curve is the simulated one assuming two quenching parameters (see the text).

The effect on the emission from **Ir-1** was investigated by using the methyl esters of other amino acids. The results are summarized in in ESI†. According to the results, tryp-Me was most effective in quenching the emission from SAP/**Ir-1**. One possibility for high quenching efficiency by tryp-Me was that an indole moiety acted as an energy acceptor from excited **Ir-1**. The electronic absorption for exciting an indole group extended to ca. 400 nm in a polar solvent, which was close to

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the edge of the emission band from **Ir-1**. Phenylalanine methyl ester acted as a quencher but was less effective than tryp-Me by more than 7 times. Little quenching was observed for alanine, valine and isoleucine methyl esters. In case of histidine methyl ester, emission increased slightly to give negative K_{SV}. The results suggested that this molecule affected the adsorption state of **Ir-1** in the ground states.

The effect was studied for **Ir-1** on adding free amino acids. No quenching occurred for alanine, histidine and tryptophan. It was interpreted that a free amino acid was adsorbed by a clay particle and fixed firmly so that it interacted with iridium(III) complexes to a negligible extent. When *N*-3, 5-dinitrobenzoyl amino alanine methyl ester (denoted as DNB-al-Me) was added, efficient quenching occurred. The details are described in the succeeding section.

Other emitting Ir(III) complexes were investigated by using *RS*-tryp-Me as a quencher. As is summarized in Table 1, efficient quenching was achieved only for the iridium(III) complexes with fluorinated ligands. One reason was that the introduction of fluorine atoms in ligands resulted in the elongation of the life-time of an excited state. As described in the succeeding section, the quenching by *RS*-tryp-Me occurred effectively only when the lifetime of an excited Ir(III) complex was longer than 1 μs.

Table 1. The quenching parameter (KSV) of iridium(III) complexes for tryptophan methyl ester as an quencher.

Complex	K_{SV} (M^{-1})
$[Ir(ppy)_2(dmbpy)]^+$	200
$[Ir(ppy)_2(C_9\text{-}bpy)]^+$	150
$[Ir(dfppy)_2(C_9\text{-}bpy)]^+$	4500
$[Ir(piq)_2(C_9\text{-}bpy)]^+$	20
Ir-1	8400

*ppy (2-phenylpyridine), dmbpy(4,4'-dimethylbipyridine), C9-bpy (4,4'-dinonylbipyridine)

*The slope of the Stern-Volmer plots for the quenching effect of trp-Me on the emission from iridium(III) complexes: [iridium(III) complex] = 2.0×10^{-5} M, [SAP] = 2.5×10^{-6} eq L^{-1}, (tryp-Me) = 1 – 6 $\times10^{-3}$ M and the solvent was 3:1 (v/v) water/methanol.

Transient emission properties: The decay rates of emission from the excited iridium(III) complexes were measured on a 3:1 (v/v) water/methanol suspension containing SAP/**Ir-1** or SAP/**Ir-2** (Figure 6).

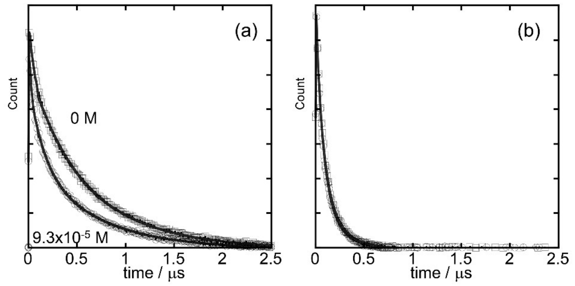

Figure 6. Decay curves of the emission at 550 nm for **Ir-1** and 600 nm for **Ir-2** when a SAP suspension containing (a) **Ir-1** or (b) **Ir-2** was irradiated with a light pulse at 355 nm: [SAP] = 1.5×10^{-4} eq L^{-1}, [**Ir-1**] = 2.0×10^{-5} M, [**Ir-2**] = 2.0×10^{-5} M and the medium 3:1 (v/v) water/methanol. The concentration of *RS*-tryp-Me was 0 M (square) and 9.3×10^{-5} M (circle) for **Ir-1** respectively. The concentration of *RS*-tryp-Me was 3.7×10^{-4} M (square) and 9.3×10^{-4} M (circle) for **Ir-2** respectively. The grey lines indicate the fitting curves according to equation (2) in the text.

The decay curves were analysed in terms of the sum of two exponential decays:

$$y = F_1 \exp(-t/\tau_1) + F_2 \exp(-t/\tau_2) \quad , \tag{2}$$

in which τ_1 and τ_2 are the fast and slow relaxation times and F_1 and F_2 their fractions, respectively. The decay curve was obtained by varying the added concentration of RS-tryp-Me. In case of Ir-1, both τ1 and τ2 decreased the increase of [RS-tryp-Me]. For both relaxation paths, the following relation was assumed to hold:

$$\tau_0/\tau = 1 + \tau_0 k_q[\text{tryp-Me}], \tag{3}$$

in which τ_0 is lifetime in the absence of *RS*-tryp-Me and k_q the bimolecular quenching rate constant, respectively. The plots according to equation (3) are given in ESI†. From the results, k_q and $\tau_0 k_q$ were obtained as given in Table 2. It was concluded that the values of $\tau_0 k_q$ for the fast and slow processes were of the same order in magnitude as K_{SV2} and K_{SV1} obtained from the stationary measurements, respectively.

In case of **Ir-2**, the decay curve was unaffected on adding 3.7×10^{-4} M of *RS*-tryp-Me. This was consistent with the results of stationary measurements in which no quenching took place for this complex. The above results lead to the following conclusion as to the occurrence of quenching: in case of **Ir-1**, its lifetime was long enough for deactivation of photon energy to occur, while in case of **Ir-2**, the lifetime was too short and the collisional intermediate returned to the ground state before the occurrence of quenching.

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Table 2. The kinetic results for the effects of *RS*-tryp-Me on the emission from SAP/**Ir-1**: [SAP] = 1.5×10^{-6} eq L^{-1}, [**Ir-1**] = 2×10^{-5} M and the medium 3:1 (v/v) water/methanol.

$\tau o/\tau$ vs. *RS*-tryp-Me concentration	τ_0 (μs)	F	k_q [M^{-1} s^{-1}]	$\tau_0 k_q$ (or K_{SV}) [M^{-1}]	K_{svav} [M^{-1}]
Fast lifetime(τ_1)	0.22	0.30	$1.60\text{x}10^{10}$	3650	1500
Slow lifetime(τ_2)	0.75	0.70	$8.24\text{x}10^{8}$	615	

Enantioselectivity: The possibility of enantioselectivity was examined by using the pure enantiomer of **Ir-1** as an emitter and *R*- or *S*-tryp-Me as a quencher. The efficiency of quenching was compared among the following four pairs: Δ-**Ir-1**/*R*-tryp-Me, Δ-**Ir-1**/*S*-tryp-Me, Λ-**Ir-1**/*S*-tryp-Me and Λ-**Ir-1**/*R*-tryp-Me. As shown in ESI†, all of these pairs gave nearly the same Stern-Volmer plots, leading to the conclusion that these pairs exhibited no observable stereoselectivity. Probably the quenching occurred even when a quencher was located too far from the chiral part of **Ir-1**.

In order to pursue the possibility of enantioselectivity further, DNB-al-Me was chosen as a quencher. The reason was that DNB-al-Me was adsorbed stereoselectively by an ion-exchange adduct of clay/Δ-$[Ru(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) (experimental section) (ESI†). It was noted that two molecules, $[Ru(phen)_3]^{2+}$ and **Ir-1**, both belonged to the tris(chelated) complexes with polypyridyl ligands. The quenching of emission from **Ir-1** was investigated for the following four pairs: Λ-**Ir-1**/*S*-DNB-al-Me, Λ-**Ir-1**/*R*-DNB-al-Me, Δ-**Ir-1**/*S*-DNB-al-Me and Δ-**Ir-1**/*R*-DNB-al-Me. As shown in Figure 7, they gave curved Stern-Volmer plots so that the results were analysed in terms of two quenching constants (eq. (1)).

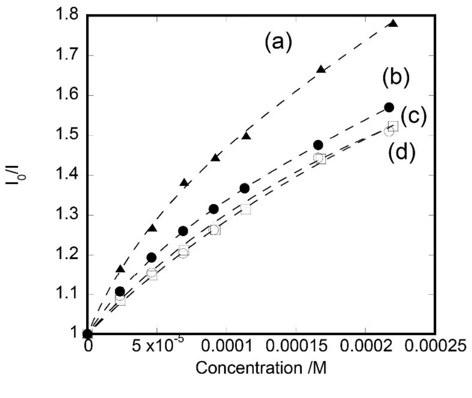

Figure 7. The Stern-Volmer plots for the quenching effect of DMB-al-Me on the emission from **Ir-1**;(a)Λ-**Ir-1**/*S*-DNB-al-Me,(b)Λ-**Ir-1**/*R*-DNB-al-Me,(c)Δ-**Ir-1**/*S*-DNB-al-Me and (d)Δ-**Ir-1**/*R*-DNB-al-Me: [SAP]= 2.5×10^{-4} eq L^{-1} and [Ir-1] = 2.0×10^{-6} M. The solvent was 3:1 (v/v) water/methanol.

Table 3. The quenching parameter (K_{SV}) of the emission from **Ir-1** for *R*- or *S*-DNB-al-Me as an quencher.

	(a)	(b)	(c)	(d)
K_{sv1}	1325	979	167	0
K_{sv2}	22092	15542	5783	6916
f_1	0.65	0.69	0.41	0.43
f_2	0.35	0.31	0.59	0.57
K_{svav}	7836	4895	3409	3940

(*) The columns denoted in the first row corresponded to (a) Λ-**Ir-1**/*S*-DNB-al-Me, (b) Λ-**Ir-1**/*R*-DNB-al-Me, (c) Δ-**Ir-1**/*S*-DNB-al-Me and (d) Δ-**Ir-1**/*R*-DNB-al-Me in Figure 7. The average Stern-Volmer constant (K_{svav}) corresponds to the initial slope at the zero concentration of a quencher.

According to Table 3, Λ-**Ir-1**/*S*-DNB-al-Me gave 1.2 times higher K_{SVav} than Λ-**Ir-1**/*R*-DNB-al-Me, while there was no significant difference between Δ-**Ir-1**/*S*-DNB-al-Me and Δ-**Ir-1**/*R*-DNB-al-Me. In other words, Λ-*R*-**Ir-1** is more effective than Δ-R-**Ir-1.** The results implied that the chiral discrimination was achieved under the coupled contribution of $\Delta\Lambda$ and *RS* chiralities. Enantioselectivity for the above systems was examined by dynamic measurements. The decay of **Ir-1** was compared among three cases of (1) Λ-**Ir-1,** (2) Λ-**Ir-1**/*S*-DNB-al-Me and (3) Λ-**Ir-1**/*R*-DNB-al-Me. As given in ESI†, the decay rate from Λ-**Ir-1**/SAP increased on adding DNB-al-Me. The effect was higher for *S*-DNB-al-Me than for *R*-DNB-al-Me. Thus the same enantioselectivity was confirmed by both the stationary and dynamic measurements.

The enantioselectivity observed for the cases of DNB-al-Me suggested that the phenyl group in DNB-al-Me was attracted by the phenylpyridyl groups in **Ir-1** through $\pi-\pi$ interaction and that the stereoselectivity appeared through the interaction at the chiral amido groups in **Ir-1**.

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. 4,4'-Bis((*R*-1,2-dimethylpropyl)aminocarbonyl-2,2'-bipyridine (*R*-pep-bpy) was synthesized according to the reported method.[31] The compound was identified by 1H-NMR spectroscopy. The cationic cyclometalated Ir(III) complex, $[Ir(dfppy)_2(R\text{-Pep-bpy})]ClO_4$, was prepared by refluxing $[Ir(dfppy)_2Cl]_2$ with an equal amount of *R*-Pep-bpy in glycerol at 180 °C for 12 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. $[Ir(piq)_2(R\text{-Pep-bpy})]ClO_4$ was synthesized in the

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same way by reacting $[Ir(piq)_2Cl]_2$ with *R*-Pep-bpy. The compounds were identified using ^{1}H-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.[25] The average SAP particle size was reported to be ca. 20 nm.

Amino acids were used as purchased from Wako Pure Chemicals. Methyl esters were prepared by reacting amino acid with thionyl chloride in methanol. DNB-al-Me was prepared by reacting *RS*-alanine methyl ester with 3, 5-dinitrobenzoyl chloride in dehydrated tetrahydrofuran. The racemic mixture was optically resolved chromatographically. The chromatogram and the CD spectra of the enantiomers are given in ESI$^+$.

Diastereomeric separation: The prepared Iridium(III) 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: ^{1}H-NMR spectra were recorded with a spectrometer (AVANCE400, Bruker). UV-visible electronic spectra were recorded with UV-vis spectrophotometer (U-2810, Hitachi Ltd., Japan). Emission spectra were measured with a fluorophotometer (FP-6500, Jasco, Japan). 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. The wavelength of excitation (λ_{ex}) was 430 nm. Φ (quantum yield) was calculated according ESI†. The value of Φ for $[Ru(bpy)_3]^{2+}$ was taken to be 0.028 from the literature.[33]

Conclusions

The effects of amino acids were studied on the emission from two kinds of iridium(III) complexes in a colloidal dispersion of synthetic saponite. Both complexes (denoted as **Ir-1** and **Ir-2**) possessed a 2,2'-bipyridine ligand attached with two amido groups in order to enhance affinity towards amino acids. The complexes were adsorbed by a colloidal particle of synthetic saponite. Such hybridization resulted in maintaining high emission level even in a medium containing water. Among the investigated amino acid methyl esters, tryptophan methyl ester exhibited remarkable quenching effects on the emission from **Ir-1**. The stereoselectivity towards *N*-3, 5-dinitrobenzoyl alanine methyl ester appeared only through the interplay of two chiral centers, or *RS* in the ligand and $\Delta\Lambda$ in the metal center, but not through each chirality alone for **Ir-1**. The results promised a possibility of developing a photo-sensor of amino acids in biological systems.

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The effect of amino acids on the emission properties of iridium(III) complexes with a colloidal particle of synthetic saponite was investigated with a purpose of developing a photo-sensor of amino acids, leading to the conclusion that the interplay of chiral coordination structure and asymmetric structure of a carbon atom achieved the enantioselectivity.

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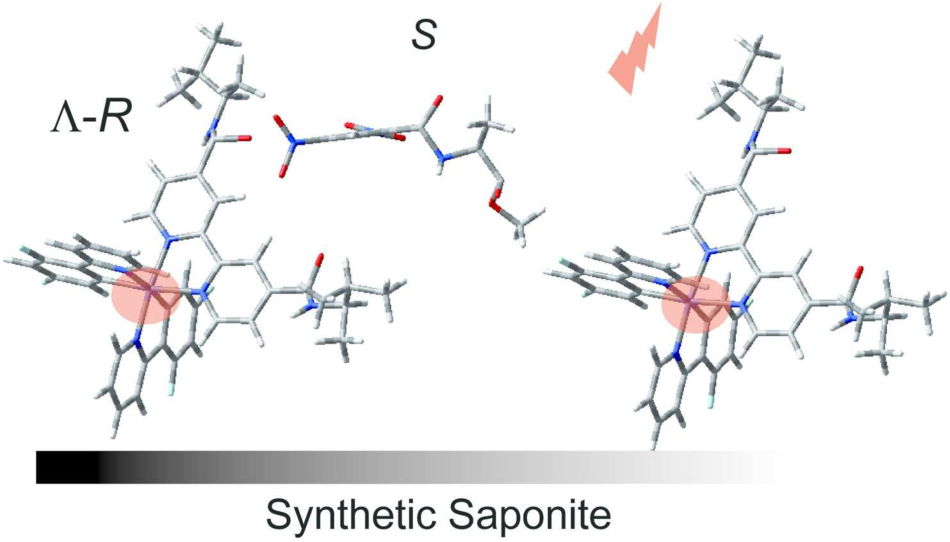

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