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Specific Chiral Sensing of Amino Acids Using Induced Circularly Polarized Luminescence of Bis(diimine)dicarboxylic Acid Europium(III) Complexes

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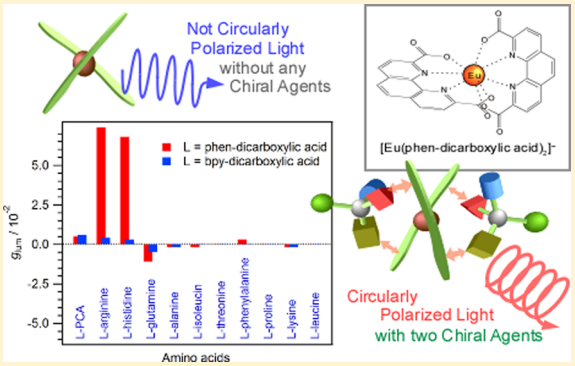
Supporting Information

ABSTRACT: The circularly polarized luminescence (CPL) from $[Eu(pda)_2]^-$ (pda = 1,10-phenanthroline-2,9-dicarboxylic acid) and $[Eu(bda)_2]^-$ (bda = 2,2′-bipyridine-6,6′-dicarboxylic acid) in aqueous solutions containing various amino acids was investigated. The europium(III) complexes exhibited bright-red luminescence assignable to the f−f transition of the Eu^{III} ion when irradiated with UV light. Although the luminescence was not circularly polarized in the solid state or in aqueous solutions, in accordance with the achiral crystal structure, the complexes exhibited detectable induced CPL (iCPL) in aqueous solutions containing chiral amino acids. In the presence of L-pyrrolidonecarboxylic acid, both $[Eu(pda)_2]^-$ and $[Eu(bda)_2]^-$ showed similar iCPL intensity ($g_{lum} \sim 0.03$ for the $^5D_0 \rightarrow {}^7F_1$ transition at 1 mol·dm^{-3} of the amino acid). On the other hand, in the presence of L-histidine or L-arginine, $[Eu(pda)_2]^-$ exhibited intense CPL ($g_{lum} \sim 0.08$ for the $^5D_0 \rightarrow {}^7F_1$ transition at 0.10 mol·dm^{-3} of the amino acid), whereas quite weak CPL was observed for $[Eu(bda)_2]^-$ under the same conditions ($g_{lum} < 0.01$). On the basis of analysis of the iCPL intensities in the presence of 12 amino acids, $[Eu(pda)_2]^-$ was found to be a good chiral CPL probe with high sensitivity (about 10^{-2} mol·dm^{-3}) and high selectivity for L-histidine at pH 3 and for L-arginine at pH 7. The mechanism of iCPL was evaluated by analysis of the fine structures in the luminescence spectra and the amino acid concentration dependence of g_{lum}. For the $[Eu(pda)_2]^-$−histidine/arginine systems, the europium(III) complexes possess coordination structures similar to that in the crystal with slight distortion to form a chiral structure due to specific interaction with two zwitterionic amino acids. This mechanism was in stark contrast to that of the europium(III) complex−pyrrolidonecarboxylic acid system in which one amino acid coordinates to the Eu^{III} ion to yield an achiral coordination structure.



INTRODUCTION

The detection and recognition of molecular chirality is relevant to a wide range of scientific fields including chemistry, biology, and medical science. The development of methods for the detection of chiral species is one of the central issues in these fields. In particular, in vivo imaging of chiral species in living cells may provide a means for an in-depth understanding of biochemical systems and the development of relevant nanotechnologies.[1−9]

Although both circular dichroism (CD) and circularly polarized luminescence (CPL) spectroscopy may be used to detect chiral species, CPL is superior as a highly spatially resolved spectroscopic technique relative to CD[9−11] because the use of luminescence probes facilitates the application of commonly utilized microscopic techniques.[12−15]

Rare-earth complexes are advantageous as luminescence probe molecules for such chiral sensing because their f−f transitions have an optical anisotropy factor (g value) that is potentially much higher than those of organic compounds.[14,16−21] Furthermore, complexes of rare-earth ions (such as Eu^{3+} and Tb^{3+}) are widely used as luminescent probe reagents or emitting sensors in medical and biochemical applications because of their excellent luminescent features such as long lifetimes even in aqueous media, high yields, and characteristic sharp spectra.[2,5,18,21−25] Thus, rare-earth complexes are potentially excellent luminescent probes for novel microscopic chiral-sensing spectroscopy.[22] It is thus required to find luminescent rare-earth complexes that exhibit strong induced CPL upon interaction with chiral species (induced CPL, iCPL).

Certain racemic rare-earth complexes such as $[Tb(dpa)_3]^{3-}$ (dpa = dipicolinic acid) are known to exhibit detectable iCPL in solutions containing chiral species.[11,14,19,26−31] iCPL originates from the Pfeiffer effect,[31,32] i.e., perturbation of the racemic equilibrium between Δ- and Λ-$[Tb(dpa)_3]^{3-}$ by interaction with the chiral molecules. Thus, the structure of $[Tb(dpa)_3]^{3-}$ itself is not changed by the chiral agents, as confirmed by the fact that the spectral profile of the total luminescence (TL) was independent of the presence of the chiral agent. Recently, we reported detectable iCPL from an achiral emissive europium(III) complex, $[Eu(bda)_2]^-$ (bda =

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2,2′-bipyridine-6,6′-dicarboxylic acid; Figure 1), in an aqueous solution of chiral pyrrolidonecarboxylic acid (PCA), although

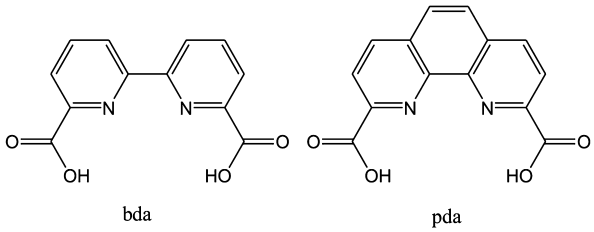

Figure 1. Ligands of $[EuL_2]^-$.

no CPL was observed in solutions without chiral amino acids.[33] On the basis of the fact that the changes in the TL spectra were accompanied by iCPL under conditions where no ligand substitutions of $[Eu(bda)_2]^-$ were recognized, it was concluded that CPL was induced by structural distortion of $[Eu(bda)_2]^-$ by interaction with the amino acid. This was caused by distortion of the structure from achiral to chiral in the molecular level, which is in contrast to the case of the Pfeiffer effect. This demonstrates that $[Eu(bda)_2]^-$ may be advantageous as a chiral-sensing probe for a luminescence microscopy detection system compared with the racemic iCPL probe. One advantage is that this system can recognize chirality even at the single molecule level, which has not been accomplished by the racemic probes. As far as we know, this is the first example of the iCPL probe using structural changes from achiral to chiral by interactions with chiral agents. Another advantage is that further enhancement of the sensitivity or selectivity as a CPL probe using relevant lanthanide complexes should be promising because of the availability of various bis(diimine)dicarboxylic acid derivatives.[34−36]

For development of the chiral-sensing method using achiral CPL probes, it is important to know what kind of chiral agents are detectable and, furthermore, to find out what kind of chemical modifications of the ligand of the probe molecules are effective for improving the sensitivity and/or selectivity of the chiral agents. In this paper, iCPL of $[Eu(pda)_2]^-$ (pda = 1,10-phenanthroline-2,9-dicarboxylic acid) and $[Eu(bda)_2]^-$ is examined in aqueous solutions containing various chiral amino acids. Recently, the Eu^{III}pda complex has been employed as an emissive pH sensor, and europium(III) complexes with pda derivatives have been examined as DNA binding markers.[35,37] $[Eu(pda)_2]^-$ exhibits bright-red f−f emission and its structure has plane symmetry, i.e., an achiral structure, in the crystal as in the case of $[Eu(bda)_2]^-$.[37] Although $[Eu(bda)_2]^-$ showed relatively weak iCPL for most of the amino acids, it is demonstrated herein that $[Eu(pda)_2]^-$ exhibits easily detectable iCPL signals only for arginine and histidine, and therefore the complex can be used as a selective and sensitive molecular probe for these chiral amino acids. The mechanism of iCPL in the europium(III) complexes was examined based on analysis of the fine structures in the luminescence spectra and the pH and concentration dependence of the iCPL intensity.

EXPERIMENTAL SECTION

The TL and CPL spectra were recorded using a laboratory-made CPL measurement system reported previously.[33]

Absorption and Emission Spectra. Emission spectra were recorded using a laboratory-made spectroscopic system reported previously.[38] Absorption spectra were recorded in a 1 cm quartz cell on a Shimadzu MPS-2000.

Materials. 2,2′-Bipyridine-6,6′-dicarboxylic acid (bda) was obtained by oxidation of 6,6′-bi-2-picoline by CrO_3 in the manner described previously.[33,39] 1,10-Phenanthroline-2,9-dicarboxylic acid (pda) was synthesized according to the literature method, except for adjustment of the reflux temperature (100 °C) and the concentration of nitric acid (63%).[40] The purity of pda was checked using UV-absorption spectroscopy, NMR, and elemental analysis. Found: C, 57.5; H, 3.61; N, 9.70. Calcd as $C_{14}H_6N_2O_4{\cdot}1.5H_2O$: C, 57.3; H, 3.09; N, 9.55. Aqueous solutions of $[EuL_2]^-$ (L = pda, bda) were prepared by mixing stoichiometric amounts of aqueous solutions of $EuCl_3$ and L. $EuCl_3$ was purchased from Sigma-Aldrich Co. Single crystals of $(C_6H_{16}N)[Eu(pda)_2]$ were obtained by recrystallization from a mixture of an aqueous solution of $EuCl_3$ and a methanolic solution of pda containing a small amount of triethylamine.

Reagent-grade arginine, histidine, ornithine, alanine, isoleucine, threonine, phenylalanine, lysine, glutamine, leucine, and PCA were purchased from Wako Pure Chemical Industries, Ltd., and proline was from Tokyo Chemical Industry Co. These materials were used without further purification. The pH of the sample solutions was adjusted using NaOH or HCl solutions using a MW101-type smart pH meter (Milwaukee Japan Co.).

RESULTS AND DISCUSSION

1. Absorption and Emission Spectra. Both $[Eu(pda)_2]^-$ and $[Eu(bda)_2]^-$ showed intense absorption bands in the region of 300 nm, assignable to an intraligand $\pi-\pi^*$ transition (Figure 2). Upon irradiation at the wavelength of the $\pi-\pi^*$

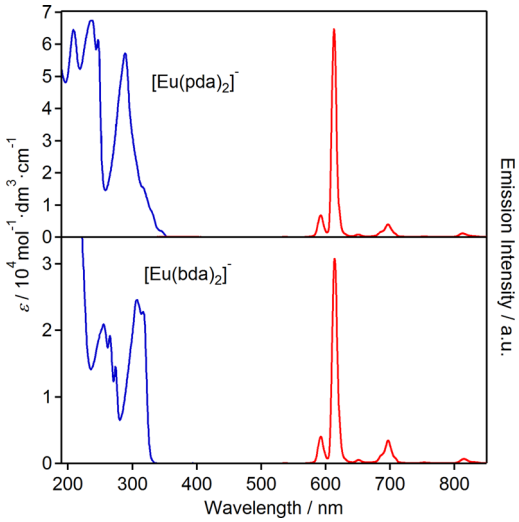

Figure 2. Absorption (blue) and emission spectra (red) of aqueous solutions of (upper) $[Eu(pda)_2]^-$ and (lower) $[Eu(bda)_2]^-$ (λ_{ex} = 310 nm, pH ~8, and [Eu] = 1.0×10^{-4} mol·dm^{-3} for emission spectra).

transition, both complexes exhibited bright emission assignable to the $^5D_0 \rightarrow {}^7F_j$ (j = 0−6) transitions of Eu^{3+} in the visible region, indicating that the ligands work as photosensitizers because of facile energy transfer to the metal center.

Figure 3 shows the emission spectra of the aqueous $[Eu(pda)_2]^-$ solution and crystalline $(C_6H_{16}N)[Eu(pda)_2]$. The europium(III) complexes are known to have achiral D_{2d} structures in the crystal.[41−43] A single peak was observed at 17220 cm^{-1} for the $^5D_0 \rightarrow {}^7F_0$ transition of the crystalline sample, which indicates that there is a single Eu^{3+} coordination site for the complex in the crystal. According to the assignment of Harbuzaru et al., this emission originates from $[Eu(pda)_2]^-$ with the structure being very close to D_{2d}.[37] On the other hand, more than three peaks (17260, 17230, and 17215 cm^{-1}) were observed in the $^5D_0 \rightarrow {}^7F_0$ emission spectrum of the solution,

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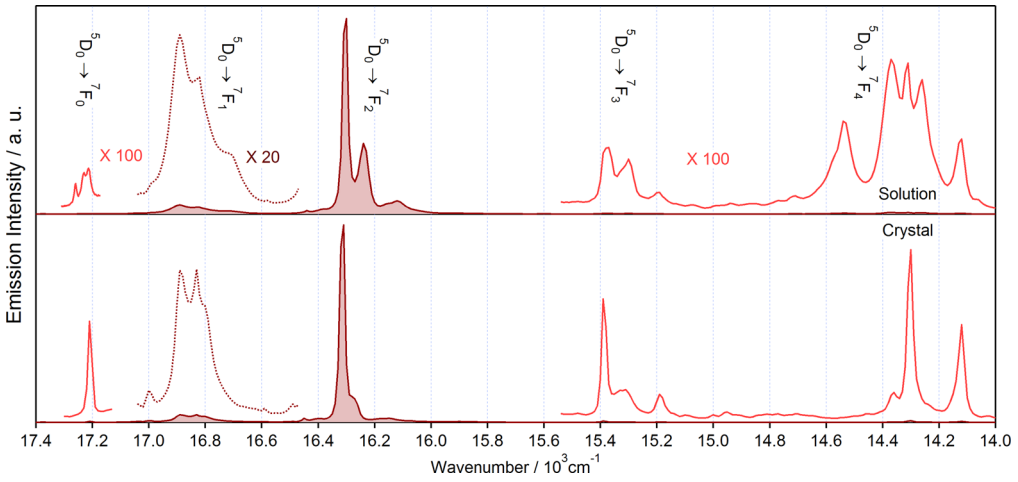

Figure 3. Emission spectra of $[Eu(pda)_2]^-$ in an aqueous solution (upper, [Eu] = 1.0×10^{-4} mol·dm^{-3}, pH ~8) and of a $(C_6H_{16}N)[Eu(pda)_2]$ crystal (lower) (λ_{ex} = 310 nm).

as shown in the upper spectrum in Figure 3. Furthermore, the fine structures of the emission bands of other transitions such as the $^5D_0 \rightarrow {}^7F_2$ band were different from those of the crystal. Such spectral differences between crystal and solution samples have also been reported for $[Eu(bda)_2]^-$.[43] The ligand concentration dependence of the emission spectra from Eu^{3+} shows that the spectral shapes are independent of the concentration of pda when the concentration is higher than twice that of $[Eu^{3+}]$ [see the Supporting Information (SI), Figure S1], indicating that the dominant emitting species in the [Eu]:[pda] = 1:2 solution is $[Eu(pda)_2]^-$. However, the appearance of multiple peaks in the $^5D_0 \rightarrow {}^7F_0$ transition in the aqueous solutions indicates the presence of several europium(III) species having structures different from that in the crystal. Given that the emission of the aqueous solutions at ambient temperature decayed single-exponentially (τ = 0.80 ms for $[Eu(bda)_2]^-$ and 0.79 ms for $[Eu(pda)_2]^-$), these species seem to be in rapid equilibrium, at least on the time scale of the lifetime of the excited states (~1 ms). Prospective species giving rise to additional $^5D_0 \rightarrow {}^7F_0$ peaks in the aqueous solution would be adducts in which a water molecule interacts with Eu^{3+}. Horrocks' analysis [$q = 1.11(1/\tau_{H_2O} - 1/\tau_{D_2O} - 0.31)$, where τ_{H_2O} = 0.79 ms and τ_{D_2O} = 1.5 ms for $[Eu(pda)_2]^-$ and τ_{H_2O} = 0.80 ms and τ_{D_2O} = 1.9 ms for $[Eu(bda)_2]^-$],[44] revealing that the number of water molecules coordinated to Eu^{3+} (q) was ~0.4 and suggesting that europium(III) complexes having one or no coordinated water molecule are in equilibrium. The three $^5D_0 \rightarrow {}^7F_0$ peaks mean that there may be more than two types of coordination of water to Eu^{3+}. The coordination of OH^- to Eu^{3+} is hardly considerable in neutral or acidic solutions (see section 4).

2. TL and iCPL Spectra of $[Eu(pda)_2]^-$ in Aqueous Solutions Containing Arginine. While no CPL signal was recorded for $[Eu(pda)_2]^-$ in aqueous solutions without any chiral agents, $[Eu(pda)_2]^-$ in aqueous solutions containing chiral arginine exhibits detectable CPL (see Figure 4 and the SI, Figure S2). Figure 4 shows the TL and CPL spectra of $[Eu(pda)_2]^-$ in aqueous solutions containing D- and L-arginine in the region of 14000−17500 cm^{-1}, which involves $^5D_0 \rightarrow {}^7F_j$ transitions (j = 0−4) of the Eu^{3+} ion. The g_{lum} value, which is defined as $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the intensities of left and right CPL, respectively, was 0.074 at

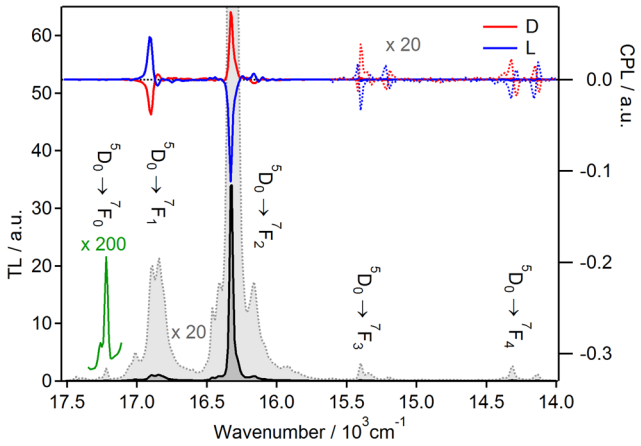

Figure 4. TL and CPL spectra of $[Eu(pda)_2]^-$ in aqueous solution containing arginine (λ_{ex} = 310 nm, [Eu] = 1.0×10^{-4} mol·dm^{-3}, [Arg] = 0.10 mol·dm^{-3}, and pH ~6).

16900 cm^{-1} ($^5D_0 \rightarrow {}^7F_1$) and −0.005 at 16300 cm^{-1} ($^5D_0 \rightarrow {}^7F_2$) for the 0.10 mol·dm^{-3} L-arginine solution. The largest g_{lum} value was observed for the $^5D_0 \rightarrow {}^7F_1$ (ΔJ = 1) transition, in accordance with the magnetic-dipole selection rule, i.e., allowed for ΔJ = 0, 1 (except 0 ↔ 0).[16] The appearance of CPL indicates that the coordination structure of the europium(III) complex is changed to a chiral structure by interaction with the coexisting arginine. The structural change is also supported by the fact that the fine structures in the TL spectra are different from those of the solution without arginine (see also the SI, Figure S2). It is noteworthy that the overall TL spectra observed for the solution containing arginine (Figure 4) were markedly similar to that of the crystal (Figure 3, lower) and, moreover, the single $^5D_0 \rightarrow {}^7F_0$ peak appeared at the same position (17220 cm^{-1}) as that in the crystal.[45] The lifetime of the f−f emission of $[Eu(pda)_2]^-$ in the H_2O solution containing arginine (1.33 ms) was the same as that for the D_2O solution, indicating that $[Eu(pda)_2]^-$ has no coordinated H_2O molecules in the arginine solutions. These findings indicate that the europium(III) species responsible for iCPL in the presence of arginine possess coordination structures similar to that in the crystal, i.e., an eight-coordinate structure, with the diimine ligands being almost perpendicular to each other. The structure of the europium(III) species was, however, considered

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to be slightly distorted from the achiral D_{2d} structure because the ratio of the integrated emission intensity of the $^5D_0 \rightarrow {}^7F_1$ (magnetic-dipole) transition to that of the $^5D_0 \rightarrow {}^7F_2$ (electric-dipole) transition (1:8.3) was greater than that for the crystal (1:5.8). Because the $^5D_0 \rightarrow {}^7F_2$ transition is symmetrically forbidden, the ratio is often used as a measure of distortion in the coordination structure of the Eu^{III} center.[46] Consequently, whereas $[Eu(pda)_2]^-$ has a D_{2d}-like structure in the aqueous solution containing arginine, its structure is slightly distorted to become chiral because of interaction with arginine molecules, thus leading to intense CPL. It is noteworthy that the single peak of the $^5D_0 \rightarrow {}^7F_0$ transition (Figure 4) indicates that the emitting europium(III) complex exists as a single species in the 1.0×10^{-2} mol·dm^{-3} L-arginine solution, indicating that most of the emitting $[Eu(pda)_2]^-$ in the solution exists as an association complex with arginine molecules, which is consistent with the amino acid concentration dependence of iCPL described in section 5. Note that the association of arginine makes the emission brighter because of elongation of the lifetime (from 0.7 to 1.3 ms) and an increase of the relative integrated emission intensity of the $^5D_0 \rightarrow {}^7F_2$ transition ($^5D_0 \rightarrow {}^7F_1$:$^5D_0 \rightarrow {}^7F_2$ = 1:6.1 and 1:8.3 without and with arginine, respectively), which is suitable for an emitting sensor.

The D_{2d}-like structure of the europium(III) species clearly rules out the occurrence of ligand substitution of pda (or bda) by amino acid molecules in the solutions. This was also confirmed by examination of the dependence of the ligand concentration on the CPL spectra in the presence of an excess of the amino acid.[33] When pda was absent, no europium(III) emission was observed for the solution containing an excess amount of arginine. In the case where mono-pda-coordinated europium(III) complexes were dominant in the solution, very weak TL and iCPL were observed, quite different from TL and iCPL of the bis-coordinated europium(III) complexes. When the ligand concentration was more than 2 times higher than that of the Eu^{III} ion, intense emission appeared and both TL and iCPL were almost independent of the ligand concentration (see the SI, Figure S3). Consequently, detectable iCPL should not originate from the arginine-coordinated europium(III) species but rather the bis-pda-coordinated species with slight structural distortion because of interaction with the chiral agents.[33] This mechanism is also operative for iCPL of $[EuL_2]^-$ in solutions of L-histidine and PCA described in the next section (see the SI, Figures S4–S7, and ref 33).

Note that the mechanism of iCPL in $[Eu(pda)_2]^-$ seems to be different from that of the $[Eu(bda)_2]^-$–PCA system reported in the previous paper.[33] In the latter case, it has been suggested that direct coordination of the COO^- group in PCA to the Eu^{3+} ion induced CPL, and thus the structure of $[Eu(bda)_2]^-$ emitting iCPL is far from D_{2d}-like, which is supported by the fact that the iCPL and TL spectra of the $[Eu(pda)_2]^-$–arginine system are different from those of $[Eu(bda)_2]^-$–PCA (see the SI, Figure S8).

3. Comparison of the g_{lum} Values for Various Amino Acids. The intensity of iCPL of $[Eu(pda)_2]^-$ and $[Eu(bda)_2]^-$ varied strongly based on the types of amino acids. Figure 5 summarizes the maximum g_{lum} values of the $^5D_0 \rightarrow {}^7F_1$ transition in iCPL of PCA, L-arginine, L-histidine, and L-glutamine at a concentration of 0.10 mol·dm^{-3} in neutral and acidic conditions. Although $[Eu(pda)_2]^-$ was found to exhibit iCPL for various amino acids (e.g., L-arginine and L-histidine), the spectra acquired in the presence of these amino acids were not significantly different (see the SI, Figures S2, S4, and S6).

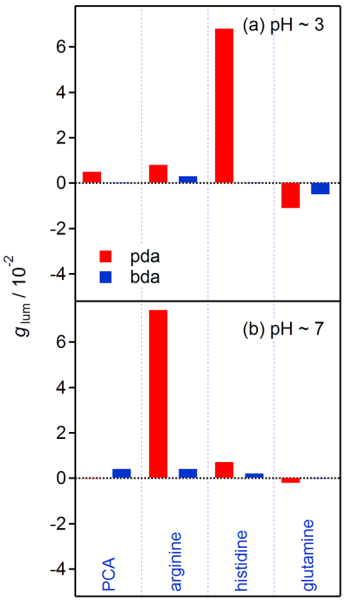

Figure 5. g_{lum} values of iCPL for $[Eu(pda)_2]^-$ and $[Eu(bda)_2]^-$ with various L-amino acids at pH ~3 (a) and ~7 (b). [Amino acids] = 0.10 mol·dm^{-3}.

For ornithine, alanine, isoleucine, threonine, phenylalanine, proline, lysine, glutamine, leucine, and PCA, the observed iCPL intensities were fairly weak under the same conditions (see the SI, Table S1). Notably, PCA induced detectable CPL with both $[Eu(pda)_2]^-$ and $[Eu(bda)_2]^-$, e.g., $g_{lum} \sim 0.03$, at higher concentrations of [PCA] = 1 mol·dm^{-3}.

Interestingly, $[Eu(pda)_2]^-$ exhibited well-detectable iCPL ($g_{lum} \sim 0.07$) only in response to L-arginine in neutral solutions and in the presence of L-histidine in acidic solutions, whereas such highly selective iCPL was not recognized for $[Eu(bda)_2]^-$. Thus, iCPL of $[Eu(pda)_2]^-$ is ascribed to a specific interaction that is very sensitive to the chemical properties of the chiral species, particularly involving the diimine ligands. These findings may provide insight for the development of chiral-sensing systems and also facilitate elucidation of the detailed mechanism of interaction from which iCPL originates.

The TL and iCPL spectra of $[Eu(pda)_2]^-$ in the presence of both L-histidine and PCA were similar to that in the presence of L-arginine (see Figure 4 and the SI, Figures S2, S4, and S6), indicating that the coordination structure of the europium(III) complex from which CPL originates is almost independent of the associating chiral agents. The results are consistent with the postulate that the chirality around the Eu^{3+} center is induced by the change in the coordination structure of $[Eu(pda)_2]^-$ to a chiral configuration such as one in which there is a flattening distortion from D_{2d} to D_2.

The addition of alanine, isoleucine, threonine, phenylalanine, proline, leucine, lysine, ornithine, glutamine, or PCA to the solution of $[Eu(pda)_2]^-$ produces a change in TL although no (or moderately) detectable CPL was recognized in these systems in the 0.1 mol·dm^{-3} solutions. These amino acids undergo some type of interaction with the europium(III) complexes to produce a certain structural change, although the structures are not chiral, or the structural change is too subtle to induce detectable iCPL. The changes of TL for lysine, ornithine, glutamine, threonine, and proline are very close to those in histidine and arginine systems (see the SI, Figure S9). On the other hand, TL changes in alanine, isoleucine, leucine,

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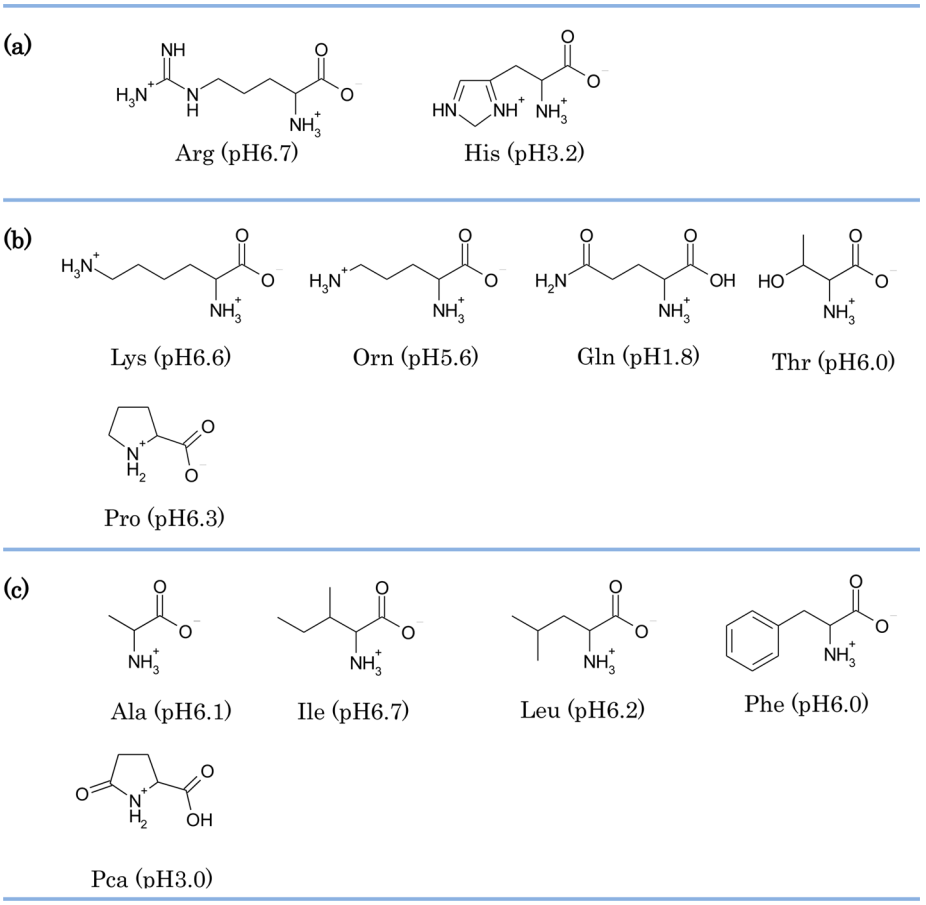

Figure 6. Classification of the amino acids examined. Group a: amino acids yielding iCPL and considerable changes in the TL spectrum. Group b: those giving no detectable iCPL but some changes in the TL spectrum. Group c: those giving no iCPL and small changes in TL. Although PCA was categorized in group c, it exhibits detectable iCPL and TL changes at concentrations higher than 0.5 mol·dm^{-3}. The values in parentheses indicate the pH values of the solutions for which TL and CPL were measured. Abbreviations: Arg, arginine; His, histidine; Lys, lysine; Orn, ornithine; Gln, glutamine; Thr, threonine; Pro, proline; Ala, alanine; Ile, isoleucine; Leu, leucine; Phe, phenylalanine; PCA, pyrrolidonecarboxylic acid.

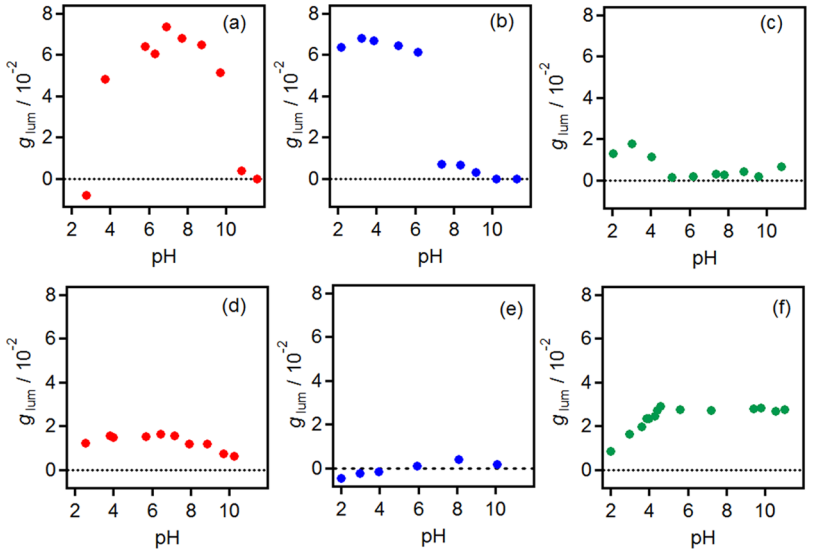

Figure 7. pH dependence of the g_{lum} values of $[Eu(pda)_2]^-$ (a–c) and $[Eu(bda)_2]^-$ (d–f) for the CPL peak of the $^5D_0 \rightarrow {}^7F_1$ transition for L-arginine (a and d), L-histidine (b and e), and PCA (c and f). The concentrations of the amino acids were 0.10 mol·dm^{-3} for arginine and histidine and 0.50 mol·dm^{-3} for PCA in $[Eu(pda)_2]^-$ and 0.70, 0.10, and 1.0 mol·dm^{-3} for arginine, histidine, and PCA in $[Eu(bda)_2]^-$, respectively (λ_{ex} = 310 nm, λ_{mon} = 592 nm, and [Eu] = 1.0 × 10^{-4} mol·dm^{-3}). Data in part f were obtained in the previous work.[33]

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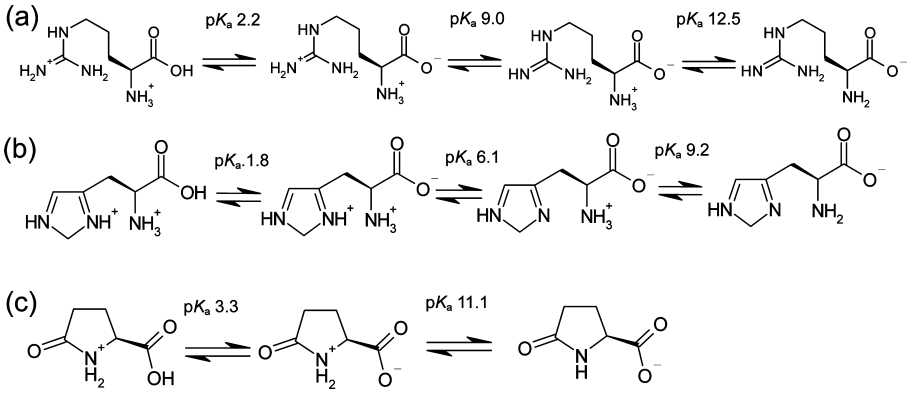
Scheme 1. Acid−base Equilibria of Arginine (a), Histidine (b), and PCA in Aqueous Solutions (c)[a]



[a] pK_a values are from the literature.[26,47].

phenylalanine, and PCA systems were smaller than the others, indicating that these amino acids do not interact so well with the europium(III) complexes (see the SI, Figure S10).

Figure 6 outlines the classification of all of the amino acids examined in this study into three groups based on the iCPL and TL spectra of $[Eu(pda)_2]^-$ in 0.1 mol·dm^{-3} solutions of the amino acids. Group a comprises amino acids yielding detectable iCPL and considerable changes in the TL spectrum. Group b is made up of those producing no detectable iCPL but some changes in the TL spectrum, and group c constitutes those producing no iCPL and changes in the TL are small. Interestingly, the amino acids belonging to groups a and b share structural similarity in that both have amino or hydroxyl groups in their substituents. On the other hand, in the group c amino acids, such amino or hydroxyl groups are absent. These facts clearly demonstrate that iCPL of $[Eu(pda)_2]^-$ originates from a structure-specific interaction between $[Eu(pda)_2]^-$ and the amino acids. In the $[Eu(bda)_2]^-$ systems, no detectable (or a minimal) TL change was recognized for the solutions containing 0.1 mol·dm^{-3} amino acids, whereas a large amount of PCA (∼1 mol·dm^{-3}) induced a detectable change in the TL spectra.[33]

Notably, small amounts of precipitates were formed after preparation of the solutions containing 10^{-4} mol·dm^{-3} of $[Eu(pda)_2]^-$ and more than $\sim10^{-2}$ mol·dm^{-3} of the amino acids, although no precipitate was observed in the case of $[Eu(bda)_2]^-$. To avoid any artifacts in the CPL measurements due to the precipitates, all of the solutions were filtered immediately prior to the measurements. The amount of precipitate was not very significant; thus, the concentration of the amino acids in the filtrate was almost unchanged from the original. Judging from the absorbance around ∼200 nm, about 97% of the amino acids remained in the solution (see the SI, Figures S11−S13).

4. pH Dependence of the g_{lum} Value. Because the chemical forms of amino acids and $[EuL_2]^-$ in aqueous solution are dependent on the pH, the pH dependences of TL and iCPL were examined in order to elucidate the chiral species involved in the specific iCPL of $[EuL_2]^-$. Parts a, b, d, and e of Figure 7 show the pH dependences of the g_{lum} value in the region of pH 2−11 for L-arginine and L-histidine. Variation of the g_{lum} value with the pH for PCA was also examined for comparison (Figure 7c, f) because PCA was used as a chiral agent for $[Eu(bda)_2]^-$ in the previous work.[33] As shown in Figure 7, the optimum pH regions for iCPL of $[EuL_2]^-$ were dependent on both the amino acid and the ligand of the europium(III) complexes. This also shows that iCPL essentially arises from specific interactions between the diimine ligands and the chiral species.

To examine the acid−base equilibria involving $[Eu(pda)_2]^-$ in aqueous solutions, the pH dependences of the TL and absorption spectra of $[Eu(pda)_2]^-$ were examined (see the SI, Figures S14 and S15). The absorption spectra of the solution containing [Eu]:[pda] = 1:2 were almost independent of the pH in the region of pH 3−11 and considerably changed in the pH region lower than 3. The former spectra could be ascribed to pda coordinated to the Eu^{3+} ion because they were quite different from that of free pda (see the SI, Figure S15). The pH dependence of the TL spectra for the solution for [Eu]:[pda] = 1:2 was well consistent with that of the absorption spectra: the spectrum at pH 1.9 was quite different from those in the region of pH 3−11. Similarity between the TL spectra at pH lower 3 and those for the [Eu]:[pda] = 1:1 solution indicates that mono-coordinated species ($[Eu(pda)]^+$) would be formed in the lower pH region. Consequently, bis-pda-coordinated europium(III) complex $[Eu(pda)_2]^-$ is dominantly formed in the region of pH 3−11 and no acid−base equilibria affecting the electronic structure of pda exist in the pH region. Small changes in the spectrum for the $^5D_0 \rightarrow {}^7F_0$ transition were recognized at pH higher than ∼9, whereas almost no change was observed in the magnetic-dipole transition $^5D_0 \rightarrow {}^7F_1$ in the region of pH 3−11 (Figure S14 in the SI). The small changes in the $^5D_0 \rightarrow {}^7F_0$ transition are probably ascribed to acid−base equilibria involving H_2O molecules coordinated to Eu^{3+}, although the molecular structures of the europium(III) species involved in the equilibria are unclear.

In the solutions of $[Eu(pda)_2]^-$ containing chiral amino acids in group a, the pH where drastic g_{lum} changes were recognized were pH 6.2 for histidine and pH 3.8 and 9.8 for arginine. It is worth noting that the TL spectra for $^5D_0 \rightarrow {}^7F_1$ were also changed in the same pH (see the SI, Figures S16 and S17). For histidine, additional changes in the TL spectrum were observed at around pH 9.2. In both amino acids, all of the pH values at which considerable changes were observed in the TL spectra of $^5D_0 \rightarrow {}^7F_1$ are very close to their pK_a values: 1.8, 6.1, and 9.2 for histidine and 2.2 and 9.0 for arginine. Because the TL spectra of $^5D_0 \rightarrow {}^7F_1$ are unchanged in the region of pH 3−11 in the absence of amino acids, these facts strongly suggest that the ionic states of histidine or arginine dominate its interaction with $[Eu(pda)_2]^-$ and thereby affect the coordinating

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structures. In particular, in the pH region where the large g_{lum} values were observed, the ionic interaction seems to be strong enough to form a single associated species because the solution showed a single peak in the $^5D_0 \rightarrow {}^7F_0$ transition (Figure 4), and the TL and CPL spectra were not changed (see the SI, Figures S16 and S17).

In these pH regions, these amino acids are dissolved as zwitterions possessing one $-COO^-$ group and two protonated amino groups (Scheme 1). In conjunction with the structural features of the amino acids in group a, this pH dependence suggests that interaction between $[Eu(pda)_2]^-$ and the amino acids plausibly occurs at three different sites: two are on the asymmetric carbon, i.e., the $-COO^-$ group and the $-NH_3^+$ group, whereas the third is another protonated amino group separated by 6–7 Å from the $-NH_3^+$ group on the asymmetric carbon. The $-COO^-$ group is expected to interact with a positively charged site of the europium(III) complex such as the metal ion. The $-NH_3^+$ moieties would form hydrogen bonds with the carboxylate groups of the pda ligands. The presence of such separated protonated amino groups is considered as one of the effective factors for highly sensitive iCPL, given that such an amino group is absent in the amino acids in group c.

About the PCA system, we found that iCPL of the $[Eu(bda)_2]^-$–PCA system was observed in the pH region where the carboxylate exists in the deprotonated form ($-COO^-$) in the previous paper.[33] Thus, it was concluded that CPL is induced by direct coordination of the amino acid to Eu^{3+} via the $-COO^-$ moiety. This mechanism, however, is not applicable for iCPL of $[Eu(pda)_2]^-$. For example, for the $[Eu(pda)_2]^-$–PCA system, large g_{lum} values were recorded in the pH region where the carboxylate exists in the protonated form ($-COOH$) and, therefore, coordination of $-COO^-$ to the Eu^{3+} ion should be less important. This is consistent with the spectral differences in the fine structure of iCPL of $[Eu(pda)_2]^-$ relative to $[Eu(bda)_2]^-$ (see the SI, Figure S8). Furthermore, the similarity of the CPL spectra of PCA, arginine, and histidine also indicates that direct coordination of $-COO^-$ to Eu^{3+} also does not occur in the $[Eu(pda)_2]^-$–arginine, –histidine, and –PCA systems (see the SI, Figures S2, S4, and S6).

5. Amino Acid Concentration Dependence of the g_{lum} Values. To elucidate the mechanism of iCPL, the amino acid concentration dependence of the g_{lum} value was assessed for PCA, L-arginine, and L-histidine at the pH where the largest g_{lum} value was observed. It was found that the concentration dependence of the g_{lum} value for the L-arginine– and L-histidine–$[Eu(pda)_2]^-$ systems that exhibit highly sensitive iCPL was markedly different from that of the other systems such as the $[Eu(pda)_2]^-$–PCA system.

For $[Eu(bda)_2]^-$, the g_{lum} value increased with increasing concentration of PCA (Figure 8).[33] Although the pH dependence of the g_{lum} value and the CPL spectra of $[Eu(pda)_2]^-$ and $[Eu(bda)_2]^-$ are different, the g_{lum} value for $[Eu(pda)_2]^-$ exhibited almost the same concentration dependence of PCA. The plots in Figure 8 were well represented by the model in which CPL arises from an association complex of *one* amino acid molecule (A) and *one* europium(III) complex (B), A·B. In this model, the g_{lum} values are represented as follows:[33]

$$I_{L/R} = R_{L/R}[A{\cdot}B]\varepsilon_{AB}k_{rAB}\tau_{AB} + 0.5[B]\varepsilon_B k_{rB}\tau_B \quad (1)$$

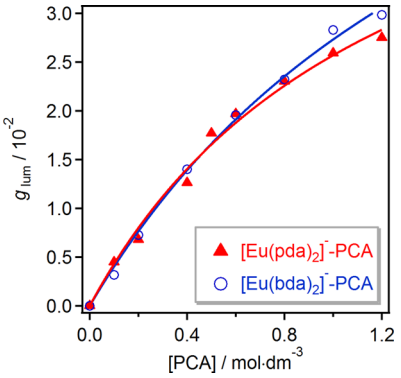

Figure 8. Plots of the g_{lum} values at 16900 cm^{-1} as a function of the concentration of PCA in aqueous $[Eu(bda)_2]^-$ [33] (open circle) and $[Eu(pda)_2]^-$ (solid triangle) solutions (λ_{ex} = 310 nm, λ_{mon} = 592 nm, [Eu] = 1.0×10^{-4} mol·dm^{-3}, pH 10 for $[Eu(bda)_2]^-$, and pH 3 for $[Eu(pda)_2]^-$).

$$g_{lum} = \frac{2(I_L - I_R)}{I_L + I_R} = \frac{2(R_L - R_R)[A{\cdot}B]\varepsilon_{AB}k_{rAB}\tau_{AB}}{[A{\cdot}B]\varepsilon_{AB}k_{rAB}\tau_{AB} + [B]\varepsilon_B k_{rB}\tau_B} = \frac{2(R_L - R_R)[A{\cdot}B]}{[A{\cdot}B] + [B]} = \frac{g_1 K_1[A]_0}{K_1[A]_0 + 1} \quad (2)$$

where $g_1 = 2(R_L - R_R)$, i.e., the g_{lum} values when all of the europium(III) species are associated with chiral agents (A·B). $R_{L/R}$ are parameters related to the left and right rotational strength of A·B ($R_L + R_R = 1$), where the value of these parameters for B is 0.5 because of its achiral structure. ε_X, k_X, and τ_X are the molar extinction coefficient, radiative rate constant, and emission lifetime of species X, respectively. Equation 2 was obtained based on the following two assumptions: (1) ε_X, k_X, and τ_X of the europium(III) complexes are not affected by association with the chiral agents.[33] (2) The concentrations of the amino acids are unchanged by the association because their concentrations are higher than those of the europium(III) complexes. Fitting the data for the g_{lum} values as a function of the concentration of the amino acid gave the equilibrium constants K_1 and g_0. The values obtained by the fitting analysis were not significantly different for the $[Eu(pda)_2]^-$ and $[Eu(bda)_2]^-$ systems: K_1 = 0.81 $mol^{-1}{\cdot}dm^3$ and g_0 = 0.058 for $[Eu(pda)_2]^-$ and K_1 = 0.55 $mol^{-1}{\cdot}dm^3$ and g_0 = 0.077 for $[Eu(bda)_2]^-$[33] (Table 1).

Table 1. Parameters for Chiral Association Species

probe	chiral agent	K_1/$mol^{-1}{\cdot}dm^3$	g_1	K_2/$mol^{-2}{\cdot}dm^6$	g_2
$[Eu(bda)_2]^-$	PCA	0.55[a]	0.077[a]		
$[Eu(pda)_2]^-$	PCA	0.81	0.058		
$[Eu(bda)_2]^-$	L-arginine	0.61	0.053		
$[Eu(pda)_2]^-$	L-arginine	0[b]	0[b]	4.9×10^4	0.078

[a]Reference 33. [b]The contribution of A·B-type species was neglected; the value was roughly estimated because these parameters were hard to determine from fitting to the current data.

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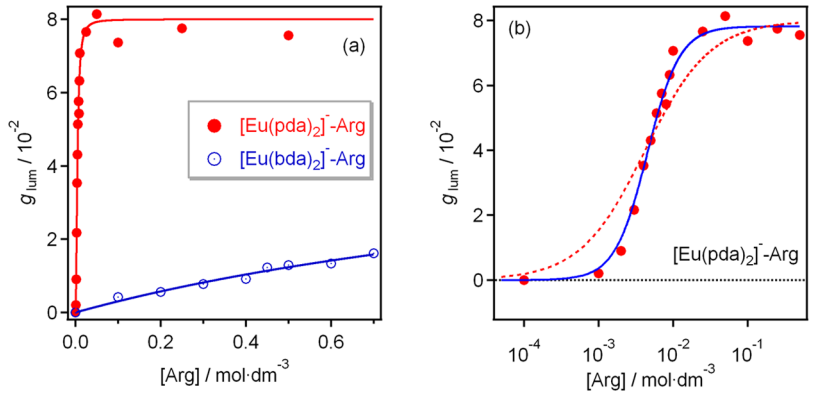

Figure 9. (a) Variation of the g_{lum} values with the L-arginine concentration for $[Eu(pda)_2]^-$ (red) and for $[Eu(bda)_2]^-$ (blue). (b) Semilogarithmic plots of the g_{lum} values for the $[Eu(pda)_2]^-$–arginine system (red circle). Red and blue indicate the fitting curves using eqs 2 and 4, respectively (λ_{ex} = 310 nm, λ_{mon} = 592 nm, [Eu] = 1.0×10^{-4} mol·dm^{-3}, and pH ~7 for $[Eu(bda)_2]^-$ and $[Eu(pda)_2]^-$).

On the other hand, $[Eu(pda)_2]^-$ and $[Eu(bda)_2]^-$ showed considerably distinctive concentration dependence of the g_{lum} value when L-arginine was used as a chiral agent (Figure 9). The g_{lum} value of $[Eu(bda)_2]^-$ increased linearly to 0.013 as the arginine concentration increased up to 1.2 mol·dm^{-3}, which was well reproduced by eq 2 using K_1 = 0.61 mol^{-1}·dm^3 and g_1 = 0.053. For the $[Eu(pda)_2]^-$–arginine system, however, the semilogarithmic plot of g_{lum} versus the amino acid concentration gave rise to a sigmoidal curve, as shown in Figure 9b: a steep increase of the g_{lum} value appeared around [Arg] = 10^{-2} mol·dm^{-3}, and the value was limited at g_{lum} = 0.08 when the concentration was higher than 10^{-2} mol·dm^{-3}. The sigmoidal curve was not well reproduced by eq 2 (see the red dashed curve in Figure 9b, which is the best-fit curve using eq 2). The fact that the observed concentration dependence was much steeper than that predicted from eq 2 strongly suggests that more than one chiral agent should be involved in the association complex. Provided that the association species of the two amino acid molecules and $[Eu(pda)_2]^-$ (A_2·B) exhibit dominant iCPL, the concentration dependence of the g_{lum} value is given as eq 4 under the same assumptions as those used for eq 2.

$$I_{L/R} = 0.5[B]\varepsilon_B k_{rB}\tau_B + R_{1L/R}[A{\cdot}B]\varepsilon_{AB}k_{rAB}\tau_{AB} + R_{2L/R}[A_2{\cdot}B]\varepsilon_{A2B}k_{rA2B}\tau_{A2B} \quad (3)$$

$$g_{lum} = \frac{2(I_L - I_R)}{I_L + I_R} = \frac{R_{2L/R}[A_2{\cdot}B] + R_1[A{\cdot}B]}{[A_2{\cdot}B] + [A{\cdot}B] + [B]} = \frac{g_2K_2[A]_0^{\,2} + g_1K_1[A]_0}{K_2[A]_0^{\,2} + K_1[A]_0 + 1} \quad (4)$$

For the $[Eu(pda)_2]^-$–arginine system, the fitting analysis gave values of g_2 = 0.078 and K_2 = 4.9×10^4 mol^{-2}·dm^6. The contribution of A·B-type species was neglected in this analysis, i.e., K_1 = 0 mol^{-1}·dm^3 and g_1 = 0, because the iCPL intensity at lower amino acid concentrations (~10^{-4} mol·dm^{-3}) was too low for determination of the K_1 values. The obtained parameters are listed in Table 1.

The histidine concentration dependence of the g_{lum} values was also evaluated for the $[Eu(pda)_2]^-$–histidine system (Figure 10). This system did not exhibit a monotonic increase

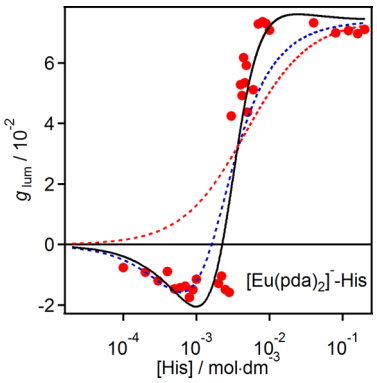

Figure 10. Semilogarithmic plots of g_{lum} values with variation of the L-histidine concentration for $[Eu(pda)_2]^-$. Red, blue, and black lines indicate the fitting curves using eqs 2, 4, and 5, respectively. The black curve was obtained for K_1 = 280 mol^{-1}·dm^3, K_2 = 4.5×10^4 mol^{-2}·dm^6, K_3 = 5.7×10^7 mol^{-3}·dm^9, g_1 = −0.14, g_2 = 0.20, and g_3 = 0.074 (λ_{ex} = 310 nm, λ_{mon} = 592 nm, [Eu] = 1.0×10^{-4} mol·dm^{-3}, and pH 3).

of the g_{lum} value. This clearly indicates that there are more than two types of chiral species in the $[Eu(pda)_2]^-$–histidine system. Of course, the concentration dependence was not reproduced by eq 2 (see the red dashed curve in Figure 10). Furthermore, the plots were not well reproduced with eq 4 (blue dashed curve) even without the assumption of K_1 = 0 mol^{-1}·dm^3 and g_1 = 0. One of the possible suggestions is that the number of chiral species giving rise to iCPL is larger than two. The black curve shown in Figure 10 was calculated using the following equation:

$$g_{lum} = \frac{2(I_L - I_R)}{I_L + I_R} = \frac{g_3K_3[A]_0^{\,3} + g_2K_2[A]_0^{\,2} + g_1K_1[A]_0}{K_3[A]_0^{\,3} + K_2[A]_0^{\,2} + K_1[A]_0 + 1} \quad (5)$$

This equation, which is applicable for three associated species, represents iCPL and looks to reproduce the observed concentration dependence of g_{lum}, as shown in Figure 10. However, it is very difficult to determine the numerous parameters from the current data, including the number of associated molecules. Furthermore, the generation of precipitations would disturb such a complicated analysis even if the uncertainty of the amino acid concentration is quite small. Thus, detailed structural analysis for this system is less fruitful. Nevertheless, the result definitively indicates that plural chiral

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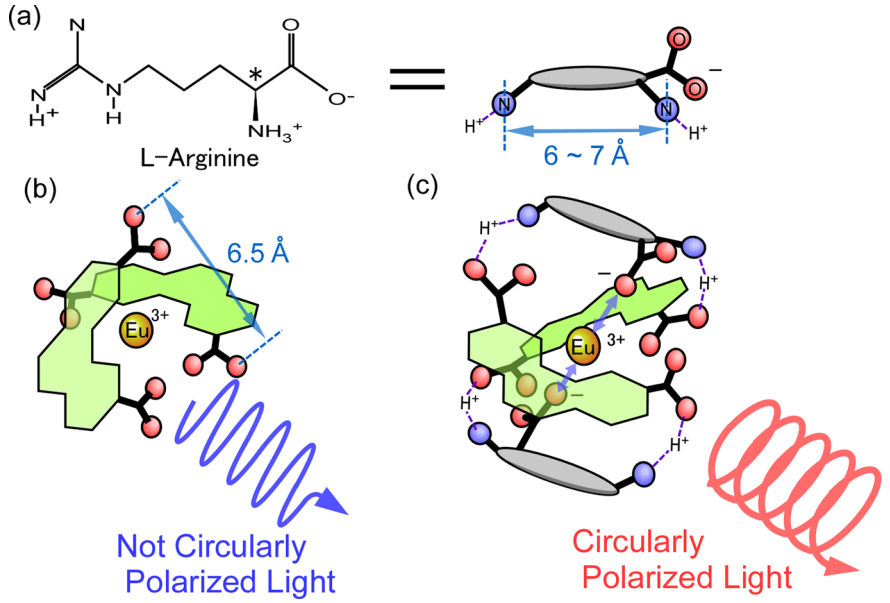

Figure 11. Schematic picture of the inducement of the chiral structure of $[Eu(pda)_2]^-$ by the amino acid. (a) Chiral agents (L-arginine). (b) Emitting probe in the perpendicular structure of ($[Eu(pda)_2]^-$). (c) Proposed model structure of the association complex of arginine and $[Eu(pda)_2]^-$. The blue arrows represent electrostatic attraction.

molecules (plausibly three or four) should be placed in the neighborhood of the probe molecule that exhibits CPL in this system.

It is worth noting that the g_{lum} values were converged to ~0.08 when the concentrations of the amino acids were larger than $\sim 10^{-2}$ mol·dm^{-3}. This indicates that there are no europium(III) complexes that are separated from the chiral agents in these solutions and suggests that the europium(III) complex exists as a single species in this concentration region. This is consistent with the TL spectrum of the $^5D_0 \rightarrow {}^7F_0$ transition in the solution of 0.10 mol·dm^{-3} showing a single peak (Figure 4).

6. Mechanisms for Highly Sensitive iCPL. Here, we consider the mechanism underlying iCPL based on the present experimental results. First, we focus on the results of iCPL generation with the various amino acids and the pH dependence. The data suggested that the amino acid molecules that induce intense CPL have two cationic moieties and one anionic carboxylate group. Naturally, it is expected that the two cationic species would bind to the carboxylate moiety on the ligands of the europium(III) complexes and participate in hydrogen bonding between the oxygen and nitrogen atoms. In this association complex, the $-COO^-$ moiety on the amino acid undergoes electrostatic interaction with the metal center. Thus, this moiety would be placed near the metal center in the association complex. It is expected that a combination of these electrostatic interactions would fix the structure of the europium(III) complex in a chiral orientation. Although the structures of free $[Eu(pda)_2]^-$ in aqueous solutions are still unclear, those of $[Eu(pda)_2]^-$ associated with arginine should be close to the crystal structure (D_{2d}-like structure), as confirmed by the similarity between these TL spectra. A proposed model structure for the association complex of arginine and $[Eu(pda)_2]^-$ based on this concept is depicted in Figure 11c. In this figure, the amino acids bridging the two ligands via hydrogen bonding induce the structural change from the true D_{2d} to D_2. Such an association is highly likely to occur given that the distance between the oxygen atoms that bind to the cationic moiety (see Figure 11b) is about 6.5 Å in the crystal structure of the europium(III) complex.[37] This distance is close to those between the cationic moieties (~6−7 Å) not only in arginine but also in other amino acids in group a (i.e., histidine) and most of group b.

Next, we pay attention to the results from evaluation of the amino acid concentration dependence of g_{lum}, which suggest that more than two chiral molecules are associated in the complex. To represent this mechanism, we propose that the symmetry of chiral $[Eu(pda)_2]^-$ in the association complex belongs to the D_2 point group as a distorted structure from true D_{2d}. If the chiral structure has D_2 symmetry, association of one amino acid molecule would facilitate association of another amino acid molecule on the opposite side, as shown in Figure 11c because the structural features of the opposite side of $[Eu(pda)_2]^-$ should be the same in D_2 symmetry. This is comparable to an allosteric effect in biological systems; i.e., first, association of the target amino acid to the probe molecule causes a change of the structure, which promotes coordination of a second probe molecule.[48] This is consistent with the fact that the amino acids exhibiting highly sensitive iCPL (i.e., amino acids belonging to group a: arginine and histidine) exhibit concentration dependence as it relates to the allosteric effect. Note that the D_2 structure is consistent with the results of analysis of the TL spectral shape, which suggests that the structure of $[Eu(pda)_2]^-$ is close to D_{2d} (but chiral).

Finally, the results of evaluation of the ligand dependence (pda and bda) of iCPL are considered. It has been demonstrated that the "allosteric effect" is very important for the highly sensitive chiral recognition system, and thus probes with highly a symmetrical structure, such as those with D_2 symmetry, are very important for this type of chiral sensing. This effect was observed in the $[Eu(pda)_2]^-$ systems but not in the $[Eu(bda)_2]^-$ system, indicating that the highly symmetrical structure is not maintained in the association complexes of $[Eu(bda)_2]^-$. This is attributed to the freedom of rotational motion along the pyridine linker. As observed in the crystal structures of several rare-earth complexes with the bda

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ligand,[42,43] bda can twist by rotation along this axis, whereas such motion is not allowed in pda.[37,41] Due to the freedom, structural distortion of $[Eu(bda)_2]^-$ may occur along the twist in the ligand in the association complex rather than flattening (D_{2d} to D_2) of the complex. This would make the symmetry of the complex lower than D_2 in the association complex. We propose this as a plausible explanation of why the allosteric effect is not operative in the $[Eu(bda)_2]^-$ system and why the $[Eu(bda)_2]^-$ system does not show highly sensitive iCPL.

The current model is highly consistent with the results obtained for the $[Eu(pda)_2]^-$–arginine system, where the arginine concentration dependence of g_{lum} was well reproduced by the two-arginine-molecule association model. In the $[Eu(pda)_2]^-$ system with histidine, the mechanism seems to be more complicated because the complex contains more than two histidine molecules, as revealed by the concentration dependence. The fact that the signs of the g_{lum} values are different in the lower and higher amino acid concentration regions (Figure 10) indicates that there are, in fact, several types of associations in the $[Eu(pda)_2]^-$–histidine system. However, the identical fine structure of CPL and TL of the arginine system and the histidine system of $[Eu(pda)_2]^-$ suggests that the structure of $[Eu(pda)_2]^-$ in the iCPL complex of histidine is not far from the D_2 structure. This indicates that the mechanism for iCPL in the histidine system is very similar to that of the arginine system shown in Figure 11.

7. Summary. Herein, the sensitivity of $[Eu(pda)_2]^-$ as a chiral probe for arginine and histidine was found to be higher than that of $[Eu(bda)_2]^-$. Our comparative study of iCPL using various amino acids revealed that iCPL is significantly affected by the electrostatic interactions between specific positions in the chiral molecules and in the probe molecules. The proposed model (depicted in Figure 11) representing the chiral structure induced by plural amino acid molecules is definitively consistent with the observations for the $[Eu(pda)_2]^-$ systems. The proposed mechanism postulates a path for the development of iCPL probe molecules; i.e., bis(diimine)europium(III) complexes that have rigid ligands with substituents that interact with $-COO^-$ and $-NH_3^+$ groups would be promising for highly sensitive CPL probe molecules.

In addition to the quite high sensitivity of iCPL of $[Eu(pda)_2]^-$ in the concentration region of $\sim 10^{-2}$ mol·dm^{-3}, $[Eu(pda)_2]^-$ offers significant advantages over $[Eu(bda)_2]^-$ for application to microscopic spectroscopy. This is because the commercially available UV-type objective lens does not transmit light of wavelength shorter than ~330 nm, whereas $[Eu(pda)_2]^-$ absorbs at wavelengths longer than 330 nm but $[Eu(bda)_2]^-$ does not. Studies of the CPL spectra of crystal systems and rare-earth complexes of various phen derivatives, which will provide more detailed mechanisms, are promising.

■ ASSOCIATED CONTENT

Supporting Information

Ligand concentration dependence of TL spectra for $[Eu(pda)_2]^-$ in the $^5D_0 \rightarrow {}^7F_j$ transition (j = 0, 1, 2), TL and CPL spectra of $[Eu(pda)_2]^-$ in the $^5D_0 \rightarrow {}^7F_1$ transition for selected amino acids and their ligand concentration dependence, TL and CPL spectra of $[Eu(pda)_2]^-$ and $[Eu(bda)_2]^-$ in the solutions containing PCA, g_{lum} values of $[Eu(pda)_2]^-$ and $[Eu(bda)_2]^-$ in solutions containing various amino acids (0.10 mol·dm^{-3}), TL spectra of $[Eu(pda)_2]^-$ in the $^5D_0 \rightarrow {}^7F_1$ transition for selected amino acids, absorption spectra of amino acids in the $[Eu(pda)_2]^-$ aqueous solutions, influence of the precipitation, pH dependence of emission spectra of the $[Eu(pda)_2]^-$ aqueous solutions, pH dependence of TL and CPL spectra of the $[Eu(pda)_2]^-$ aqueous solutions for selected amino acids. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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