Inorganic Chemistry

Article

pubs.acs.org/IC

Chiral Sensing Using an Achiral Europium(III) Complex by Induced Circularly Polarized Luminescence

Munetaka Iwamura,* Yoshihiro Kimura, Risa Miyamoto, and Koichi Nozaki

Graduate School of Science and Engineering, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan

Supporting Information

ABSTRACT: $[Eu(bda)_2]^-$ (bda = 2,2′-bipyridine-6,6′-dicarboxylic acid) produces intense circularly polarized luminescence (CPL) in aqueous solutions in the presence of (*S*)-2-pyrrolidone-5-carboxylic acid upon UV irradiation, although the molecular structure of the europium(III) complex is achiral. The mechanism for the induction of CPL was preliminarily attributed to distortions induced by association with an amino acid to generate chirality in the achiral complex. The optical anisotropy factor (g_{lum} value) for the $^5D_0 \rightarrow {}^7F_1$ transition was 0.03 in the presence of 1.0 mol dm^{-3} of the amino acid. Analysis of the CPL intensity as a function of the amino acid concentration gave an association constant between those of $[Eu(bda)_2]^-$ and the amino acid, $K_{aso} = 0.55 \pm 0.09$ mol^{-1} dm^3. These results demonstrate the potential of $[Eu(bda)_2]^-$ to act as a luminescent chiral-sensing reagent in microscopic spectroscopy.

INTRODUCTION

Complexes of rare-earth ions such as Eu^{3+} and Tb^{3+} are widely used as luminescent probe reagents in medical and biochemical applications because of their excellent luminescent features such as long lifetimes even in aqueous media, high intensity, and characteristic sharp spectra.[1−5] It is well-known that chiral species such as amino acids and sugar play key roles in medical and biochemical systems, and, consequently, in vivo imaging of such chiral species in living cells using circularly polarized spectroscopy may provide a means for understanding biochemical systems.[1,6−13] Rare-earth complexes are advantageous for such chiral sensing because their f−f transitions have optical anisotropy factors (*g* values) that are potentially much higher than those of optical transitions within organic compounds.[14,15] Circularly polarized luminescence (CPL) is superior to circular dichroism (CD) for the detection of the chirality of f−f transitions, which have characteristically small absorption coefficients.[7,16−24] Furthermore, CPL is more suitable for highly spatially resolved spectroscopy than CD because CPL detects luminescence from probes using established luminescent probe techniques.[2] Thus, finding luminescent rare-earth complexes with strong CPL is crucial to the development of novel microscopic chiral-sensing spectroscopic techniques.

Our focus has been on "induced CPL" because this represents a promising technique for the realization of highly sensitive chiral sensing.[16−19,25] When optical activity is "induced" in a probe reagent by a vicinal chiral species, the spatial distribution of the chiral species can be determined through the detection of induced CPL signals. Brittain and Muller and Riehl have reported the induction of CPL by the addition of chiral amino acids to a racemic solution of terbium(III) complexes with D_3 symmetry ($[Tb(dpa)_3]^{3-}$, where dpa = dipicolinic acid).[16,17,26,27] In this system, CPL was induced by the perturbation of the racemic equilibria due to the chiral agents.

In this work, we employed different types of probes having an *achiral* structure but showing intense CPL signals as a result of the interaction with chiral agents.[18,28] Because this type of induced CPL originates only from the probe molecules interacting with chiral agents,[6] the induced CPL is expected to be suitable for highly sensitive and background-free chiral sensors and therefore applicable to microscopic chiral-sensing systems at the single-molecule level, which cannot be achieved in the case of using conventional racemic probes. Because studies of this type of induced CPL remain sparse,[28] the development of achiral rare-earth complexes that show a strong CPL signal in the presence of chiral molecules is a fruitful exercise and will contribute to the further development of molecular and biochemical spectroscopy using CPL.

A complex $[Eu(bda)_2]^-$ (Figure 1a; bda = 2,2′-bipyridine-6,6′-dicarboxylic acid) has been known to exhibit intense

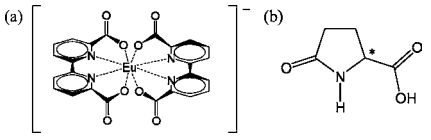

Figure 1. (a) $[Eu(bda)_2]^-$ and (b) 2-pyrrolidone-5-carboxylic acid.

emission under UV irradiation.[29,30] In this paper, we report induced CPL from $[Eu(bda)_2]^-$ in the presence of chiral 2-pyrrolidone-5-carboxylic acid (Figure 1b) in aqueous solutions.

Received: October 31, 2011
Published: March 13, 2012

The complex is expected to have an achiral structure in solution because lanthanide complexes of bis(bda) and its derivatives have structures close to D_{2d} in crystals, wherein two ligands are attached to the metal center perpendicularly.[30−32]

EXPERIMENTAL SECTION

Measurements. *CPL Measurements.* Total luminescence (TL) and CPL spectra were recorded by a laboratory-made spectroscopic measurement system. Sample solutions in a 1 cm × 1 cm quartz cell were irradiated with UV light from a Xe−Hg arc lamp (Hamamatsu Photonics, L2423) through a liquid light guide (220−600 nm, 0.12 in. core, Tokyo Instruments, Inc.) and optical filters. Luminescence of the samples was detected from the opposite side or right side of the excitation. Right or left circularly polarized emissions from the sample were converted to linear polarized light of which the polarization angle was rotated to ±45° from the vertical in a photoelastic modulator (PEM; HINDS Instruments, PEM-100), which was controlled to work as a $\lambda/4$ plate of the monitoring wavelength. A 45°-angled linear polarizer was set behind the PEM to chose the +45° linear polarized light, and the translated light was monochromated through a wavenumber double monochromator (f = 800 mm, Jasco R800) and detected by a photomultiplier tube (Hamamatsu Photonics, R943-02). The emission signals of the right (I_R) and left (I_L) polarized emission were recorded separately by a gated photon counter (Stanford SR400), the gate of which was synchronized with the PEM. The spectroscopic resolution of the system was 0.2 cm^{-1}.

Absorption and Emission Spectra. Emission spectra were recorded by a laboratory-made spectroscopic system, the details of which were reported previously.[33] A grating monochromator (Jobin Yvon, Triax 1900) with a CCD image sensor (Hamamatsu, S7031) was used. The spectral sensitivity of the spectrofluorimeter was corrected using a Br lamp (Ushio, IPD 100 V 500WCS). Absorption spectra were recorded in a 1-mm quartz cell on a Shimadzu MPS-2000.

Emission Lifetime Measurements. Time profiles of the emission intensity were recorded by a laboratory-made time-resolved emission measurement system reported previously.[34] Sample solutions in a 1 cm × 1 cm quartz cell were irradiated with the fourth harmonics (266 nm) of a Q-switched Nd^{3+}:YAG laser pulse (1064 nm, 10 Hz, Continuum, Surelite I-10).

Materials. 2,2′-Bipyridine-6,6′-dicarboxylic acid (bda) was synthesized by oxidation of 6,6′-bis(2-picoline) by CrO_3 according to the method in the literature.[29] 6,6′-Bis(2-picoline) was purchased from Tokyo Chemical Industry Co. The purity of bda was checked by NMR and elemental analysis. $C_{12}H_8O_4N_2$. Calcd: C, 59.02; H, 3.30; N, 11.47. found: C, 58.88; H, 3.54; N, 11.48. Aqueous solutions of $[Eu(bda)_2]^+$ were prepared by mixing stoichiometric amounts of $EuCl_3{\cdot}6H_2O$ and bda aqueous solution. $EuCl_3{\cdot}6H_2O$ (99.9%) was purchased from Sigma-Aldrich. Reagent-grade (*S*)- and (*R*)-2-pyrrolidone-5-carboxylic acid were purchased from Wako Chemical Corp. and used without further purification. The pH of the sample solutions was adjusted using NaOH solutions.

RESULTS AND DISCUSSION

Intense emission of $[Eu(bda)_2]^-$ upon UV irradiation is exhibited by efficient sensitization of Eu^{3+} emission by the bipyridine moieties.[29,30] Figure 2 shows the absorption spectrum of an aqueous solution of $[Eu(bda)_2]^-$. The absorption band at 310 nm is assignable to the $\pi-\pi^*$ transition of the bipyridine moieties. The absence of free ligand absorption bands at 290 nm indicates that $[Eu(bda)_2]^-$ is stable in aqueous solutions.[30] Photoirradiation of the solution at 310 nm produces bright-red luminescence assignable to the f−f transitions ($^5D_0 \rightarrow {}^7F_j$, j = 0−6) of Eu^{3+} (Figure 2). The absence of broad luminescence arising from the ligand-centered transitions is indicative of efficient ligand-to-metal energy

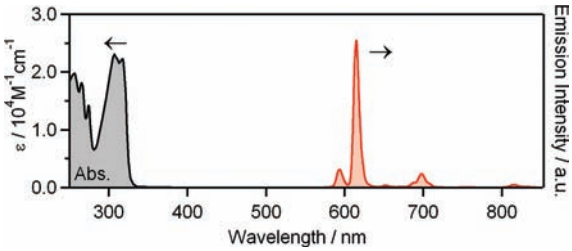

Figure 2. Absorption (black line) and corrected emission (red line) spectra of $[Eu(bda)_2]^-$ in an aqueous solution (λ_{ex} = 310 nm; [Eu] = 1.0 × 10^{-4} mol dm^{-3}).

transfer; i.e., ligand-centered excited states were completely quenched by the Eu^{3+} ion. Time profiles of the Eu^{3+} emission intensity at 612 nm, observed after excitation of a basic solution of $[Eu(bda)_2]^-$ using the fourth harmonic (266 nm) of a Q-switched Nd^{3+}:YAG laser, were well reproduced as a single-exponential decay with a lifetime (τ) of 802 μs (Figure S1 in the Supporting Information). These facts indicate that the emissive species in the basic solution are discrete, i.e., $[Eu(bda)_2]^-$, as previously illustrated by Bünzli et al.[30]

Figure 3 shows the CPL ($I_L - I_R$, where I_L and I_R are the emission intensities of left and right circularly polarized light, respectively) and TL ($I_L + I_R$) spectra for aqueous solutions of

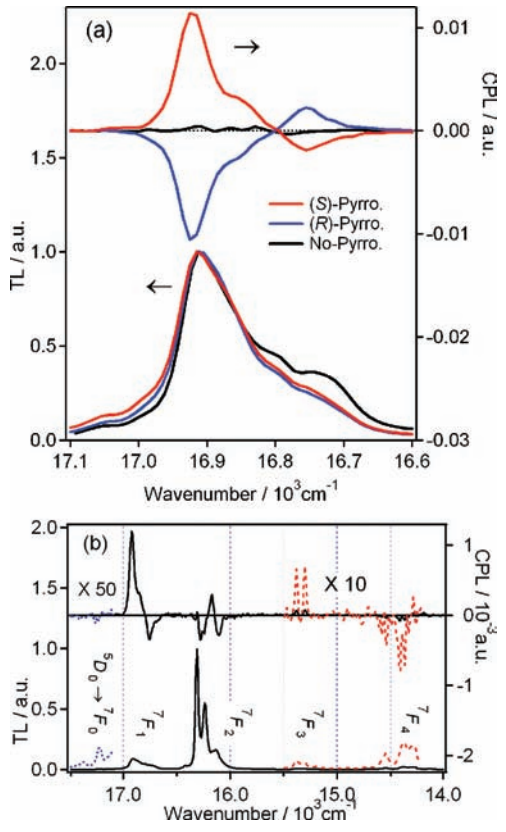

Figure 3. CPL (upper) and TL (lower) spectra of aqueous $[Eu(bda)_2]^-$ solutions. (a) Spectra observed in the region of 17100−16600 cm^{-1} in the presence and absence of (*S*)- and (*R*)-2-pyrrolidone-5-carboxylic acid. The TL spectra were normalized to the peak of the $^5D_0 \rightarrow {}^7F_1$ transition. (b) Spectra in the wide region of 17500−14000 cm^{-1} with (*S*)-2-pyrrolidone-5-carboxylic acid. Intensities were normalized to the TL peak of the $^5D_0 \rightarrow {}^7F_2$ transition (λ_{ex} = ca. 310 nm; [Eu] = 1.0 × 10^{-4} mol dm^{-3}).

dx.doi.org/10.1021/ic202355s | Inorg. Chem. 2012, 51, 4094−4098

$[Eu(bda)_2]^-$. Spectra denoted by red, blue, and black lines in Figure 3a are the TL and CPL spectra of the $^5D_0 \rightarrow {}^7F_1$ transition of the Eu^{3+} ion in the presence and absence of 1.0 mol dm^{-3} (*S*)- and (*R*)-2-pyrrolidone-5-carboxylic acid, respectively. In the absence of the amino acid, no CPL spectrum was observed, as expected on the basis of the achiral structure of $[Eu(bda)_2]^-$. However, the addition of (*S*)-pyrrolidonecarboxylic acid to the $[Eu(bda)_2]^-$ solution produced intense CPL signals. As shown in Figure 3a, the CPL signals in the solution containing (*R*)-2-pyrrolidone-5-carboxylic acid were exact mirror images of those of the (*S*)-amino acid, affirming that the observed CPL signals are due to the Eu^{3+} ion within the chiral structure and not due to artifacts.

In the visible region of 17500−14000 cm^{-1}, five f−f transitions of the Eu^{3+} ions corresponding to $^5D_0 \rightarrow {}^7F_j$ (j = 0−4) were observed in the TL spectrum (lower portion of Figure 3b).

The CPL of the $^5D_0 \rightarrow {}^7F_1$ magnetic-dipole transition at 16900 cm^{-1} (upper region, Figure 3b) gave the largest g_{lum} value of ∼0.03, where g_{lum} is defined as

$$g_{lum} = 2(I_L - I_R)/(I_L + I_R) \quad (1)$$

Large g_{lum} values have often been observed for certain chiral europium(III) complexes according to the magnetic-dipole selection rule, $\Delta J = 0, 1$ (except $0 \leftrightarrow 0$).[14]

The fact that $[Eu(bda)_2]^-$ exhibited CPL signals indicates that certain changes in the coordination structure are induced by the chiral agent, because the complex is expected to have an achiral structure in solution, where chiral agents are absent.[30−32] It is noteworthy that the shapes of the TL spectra were altered slightly by the addition of the amino acid, as shown in Figure 3a. These results also indicate that the coordination structure of the europium(III) complex changed upon its interaction with the amino acid. Furthermore, the emission intensity at 615 nm (16300 cm^{-1}), which is assigned to the $^5D_0 \rightarrow {}^7F_2$ transition, decreased by 10% with the addition of the amino acid, whereas the intensity in the $^5D_0 \rightarrow {}^7F_1$ transition was independent of the amino acid (Figure S2 in the Supporting Information). (Note that the absorption intensity at excitation is independent of the amino acid; see Figure S3 in the Supporting Information.) In the case of europium(III) complexes, the oscillator strength of the $^5D_0 \rightarrow {}^7F_2$ transition depends on the coordination structure in the complex, while the $^5D_0 \rightarrow {}^7F_1$ transition is not so dependent.[35] Therefore, we could confirm that the appearance of induced CPL signals was accompanied by significant changes in the coordination structure of the europium(III) complex. These features are different from those of induced CPL in racemic solutions of D_3-type complexes, in which no structural change was observed in the TL spectra upon the addition of chiral species.[16,26] Thus, one possible interpretation of the induced CPL in achiral $[Eu(bda)_2]^-$ is that association with an amino acid induces a structural change to achieve chirality, e.g., from D_{2d} symmetry to a Δ or Λ structure in the D_2 point group or lower symmetric group. Another possibility is ligand substitution: the bda ligand in $[Eu(bda)_2]^-$ may have been replaced by the chiral amino acid to generate a chiral europium(III) complex because the amino acid is present in fairly high concentration (1.0 mol dm^{-3}).

To elucidate the mechanism by which CPL is induced in $[Eu(bda)_2]^-$, the concentration dependence of the TL/CPL spectra on bda was examined while keeping the concentrations of both Eu^{3+} (1.0×10^{-4} mol dm^{-3}) and the amino acid (1.0 mol dm^{-3}) constant. In the absence of bda, no luminescence was observed under the present conditions for the emission measurements, indicating that europium(III) complexes having no bda are essentially nonemissive. When the concentration of bda was equimolar or lower than that of the Eu^{3+} ion ($[Eu^{3+}]$:[bda] = 1:1 and 1:0.5), the solution exhibited emission upon 310 nm excitation, whereas the spectral profile of the TL of the $^5D_0 \rightarrow {}^7F_1$ emission was different from that of $[Eu(bda)_2]^-$ ($[Eu^{3+}]$:[bda] = 1:2); the peak of the latter was red-shifted by 40 cm^{-1} relative to $[Eu^{3+}]$:[bda] = 1:0.5, and the g_{lum} value of the 1:0.5 complex was smaller than that of $[Eu(bda)_2]^-$ (Figure S4 in the Supporting Information). Because the mono-bda-coordinated europium(III) complex is dominant in solution at relatively low concentrations of bda, the emitting species in the solution is expected to be a complex containing both bda and the amino acids (A), such as $[Eu(bda)(A)_n]^-$.[36] In addition, the CPL intensity of a $[Eu^{3+}]$:[bda] = 1:3 solution (Figure S4 in the Supporting Information) was almost the same as that of the stoichiometric solution of the $Eu^{III}(bda)_2$ complex. These results indicated that the strong CPL signals that appeared in the presence of the chiral amino acid must be ascribed to interaction of the $Eu^{III}(bda)_2$ complex with the chiral molecules. It is also postulated that the strong CPL from $[Eu(bda)_2]^-$ is induced by certain structural distortions that induce chirality in the achiral complex as a result of association with the amino acid.

As shown in Figure 4a, the g_{lum} value of the f−f emission at 16900 cm^{-1} increased as the concentration of the amino acid

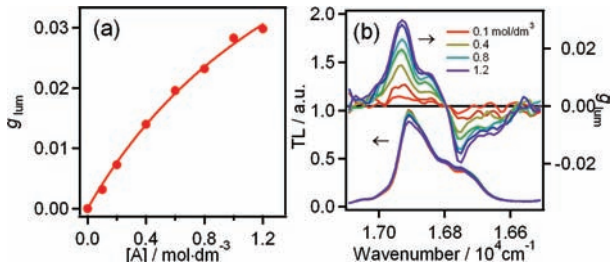

Figure 4. (a) g_{lum} values at 16900 cm^{-1}. (b) Dependence of g_{lum} (upper) and TL (lower) spectra of $[Eu(bda)_2]^-$ on the concentration of (*S*)-2-pyrrolidone-5-carboxylic acid.

increased, which is consistent with the proposed mechanism whereby CPL is induced by association with the amino acid. The association constant was obtained from the following analysis. The intensities of the left and right components of the CPL are represented as

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

where [A], [B], and [A·B] denote the concentrations of the amino acid, $[Eu(bda)_2]^-$, and the association complex, respectively. R_L and R_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. The terms τ_i, k_{ri}, and ε_i represent the lifetime, the radiative rate constant, and the absorption coefficient of species i, respectively. Here, we assumed that the radiative rate k_{rAB} is the same as k_{rB} because the spectral profile remained largely unchanged after the association, as shown in Figure 3, and the radiative rate of the $^5D_0 \rightarrow {}^7F_1$ transition is not sensitive to the structure.[37] In addition, the fact that the absorbance around 310

dx.doi.org/10.1021/ic202355s | *Inorg. Chem.* 2012, 51, 4094−4098

nm was independent of the concentration of the amino acid (Figure S3 in the Supporting Information) indicates that the value of ε_{AB} is the same as that of ε_B. Thus, g_{lum} is represented as

$$g_{lum} = \frac{2(I_L - I_R)}{I_L + I_R} = \frac{2(R_L - R_R)[A\cdot B]\cdot\tau_{AB}}{[A\cdot B]\cdot\tau_{AB} + [B]\cdot\tau_B} = \frac{2(R_L - R_R)K_{aso}[A]_0}{K_{aso}[A]_0 + \frac{\tau_B}{\tau_{AB}}} \quad (3)$$

where K_{aso} is an equilibrium constant of association between one amino acid molecule and $[Eu(bda)_2]^-$ defined by eq 4.

$$K_{aso} = \frac{[A\cdot B]}{[A][B]} \quad (4)$$

Because [A] is much higher than [B] under the present conditions (where [B] = 1.0×10^{-4} mol dm^{-3} and [A] is 0.1−1 mol dm^{-3}), [A] can be replaced by the total concentration of the amino acid in the solution [A_0]. The values τ_B and τ_{AB} are the emission lifetimes of $[Eu(bda)_2]^-$ and the association complex, respectively. Because the emission lifetime of the $[Eu(bda)_2]^-$ solution ([Eu]:[bda] = 1:2) containing the amino acid was not markedly different (τ = 0.75 ms; Figure S1 in the Supporting Information) from that without the amino acid (τ = 0.80 ms) in the present case, τ_A/τ_{AB} was assumed to be 1. The fitting of eq 3 to the plots gave a K_{aso} value of 0.55 ± 0.09 mol^{-1} dm^3.

We have examined the pH dependence of the induced CPL because the chemical speciation of 2-pyrrolidone-5-carboxylic acid in aqueous solution is dependent on the pH, as shown in Scheme 1. The pK_{a1} and pK_{a2} values for 2-pyrrolidone-5-carboxylic acid are 3.32 and ∼11, respectively.[16]

Scheme 1. Acid−Base Equilibria of 2-Pyrrolidone-5-carboxylic Acid in Aqueous Solutions

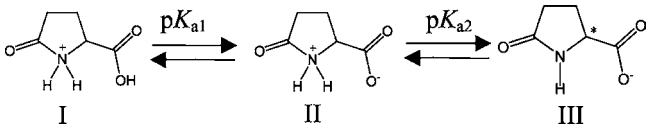

Figure 5 shows variation in the g_{lum} values at 16900 cm^{-1} with the pH. The g_{lum} values decreased when the pH of the solution was below 4. In the lower pH region, the amino acid exists mainly as the positively charged species I, and therefore the electrostatic attraction between $[Eu(bda)_2]^-$ and the amino acid should be stronger. However, the pH dependence of the

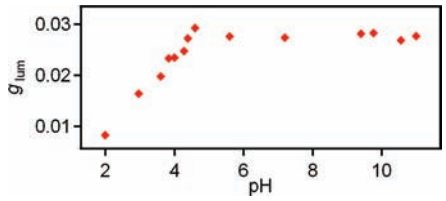

Figure 5. Dependence of the g_{lum} values of $[Eu(bda)_2]^-$ on the pH in aqueous solutions containing 1.0 mol dm^{-3} 2-pyrrolidone-5-carboxylic acid.

g_{lum} values clearly indicates that species I is not the crucial species for the induction of CPL, whereas associations with species II and III are important. Moreover, the addition of 1.0 mol dm^{-3} NaCl to the solution did not produce any effects on the CPL spectra. These findings clearly indicate that electrostatic attraction is not the dominant interaction in the generation of induced CPL. The pH dependence suggests that the chirality around Eu^{3+} is generated by the additional coordination of the chiral amino acid to the metal center in $[Eu(bda)_2]^-$ because the carboxylate anion, which is generated on the amino acid in the higher pH region, coordinates favorably with the Eu^{3+} ion. Because the coordination of two bda ligands to Eu^{3+} is essential for the induced CPL as mentioned above, the associated species must involve two bda ligands, e.g., $[Eu(bda)_2(A)]^-$. The additional coordination of the chiral molecule(s) distorts the coordination structure of the bda ligands to generate a chiral structure. More information on the molecular structures of the association complex of $[Eu(bda)_2]^-$ and the chiral species is necessary to reveal the detailed chiral-sensing mechanisms.

Water molecules are likely to coordinate to the Eu^{3+} ion in aqueous solutions, and the numbers of coordinated water molecules to $[Eu(bda)_2]^-$ and $[Eu(bda)_2(A)]^-$ would provide a good understanding of the mechanism of the induced CPL. However, the coordination number q estimated from Horrocks' equation as $q = 1.11(1/\tau_{H_2O} - 1/\tau_{D_2O} - 0.31)$[38] remained unchanged in solution with and without the amino acid. The lifetime observed for $[Eu(bda)_2]^-$ in D_2O was 2.1 ms without the amino acid and 1.9 ms with the amino acid, thereby giving q of 0.5 (τ_{H_2O} = 0.8 ms in both solutions), which is very close to that estimated by Bünzli et al. (q = 0.5 ± 0.1).[30] These results imply that the coordination number of water is small in both solutions, i.e., with and without the amino acid.

In this work, induced CPL from the achiral rare-earth complex $[Eu(bda)_2]^-$ was observed for the first time. On the basis of the ligand concentration and pH dependence of the CPL intensity, it was proposed that the induced CPL arises from the distortion of the achiral structure of $[Eu(bda)_2]^-$ to a chiral motif; the distortion is thought to be induced by association with the chiral amino acid via the carboxylate anion. $[Eu(bda)_2]^-$ exhibits undisputed potential as an emissive probe molecule for chiral-sensing systems, including microscope spectroscopy and single-molecule spectroscopy. Because a much larger number of derivatives are known for bipyridine ligands than for dpa ligands, the chiral sensitivity of the system can be further developed by the chemical modification of the ligands.[30−32,39] Currently, other chiral systems such as other amino acids, sugar, and DNA are under scrutiny in our laboratory as well as modifications of the bda ligand. These will contribute to elucidation of the mechanism of chiral sensing and the development of such agents.

■ ASSOCIATED CONTENT

Supporting Information

Emission time profiles, absorption and emission spectra of $[Eu(bda)_2]^-$ in aqueous solutions with and without the amino acid, TL and CPL spectra for the solutions with low concentrations of the ligand. This material is available free of charge via the Internet at http://pubs.acs.org.

dx.doi.org/10.1021/ic202355s | Inorg. Chem. 2012, 51, 4094−4098

AUTHOR INFORMATION

Corresponding Author

*E-mail: miwamura@sci.u-toyama.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by KAKENHI (23750060), Grant-in-Aid for Young Scientists (B), and Grant-in-Aid for Scientific Research (C) (22550057). We extend our appreciation to Prof. Tsubomura of Seikei University for allowing us to use the photon counter and for his kind discussions.

REFERENCES

(1) Tsukube, H.; Shinoda, S. *Chem. Rev.* **2002**, *102*, 2389.
(2) Selvin, P. R. *Annu. Rev. Biophys. Biomol. Struct.* **2002**, *31*, 275.
(3) Andolina, C. M.; Morrow, J. R. *Eur. J. Inorg. Chem.* **2011**, 154.
(4) Eliseeva, S. V.; Bünzli, J. C. G. *Chem. Soc. Rev.* **2010**, *39*, 189.
(5) Bünzli, J. C. G.; Piguet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048.
(6) Hassey, R.; Swain, E. J.; Hammer, N. I.; Venkataraman, D.; Barnes, M. D. *Science* **2006**, *314*, 1437.
(7) Hembury, G. A.; Borovkov, V. V.; Inoue, Y. *Chem. Rev.* **2007**, *108*, 1.
(8) Claborn, K.; Puklin-Faucher, E.; Kurimoto, M.; Kaminsky, W.; Kahr, B. *J. Am. Chem. Soc.* **2003**, *125*, 14825.
(9) Tsukube, H.; Shinoda, S.; Tamiaki, H. *Coord. Chem. Rev.* **2002**, *226*, 227.
(10) Borovkov, V. V.; Lintuluoto, J. M.; Inoue, Y. *J. Am. Chem. Soc.* **2001**, *123*, 2979.
(11) Takeuchi, M.; Mizuno, T.; Shinkai, S.; Shirakami, S.; Itoh, T. *Tetrahedron: Asymmetry* **2000**, *11*, 3311.
(12) Kubo, Y.; Ohno, T.; Yamanaka, J.-i.; Tokita, S.; Iida, T.; Ishimaru, Y. *J. Am. Chem. Soc.* **2001**, *123*, 12700.
(13) Matsugaki, A.; Takechi, H.; Monjushiro, H.; Watarai, H. *Anal. Sci.* **2008**, *24*, 297.
(14) Richardson, F. S. *Inorg. Chem.* **1980**, *19*, 2806.
(15) Berova, N.; Nakanishi, K.; Woody, R. W. *Circular Dichroism: Principles and Applications*; Wiley-VCH: New York, 2000.
(16) Brittain, H. G. *Inorg. Chem.* **1981**, *20*, 3007.
(17) Muller, G.; Riehl, J. P. *J. Fluoresc.* **2005**, *15*, 553.
(18) Muller, G. *Dalton Trans.* **2009**, 9692.
(19) Muller, F. C.; Muller, G.; Riehl, J. P. *Chirality* **2007**, *19*, 826.
(20) Coruh, N.; Riehl, J. P. *Biochemistry* **1992**, *31*, 7970.
(21) Coruh, N.; Riehl, J. P. *Collect. Czech. Chem. Commun.* **1991**, *56*, 3028.
(22) Riehl, J. P.; Coruh, N. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 263.
(23) Aspinall, H. C. *Chem. Rev.* **2002**, *102*, 1807.
(24) Crassous, J. *Chem. Soc. Rev.* **2009**, *38*, 830.
(25) Yuasa, J.; Ohno, T.; Miyata, K.; Tsumatori, H.; Hasegawa, Y.; Kawai, T. *J. Am. Chem. Soc.* **2011**, *133*, 9892.
(26) Moussa, A.; Pham, C.; Bommireddy, S.; Muller, G. *Chirality* **2009**, *21*, 497.
(27) Tsukube, H.; Hosokubo, M.; Wada, M.; Shinoda, S.; Tamiaki, H. *Inorg. Chem.* **2001**, *40*, 740.
(28) Morita, M.; Rau, D.; Takaba, H.; Herren, M. *Microelectron. Eng.* **2000**, *51*−*2*, 605.
(29) Mukkala, V.-M.; Kwiatkowski, M.; Kankare, J.; Takalo, H. *Helv. Chim. Acta* **1993**, *76*, 893.
(30) Bünzli, J.-C. G.; Charbonniere, L. J.; Ziessel, R. F. *J. Chem. Soc., Dalton Trans.* **2000**, 1917.
(31) Fan, L.-L.; Li, C.-J.; Meng, Z.-S.; Tong, M.-L. *Eur. J. Inorg. Chem.* **2008**, 3905.
(32) Kelly, N. R.; Goetz, S.; Batten, S. R.; Kruger, P. E. *CrystEngComm* **2008**, *10*, 68.
(33) Siddique, Z. A.; Yamamoto, Y.; Ohno, T.; Nozaki, K. *Inorg. Chem.* **2003**, *42*, 6366.
(34) Obara, S.; Itabashi, M.; Okuda, F.; Tamaki, S.; Tanabe, Y.; Ishii, Y.; Nozaki, K.; Haga, M. *Inorg. Chem.* **2006**, *45*, 8907.
(35) Ofelt, G. S. *J. Chem. Phys.* **1962**, *37*, 511.
(36) The emission intensity is comparable with the solution of 2:1. In the case of the solution without the amino acid, the emissions from the solutions of 1:1 and 1:0.5 are much weaker than that of 2:1. This is due to ligation of water in the empty site of Eu^{3+} in $[Eu(bda)]^{+}$, and it is evidence of ligation of the amino acid in the case of the solution with the amino acid.
(37) Harada, T.; Nakano, Y.; Fujiki, M.; Naito, M.; Kawai, T.; Hasegawa, Y. *Inorg. Chem.* **2009**, *48*, 11242.
(38) Supkowski, R. M.; Horrocks, W. D. *Inorg. Chim. Acta* **2002**, *340*, 44.
(39) Zhang, Y.-N.; Liu, J.-Q.; Wang, T.; Wen, G.-L.; Yang, G.-P.; Wang, Y.-Y.; Shi, Q.-Z. *J. Mol. Struct.* **2008**, *878*, 116.