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Chiroptical Spectra of a Series of Tetrakis((+)-3-heptafluorobutylyrylcamphorato)lanthanide(III) with an Encapsulated Alkali Metal Ion: Circularly Polarized Luminescence and Absolute Chiral Structures for the Eu(III) and Sm(III) Complexes

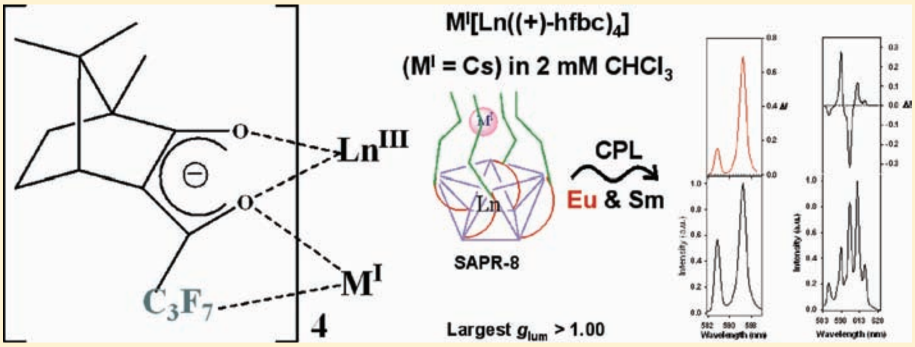
Jamie L. Lunkley,[‡] Dai Shirotani,[†] Kazuaki Yamanari,[†] Sumio Kaizaki,[§] and Gilles Muller*,[‡]

[‡]Department of Chemistry, San José State University, One Washington Square, San José, California 95192-0101, United States

[†]Institute for Higher Education Research and Practice, Osaka University, Toyonaka, Osaka, 560−0043, Japan

[§]Venture Business Laboratory, Osaka University, Suita, Osaka, 565-0871, Japan

S *Supporting Information*



ABSTRACT: The luminescence and circularly polarized luminescence (CPL) spectra of $M^I[Eu((+)\text{-}hfbc)_4]$ show a similar behavior to the exciton CD in the intraligand $\pi-\pi^*$ transitions when the alkali metal ions and solvents are manipulated. There is a difference in susceptibility in solvation toward the alkali metal ions but not toward the Eu(III) ion, as in the case of axially symmetric DOTA-type compounds. The remarkable CPL in the 4f−4f transitions provide much more information on the stereospecific formation of chiral Eu(III) complexes, since CPL spectroscopy is limited to luminescent species and reflects selectively toward helicity of the local structural environment around the lanthanide(III). While in comparison, exciton CD reveals the chiral structural information from the helical arrangement of the four bladed chelates. Of special importance, the observation of the highest CPL activities measured to date for lanthanide(III)-containing compounds (i.e., Eu and Sm) in solution supports the theory that the chirality of lanthanide(III) in the excited state corresponds to that in the ground state, which was derived from the exciton CD.

■ INTRODUCTION

Circular dichroism (CD) spectroscopy allows one to detect the differential absorption of left- and right-handed circularly polarized light. CD is widely recognized as one of the most important techniques for elucidation of metal complexes as well as three-dimensional protein structure under conditions approaching those found in the intracellular environment,[1−8] although CD gives less specific structural information than X-ray crystallography or NMR spectroscopy.

Since commercial CD instrumentation became available in the 1960s, considerable effort was devoted to the development of reliable rules relating CD sign patterns to absolute configurations or conformations of coordination compounds.[3,4,7,9,10] Although some progress was made toward this goal, it was noticed that predictions of chiral structures from CD spectra were usually possible when, in the electronic $\pi-\pi^*$ transitions, the coupling of electronic dipole transition moments in a chiral arrangement occurred (this is referred to as "exciton coupling"). This latter method, which is used to predict the chiral configuration of organic compounds acting as bidentate ligands, is based on the sign of the CD couplet observed in the electronic $\pi-\pi^*$ transitions around 300 nm.[11]

Even with advancements in CD instrumentation and with the development of modified techniques including the spectroscopic approach of comparing observed spectra of vibrational CD (VCD), exciton CD, electronic CD (ECD), or optical rotation values with the DFT calculated ones,[4,12−22] it was observed that there were often exceptions and complications in the establishment of reliable structure−spectra relations for metal-containing compounds. The origin of such complications commonly resulted from the fact that small changes of

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substituents and/or their location within the systems of interest were accompanied by unpredictable changes in the CD sign.[3,4,7] This is certainly one of the reasons why it is important to use various chiroptical spectroscopic tools for obtaining chiral molecular structural information because singular methods may provide partial information or give ambiguous conclusions.[23]

Consequently, an attractive complementary tool is the use of lanthanide(III), Ln(III), luminescence spectroscopy, especially circularly polarized luminescence (CPL) spectroscopy, which is the emission analog to CD. CPL is observed as the difference in the emission intensity of left versus right circularly polarized light. It is common to report the degrees of CPL in terms of the luminescence dissymmetry factor, $g_{\mathrm{lum}}(\lambda)$, which is defined as follows: $g_{\mathrm{lum}}(\lambda) = 2\Delta I/I = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R respectively refer to the intensity of left and right circularly polarized emissions. A value of 0 for g_{lum} corresponds to no circular polarization, while the absolute maximum value is 2. Several reviews that have been published in recent years summarize the important structural information that can be deduced with the CPL technique. This latter becomes increasingly useful as a probe to identify the existence of chiral species and is, also, an indicator of changes in chiral structure.[4,24−31]

Unlike CD spectroscopy, there were only a few attempts to develop reliable empirical relationships between chiral structures and CPL sign patterns.[32−35] Although CPL is primarily used in the study of Ln(III)-containing systems, one may envisage that a similar structure−spectra relation for metal-containing compounds may be developed for the CPL spectroscopy. However, such a development may be limited to chiral metal complexes containing Ln(III) ions since the difference in absorption or emission of circularly polarized light may approach 50%, that is, if one studies the intraconfigurational f−f transitions that obey the magnetic dipole transition selection rules ($\Delta J = 0 \pm 1$, except $0 \leftrightarrow 0$).[36,37] On the other hand, it is very unlikely that chiral organic systems will show a difference in absorption or emission of circularly polarized light greater than 0.1%. In addition to the fact that the nature of the 4f electronic states makes the calculation of the observed CD or CPL very difficult, one must also envisage the use of chiral high symmetric Ln(III)-based systems which would lead to strong CPL activities. This would be a necessary step to make reliable predictions. In recent reports, Ln(III)-containing systems with, e.g., chiral 2-hydroxyisophthalamide-, pyridyldiamine-, 1-hydroxy-2-pyrydinone-, pybox-, or macrocyclic-based ligand derivatives exhibited g_{lum} values as high as 0.5,[10,25,38−45] whereas chiral organic molecules exhibited almost always g_{lum} values less than 1×10^{-2}.[4,24,25]

Working along these lines, we recently showed the importance of using CPL for studying only luminescent chromophores present in solution containing cesium and sodium tetrakis(3-heptafluorobutylryl-(+)-camphorato = (+)-hfbc) Eu(III) complex solutions, $\mathrm{M^I[Ln((+)\text{-}hfbc)_4]}$ ($\mathrm{M^I}$ = Na or Cs), in $CHCl_3$ and EtOH.[46] Of special importance, we showed a concentration-dependent exciton CD due to the dissociation of the tetrakis(+)-hfbc Eu(III) compound into the tris(+)-hfbc Eu(III) complex, but more importantly, the former species exhibited the highest CPL activity ever observed for any CPL studies of Ln(III)-containing systems in solution (g_{lum} values amounted to +1.38 or +1.32 at 595 nm in $CHCl_3$ or EtOH, respectively). The CPL activity of the latter compound, however, was negligible. It is worth mentioning that these systems of interest were isolated and structurally characterized by ^{19}F NMR, CD and VCD.[47−50] It was shown that the solution structure was supposed to take a square antiprism eight coordination (SPAR-8) with Δ-configurational chirality on the basis of the exciton CD spectra.

Taking advantage of the strong CPL activity exhibited by these systems, we propose to explore the possibility of developing a reliable empirical relationship between their chiral structure and CPL spectra. Consequently, in this work, the luminescence and CPL of $\mathrm{M^I[Eu((+)\text{-}hfbc)_4]}$ complexes ($\mathrm{M^I}$ = Na, K, Rb, and Cs) in $CHCl_3$, CH_3CN, and EtOH as well as of $\mathrm{Cs[Sm((+)\text{-}hfbc)_4]}$ in $CHCl_3$ were examined in order to reveal the detailed chiral configuration in solution. This is a preliminary step that is necessary if one wants to understand the chiroptical spectral−structure relationships with variation of $\mathrm{M^I}$ ions and solvents. Of special interest is the importance of using CPL for selectively studying only luminescent chromophores present in the studied systems. This is in contrast to CD, which is affected by most chromophores and/or equilibrium mixtures in an additive manner. Finally, preliminary conclusions made relative to the goal mentioned above will be discussed.

■ EXPERIMENTAL SECTION

The $\mathrm{M^I[Eu((+)\text{-}hfbc)_4]}$ ($\mathrm{M^I}$ = Na, K, Rb, Cs) and $\mathrm{Cs[Sm((+)\text{-}hfbc)_4]}$ compounds were obtained as crystals using the reported method.[49,50] Luminescence spectra were measured on a Perkin-Elmer LB 50 spectrophotometer. Luminescence measurements were performed in $CHCl_3$, CH_3CN, and EtOH solutions. CPL and total luminescence spectra were recorded on an instrument previously described in the literature.[44,51] A circular analyzer consisting of an oscillating photoelastic polarization modulator (PEM) followed by a high-quality linear polarizer is located between the emitting sample and the emission monochromator. This circular analyzer allows detection of the net circular polarization in the luminescence. Detection of the alternating emitted left and right polarized light is accomplished using a thermoelectrically cooled photomultiplier tube (PMT), operating in a differential photon-counting mode. The photon pulses corresponding to the intensity of left and right circularly polarized emitted light are collected with two separate digital counters. It should be added that the various elements including linear polarizers, sample containers, filters, mirrors, and the PEM, which is not a perfect optical element, may lead to systematic sources of error. The standard deviation, σ_d, in the measurement of the luminescence dissymmetry factor, g_{lum}, is defined as follows: $\sigma_d = (2/N)^{1/2}$, where N is the total number of photon pulses counted. One can see that the determination of accurate g_{lum} values can be done in a short time for transitions associated with large g_{lum} values of highly luminescent compounds. However, a longer time of collection is required for transitions associated with small g_{lum} values of weakly luminescent systems for achieving the same percent error. As the time required for measuring a CPL spectrum is dependent on the intensity of the luminescence of the system of interest and the "chirality" of the transition analyzed, the photon pulses are collected for the same amount of time at each wavelength. As a result, the relative error at each of these wavelengths is the same in the CPL spectrum measured. The light source for excitation was a continuous-wave 1000 or 450 W xenon arc lamp from a Spex FluoroLog-2 spectrofluorimeter, equipped with excitation and emission monochromators with dispersions of 4 nm/mm (SPEX, 1681B).

■ RESULTS AND DISCUSSION

Luminescence Spectra of Eu(III)−(+)-hfbc Complexes. The luminescence spectra of $\mathrm{[Eu((+)\text{-}hfbc)_3]}$ and $\mathrm{M^I[Ln((+)\text{-}hfbc)_4]}$ ($\mathrm{M^I}$ = Na, K, Rb, and Cs) were recorded in 2 and 0.2 mM EtOH as well as in 0.035 mM $CHCl_3$ and

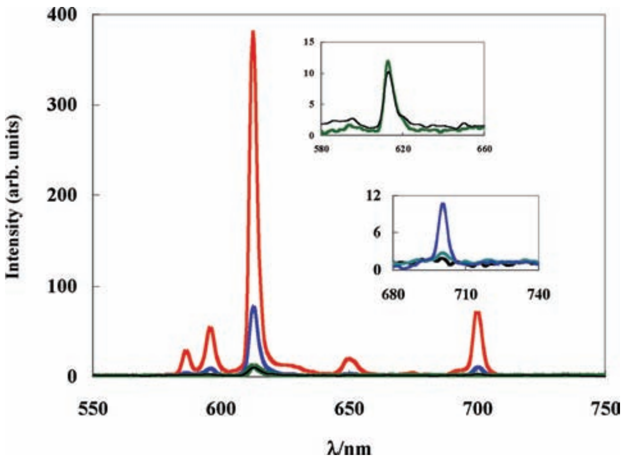

Figure 1. Total luminescence spectra of $M^I[Eu((+)\text{-hfbc})_4]$ in 0.035 mM $CHCl_3$ solution: Cs–Eu (red), Rb–Eu (blue), K–Eu (green), and Na–Eu (black).

CH_3CN (Figure 1 and Figures S1–S3, Supporting Information).

Although no characteristic luminescence of $[Eu((+)\text{-hfbc})_3]$ is detectable in $CHCl_3$ solution, it was possible to observe a very weak luminescence of this complex in EtOH solution (Figure S1, Supporting Information). These overall poor luminescent properties of $[Eu((+)\text{-hfbc})_3]$ probably derive from the excitation energy loss from vibrational deactivation quenching processes involving the complex itself and/or solvent molecules.[52] On the other hand, the characteristic luminescence of $Cs[Eu((+)\text{-hfbc})_4]\cdot H_2O$ was observed in EtOH, $CHCl_3$, and CH_3CN solutions (Figures S1 and S2, Supporting Information). The intensity is so strong that the naked-eye red luminescence can be observed in $CHCl_3$ and CH_3CN solutions. It is worth mentioning that a solvent dependence on the luminescence properties is similar to those for the exciton CD and CPL for similar $M^I[Ln((+)\text{-hfbc})_4]$ complexes where M^I varied from Na, K, Rb, to Cs (Figure 1 and Figure S3, Supporting Information).

Since the splitting of the ^7F_J levels is dependent on the local symmetry of the Eu(III) ion, which is mainly governed by the chemical environment around the Eu(III) ion, it is interesting to note that the $M^I[Ln((+)\text{-hfbc})_4]$ complexes are assumed to take a D_4 or C_4(*llll*) (*l* between different squares) configuration. One would expect that for such a symmetry environment the luminescence spectrum reveals a single emission peak[53] for the $^5D_0 \rightarrow {}^7F_2$ transition. Although the luminescence spectra of $M^I[Ln((+)\text{-hfbc})_4]$ were recorded in solution (Figure 1 and Figures S1–S3, Supporting Information), it can be noted that the broad band observed for the emission peak of the $^5D_0 \rightarrow {}^7F_2$ transition is consistent with what would be expected for a D_4 or C_4(*llll*) configuration. Another piece of information that can be gained from the total luminescence spectra of $M^I[Ln((+)\text{-hfbc})_4]$ is that the luminescence intensities is dependent on the nature of the alkali metal ions. The luminescence spectra of a series of $M^I[Ln((+)\text{-hfbc})_4]$ with variation of alkali metal ions in $CHCl_3$ and CH_3CN solutions are shown in Figure 1 and Figure S3, Supporting Information. Of special importance, one can see that the luminescence intensities increase with increasing alkali metal ion radii in the order of Na < K<Rb < Cs in $CHCl_3$ solution, whereas the luminescence intensities remain almost the same in CH_3CN solution. This luminescence intensity behavior is parallel to that of the CD couplet of $M^I[Ln((+)\text{-hfbc})_4]$ observed in $CHCl_3$ and CH_3CN solutions.[47] Since the CD spectra in the UV region revealed that there is a dissociated mixture of chiral SAPR-8–M–Ln

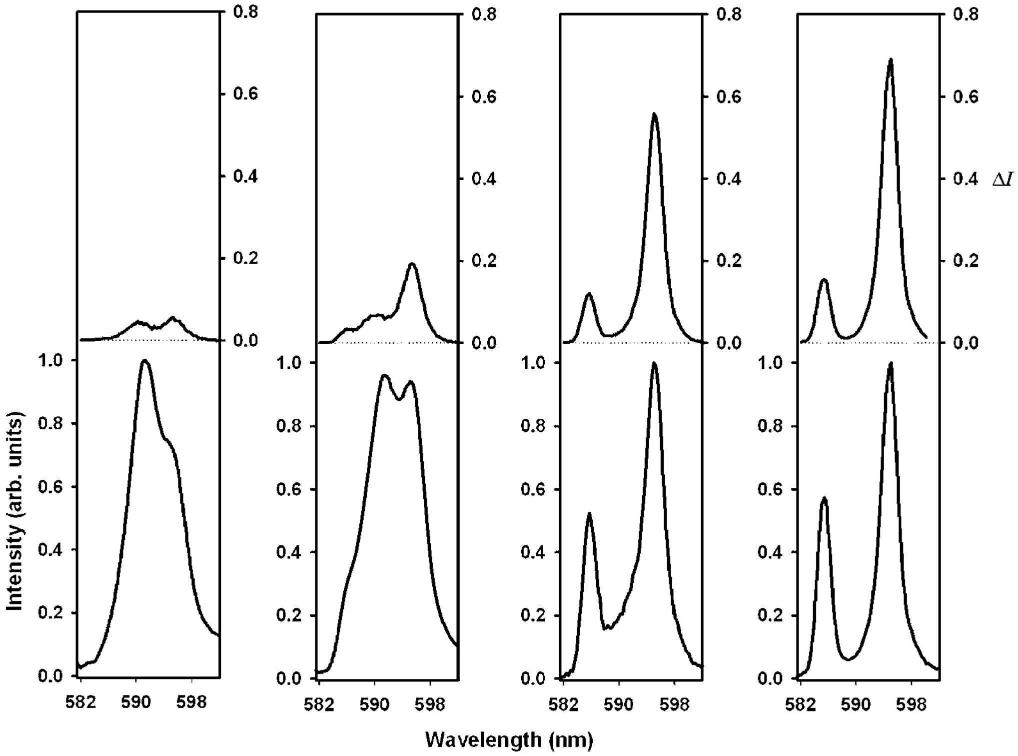

Figure 2. CPL (upper curves) and total luminescence (lower curves) spectra of the $^5D_0 \rightarrow {}^7F_1$ transition of $M^I[Eu((+)\text{-hfbc})_4]$ in 2 mM $CHCl_3$ solution at 295 K, following excitation at 352 nm. From left to right: Na–Eu, K–Eu, Rb–Eu, and Cs–Eu.

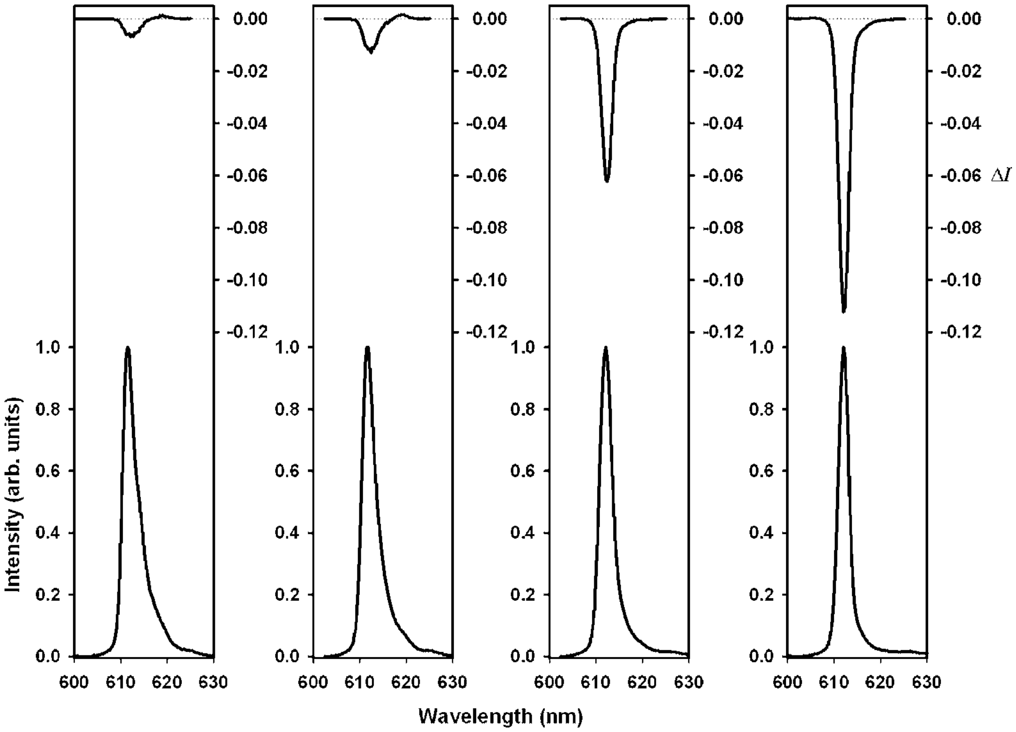

Figure 3. CPL (upper curves) and total luminescence (lower curves) spectra of the $^5D_0\rightarrow{}^7F_2$ transition of $M^I[Eu((+)\text{-hfbc})_4]$ in 2 mM $CHCl_3$ solution at 295 K, following excitation at 352 nm. From left to right: Na–Eu, K–Eu, Rb–Eu, and Cs–Eu.

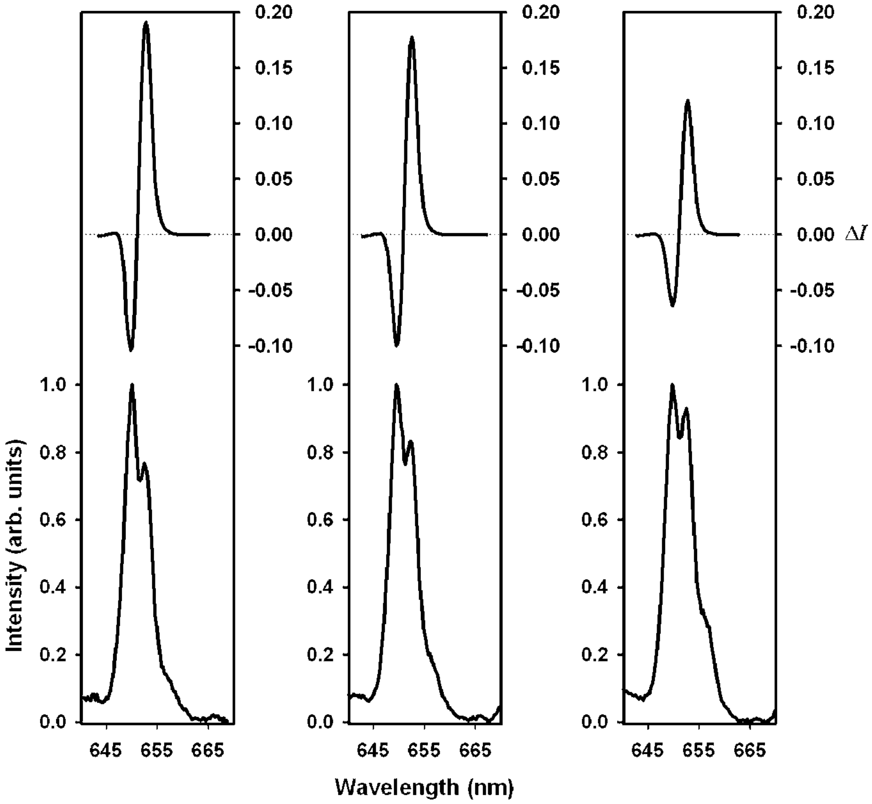

Figure 4. CPL (upper curves) and total luminescence (lower curves) spectra of the $^5D_0\rightarrow{}^7F_3$ transition of $Cs[Eu((+)\text{-hfbc})_4]$ in 2 mM EtOH (left), CH_3CN (middle), and $CHCl_3$ (right) solutions at 295 K, following excitation at 352 nm.

complexes ($[Ln((+)\text{-hfbc})_3]$ and M((+)-hfbc) in EtOH and chiral SAPR-8–M–Ln complexes and pseudo-achiral DD-8–M–Ln complexes in $CHCl_3$), one can conclude that the alkali metal dependence on the luminescence intensities of $M^I[Ln((+)\text{-hfbc})_4]$ in $CHCl_3$ results from such a speciation in solution. This can be explained by the fact that the chiral configuration around the Eu(III) ion in $\Delta\text{-}M^I[Eu((+)\text{-hfbc})_4]$ as well as the degree of dissociation of the chiral SAPR-8–M–

Table 1. g_{lum} Values of $M^I[Eu((+)\text{-hfbc})_4]$ (M^I−Eu with M^I = Na, K, Rb, and Cs) Complexes in 2 mM $CHCl_3$, EtOH, and CH_3CN at 295 K, Following Excitation at 335−360 nm

g_{lum} (λ nm)	$^5D_0 \rightarrow {}^7F_1$ $CHCl_3$	$^5D_0 \rightarrow {}^7F_1$ EtOH	$^5D_0 \rightarrow {}^7F_1$ CH_3CN	$^5D_0 \rightarrow {}^7F_2$ $CHCl_3$	$^5D_0 \rightarrow {}^7F_2$ EtOH	$^5D_0 \rightarrow {}^7F_2$ CH_3CN	$^5D_0 \rightarrow {}^7F_3$ $CHCl_3$	$^5D_0 \rightarrow {}^7F_3$ EtOH	$^5D_0 \rightarrow {}^7F_3$ CH_3CN
Na−Eu	+0.08 (591)	+0.05 (591)	+0.25 (585)	−0.02 (612)	−0.01 (612)	−0.04 (612)	not measured	not measured	not measured
	+0.15 (595)	+0.06 (595)	+0.39 (595)						
K−Eu	+0.14 (591)	+0.23 (585)	+0.22 (585)	−0.02 (612)	−0.03 (612)	−0.04 (612)	not measured	not measured	not measured
	+0.39 (595)	+0.48 (595)	+0.38 (595)						
Rb−Eu	+0.47 (585)	+0.47 (585)	+0.35 (585)	−0.12 (612)	−0.10 (612)	−0.07 (612)	not measured	not measured	not measured
	+1.12 (595)	+1.08 (595)	+0.62 (595)						
Cs−Eu	+0.55 (585)	+0.53 (585)	+0.41 (585)	−0.23 (612)	−0.19 (612)	−0.10 (612)	−0.20 (650)	−0.17 (650)	−0.12 (650)
	+1.38 (595)	+1.32 (595)	+0.79 (595)				+0.51 (653)	+0.43 (653)	+0.27 (653)

Ln complexes in solution are controlled by the size of the alkali metal ions. It is interesting to note that this alkali metal dependence is much less pronounced for CH_3CN solutions. Although the luminescence intensity, which is very difficult to predict, is dependent on the type of *β*-diketonates and, more importantly, on the type of complex, it was shown that the fine structure of the luminescence spectra of tetrakis Eu(III) complexes were influenced by the counterions in nonpolar solvents. However, in contrast, in polar solvents they are cation-independent.[52]

CPL Spectra of Eu(III)−(+)-hfbc$^-$ Complexes. To get better insight into the influence of the alkali metal ions on the chiroptical properties of $M^I[Ln((+)\text{-hfbc})_4]$ in CH_3CN, $CHCl_3$, and EtOH solutions, we have resorted to CPL to determine whether or not the solvents and/or the alkali metal ions influence the chiral structure of the compounds of interest.

The CPL spectra of 2 mM $CHCl_3$ solutions of $M^I[Eu((+)\text{-hfbc})_4]$ (M^I = Na, K, Rb, Cs) are plotted in Figure 2 in the spectral range of the $^5D_0 \rightarrow {}^7F_1$ transition, which is particularly well-suited for CPL measurements, since it satisfies the magnetic-dipole selection rule, $\Delta J = 0 \pm 1$ (except $0 \leftrightarrow 0$).[36] Although one would predict that the CPL would be large for this magnetic-dipole-allowed $^5D_0 \rightarrow {}^7F_1$ transition, we also measured the CPL spectra of the $^5D_0 \rightarrow {}^7F_2$ and $^7F_3$ transitions of Eu(III) for the compounds of interest, even if these two transitions do not satisfy the magnetic-dipole selection rule (see Figures 3 and 4 and Table 1). As one would expect, the CPL signal of the two latter transitions is less pronounced than for the $^5D_0 \rightarrow {}^7F_1$ transition but still measurable. For instance, CPL peaks are observed for the $^5D_0 \rightarrow {}^7F_1$ (g_{lum} = +1.38 at 595 nm), $^5D_0 \rightarrow {}^7F_2$ (−0.23 at 612 nm), and $^5D_0 \rightarrow {}^7F_3$ transitions (−0.20 and +0.51 at 650 and 653 nm) in the CPL spectra of a 2 mM $CHCl_3$ solution of $Cs[Eu((+)\text{-hfbc})_4]$.

One can conclude that the detection of CPL signals for a series of the M^I−Eu complexes confirmed the presence of stable chiral emitting species on the luminescence time scale. The g_{lum} values of $M^I[Eu((+)\text{-hfbc})_4]$ (Na−, K−, Rb−, Cs−Eu) amounted to +0.15, +0.39, +1.12, and +1.38 at 595 nm, respectively. Like the luminescence intensity behavior, the magnitude of the g_{lum} values is also affected by the alkali metal ion sizes. The larger CPL components are observed in the M−Eu complexes with the larger alkali metal ions, since the magnitude of the g_{lum} values follows the Na−Eu < K−Eu < Rb−Eu <Cs−Eu trend both in $CHCl_3$ and EtOH solutions (Figures 2−4 and Table 1). For instance, the g_{lum} ($^5D_0 \rightarrow {}^7F_1$) values of the Cs−Eu complex is 9 vs. 22 times as large as that of the Na−Eu compound (+1.38 and +1.32 vs. +0.15 and +0.06) in $CHCl_3$ and EtOH solutions, respectively. In addition, the difference in g_{lum} values for the Na−Eu complex between the $CHCl_3$ and EtOH solutions is larger (2.6 times) than that of other M−Eu complexes (<ca. 1.6 times). It is interesting to note that the Na−La complex gives no CD couplet but only a single positive CD in 2−0.02 mM EtOH and a CD couplet in 2 mM $CHCl_3$, whereas other M^I−La compounds show CD couplets in both 2 mM $CHCl_3$ and 2 mM EtOH.[47,49,50] The observation of a couplet CD indicates the existence of a chiral helical configuration, whereas a single CD suggests the disruption of the chiral configuration toward $[Ln((+)\text{-hfbc})_3]$ as a result of the facile solvation by EtOH. It is also interesting to note that the g_{lum} values of M−Eu solutions are quite larger than those of $[Eu((+)\text{-hfbc})_3]$. This strongly suggests that chiral stereoselectivity for tetrakis-(+)-hfbc complexes is retained by alkali metal ions. In a preliminary report, we showed that the g_{lum} values obtained for $[Eu((+)\text{-hfbc})_3]$ and $M^I[Eu((+)\text{-hfbc})_4]$ complexes had opposite signs but, more importantly, that the CPL activity of $[Eu((+)\text{-hfbc})_3]$ was almost negligible (+0.003 vs. −0.19 for Cs−Eu at 612 nm in 2 mM EtOH, see Table S1, Supporting Information).[46] This strongly implied that the helical Δ-SAPR(C_4) arrangement of the four (+)-hfbc ligands in the M−Eu complexes accounted for the CPL pattern of the M−Eu complexes, which in turn was controlled by the metal alkali ion sizes. Thus, the 9-fold decrease in the magnitude of the g_{lum} values of the Na−Eu may be attributed from a less chiral environment for the Eu(III) ion in Na−Eu compared to Cs−Eu (Figure 2 and Table 1). Comparing CD spectroscopy, where all of the absorbing chromophores contribute to the observed absorption measurement (i.e., variation in the CD due to the contribution of both $Cs[Eu((+)\text{-hfbc})_4]$ and $[Eu((+)\text{-hfbc})_3]$ or DD-8−Cs−Eu species present in solution),[47] CPL spectroscopy is limited to only luminescent species. More importantly, the sign and magnitude of CPL are mainly affected by the degree of helical twist of the complex, the nature of the ligand field, and by modulating the polarizability[54,55] of the axial donor group solvation. In other words, the CPL signal reflects the time-averaged local helicity around the Ln(III) ion (i.e., the magnitude of g_{lum} values increases with an increase in the degree of conformational rigidity of the complex).[24]

Although the effect of the alkali metal ions on the CPL activity of a series of $M^I[Eu((+)\text{-hfbc})_4]$ is an important factor in the stereospecific formation of the helical arrangement of the four (+)-hfbc ligands around the Eu(III) ion, one must also consider the influence of the solvent and, in particular, the complex speciation on the chiroptical properties of these systems of interest. As one may expect, a solvent dependence is also observed since the magnitude of the g_{lum} values (+0.79, +0.62, +0.38, +0.39; +1.38, +1.12, +0.39, +0.15; and +1.32, +1.08, +0.48, +0.06 at 595 nm, Table 1) varies among the Cs−, Rb−, K−, and Na−Eu complexes, respectively, in 2 mM MeCN, $CHCl_3$, and EtOH solutions. This observation suggests that the solvent effect is probably due to the difference in susceptibility to the solute−solvent interaction (hydrogen bond) toward the fluorocarbon of (+)-hfbc and/or the solvation toward the alkali metal ion but not toward the Eu(III) ion, unlike the case of axially symmetric DOTA-type complexes.[25,45] However, it is quite interesting to note that the CPL activity of Cs−Eu is not concentration-dependent. In 0.2 mM $CHCl_3$ or EtOH, the g_{lum} ($^5D_0 \rightarrow {}^7F_1$) value is +1.38 or +1.32, which is the same as the one observed for a 2 mM complex solution in $CHCl_3$ or EtOH (Table S1, Supporting Information). On the other hand, the CD intensities in the intraligand transition were concentration-dependent in EtOH (going from a weaker CD couplet to a single CD band with lowering the concentration), while there is a smaller concentration dependence in CH_3CN.[47,49,50] In our previous report, we showed that the variation in the CD couplet was due to the contribution of two different species present in solution, SAPR-8− Cs[Eu((+)-hfbc)$_4$] and [Eu((+)-hfbc)$_3$] or pseudo-achiral DD-8−[Eu((+)-hfbc)$_4$].[47]

As in our previous report,[46] the existence of [Eu((+)-hfbc)$_3$] was substantiated by both the concentration-dependent CD couplet (i.e., the 0.2 mM EtOH Na−Eu and 0.02 mM EtOH Cs−Eu complex solutions gave a single positive CD band similar to that of [Eu((+)-hfbc)$_3$], confirming that [Eu((+)-hfbc)$_3$] was the predominant species in the M^I−Eu solutions at lower concentration) and, more specifically, by the observation of two distinctive $^5D_0 \leftarrow {}^7F_0$ excitation peaks of the 2−0.2 mM Cs−Eu complex solutions and the coincidence of only one peak around 579.3 nm of 0.02 mM Cs−Eu and 2−0.02 mM [Eu((+)-hfbc)$_3$]. This is also confirmed by comparing the luminescence spectra and the CPL activities of [Eu((+)-hfbc)$_3$] and Cs−Eu. As shown in Figure S1 (Supporting Information), the $^5D_0 \rightarrow {}^7F_2$ luminescence peaks of the Cs−Eu in 2 mM solution are more intense by ca. 84 times than those of [Eu((+)-hfbc)$_3$]. This suggests that the contribution of [Eu((+)-hfbc)$_3$] to the luminescence properties of the Cs−Eu complex solution is almost negligible.

As already discussed above, this is even more obvious when one considers the large difference in the CPL activity of both species in EtOH (g_{lum} values of only +0.002 or +0.003 vs. twice −0.19 in the spectral range of the $^5D_0 \rightarrow {}^7F_2$ transition, Table S1, Supporting Information). It is also noticeable that a constant CPL activity is observed even if the Cs−Eu is a minor species in solution (i.e., 0.2 mM complex solution). This is explained by the fact that the Cs−Eu exhibits strong CPL activity in solution, whereas the CPL activity of [Eu((+)-hfbc)$_3$] is negligible (lack of the influence of the helical Δ-SAPR(C_4) arrangement of the four (+)-hfbc ligands as observed in M^I[Eu((+)-hfbc)$_4$]). This is also true for the various M^I−Eu complexes studied in EtOH, since larger g_{lum} values of M−Eu (−0.19 for Cs, −0.10 for Rb, −0.03 for K, and −0.01 for Na) than [Eu((+)-hfbc)$_3$] (+0.003 and +0.002) at 612 nm were obtained (Table 1 and Table S1, Supporting Information).

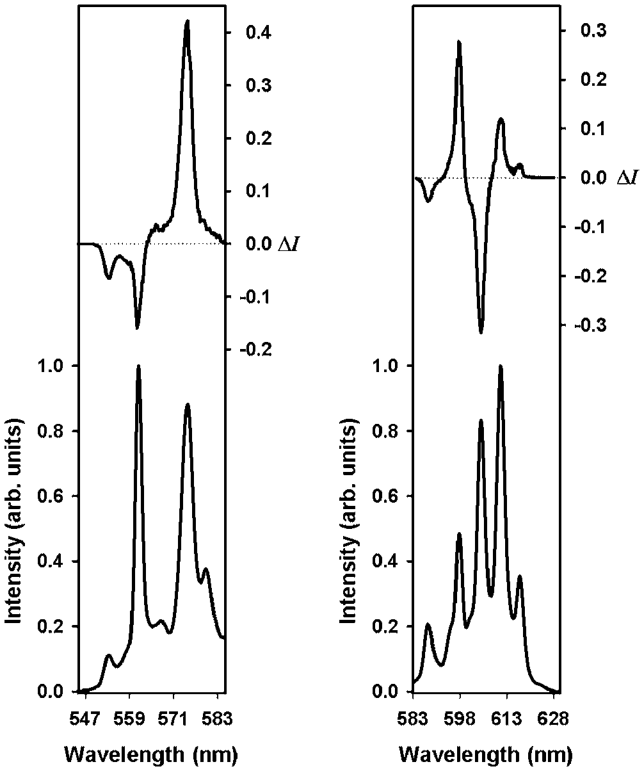

Figure 5. CPL (upper curves) and total luminescence (lower curves) of the $^4G_{4/2} \rightarrow {}^6H_{5/2}$ (left) and $^4G_{4/2} \rightarrow {}^6H_{7/2}$ (right) transitions of Cs[Sm((+)-hfbc)$_4$]·H_2O in 2 mM $CHCl_3$ solution at 295 K, following excitation at 338 nm.

Finally, we were also able to record the CPL spectra of the Cs−Sm compound in $CHCl_3$ solution upon UV excitation (Figure 5). The CPL spectrum of the two magnetic-dipole-allowed $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{5/2}$ transitions displays several peaks corresponding to crystal-field splitting of the electronic level. The observed CPL values are the largest ever measured for Sm(III) compounds ($g_{lum} > 1$), as summarized in Table 2. To the best of our knowledge, there are only a few examples of CPL spectra for chiral and/or racemic Sm(III) complexes with chiral and/or achiral ligands, respectively.[40,41,56] However, none of these systems have a CPL value comparable to our compound. Although one may expect simpler CPL spectra for Eu(III)-containing compounds (the splitting of the ^7F_j levels is less important than those for the analogous Sm(III) or other luminescent Ln(III) complexes) which are more amenable to chiroptical spectra−structural interpretation, the strong CPL activity of the Cs−Sm complex also supports the findings of the Eu(III)-based systems (importance of the helical structure) and that it is not only relevant for one given Ln(III) ion. However, one may expect differences in the CPL activity if

Table 2. g_{lum} Values of Cs[Sm((+)-hfbc)$_4$]·H_2O in 2 mM $CHCl_3$ at 295 K, Following Excitation at 338 nm

electronic transitions	g_{lum} (λ nm)
$^4G_{5/2} \rightarrow {}^6H_{5/2}$	−1.15 (553)
	−0.35 (561)
	+0.96 (575)
$^4G_{5/2} \rightarrow {}^6H_{7/2}$	−0.45 (588)
	+1.15 (598)
	−0.76 (605)
	+0.24 (611)
	+0.15 (617)

the local structural environment around the Ln(III) is slightly perturbed due to the effect of the Ln(III) ion size.

CPL-Based Chiroptical Spectra−Structural Relationship. Although the application of the exciton CD is a relatively successful method for the determination of absolute configuration of transition metal compounds,[4,11,20−22] however, its application to the 4f−4f transitions of Ln(III) systems is much more complicated. This results from the fact that these compounds are often too labile in solution (hindered fixing of the chiral structure in solution) and from the nature of the 4f electronic state, for which the intensity of 4f−4f transitions is too weak to record reliable ECD spectra (requirement of working with high concentration and long cell path lengths), but it is mainly because they are less understood in theory. However, one may envisage investigating a potential correlation between the chiral structure of metal-containing compounds and their chiral spectral features using a combination of chiroptical tools such as CD and CPL. In other words, one may want to compare the signs for the exciton CD and CPL bands of the systems of interest with the expectations of identical findings. The key point is to identify the ideal compound target that may satisfy the various requirements of the aforementioned techniques (i.e., observation of clear exciton CD bands, Ln(III)-based coordination compounds that possess a high symmetry, strong chiroptical properties measurable by CD and CPL). The main requirements for such analyses are probably the use of enantiopure Ln(III)-containing edifices (chiral structure due to the arrangement of ligand molecules around the luminescent center) or related compounds for which the presence of at least one asymmetric carbon atom in the ligand molecule(s) surrounding the Ln(III) ion results in a complete diastereomeric resolution of the Ln(III)-based systems. Additionally, these compounds necessitate the possession of a defined high symmetry (i.e., C_4-symmetric species or at least with a trigonal symmetry) and a conformational rigidity in solution on the time scale of the measurement (i.e., CPL and CD). In fact, one may want to consider Ln(III)-containing edifices that possess a limited number of individual crystal field levels. That is the reason why the use of low-symmetric Ln(III) complexes would be more problematic since they would result in more complexed CD and CPL spectra and, therefore, complicate the identification and/or assignment of the various components of the studied transitions. As already mentioned earlier, the choice of studying Eu(III) compounds would also lead to simpler CPL spectra since the splitting of the ^7F_j levels is less important than for the other luminescent Ln(III) complexes.

Working along these lines, it was observed that our systems of interest, the $M^I[Eu((+)\text{-hfbc})_4]$ complexes, which are stereospecifically formed with helically four-bladed chiral Δ-SAPR−(C_4(*llll*)) configurations with the aid of CF···M^I intramolecular interactions (supported by X-ray crystallography, NMR, and/or chiroptical techniques),[46−50] followed a similar CD sign pattern to that of the C_4-symmetric chiral tetraamide-based (*S*)-Δ-Eu(III) compounds with naphtyl groups[57,58] (the strong exciton coupling exhibited by the (*S*)-Δ-Eu(III) complex was associated with a negative CD sign). That is, a negative CD couplet around 300 nm in $CHCl_3$, and for the different alkali metal ions Na, K, Rb, and Cs, though, a part of Δ-SAPR-(C_4(*llll*))−M−Ln complexes turns to pseudo-achiral DD-8−D_{2d}−M−Ln complexes in $CHCl_3$ solutions. An identical finding was observed for MeCN, whereas the CD pattern in a dilute EtOH solution was similar to that of the CD of $[Eu((+)\text{-hfbc})_3]$, suggesting the dissociation of $M^I[Eu((+)\text{-hfbc})_4]$ into $[Eu((+)\text{-hfbc})_3]$.[47] This dissociation was also corroborated by CPL and the $^5D_0{\leftarrow}^7F_0$(Eu) excitation spectroscopy.[46,47] Similarly, the $M^I[Eu((+)\text{-hfbc})_4]$ complexes showed that the CPL sign was following a parallel pattern among the various alkali metals and solvents studies (M^I = Na, K, Rb, Cs, and $CHCl_3$, EtOH, and MeCN). It was observed that the two components at 585 and 595 nm of the magnetic-dipole-allowed $^5D_0{\rightarrow}^7F_1$ were positive. It is interesting to note that the single and two components of the $^5D_0{\rightarrow}^7F_2$ and $^5D_0{\rightarrow}^7F_3$ transitions were also showing a similar pattern consisting of negative and negative−positive CPL signs at around 612 nm and 650 and 653 nm for the various M^I and solvents investigated, respectively. Although the CPL sign pattern result is comparable to the magnetic-dipole-allowed $^5D_0{\rightarrow}^7F_1$ transition, one must be aware that these two transitions, $^5D_0{\rightarrow}^7F_2$ and $^5D_0{\rightarrow}^7F_3$, are not theoretically the most favorable chiroptical transition-like probes to be considered since they do not obey the magnetic-dipole rule.

Since the magnitude of the g_{lum} values for the magnetic-dipole-allowed $^5D_0{\rightarrow}^7F_1$ transition is so large (>1) and considering that this behavior is parallel to the large exciton CD couplet observed for the systems of interest (i.e., $Cs[Eu((+)\text{-hfbc})_4]$ exhibits strong CPL and exciton CD activities in 2 mM $CHCl_3$), one may anticipate that the local symmetry of the Eu(III) site in $M^I[Eu((+)\text{-hfbc})_4]$ is retained. Thus, the helical Δ-SAPR(C_4) arrangement of the four (+)-hfbc ligands in $M^I[Eu((+)\text{-hfbc})_4]$ accounts for the CPL pattern of the M^I−Eu complexes. In other words, the strong CPL activity observed supports that the chirality of the Eu(III) ion of $M^I[Eu((+)\text{-hfbc})_4]$ in the excited state corresponds to that in the ground state derived from the exciton CD. It should also be mentioned that these findings were also corroborated by the detection of strong CPL and exciton CD activities for the analogous complex with Sm(III) instead of Eu(III).

CONCLUSIONS

Although the findings are of a preliminary nature, they support the fact that one may be able to develop a "helicity rule" aimed at determining a Δ or Λ helicity configuration based upon CPL sign patterns when the chiral systems of interest possess high and defined symmetries and, thus, exhibit strong CPL activities. It was observed that a positive component at around 595 nm for the magnetic-dipole-allowed $^5D_0{\rightarrow}^7F_1$ transition of $M^I[Eu((+)\text{-hfbc})_4]$ indicates a Δ configuration for the local helicity environment around the Eu(III) ion, whereas the exciton CD in the intraligand $\pi-\pi^*$ transitions of (+)-hfbc$^-$ shows a negative CD couplet around 300 nm. It is interesting to note that almost a similar pattern was observed in the CPL and UV CD for the Eu(III) and Sm(III) complexes with the chiral 2-hydroxyisophthalamide octadentate ligand.[40] That is, a negative−positive exciton CD is observed in the UV region for the Δ−Ln complexes, while a positive ($^5D_0{\rightarrow}^7F_1$) and positive−negative ($^4G_{4/2}{\rightarrow}^6H_{7/2}$) CPL signs are observed for the Δ-Eu(III) and Sm(III) compounds, respectively. Although these complexes may not present the same structure as ours, they also exhibit strong CPL activities (mainly the Eu(III) compound). Consequently, the combination of these observations may open new perspectives for the potential development of an empirical spectra/structure correlation based upon chiroptical spectral information. Research in these directions is currently underway.

To conclude, it is possible to make more selective measurements of chiral Ln(III)-based species using the CPL spectroscopy. These are significant results, indicating that CPL is a useful technique in analyzing solution chiroptical chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1−S3 (total luminescence spectra of $M^I[Eu((+)\text{-}hfbc)_4]$ and $[Eu((+)\text{-}hfbc)_3]$ in 0.035, 0.2, and/or 2 mM $CHCl_3$, EtOH, and/or CH_3CN) and Table S1 (CPL results for $M^I[Eu((+)\text{-}hfbc)_4]$ (M^I = Cs and Na) and $[Eu((+)\text{-}hfbc)_3]$ in 0.2 and 2 mM $CHCl_3$ and EtOH). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gilles.muller@sjsu.edu.

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