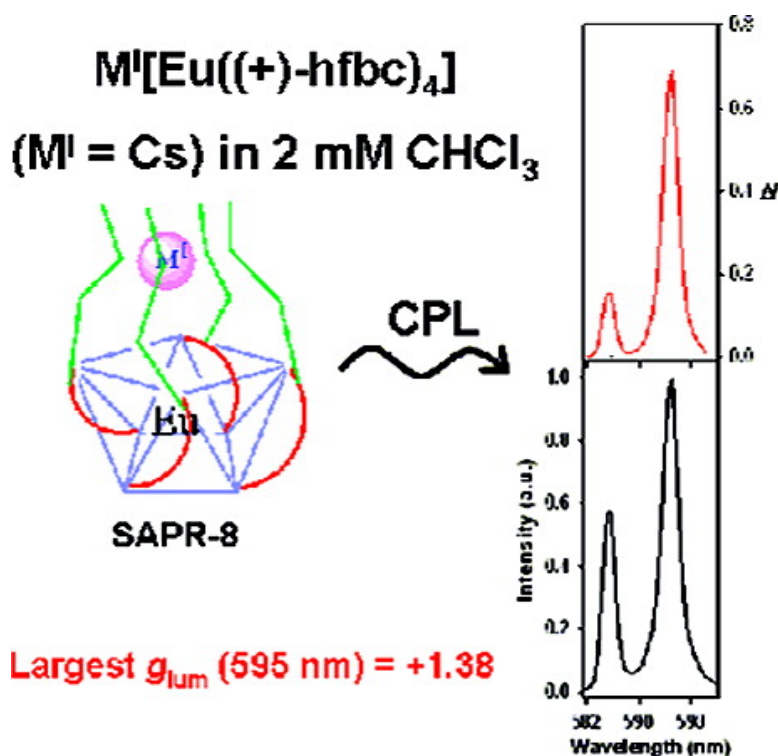


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## Extraordinary Circularly Polarized Luminescence Activity Exhibited by Cesium Tetrakis(3-heptafluoro-butylryl-(+)-camphorato) Eu(III) Complexes in EtOH and CHCl<sub>3</sub> Solutions

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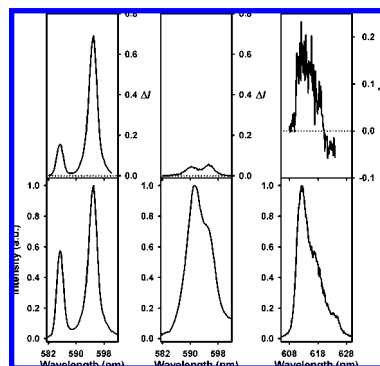
Received July 21, 2008; E-mail: gilles.muller@sjsu.edu.

Circularly polarized luminescence (CPL) spectroscopy is the emission analogue to circular dichroism (CD) spectroscopy.<sup>1</sup> It is common to report the degree of CPL in terms of the luminescence dissymmetry factor,  $g_{\text{lum}}(\lambda)$ , which is defined as follows:  $g_{\text{lum}}(\lambda) = 2\Delta I/I = 2(I_L - I_R)/(I_L + I_R)$ , where  $I_L$  and  $I_R$  refer, respectively, to the intensity of left and right circularly polarized emissions. A value of 0 for  $g_{\text{lum}}$  corresponds to no circular polarization, while the absolute maximum value is 2. Although the development of useful correlation between CPL spectrum and chiral structure is still limited,<sup>1</sup> a study by Bruce et al.<sup>2</sup> conducted on well-defined DOTA-based macrocyclic Eu(III) complexes led to the following conclusion. The sign and magnitude of CPL are affected by the degree of helical twist of the complex, the nature of the ligand field, and the axial donor group solvation. Of special importance is that the CPL will reflect the time-averaged local helicity around the lanthanide(III) ion (i.e., the magnitude of  $g_{\text{lum}}$  values increases with an increase in the degree of conformational rigidity of the complex).

To date, the largest  $g_{\text{lum}}$  value reported in the literature was for the commercially available NMR shift reagent tris(3-trifluoro-acetyl-(+)-camphorato)europium(III), [Eu(+)-facam]<sub>3</sub>, in dry DMSO ( $g_{\text{lum}}$  value of  $-0.78$  at 588.2 nm),<sup>3,4</sup> whereas lanthanide-containing systems with chiral 2-hydroxyisophthalamide-, pyridyl diamide-, 1-hydroxy-2-pyridinone-, or DOTA-based ligand derivatives exhibited  $g_{\text{lum}}$  values as high as 0.5.<sup>1,4-8</sup>

Recently, we reported on the isolation and structural characterization of sodium or cesium tetrakis(3-heptafluoro-butylryl-(+)-camphorato) lanthanide(III) complexes, M<sup>I</sup>[Ln(+)-hfbc]<sub>4</sub>, by X-ray analysis and/or CD spectroscopy. The solution structure is supposed to take a square antiprism eight coordination (SAPR-8) with  $\Delta$ -configurational chirality on the basis of the exciton CD spectra.<sup>9,10</sup> In this communication, the CPL as well as CD of M<sup>I</sup>[Eu(+)-hfbc]<sub>4</sub> complexes (M<sup>I</sup> = Cs and Na) in CHCl<sub>3</sub> and EtOH were examined in order to reveal the detailed chiral configuration in solution. Of special interest is the importance of using CPL for selectively studying only luminescent chromophores present in the systems of interest, in contrast to CD, which is affected by most chromophores and/or equilibrium mixtures in an additive manner. The M<sup>I</sup>[Eu(+)-hfbc]<sub>4</sub> (M<sup>I</sup> = Cs and Na) compounds were obtained as crystals by the reported method (see Supporting Information).<sup>9,10</sup>

The CPL spectra of 2 mM solutions of M<sup>I</sup>[Eu(+)-hfbc]<sub>4</sub> (M<sup>I</sup> = Cs and Na) in CHCl<sub>3</sub> are plotted in Figure 1 in the spectral range of the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> transition, which is particularly well-suited for CPL measurements since it satisfies the magnetic-dipole selection rule,  $\Delta J = 0, \pm 1$  (except 0 ↔ 0), respectively. As shown in Figure 1, the detection of a CPL signal confirmed the presence of stable



**Figure 1.** CPL (upper curves) and total luminescence (lower curves) spectra for the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> transition of the 2 mM Cs[Eu(+)-hfbc]<sub>4</sub> (left) and Na[Eu(+)-hfbc]<sub>4</sub> (middle) solutions in CHCl<sub>3</sub>, and for the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition of the 2 mM [Eu(+)-hfbc]<sub>3</sub> solution (right,  $\Delta I \times 10^2$ ) in EtOH at 295 K, upon excitation at 352 and 335 nm, and 359 nm, respectively.

**Table 1.** Summary of CPL Results for M<sup>I</sup>[Eu(+)-hfbc]<sub>4</sub> (M<sup>I</sup> = Cs, Na) and [Eu(+)-hfbc]<sub>3</sub> at 295 K ( $\lambda_{\text{exc}} = 335\text{--}359$  nm Range)

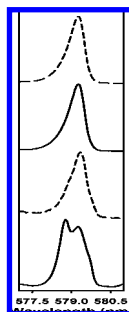
complex	solvent	solvent concn [mM]	( <sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub> (nm))	( <sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>2</sub> (nm))
Cs[Eu(+)-hfbc] <sub>4</sub>	EtOH	2	+1.32 (595)	-0.19 (612)
		0.2	+1.32 (595)	-0.19 (612)
	CHCl <sub>3</sub>	2	+1.38 (595)	-0.23 (612)
0.2		+1.38 (595)	-0.23 (612)	
Na[Eu(+)-hfbc] <sub>4</sub>	EtOH	2	+0.06 (595)	-0.01 (612)
		0.2	-0.01 (612)	-0.01 (612)
	CHCl <sub>3</sub>	2	+0.15 (595)	-0.02 (612)
0.2		-0.02 (612)	-0.02 (612)	
[Eu(+)-hfbc] <sub>3</sub>	EtOH	2	+0.003 (612)	+0.003 (612)
		0.2	+0.002 (612)	+0.002 (612)

chiral emitting species on the luminescence time scale. The  $g_{\text{lum}}$  values of the M<sup>I</sup>[Eu(+)-hfbc]<sub>4</sub> (M<sup>I</sup> = Cs and Na) complexes amounted to +1.38 and +0.15 at 595 nm, respectively. The magnitude of the  $g_{\text{lum}}$  values is affected by the alkali metal ion sizes (9-fold difference between Cs–Eu and Na–Eu). And also the solvent dependence is observed; 1- and 2.5-fold differences in the magnitude of the  $g_{\text{lum}}$  values were observed between the 2 mM Cs–Eu and Na–Eu complex solutions in CHCl<sub>3</sub> and EtOH, respectively (+1.38 vs +1.32 and +0.15 vs +0.06 at 595 nm, Table 1).

We have resorted to the <sup>5</sup>D<sub>0</sub> ← <sup>7</sup>F<sub>0</sub> (Eu) excitation spectroscopy to study the speciation of the Cs–Eu complex solution and investigate its influence on the CPL results, upon monitoring at 612 nm in the spectral range of the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> emission transition. In Figure 2 we show the <sup>5</sup>D<sub>0</sub> ← <sup>7</sup>F<sub>0</sub> excitation spectra of the 2 and 0.2 mM Cs–Eu complex solutions in EtOH. These spectra show two peaks centered around 578.8 and 579.3 nm, and predominantly

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**Figure 2.**  $^5D_0 \leftarrow ^7F_0$  excitation spectra of the 2 (solid lines) and 0.2 mM (dashed lines)  $Cs[Eu((+)-hfbc)_4]$  (first two spectra from bottom) and  $[Eu((+)-hfbc)_3]$  (last two spectra from bottom) solutions in EtOH at 295 K, respectively. The luminescence was monitored at about 612 nm.

one peak centered at 579.3 nm for the 2 and 0.2 mM  $Cs-Eu$  complex solutions, respectively. These results confirm the presence of different species in solution. It is interesting to note that the CPL activities of the  $Cs-Eu$  and  $Na-Eu$  complexes are not concentration dependent (see  $g_{lum}$  values at 612 nm in Table 1). However, the CD intensities in the intraligand transition are concentration dependent in EtOH; going from a weaker exciton couplet to a single CD band with lowering the concentration,<sup>9,10</sup> while little concentration dependence was observed in  $CHCl_3$  (Supporting Information, Figures S1, S2). These observations suggest that the large CPL activity observed for the  $Cs-Eu$  complex solution originates from the tetrakis (+)-hfbc  $Eu(III)$  complex still present at lower concentrations. Unlike the CPL activity, the variation in the exciton CD activity is due to the contribution of both species present in solution.

This was confirmed by comparing the  $^5D_0 \leftarrow ^7F_0$  excitation spectra of the  $[Eu((+)-hfbc)_3]$  solutions with that of the  $Cs-Eu$  complex. These  $^5D_0 \leftarrow ^7F_0$  excitation spectra of the 2 and 0.2 mM  $[Eu((+)-hfbc)_3]$  solutions showed one main peak centered around 579.3 nm in Figure 2. On the other hand, the 0.2 mM  $Na-Eu$  and 0.02 mM  $Cs-Eu$  solutions in EtOH give a single positive CD band similar to that of the  $[Eu((+)-hfbc)_3]$  (Figures S1, S2). These facts confirm that the predominant species in the  $M^I-Eu$  solutions at lower concentration is due to the presence of the  $[Eu((+)-hfbc)_3]$  compound. This is consistent with the CPL results. Unlike the  $Cs-Eu$  and  $Na-Eu$  complexes ( $g_{lum}$  values of  $-0.19$  and  $-0.01$  at 612 nm, respectively), the CPL signal of the 2 and 0.2 mM  $[Eu((+)-hfbc)_3]$  solutions in EtOH is very weak ( $g_{lum}$  values of  $+0.003$  and  $+0.002$  at 612 nm, respectively, Table 1). In addition, the  $g_{lum}$  values obtained for  $[Eu((+)-hfbc)_3]$  and  $M^I-Eu$  complexes have opposite signs. These observations suggest that the concentration dependence of the  $^5D_0 \leftarrow ^7F_0$  excitation spectra for the  $Cs-Eu$  solution and of the CD of the  $M^I-Eu$  complexes result from the dissociation of the tetrakis (+)-hfbc  $Eu(III)$  complex ( $Cs-Eu$ ) into the tris (+)-hfbc  $Eu(III)$  compound,  $[Eu((+)-hfbc)_3]$ . On the other hand, the constant CPL activity observed for the  $M^I-Eu$  complex solution upon 10-fold dilution is due to the helical  $\Delta$ -SAPR( $C_4$ ) arrangement of the four (+)-hfbc ligands,<sup>9,10</sup> even if  $M^I[Eu((+)-hfbc)_4]$  is the minor species in solution at lower concentrations. This latter species shows strong CPL activity in solution, whereas the CPL activity of  $[Eu((+)-hfbc)_3]$  is almost negligible, as corroborated by its CPL data (Figure 1 and Table 1).

It is also interesting to note that the difference of the line shape of the  $^5D_0 \rightarrow ^7F_1$  emission bands between the two total luminescence spectra of  $M^I[Eu((+)-hfbc)_4]$  suggests a difference in local crystal field around the  $Eu(III)$  ions (Figure 1). 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. Knowing that the constant CPL activity (it is not concentration dependent) is due to the helical  $\Delta$ -SAPR( $C_4$ ) arrangement of the four (+)-hfbc ligands in  $M^I[Eu((+)-hfbc)_4]$ , the 9-fold decrease in the magnitude of the CPL signal of the  $Na-Eu$  complex results from a less chiral environment for the  $Eu(III)$  ion in  $Na-Eu$  compared to  $Cs-Eu$  (Figure 1 and Table 1). This observation suggests that the helical  $\Delta$ -SAPR( $C_4$ ) arrangement of the four (+)-hfbc ligands in  $CHCl_3$  and EtOH accounts for the CPL pattern of the  $M^I-Ln$  complexes, which in turn is controlled by the alkali metal ion sizes. The solvent and alkali metal ion effects are due to the difference in susceptibility to solvation toward the alkali metal ion, but not toward the  $Eu(III)$  ion unlike the case of axially symmetric DOTA-type complexes.<sup>1,2</sup> A complete study of such effects on the CPL activity of  $M^I[Ln((+)-hfbc)_4]$  will be described in a forthcoming publication.

In conclusion, the observation of a constant and large CPL activity substantiates the stereospecific formation of chiral  $\Delta$ -SAPR- ( $C_4$ ) configurations with aid of  $M^I \cdots FC$  (fluorocarbon) interactions as revealed by the X-ray analysis more clearly than the exciton CD spectra.<sup>9,10</sup> It is also found that the  $Cs-Eu$  and  $Na-Eu$  complexes are dissociated in an equilibrium with the  $[Eu((+)-hfbc)_3]$  at lower concentrations. Knowing that the absolute maximum  $g_{lum}$  value is 2, the reported  $g_{lum}$  values for the  $Cs[Eu((+)-hfbc)_4]$  complex in EtOH and  $CHCl_3$  solutions are the highest ever observed for any CPL studies of lanthanide-containing compound solutions described in the literature. The observation of large CPL activities with variation of  $M^I$  ions and solvents opens new perspective for the studies aimed at understanding the chiroptical spectral-structure relationships and their important roles in configurational chirality for chemical sensors, NMR shift reagents, or chiral catalysis.

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**Supporting Information Available:** Experimental section and Figures S1 and S2 (CD spectra of  $M^I[Eu((+)-hfbc)_4]$  ( $M^I = Cs$  and  $Na$ ) and  $[Eu((+)-hfbc)_3]$  in EtOH and/or  $CHCl_3$ ). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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