Lanthanide Spectroscopy

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Detection of Circularly Polarized Luminescence of a Cs-Eu^{III} Complex in Raman Optical Activity Experiments

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Abstract: *Circularly polarized luminescence (CPL) spectra are extremely sensitive to molecular structure. However, conventional CPL measurements are difficult and require expensive instrumentation. As an alternative, we explore CPL using Raman scattering and Raman optical activity (ROA) spectroscopy. The cesium tetrakis(3-heptafluoro-butylryl-(+)-camphorato) europium(III) complex was chosen as a model as it is known to exhibit very large CPL dissymmetry ratio. The fluorescent bands could be discriminated from true Raman signals by comparison of spectra acquired with different laser excitation wavelengths. Furthermore, the ROA technique enables fluorescence identification by measuring the degree of circularity. The CPL dissymmetry ratio was measured as the ROA circular intensity difference of 0.71, the largest one ever reported. The alternative CPL measurement enhances applications of lanthanides in analytical chemistry and chemical imaging of biological objects.*

Molecular probes based on luminescent lanthanide(III) complexes are commonly employed for analytical and biomedical applications, such as therapeutic and diagnostic tools.[1] They were also suggested as memory devices compatible with the technology of quantum computing.[2] Their unique properties are given by the exceptional lanthanide electronic structure, such as shielding of the f-electrons from the environment by the outer s-shell, and a plethora of electronic transitions, often observable only because of the relativistic effects.[3]

Circularly polarized luminescence (CPL) of lanthanides appears particularly attractive as the spectra provide more information and are highly sensitive to fine structural details compared to unpolarized luminescence.[4] The electric-dipole semi-forbidden electronic transitions in lanthanides exhibit relatively large magnetic dipole and electric quadrupole components,[5] providing high CPL intensities.[6] For example, the dissymmetry factor, $g = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R refer to respective intensities of left- and right-circularly polarized emission, can reach almost the limit of 2 in some lanthanide complexes,[4b] whereas values of 10^{-2}–10^{-3} are typically encountered in most chiral organic molecules. For the heterobimetallic complex studied here, Δ-CsEu[(+)-hfbc]$_4$ (hfbc = 3-heptafluorobutyryl camphorate, Figure 1), a g-value of 1.38 was measured.[7] To date, this is the highest value found for a lanthanide complex and is one of the highest experimental g-values ever reported.

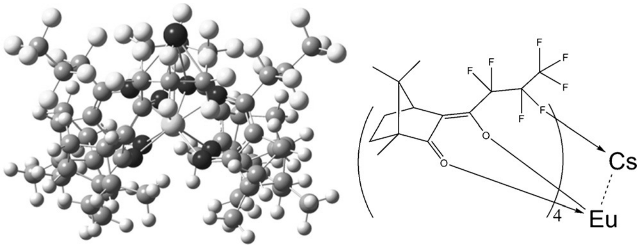

Figure 1. Calculated geometry and chemical structure of the Δ-CsEu-[(+)-hfbc]$_4$ complex.

Although Raman optical activity (ROA) spectrometers in the scattered circular polarized (SCP) mode also detect difference of right- and left circularly polarized emitted intensities, the potential of ROA spectroscopy for chiral lanthanide complexes has remained rather unexplored. The instrumentation has been commercially available since about 2003[8] and method has already become a powerful tool for structural elucidation of chiral molecules.[9] The ROA analogue of the dissymmetry factor is the circular intensity difference (CID).[8] For SCP modulation with unpolarized excitation radiation, the difference can be expressed as CID = $(I_R - I_L)/(I_R + I_L)$. Therefore, if CPL is measured on an SCP ROA instrument, CID = $-g/2$.

The green 532 nm laser, commonly used for ROA, resonates with the $^7F_0 \rightarrow {}^5D_0$ electronic transition in the Eu^{III} ion, and can be used to the boost the signal.[10] The CPL component in scattered radiation was previously proposed for sensitive chirality detection of optically active alcohols and ketones chelated with an achiral Eu(fod)$_3$ complex, although the phenomenon was rather incorrectly referred to as induced resonance ROA (IRROA).[11] Recently, we also reported a comparative study of electronic and vibrational optical activity in a chiral bipyridine Eu^{III} complex,[12] where a very

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high CID of approximately 10^{-2} was observed in its ROA spectrum.

The CsEu[(+/−)-hfbc]$_4$ complex investigated in the present study highlights the ability of ROA spectroscopy to measure CPL. Raman and ROA spectra of the complex enantiomers dissolved in chloroform are plotted in Figure 2. Note that while typical CID values of organic molecules rarely exceed 10^{-3}, about 85 % of the emitted photons by the Δ enantiomer at 595 nm are left-circularly polarized.[7,13] This luminescence appears at 1989 cm^{-1} in the Raman spectrum, resulting in CID = 0.71 for the Λ enantiomer. As typical for similar europium complexes,[10–12] the Raman signal is dominated by europium fluorescent transitions at 1722 and 1989 cm^{-1}. Pure vibrational Raman spectrum of the ligand (Supporting Information, Figure S2) is not visible in the scale of Figure 2. Only vibrational Raman bands of the CHCl$_3$ solvent are comparable in intensity with the fluorescence peaks. The 1989 and 1722 cm^{-1} fluorescence bands are accompanied by CPL measured as ROA, negative for the Δ-enantiomer, and nearly a mirror-image for Λ-enantiomer. Weaker fluorescent bands appear in the wavenumber region below 1300 cm^{-1}, perhaps mixed with a weak ROA signal induced in chloroform.

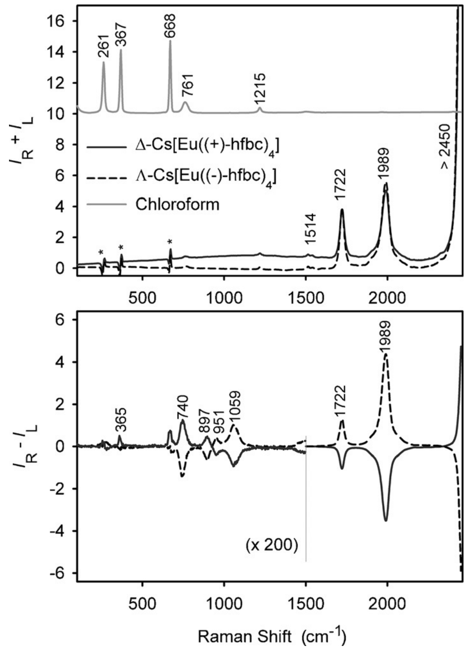

Figure 2. Raman ($I_R + I_L$) and ROA ($I_R - I_L$) spectra of the CsEu[(+/−)-hfbc]$_4$ complex enantiomers in 2 mM solutions in chloroform with 532 nm laser excitation. In the upper panel, Raman spectrum of pure chloroform is shown as well, and ROA intensities within 100–1500 cm^{-1} are multiplied by 200. The higher Raman background in the Δ enantiomer (solid line) is caused by fluorescent impurities; subtraction of the chloroform signal from the complex Raman spectra causes minor artifacts denoted by the asterisk (*).

The small difference between the measured CID of 0.71 and a theoretical value of 1.38/2 = 0.69 calculated from the fluorescence measurement is potentially explained by experimental error and different experimental conditions. For example, both the Raman and ROA signals are very dependent on temperature (Supporting Information, Figure S3). Raman and ROA peaks at 2450, 1989, and 1722 cm^{-1} are getting smaller as the temperature increases, which was previously observed for europium(III) luminescence as well.[5] The europium fluorescent bands in this way also differ from the relatively temperature-independent chloroform bands.

Another interesting means that the ROA technique offers to distinguish fluorescence bands from the Raman ones is measurement of the degree of circularity (DOC, defined in the same way as CID, $(I_R - I_L)/(I_L + I_R)$, but for incident right- or left- circularly polarized light.[14] Note that the sample is irradiated by unpolarized light for SCP ROA. The DOC thus indicates how the sample "remembers" the incident polarization. We plot separately the sum and differential intensities of the Δ-enantiomer in Figure 3, indicating the incident polarization as the upper index. Indeed, chloroform can be clearly distinguished where the differential sums entering DOC change sign according to the incident polarization. This includes small signal of a combination transition at 2405 cm^{-1}. On the other hand, the DOC signal of the complex is of one-sign, DOC = CID, and the intensity difference is thus the same as ROA. In other words, the initial polarization is lost during the fluorescence process.

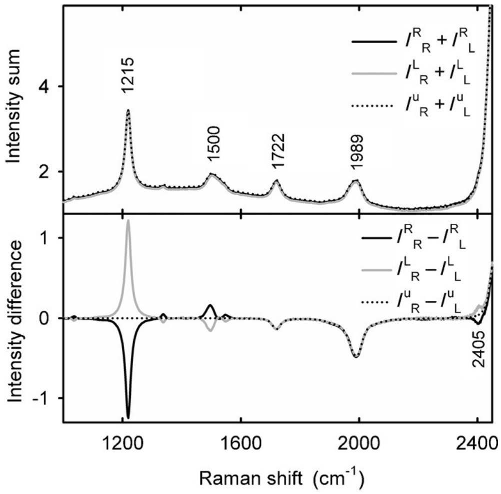

Figure 3. Sum and differential intensities of the Δ-CsEu[(+)-hfbc]$_4$ complex in CHCl$_3$ measured with 532 nm excitation, at 55 °C, and with different incident polarizations indicated by the upper index.

Finally, and perhaps most directly, the fluorescence and true Raman bands can be discriminated in the Raman spectrum using different laser colors. For a fluorescent transition, the wavelength of the emitted light is constant, which causes different apparent Raman shifts with different excitation wavelengths. For a Raman transition, emitted wavelength changes, and the Raman shift difference with respect to the excitation is constant. This is documented in Figure 4, where chloroform and chloroform complex solution Raman spectra measured with 404 nm and 532 nm excitation are compared. The spectra were measured on a different

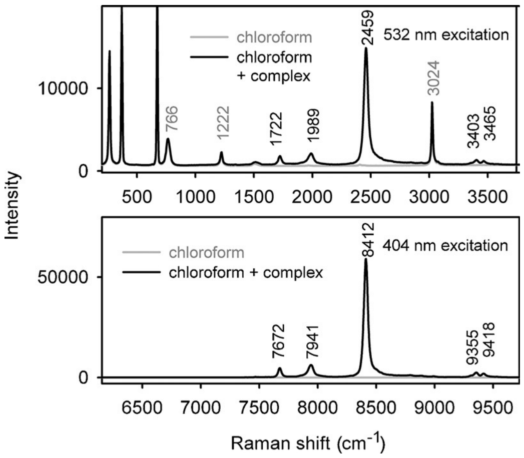

Figure 4. Raman spectra of chloroform and Δ-CsEu[(+)-hfbc]$_4$ complex chloroform solution measured with 532 nm and 404 nm excitation wavelengths. For 404 nm, the complex fluorescence bands are shifted by about 5953 cm^{-1}.

spectrometer (Raman microscope; see the Experimental Section) than those in Figure 3; thus, the 2459, 3404, and 3465 cm^{-} complex signals are visible for the 532 nm excitation, as well as the 1722 cm^{-1} and 1989 cm^{-1} complex bands. All five of these fluorescent transitions shift by about 5953 cm^{-1} in the Raman spectrum obtained with the 404 nm excitation, whereas the chloroform Raman bands do not change positions (see also Figure S4 for the chloroform Raman bands only).

Observed fluorescence bands in the Raman and ROA spectra are summarized in Table 1. Their assignment is based on the crystal field theory[15] and parameterized description of lanthanide electronic states.[5] The europium electronic levels are relatively independent of the environment, and the energies observed for the Δ-enantiomer in the present study correspond well, for example, with those identified in the Cs$_2$NaEuCl$_6$ crystal[15] and many other measurements.[7,16] Software for computation of accurate complex excitation energies is currently not available to us. From the shape of molecular orbitals calculated at the approximate B3LYP(6-31+G* basis set on O and F atoms, MWB46 and MWB28 basis sets and pseudopotentials on Eu and Cs, respectively, and 6-31G* basis set on the rest, multiplicity = 7),[17] we can at least qualitatively see the extent of the mixing between the europium and complex electronic states. In Figure 5, two α-orbital pairs are shown. The first comprises molecular orbitals number 280 (occupied) and 296 (virtual), with a high participation of Eu atomic f-orbitals. A large transition magnetic dipole between them indicates a high-dissymmetry value, but the transition electric dipolar strength is very small. In the second pair (280 and 286), the latter virtual orbital 286 is located mostly in the organic part of the complex, which causes a decrease of the dipole strength, but the dissymmetry factor significantly decreases. These results confirm that the circularly polarized luminescence must come from europium-centered transitions perturbed by the external crystal field of the complex.[5] The calculations and a previous study based on excitation and circular dichroism spectra also suggest that the role of the cesium in the complex is rather minor and the main spectral features come from the europium transitions.[16a]

Table 1: Observed luminescence bands in the Raman Δ-CsEu[(+)-hfbc]$_4$ spectra and their assignments.

Wavelength[nm]	Raman shift [cm^{-1}] 532 nm excitation	 404 nm excitation	Transition[15]
652	3465	9418	$^5D_0 \rightarrow {}^7F_3$
650	3404	9355	$^5D_0 \rightarrow {}^7F_3$
612	2458	8412	$^5D_0 \rightarrow {}^7F_2$
595	1989	7941	$^5D_0 \rightarrow {}^7F_1$
586	1722	7672	$^5D_0 \rightarrow {}^7F_1$ $^5D_1 \rightarrow {}^7F_3$
579	1514	7468	$^5D_0 \rightarrow {}^7F_0$
564	1059	7012	
560	951	6901	
559	897	6856	
554	740	6695	
542	365	≈6316	

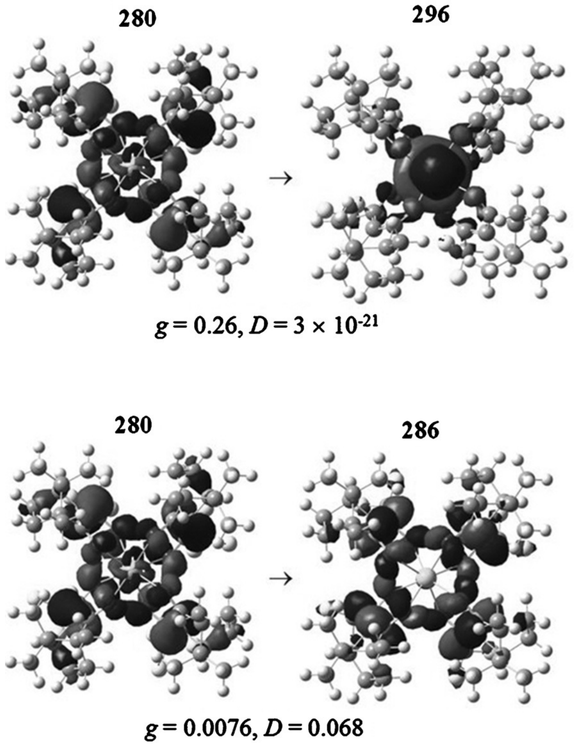

Figure 5. Example of calculated molecular orbitals in the Δ-CsEu[(+)-hfbc]$_4$ complex, and dipolar strengths (*D*) and dissymmetry factors (*g*) calculated from the 280 (occ.)→296 (virt.) and 280 (occ.)→286 (virt.) transition matrix elements. The Cs atom is pointing backward. The orbital shapes highlight the interactions between the Eu^{III} and organic electronic structures favorable for high CPL efficiency.

We conclude that we could measure the Raman scattering and Raman optical activity of the CsEu[(+/−)-hfbc]$_4$ complex, and using various means we could reliably distinguish the fluorescence signal from the true Raman bands. ROA spectroscopy thus appears to be a useful tool to monitor circular polarized luminescence of chiral europium(III) complexes, and can be used as a sensitive molecular and chirality probe in material and life sciences.

Methods

Enantiomeric complexes of CsEu[(+/−)-hfbc]$_4$ were synthesized following a previously-described procedure.[18] Raman, backscattered SCP ROA and DOC spectra were acquired on a BioTools spectrometer operating with laser excitation at 532 nm at a resolution of 7 cm^{-1}. 100 μL of the sample chloroform solution was placed in a fused silica cell; the laser power at the sample was 10 mW (complexes) and 60 mW (ligand). Collection times and concentrations were 75 min and 2 mM (complexes), and 16 h and 1M (ligand). The intensity was calibrated with a NIST standard reference material (SRM 2242). For Figure 2, solvent signal was subtracted in the Raman spectra of the complex. Raman/luminescence spectra were also measured on a Raman microscope (Alpha300R+, Witec) equipped with three different laser sources (404 nm, 532 nm, and 785 nm, the sample was placed in a glass capillary). The calculations were performed with the Gaussian 09 program,[17] using the B3LYP functional. The 6-311++G(d,p) basis set was used for the ligand ROA spectra. For computations of the geometry and orbitals of the complex, the 6-31+G(d) basis set was used for the O and F, and the 6-31G(d) basis set for the C and H atoms. The MWB46 and MWB28 pseudopotentials were used for Cs and Eu, respectively. In all cases, the solvent was mimicked with the polarizable continuum solvent model (PCM).

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