

Circularly Polarised Luminescence in Enantiopure Samarium and Europium Cryptates

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Abstract: Circularly polarised luminescence (CPL) is a chiroptical phenomenon gaining more and more attention, as the availability of the necessary spectrometers is getting better and first applications in bioimaging or for the preparation of OLEDs (organic light emitting diodes) are coming within range. Until now most examples of distinctly CPL-active compounds were europium and terbium complexes though theoretically the electronic structure of samarium should be as suitable as the one of terbium. This discrepancy can be accounted for by the high susceptibility of samarium to non-radiative deactivation processes. The aim of this study was to strategically circumvent this difficulty by the use of a ligand scaffold which has already proven to efficiently suppress these processes, namely the cryptates. The prepared partly deuterated samarium and europium complexes indeed exhibit distinct circularly polarised luminescence with dissymmetry factors up to $g_{lum} = +0.13$ (Sm^{III}) or $g_{lum} = -0.19$ (Eu^{III}).

Introduction

Chirality is an ubiquitous concept in science and technology and of special importance in chemistry and related fields. The handedness of molecules is crucial for various phenomena. Many of these phenomena depend on the interplay of chiral matter with (polarised) light, e.g. optical rotation, circular dichroism (CD) or circularly polarised luminescence (CPL). Especially the latter is of special interest for various applications. A compound which exhibits CPL emits different intensities of left and right circularly polarised light at specific wavelengths after excitation with unpolarised light.^[1] This property is usually quantified by means of the luminescence dissymmetry factor g_{lum} which is defined as quotient of the difference of the intensities of left and right polarised light ($I_L - I_R$) and the half of the total intensity ($I_L + I_R$):

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

The luminescence dissymmetry factor of a given transition a→b depends on the ratio of the transition's rotatory strength R_{ab} and the oscillator strength D_{ab} . The rotatory strength is determined by the magnitudes and the relative orientation of the magnetic and electric dipole transition moments ($R_{ab} = |M_{ab}| |P_{ab}| \cos \tau_{ab}$), whereas the oscillator strength can be approximated as the square of the electric dipole moment ($D_{ab} = |P_{ab}|^2$), giving:^[1b]

$$g_{lum} = \frac{4 R_{ab}}{|D_{ab}|} = \frac{4 |M_{ab}| \cos \tau_{ab}}{|P_{ab}|} \quad (2)$$

The dependence on the angle τ_{ab} between the magnetic and electric dipole transition moments points towards the high sensitivity of CPL towards subtle changes in the coordination geometry. This makes it a useful tool in the study of biomolecules.^[2] Also, the circularly polarised nature of the emitted light offers great potential for applications, e.g. in bioimaging, as it enables a substantial improvement of the signal to noise ratio.^[3] Another field which will greatly benefit from circularly polarised luminescence are innovative organic light emitting diodes (OLEDs).^[4] In the past few years CPL has evolved from a quite exotic speciality measured on custom-built devices to a more established technique. Subsequently, attempts to realise applications in the fields mentioned above are getting more concrete.

For all kinds of applications, substances with high g_{lum} values are desired. While for purely organic molecules usually values in the range of 10^{-4} to 10^{-2} are reported,^[1f] a special class of coordination compounds, namely lanthanoid complexes, may reach g_{lum} values between 0.1 and 1.38 (or up to 1.45 in the solid state).^[1,5] This is not the only exceptionality of lanthanoid complexes, other peculiarities like long luminescence lifetimes, very sharp emission spectra or very high magnetic anisotropies have led to a flourishing research on these compounds in the past years.^[6]

Both the general electronic structure of the lanthanoid and the influence of the crystal field control the CPL properties of a lanthanoid complex. From equation (2) it becomes evident that the highest luminescence dissymmetry factors can be expected for transitions which are magnetic dipole allowed and electric dipole forbidden and satisfy the magnetic dipole selection rule ($\Delta J = 0, \pm 1$; except $J' = J'' = 0$). Already in 1980 Richardson identified the transitions of the lanthanoids for which the highest dissymmetry factors can be expected.^[7] The $^5D_0 \rightarrow ^7F_1$ transition of Eu^{III} with its purely magnetic dipole character offers by far the best prerequisites for observing large dissymmetry factors. But also the electronic structures of e.g. Tb^{III} and Sm^{III} allow for sizeable g_{lum} values. Although Richardson's classification of the

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transitions has proven to be very reliable and successful, the influence of the coordination situation around the lanthanoid is only poorly understood until now. Also against the background of the lanthanoid's intrinsic kinetic lability it is very difficult to establish correlations of structural features of a complex and its CPL properties such as the magnitude of the luminescence dissymmetry factor or the shape of the CPL spectrum. Yet there have been some efforts.^[8]

A wealth of europium complexes exhibiting CPL has been reported until now, in line with this metal's exceptional suitability for observing CPL.^[9] Though the electronic nature of the $^5D_4 \rightarrow ^7F_5$ transition of terbium is less favourable for the observance of CPL, the generally high luminescence of this lanthanoid is beneficial for the detection of CPL and many examples have been reported.^[10] Following Richardson's classification of the transitions of lanthanoids, the suitability for the observance of CPL of the $^4G_{5/2} \rightarrow ^6H_{5/2}$ transition of samarium should be comparable to the one of the $^5D_4 \rightarrow ^7F_5$ transition of terbium. But in contrast to terbium, samarium complexes are usually only weakly luminescent, which is due to this lanthanoid's high susceptibility to multiphonon quenching. Consequently, the study of CPL has to a certain degree been limited to complexes of europium and terbium so far. To the best of our knowledge, until now **four** molecular samarium complexes were known to exhibit CPL in solution.^[5b,11] For these compounds which were studied as enantiopure samples also dissymmetry factors were reported. The ligands used for the preparation of these compounds are shown in Figure 1. The most intense samarium-centered CPL was found for $\text{Cs}[\text{Sm}((+)\text{-hfbc})_4]$ with maximum g_{lum} values of -1.15 ($^4G_{5/2} \rightarrow ^6H_{5/2}$) and $+1.15$ ($^4G_{5/2} \rightarrow ^6H_{7/2}$). The respective europium complex $\text{Cs}[\text{Eu}((+)\text{-hfbc})_4]$ ^[5] exhibits the highest g_{lum} value ($+1.38$ in CHCl_3) reported so far, which points towards an exceptional suitability for CPL of the coordination geometry and electronic structure of the ligand found in these complexes. The fact that the g_{lum} value of the samarium compound reaches the same order of magnitude as the europium compound gives evidence of the high potential of samarium-centered CPL. Remarkably high g_{lum} values were also found for the complexes of Sm^{III} and the pyridyldiamide **A** (up to 0.50 for $^4G_{5/2} \rightarrow ^6H_{5/2}$ and up to 0.28 for $^4G_{5/2} \rightarrow ^6H_{7/2}$).^[11e] The complex of Sm^{III} and the 2-hydroxyisophthalamide **B** is the third example of a samarium complex for which g_{lum} values were reported (-0.027 for $^4G_{5/2} \rightarrow ^6H_{5/2}$ and -0.028 for $^4G_{5/2} \rightarrow ^6H_{7/2}$).^[11d] In the case of the complex consisting of the disuccinate edds and Sm^{III} only for the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition (which is typically more luminescent) a g_{lum} value ($+0.066$) could be reported.^[11f] Interestingly, in two of these **four** examples, for the $^4G_{5/2} \rightarrow ^6H_{5/2}$ and the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transitions identical g_{lum} values were reported, though according to Richardson's classification one would expect the dissymmetry factor to be considerably higher in the case of the $^4G_{5/2} \rightarrow ^6H_{5/2}$ transition.

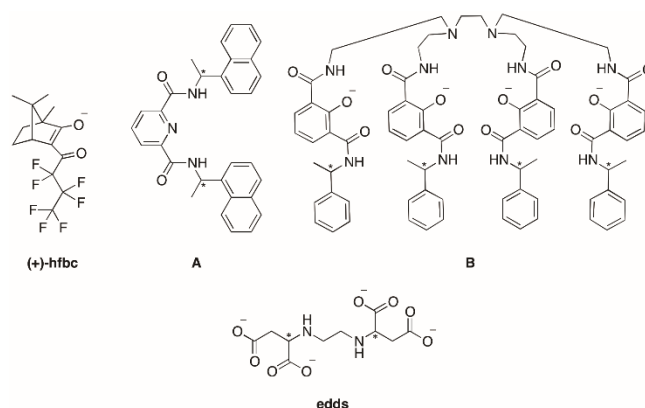


Figure 1. Ligands used for the preparation of CPL-active samarium complexes. (+)-hfbc = (+)-3-heptafluorobutyrylcamphorate^[5b], **A** = pyridine-2,6-dicarboxylic acid bis-[(1-naphthalen-1-yl-ethyl)-amide]^[11e], **B** = 1-phenylethylamine substituted 2-hydroxyisophthalamide^[11d], **edds** = ethylenediamine-*N,N'*-disuccinate^[11f].

Rigidified bipyridine cryptands (Fig. 2) are C_2 -symmetric and offer an extremely high conformational and configurational stability. The propeller-like arrangement of the three bipyridine units results in helical (*M/P*) or axial chirality (*R_a/S_a*). Usually, lanthanoid cryptates are synthesised as racemic mixture of two enantiomers, but it has been shown that it is also possible to prepare these complexes selectively in an enantiopure fashion.^[12]

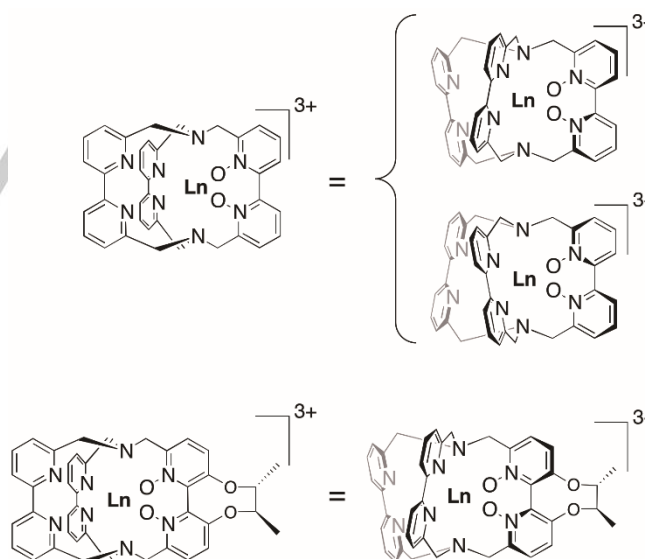


Figure 2. Rigidified lanthanoid cryptates are usually isolated as racemic mixture (top). By attachment of a stereogenic element to one of the bipyridine units a preorganisation of the building blocks and enantiopure synthesis can be achieved (bottom).^[12]

The luminescence properties of the racemic lanthanoid cryptates have already been studied in detail.^[13] The three bipyridine units

around the lanthanoid ion cause both an efficient shielding from surrounding solvent molecules and an efficient indirect population of the excited state of the lanthanoid via the so called *antenna effect*^[6a-d], affording lanthanoid complexes with long luminescence lifetimes and good quantum yields.^[14]

Lanthanoids for which the energetic difference between the electronic states is typically small (e.g. Sm^{III} or Yb^{III}) are especially sensitive towards nonradiative deactivation processes caused by multiphonon quenching. Past studies have shown that deuterated derivatives of the cryptates have a special ability to protect this group of lanthanoids against nonradiative deactivation processes, leading to extraordinarily long luminescence lifetimes of the corresponding Yb^{III} and Sm^{III} complexes in deuterated solvents.^[13d-e] In the case of Sm^{III} this also leads to very promising conditions for the observance of CPL. The aim of this work was to realise an enantiopure samarium cryptate and study whether such a compound is indeed suitable to enlarge the repertory of samarium complexes exhibiting CPL.

Results and Discussion

Complex Design. As shown before, it is possible to prepare lanthanoid cryptates in an enantiopure form (Fig. 2).^[12] For this purpose a tether derived from (*S,S*)-2,3-butanediol is attached to the *N,N'*-dioxide modified bipyridine unit of the ligand scaffold. ¹H NMR experiments on samples of corresponding lanthanoid cryptates in enantiopure solvents (methyl L-lactate and methyl D-lactate) already gave evidence of the enantiopurity of the samples. Due to the presence of transitions with small energetic differences ΔE between the electronic states, samarium complexes are especially sensitive towards non-radiative deactivation processes and some additional efforts are necessary to prepare luminescent samarium complexes. Generally, deuteration of the ligand scaffold can suppress multiphonon quenching processes efficiently, most efficiently in the case of the benzylic positions.^[13c-d,14,15] Furthermore the deuteration of only the benzylic positions of the non-oxidised bipyridine units offers an acceptable tradeoff between efficient ligand synthesis and the improvement of the luminescence properties. The synthesis of the resulting enantiopure and partly deuterated ligand core has already been reported.^[12] This ligand offers optimal preconditions for the preparation of a CPL-active samarium compound (Fig. 3). Additionally the respective europium complex was prepared. The special electronic structure of Eu^{III} is not only suitable for observing CPL but it also offers the extraction of additional information from the study of the photophysical properties like for example the radiative luminescence lifetime τ_{rad} , which is not always easily accessible in the case of the other lanthanoids.

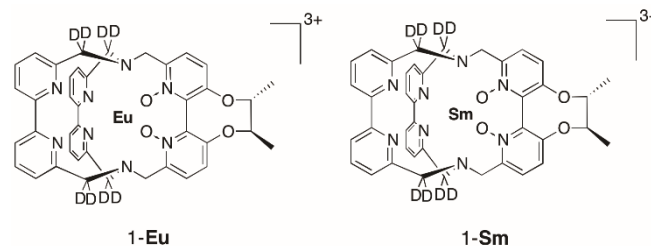
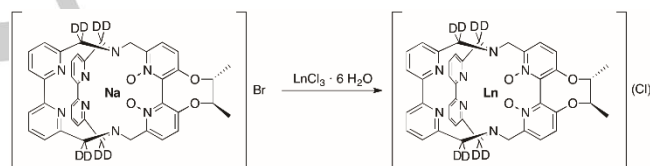


Figure 3. Enantiopure, luminescent lanthanoid cryptates prepared for this study.

Synthesis. The synthesis of the ligand and the corresponding samarium and europium complexes was performed analogously to procedures already described (Scheme 1).^[12] Experimental details for the preparation of the lanthanoid complexes **1-Sm** and **1-Eu** from the sodium complex are given in the experimental section. After complex synthesis, the obtained crude products were purified via recrystallisation. Analytical HPLC (high performance liquid chromatography) runs were performed to check the purity of the isolated compounds, whereby no remains of the sodium cryptate were detected (see experimental section and supporting information).



Scheme 1. Preparation of the enantiopure, partly deuterated lanthanoid cryptates from the corresponding sodium cryptates.

Chemical Structure in Solution – Nuclear Magnetic Resonance. The spectra of **1-Sm** and **1-Eu** consist of relatively sharp signals, giving evidence of the expected rigid structure, the presence of only one species in solution and the C₂-symmetry of the complexes.

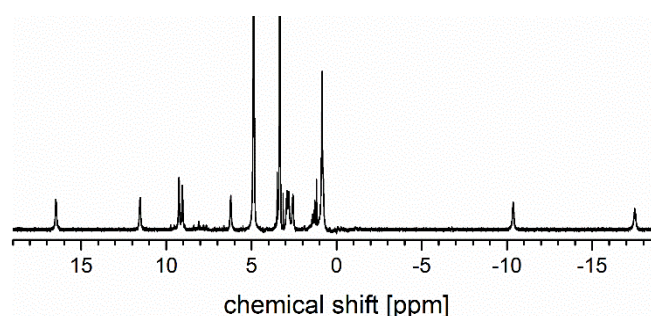


Figure 4. ¹H NMR (CD₃OD, 400 MHz) of **1-Eu**.

The pronounced magnetic susceptibility anisotropy of **1-Eu** leads to considerable shifts of the signals in the ^1H NMR spectrum (CD_3OD) of the compound (Fig. 4). The signals are distributed over about 35 ppm, and most of them are well separated from each other. Only in the range between 2.5 to 3.0 ppm and 1.0 to 0.7 ppm signals are overlapping, so that an individual integration is not possible. In total ten signals with an integral of two protons and one multiplett of two overlaid signals with a total integral of eight protons can be identified, perfectly mirroring the expected C_2 -symmetry of the molecule. Usually the pseudocontact component of the paramagnetic shift that a signal experiences will be more pronounced when the corresponding nucleus is spatially close to the paramagnetic center. In compliance with that, in previous detailed NMR studies on paramagnetic lanthanoid cryptates the most shifted signals could always be assigned to the benzylic protons.^[12,13c] Accordingly, the strongly shifted signals at about -10 and -17.5 ppm most likely correspond to the protons in the benzylic position, which is also in agreement with the NMR data reported for the unfunctionalised europium cryptate and a study on a modified europium cryptate, in which for the respective protons very similar lanthanoid induced shifts were found.^[13b,16] Because of their long distance from the lanthanoid, the signal of the methyl groups (0.85 ppm, overlaid with another signal of two protons) is experiencing only a slight shift compared to the diamagnetic analogue.^[12]

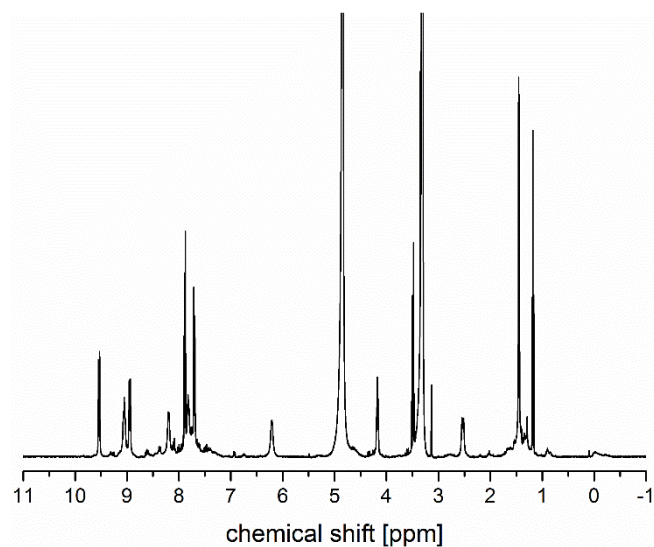


Figure 5. ^1H NMR (CD_3OD , 400 MHz) of **1-Sm**.

As for **1-Eu**, the spectrum of **1-Sm** (in CD_3OD) gives evidence of the C_2 -symmetry of the complex (Fig. 5). The eight partly overlapping signals between 7.5 ppm and 9.8 ppm with integrals of two protons each correspond to the aromatic protons of the ligand and the signal at 1.45 ppm with an integral of six protons can be assigned to the methyl groups. Sm^{III} is only slightly paramagnetic, yet some signals experience a considerable shift.

Whereas in the diamagnetic **1-Lu**^[12] no signals could be detected in the ranges between 1.5 ppm to 3.0 ppm and between 5.0 ppm to 7.5 ppm, in the spectrum of **1-Sm** two signals can be detected in these ranges. As these signals experience the strongest paramagnetic shifts they most likely correspond to the protons which are closest to the lanthanoid, namely the benzylic protons. In contrast, the two remaining protons of the tether are relatively apart from the paramagnetic center. Their ^1H NMR signal will not experience a considerable paramagnetic shift and can be detected at about 4.2 ppm.

In conclusion, the ^1H NMR spectra of both compounds under study give evidence of the presence of one C_2 -symmetric species in solution. As expected the structure of the complexes is well defined and no exchange or rearrangement processes are observable.

Steady-State Emission Spectra. In accordance to the findings from the analysis of the ^1H NMR spectra, the high resolution luminescence spectrum of **1-Eu** (Fig. 6) is completely consistent with one C_2 -symmetric Eu^{III} -species, exhibiting one $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition and three sublevels of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition.^[16] As **1-Sm** is highly luminescent, a partial resolution of the transition's fine structure was possible, by the use of a narrow emission monochromator slit width (1nm) (Fig. 7). In addition the transitions in the near-infrared could also be detected (Fig. 8).

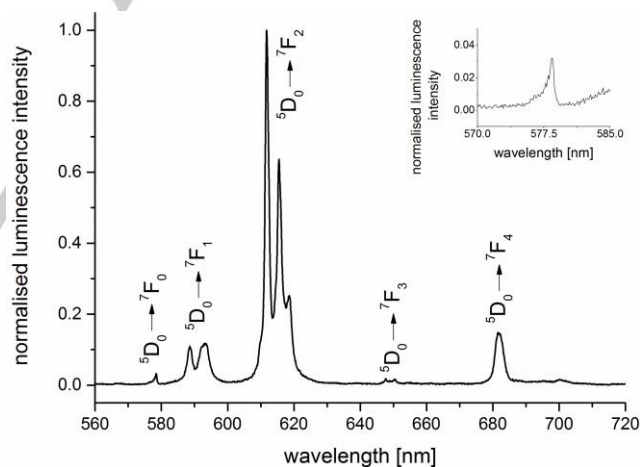


Figure 6. Emission spectrum of **1-Eu** in CD_3OD at room temperature. $\lambda_{\text{exc}} = 305 \text{ nm}$, $A_{305\text{nm}} = 0.22$. Insert: Magnification of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition.

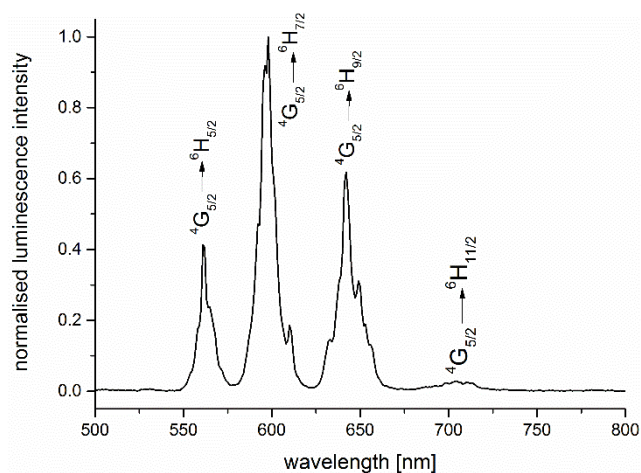


Figure 7. Emission spectrum of **1-Sm** in CD₃OD at room temperature. $\lambda_{\text{exc}} = 320$ nm, $A_{320\text{nm}} = 0.26$.

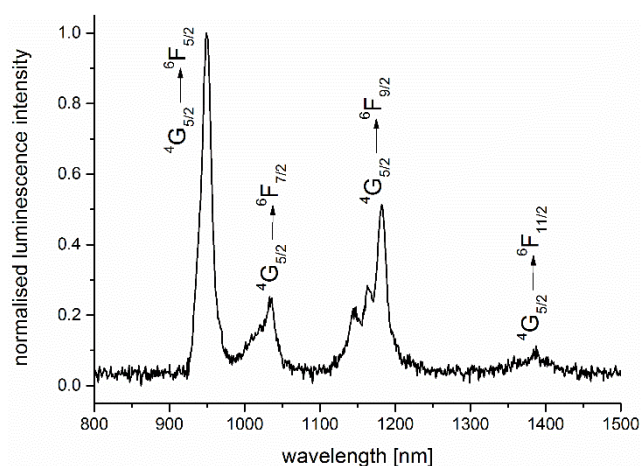


Figure 8. Near-infrared emission spectrum of **1-Sm** in CD₃OD at room temperature. $\lambda_{\text{exc}} = 320$ nm, $A_{320\text{nm}} = 0.26$.

Luminescence Lifetimes and Quantum Yields. For both complexes **1-Sm** and **1-Eu** the luminescence lifetimes τ_{obs} and absolute quantum yields $\phi_{\text{Ln}}^{\text{L}}$ were determined (see Table 1). Both complexes exhibit a monoexponential decay (see supporting information), which is another evidence of the stable and well defined structure of **1-Sm** and **1-Eu** in solution. As expected, τ_{obs} and $\phi_{\text{Ln}}^{\text{L}}$ are significantly higher in the case of **1-Eu**. In a rough approximation, due to the absence of C/H- and O/H-oscillators, CD₃OD, CD₃CN and D₂O can be assumed to be solvents which do not cause nonradiative deactivation of the excited lanthanoid. Indeed at least the O/D-oscillators will cause some nonradiative deactivation and analogously to general experiences shorter lifetimes can be expected for measurements in D₂O and longer lifetimes for measurements in CD₃CN.^[19] Keeping this in mind, a rough comparison of lifetime data measured in these solvents is possible.

The determined luminescence lifetime τ_{obs} of **1-Eu** in CD₃OD is about one third higher than the previously reported value for the

unfunctionalised europium cryptate in D₂O ($\tau_{\text{obs}} = 1.15$ ms).^[13a] This increase of the lifetime can be accounted for by the partial deuteration of the ligand scaffold by which eight of the quite efficient C/H-oscillators are replaced by less efficient C/D-oscillators. Interestingly the overall quantum yield $\phi_{\text{Ln}}^{\text{L}}$ of **1-Eu** is almost one order of magnitude smaller than the value for the previously reported unfunctionalised compound ($\phi_{\text{Ln}}^{\text{L}} = 30\%$, in D₂O).^[13a] Due to the purely magnetic dipole character of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition of Eu^{III} the intrinsic luminescence lifetime τ_{rad} of the corresponding complexes is proportional to the ratio of integrated total emission intensity I_{tot} and the integrated emission intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition (I_{MD}).^[19] Consequently it can be obtained directly from the corrected steady state emission spectrum:

$$\frac{1}{\tau_{\text{rad}}} = A_{\text{MD},0} \times n^3 \left(\frac{I_{\text{tot}}}{I_{\text{MD}}} \right) \quad (3)$$

Where $A_{\text{MD},0}$ corresponds to the probability of spontaneous emission of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition *in vacuo* (14.65 s⁻¹) and n is the refractive index of the surrounding medium (1.326 for CD₃OD). The intrinsic quantum yield $\phi_{\text{Ln}}^{\text{L}}$ of **1-Eu** can be determined as the quotient of the observed luminescence lifetime τ_{obs} and the intrinsic luminescence lifetime τ_{rad} .

The sensitisation efficiency $\eta_{\text{sens}} (= \phi_{\text{Ln}}^{\text{L}} / \phi_{\text{Ln}}^{\text{Ln}})$ determined for **1-Eu** is somewhat lower than expected, which indicates some kind of energetic mismatch between the ligand and the trivalent europium ion. A less efficient energy transfer from the ligand to the lanthanoid would also explain the relatively low overall quantum yield. Indeed the introduction of the tether at the oxidised bipyridine unit is likely to alter the electronic structure at the ligand. Nevertheless, the UV/Vis spectra of the complexes (see supporting information) correspond to the spectra typically obtained for tris(2,2'-bipyridine)-*N,N*-dioxide cryptates.

As expected, the luminescence lifetime of the partly deuterated **1-Sm** in CD₃OD lies between the luminescence lifetimes determined for the undeuterated and the perdeuterated unfunctionalised analogues in CD₃CN (31 and 394 μs , respectively).^[13c] The threefold increase compared to the

Table 1. Luminescence lifetimes τ_{obs} , radiative lifetimes τ_{rad} , intrinsic quantum yields $\phi_{\text{Ln}}^{\text{L}}$, overall quantum yields $\phi_{\text{Ln}}^{\text{L}}$ and sensitisation efficiencies η_{sens} of **1-Eu** and **1-Sm** in CD₃OD.

compound	τ_{obs}	τ_{rad}	$\phi_{\text{Ln}}^{\text{L}}$ [a]	$\phi_{\text{Ln}}^{\text{L}}$ [b]	η_{sens} [c]
1-Eu	1.6 ms [d]	4.2 ms	5.9%	38 %	15 %
1-Sm	90 μs [e]	-	0.26%	-	-

[a] Determined using quinine in 0.5 M H₂SO₄ as reference compound, see supporting information and reference [20]. [b] $\phi_{\text{Ln}}^{\text{L}} = \tau_{\text{obs}} / \tau_{\text{rad}}$. [c] $\eta_{\text{sens}} = \phi_{\text{Ln}}^{\text{L}} / \phi_{\text{Ln}}^{\text{Ln}}$. [d] $\lambda_{\text{exc}} = 320$ nm, $\lambda_{\text{em}} = 610$ nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$). [e] $\lambda_{\text{exc}} = 320$ nm, $\lambda_{\text{em}} = 597$ nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$).

undeuterated compound, despite the more pronounced non-radiative deactivation in CD₃OD, points towards the high impact of the oscillators in the benzylic positions of the ligand scaffold.

Chiroptical Properties: Circular Dichroism and Circularly Polarised Luminescence. The normalised CD spectra of **1-Eu** and **1-Sm** (Fig. 9) are quite similar to the previously reported CD spectra of enantiopure, unfunctionalised Lu^{III}-cryptates.^[21] This indicates that the geometry of the ligand around the lanthanoid and the helicity is comparable to the one found in unfunctionalised lanthanoid cryptates.

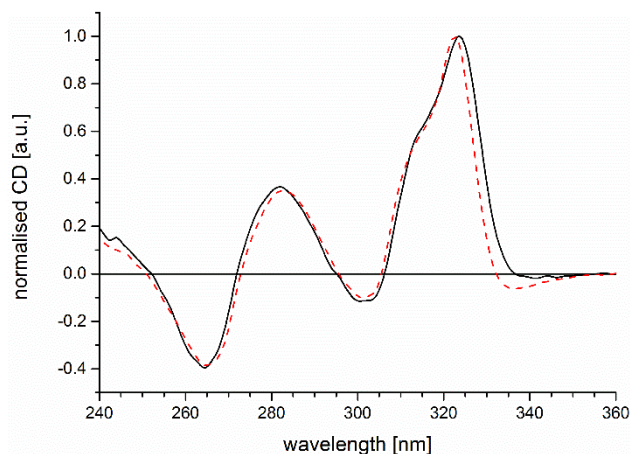


Figure 9. CD spectra of **1-Eu** (black, solid line) and **1-Sm** (red, dashed line) in CD₃OD (3 mM) at room temperature. Both spectra were independently normalised on a scale of 0 to 1.

After the complexes were found to meet the photophysical and structural expectations, finally circularly polarised luminescence was studied. The spectra of both complexes feature transitions with distinct rotatory strengths. Figures 10 and 11 show the normalised CPL (with the luminescence dissymmetry factors g_{lum}) and total emission spectra of **1-Eu** and **1-Sm**. In the case of **1-Sm** the $^4G_{5/2} \rightarrow ^6H_{5/2}$ and the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition exhibit distinct rotatory strengths, leading to g_{lum} values of up to +0.13 ($^4G_{5/2} \rightarrow ^6H_{5/2}$) (Fig. 10). In the case of the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition the opposite signs of the components of the transition give additional information about the fine structure of the band, which could not be resolved in the total luminescence spectrum, not even in the high resolution spectrum (Fig. 7). For this transition g_{lum} values of -0.03 and +0.03 were determined. Consequently, in the case of **1-Sm** Richardson's prediction of the $^4G_{5/2} \rightarrow ^6H_{5/2}$ transition exhibiting more intense CPL than the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition was experimentally confirmed. In the CPL spectrum of **1-Eu**, the $^5D_0 \rightarrow ^7F_2$ transition is split into two components with opposite signs (Fig. 11). On the other hand the $^5D_0 \rightarrow ^7F_1$ transition exhibits opposite sign with respect to the major CPL component associated with the hypersensitive transition and quite similar rotatory strengths, as it can often be observed in CPL spectra of Eu-complexes. Resulting from the lower total luminescence intensity of the $^5D_0 \rightarrow ^7F_1$ transition (and in

congruence with Richardson's classification), the corresponding luminescence dissymmetry factor g_{lum} is about one order of magnitude higher than the one allied to the $^5D_0 \rightarrow ^7F_2$ transition. Interestingly the maximum g_{lum} values determined for **1-Sm** and **1-Eu** are in the same order of magnitude, as it had already been reported for Cs[Ln((+)-hfbc)₄].^[5b] Consequently the results reported herein give another evidence for the high potential of samarium-centered CPL.

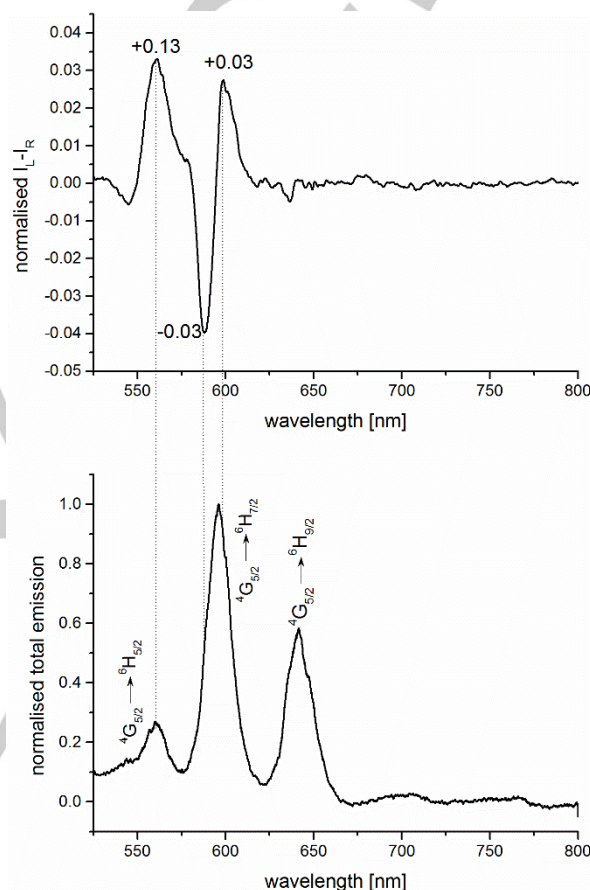


Figure 10. Normalised CPL spectrum (top) with the luminescence dissymmetry factors g_{lum} and total emission spectrum (bottom) of **1-Sm** ($\lambda_{exc} = 254$ nm, $c = 3$ mM in CD₃OD).

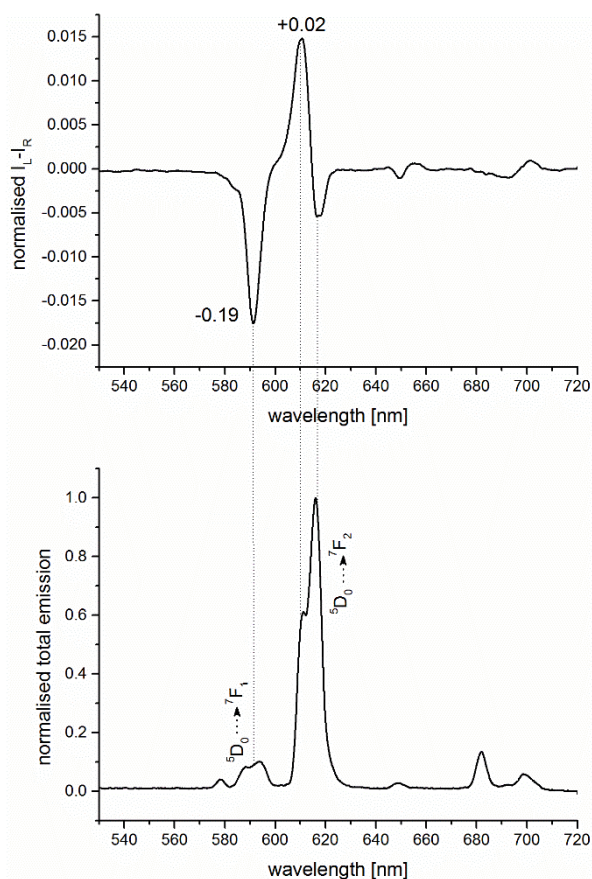


Figure 11. Normalised CPL spectrum (top) with the luminescence dissymmetry factors g_{lum} and total emission spectrum (bottom) of **1-Eu** ($\lambda_{exc} = 254$ nm, $c = 3$ mM in CD_3OD).

Conclusions

In summary we could show that enantiopure cryptates are indeed a well suited scaffold for the observance of circularly polarised luminescence. In the partly deuterated ligand scaffold under study the lanthanoid ion is efficiently protected against nonradiative deactivation processes, which is especially helpful in the case of the less luminescent lanthanoids such as samarium. As already observed for other ligand scaffolds in which samarium and europium exhibit distinct CPL-activity, in our study g_{lum} values in the same order of magnitude were determined for the europium ($g_{lum} = -0.19$) and the samarium complex ($g_{lum} = +0.13$). This points to the high potential of samarium CPL which is accessible when the non-radiative deactivation can be controlled, as it is possible in lanthanoid cryptates. The well defined structure in solution of these complexes may be of help for a more detailed understanding of the origin of CPL and the extraordinarily high stability of these complexes under various conditions makes the lanthanoid cryptates promising candidates for upcoming applications of CPL.

Experimental Section

General. The synthesis of the ligand and respective Yb^{III} and Lu^{III} complexes has already been reported elsewhere.^[12] Chemicals were purchased from commercial suppliers and used as received unless stated otherwise. CH_3CN for the synthesis of the cryptates was HPLC grade. NMR spectra were measured at 26°C on a Bruker AVII+400 (1H : 400 MHz) and analysed using MestReNova 7 (Mestrelab Research) and Origin 9.0 (OriginLab). Deuterated solvents had deuterium contents > 99.8%D and were used as commercially available without additional purification or drying procedures. To confirm the purity of the complexes, samples were taken up in a minimum of CH_3CN/H_2O (1:1, v/v), filtered (0.45 μm nylon membrane filters) and subjected to analytical reversed-phase HPLC (RP-18e, 125 \times 4 mm - 5 μm , flow rate: 1 mL min^{-1} , UV detection: 300 nm) with H_2O (degassed, +1% TFA, v/v) as mobile phase A, CH_3CN (degassed, HPLC grade) as mobile phase B, and the following gradient: 0 min: 85%A/15%B; 5 min 85%A/15%B; 19 min: 45%A/ 55%B; 25 min: 45%A/55%B; 40 min: 85%A/15%B; 50 min: 85%A/ 15%B.

Photophysical measurements. Steady state emission spectra were acquired on a Horiba Fluorolog-3 DF spectrofluorimeter using quartz cuvettes (suprasil, 1 cm pathlength) at room temperature. The excitation light source was a 450 W xenon lamp. Emission was monitored at 90° using a Hamamatsu R2658P PMT (UV/vis/NIR, 200 nm < λ_{em} < 1010 nm) or a Hamamatsu H10330-75 PMT (NIR, 950 nm < λ_{em} < 1700 nm). Spectral selection was achieved by single grating monochromators (excitation: 1200 grooves/nm, blazed at 300 nm, visible emission: 1200 grooves/nm, blazed at 500 nm, NIR emission: 600 grooves/nm, blazed at 1000 nm). Luminescence decay profiles were determined with the same instrumental setup as described above for the steady state experiments. The light source for the recording of the decay profiles was a 70 W xenon flash lamp (pulse width ca. 1.5 μs FWHM). Lifetime data analysis (deconvolution, statistical parameters, etc.) was performed using the software package DAS from Horiba. Lifetimes were determined by fitting the middle and tail portions of the decays. The absolute quantum yields ϕ_{Ln}^L of **1-Eu** and **1-Sm** were determined with two independent sets of samples each, using quinine sulfate in 0.5 M H_2SO_4 as quantum yield standard ($\Phi = 54.6\%$).^[20] For analysis the optically dilute method was employed:^[20]

$$\phi_x = \phi_s \times \left(\frac{Grad_x}{Grad_s} \right) \times \left(\frac{n_x}{n_s} \right)^2 \quad (4)$$

where ϕ_x/ϕ_s are the quantum yields of the sample (x) or the standard (s), $Grad_x/Grad_s$ are the linearly fitted slopes from the plot of the integrated luminescence intensity of the sample (x) or the standard (s) versus the absorbance at the excitation wavelength and n_x/n_s are the refractive indices of the medium or the sample (here: CD_3OD , $n_x = 1.326$) or the standard (here: $n_s = 1.33$). For the determination of ϕ_{Eu}^L an excitation wavelength of 317 nm was chosen, for the determination of ϕ_{Sm}^L an excitation wavelength of 310 nm was chosen. All spectra were corrected and the integrated intensity of the second order peaks in the spectra of the lanthanoid complexes were subtracted from the integrated luminescence intensity. The estimated uncertainties in ϕ_{Ln}^L are $\pm 15\%$.

Chiroptical measurements. ECD (electronic circular dichroism) spectra were recorded using a Jasco J-715 spectropolarimeter, in 3 mM CD_3OD solution in a 0.1 mm optical path cell (4 accumulations). CPL spectra were measured using the home-built spectrofluoropolarimeter described in ref. [8h]. The samples were irradiated by a 90° geometry employing as the source an UVC high pressure mercury lamp ($\lambda_{max} = 254$ nm), the following acquisition parameters were used: accumulations = 2, integration time = 8 sec, scan-speed = 0.5 nm/sec

Synthesis. *Europium complex 1-Eu.* The sodium cryptate 1-Na (5.02 mg, 6.25 μmol , 1.0 equiv.) and $\text{EuCl}_3 \cdot 6 \text{H}_2\text{O}$ (3.44 mg, 9.38 μmol , 1.5 equiv.) were suspended in 7 mL dry CH_3CN (HPLC grade) and heated to reflux temperature, whereby the mixture got turbid. After 40 h the volatiles were removed. The remaining solid was dried *in vacuo*, afterwards taken up in a minimum amount of CH_3OH and filtered over cotton. The yellow solution was overlaid with Et_2O and stored at 4°C overnight. Afterwards the precipitate was collected on a membrane filter, washed with cold Et_2O and dried to give a faintly yellow solid (3.62 mg, 3.81 μmol , 61%). ^1H NMR (400 MHz, CD_3OD): $\delta = 16.49$ (s, 2H), 11.54 (s, 2H), 9.25 (s, 2H), 9.03 (s, 2H), 6.19 (s, 2H), 3.09 – 2.43 (m, 6H), 1.00 – 0.66 (m, 8H), -10.40 (s, 2H), -17.53 (s, 2H) ppm. Analytical HPLC: $t_r = 13.7$ min (see Figure S1 in the supporting information).

Samarium complex 1-Sm. 5.02 mg (6.25 μmol , 1.0 equiv.) of the sodium cryptate 1-Na together with $\text{SmCl}_3 \cdot 6 \text{H}_2\text{O}$ (3.42 mg, 9.38 μmol , 1.5 equiv.) were suspended in 7 mL dry CH_3CN (HPLC grade) and heated to reflux temperature. After 40 h the volatiles were removed and the crude product was treated as described for **1-Eu** to yield 3.61 mg (3.80 μmol , 61%) of a faintly yellow solid. ^1H NMR (400 MHz, CD_3OD): $\delta = 9.54$ (d, $J = 8.13$ Hz, 2H), 9.11 – 9.00 (m, 2H), 8.95 (d, $J = 7.30$ Hz, 2H), 8.26 – 8.14 (m, 2H), 7.93 – 7.65 (m, 8H), 6.21 (br s, 2H), 4.17 (br s, 2H) 2.62 – 2.43 (m, 2H), 1.52 – 1.39 (m, 6H) ppm. Analytical HPLC: $t_r = 14.0$ min (see Figure S2 in the supporting information).

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