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Unlocking same-sign CPL: solvent effects on spectral form and racemisation kinetics in nine-coordinate chiral europium(III) complexes

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Understanding the factors that shape the circularly polarised luminescence (CPL) emission profiles of europium(III)-based CPL emitters to have specific sign properties, *e.g.* monosignate individual CPL transitions, is key to design novel complexes for applications ranging from advanced security inks to bio-probes for live cell imaging. In order to correlate structure and spectral characteristics, a photophysical and kinetic investigation has been conducted on a series of coordinatively saturated nine-coordinate europium(III) systems based on 1,4,7-triazacyclononane. We highlight that lanthanide emission is sensitive to changes in the ligand field by showing the linear dependence of total emission intensity ratios as a function of solvent polarity, for europium(III) complexes displaying an internal charge transfer (ICT) excited state. This sensitivity increases by a factor of 20 when studying changes in CPL spectra, rendering these complexes accurate probes of local polarity. Solvent polarity, solvent-specific effects, and the nature of the chromophores' coordinating donor atoms strongly influence the kinetic stability of europium(III) complexes with respect to enantiomer interconversion. Notably, we show that the choice of donor groups to coordinating to europium(III) and the nature and polarity of the solvent affects the rate of racemisation, leading to systems with very long half-lives at room temperature in non-polar media.

Introduction

It is often assumed that lanthanide luminescence is fundamentally independent of the metal coordination environment, owing to the effective shielding experienced by the 4*f* orbitals. Recent findings highlight the striking effect of solvent polarity in determining emission spectral form for coordinatively saturated complexes, including circularly polarised luminescence (CPL) spectra.[1] The present work extends the scope of the study performed by Fradgley *et al.* to *quasi*-C_3 symmetric complexes, named **[Eu.L$^{1-3}$]**, (Figure 1).[2,3] The lower symmetry removes the degeneracy of some transitions, leading to greater complexity in the spectral profile.[4–8]

The structurally related complexes **[Eu.L$^{1-3}$]**, possessing one, two, and three antennae, are used to probe the effect of small variations in the coordination environment.

The ligand field and hence the spectral properties of europium(III) complexes, are also affected by the nature and polarisability of the chromophores' donor groups. Since the polarisability of the chromophores is a function of solvent polarity, we expect to see solvent dependent changes in luminescence for such complexes. Understanding how solvent polarity shapes the CPL emission profile is a prerequisite to devising novel Eu(III) complexes with desirable chiroptical properties for applications such as *in vivo* sensing and security tagging. This issue is particularly relevant, as the rapid detection of CPL is facilitated by having relatively broad monosignate transitions within a given manifold in the CPL fingerprint spectrum.

Macrocyclic Eu(III) complexes of nonadentate ligands do not normally suffer from ligand dissociation in aqueous media and are not quenched by dissolved oxygen.[2,9] The presence of pyridylalkynylaryl chromophores in the ligand also allows efficient multiphoton excitation.[10,11] Controlling the sign and intensity of individual CPL transitions within a single emission manifold is key to tailor CPL spectra for specific purposes. Compared to total emission, CPL spectra may have increased resolution of individual transitions,[12–16] providing valuable insight into individual sub-transition energy states. In this case, the ideal highly resolved and informative CPL spectrum often consists of a sequence of opposing sign transitions within a single emission manifold. An interesting potential application of such a situation is in tailored CPL spectral fingerprint barcoding.[17] Conversely, a monosignate spectrum is ideal in circumstances where the goal is to maximise the number of photons having a defined CP handedness within a single emission manifold,. In this case, applications include CPL microscopy[10] and photography[18] using low-cost broad band-pass filters or wide detection slits.

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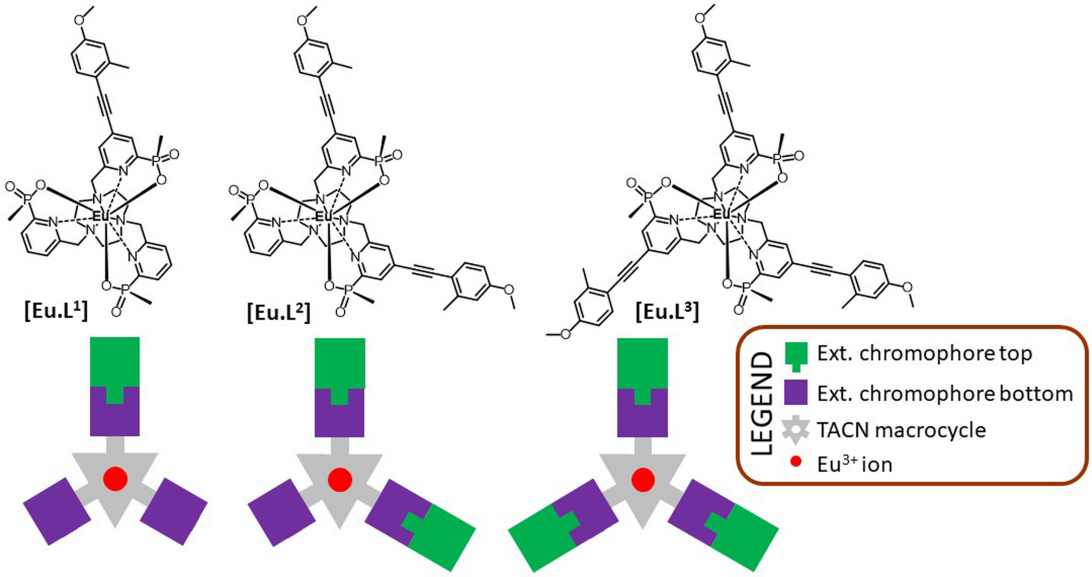

Figure 1. Structures and schematic representation of [**Eu.L**$^{1-3}$].

Solvent effects and Racemisation kinetics

Solvatochromism refers to the reversible change in either absorption or emission spectral features of a fluorophore in different solvents. These changes are typically rationalised in terms of the differential effect that solvent polarity has in shifting the ground and first excited states of the emissive species, thereby affecting this energy difference. Fluorophores typically have a larger electric dipole moment in the excited state compared to the ground state. Emission wavelengths decrease with increasing solvent polarity because while both the ground state and excited state of a fluorophore can be stabilised, the excited state is usually stabilised to a greater extent, resulting in a red shifted (bathochromic) emission in more polar solvents. In certain cases, *e.g.* for fluorophores which can access an internal charge transfer (ICT) state, solvent polarity effects are also observed in absorption spectra.[19] Being an excited state characterised by a strong charge separation and therefore a high electric dipole moment, the energy of the internal charge transfer state is altered by solvent polarity. As a consequence, variations in the spectral profile and shifts in absorption maxima can also be observed, in addition to the more commonly observed changes in emission spectra.[19]

Recent work from Fradgley *et al.* has continued to challenge the dogma that lanthanide emission is insensitive towards changes in the ligand field, by showing that solvatochromism behaviour is not restricted to hypersensitive transitions.[1] The reference compounds examined were coordinatively saturated chiral europium(III) complexes, in which solvent molecules cannot access the first coordination shell of the lanthanide ion due to preferential nonadentate binding of the ligand donor atoms. This situation excludes the possibility that the observed change is due to first-shell solvent ion interactions. As anticipated, europium(III) complexes that can access ICT excited states show marked solvatochromism in absorption. The small wavelength shifts in emission and variations of emission intensity were rationalised in terms of the changes of the ligand field experienced by the lanthanide centre in the different solvents alongside a profound effect on the CPL emission profile, sign orientation and sequence.

The enantiomeric purity of enantioenriched samples decreases with time in the presence of an accessible pathway for enantiomer interconversion via racemisation. The energy barrier to the enantiomer interconversion process determines the time-dependence of the stability of a given compound towards racemisation. Enantiomers may be not isolable in the case of rapid interconversion or, conversely, can be virtually impossible to racemise.

Premature racemisation of samples is undesirable for applications such as security inks,[20] CPL calibration standards, and CPL microscopy standards.[10] High stability towards racemisation is crucial for applications where the temperature can range from prolonged exposure to 37 °C (*e.g.* live cell imaging) to brief 150 °C incursions (*e.g.* bank note lamination).

TACN-based europium(III) complexes possess a tricapped trigonal prismatic coordination geometry. The complex exists as a racemic mixture of two enantiomers (*RRR*)-$\Lambda(\delta\delta\delta)$ and (*SSS*)-$\Delta(\lambda\lambda\lambda)$, where *R* and *S* refer to the configuration of the phosphorus atom (since metal coordination renders the P centre stereogenic), δ and λ refer to the torsion angle in the NCCN chelate ring, and Δ and Λ to the propeller (arm) chirality defined by the $NCCN_{py}$ torsion angles, (Figure 2). Although a larger number of diastereomeric combinations is possible in principle, interlinked steric requirements force the complex to exist as the two enantiomers (*RRR*)-$\Lambda(\delta\delta\delta)$ and (*SSS*)-$\Delta(\lambda\lambda\lambda)$ only. The high energy barrier to racemisation allows for enantiomer isolation by chiral HPLC.

In principle, the process of enantiomer interconversion could involve cooperative arm rotation or inversion of the nine-membered macrocycle ring. The energy barrier increases

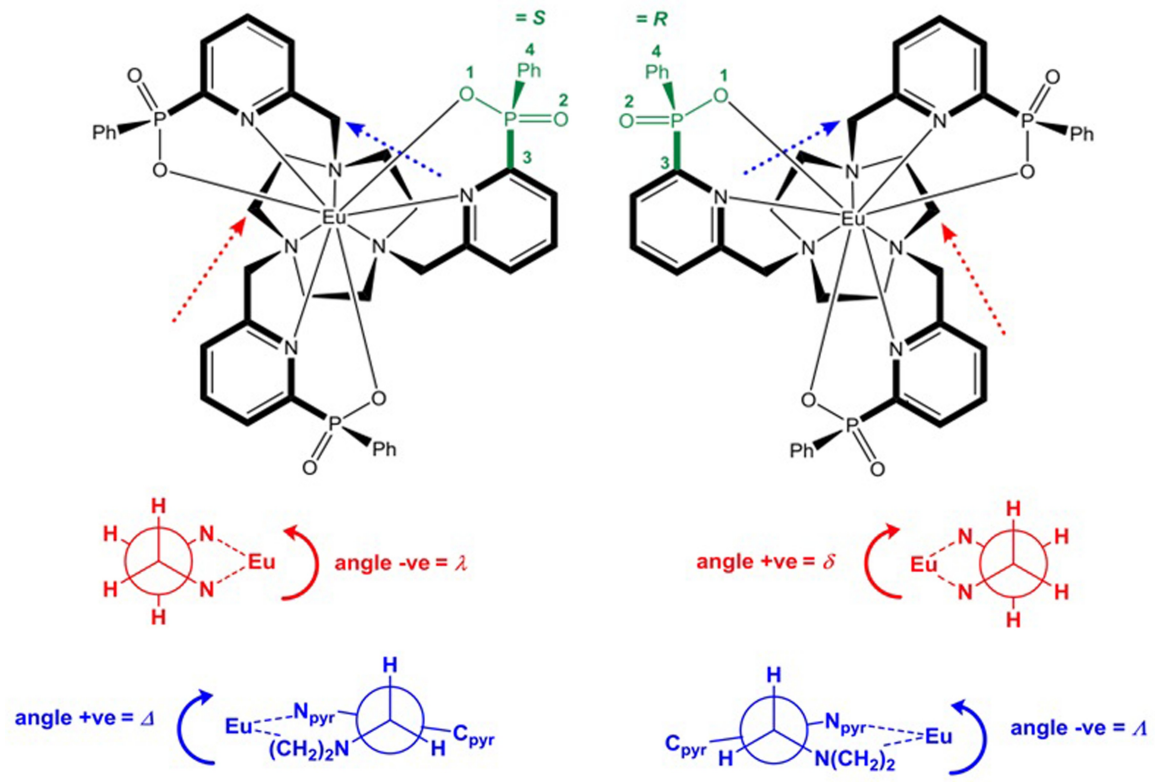

Figure 2. Stereochemistry of (*SSS*)-*Δ*(*λλλ*) (*left*) and (*RRR*)-*Λ*(*δδδ*) (*right*) enantiomers characteristic of TACN-based europium(III) complexes. Stereochemistry at P (*green*) and Newman projections of the C–C bond of ring NCCN (*red*) and $NCCN_{py}$ (*blue*) chelates are shown.

dramatically with the degree of steric hindrance. It is known that the three donor groups carboxylate, methylphosphinate, and phenylphosphinate display increasing stability towards racemisation.[21] In the present work, other factors impacting the racemisation kinetics of TACN-based europium(III) complexes were investigated, including solvent polarity and the size and nature of the electric dipole moment of the chromophore. For further insights and background information on the importance of solvent effects and racemisation kinetics please refer to the relevant section of the Supplementary Information file.

Results and Discussion

Solvent effects

An investigation of the variation of spectral form in total emission and CPL as a function of solvent polarity was performed with [**Eu.L**$^{1-3}$], *i.e.* the uncharged Eu(III) complexes bearing one, two, and three extended chromophore antennae, respectively. The spectral form of both total emission and CPL spectra was found to be solvent dependent, (Figure 3 and Figure SI 1). Previous studies have highlighted the sensitivity of the electric dipole allowed $\Delta J=2$ and $\Delta J=4$ manifolds in Eu(III) complexes to solvent effects.[1] The three bands within the $\Delta J=2$ manifold are labelled ***A***, ***B***, and ***C***; the five transitions within the $\Delta J=4$ manifold are labelled ***D-H***, where ***G*** and ***H*** are resolved only in CPL spectra. In the total emission spectra of [**Eu.L**$^{1-3}$], the most intense transition ***A*** centred at 613.5 nm does not show any solvent dependence, whereas transition ***B*** exhibits a bathochromic (red−) shift ($\Delta\lambda=1.5$ nm going from EtOAc to MeOH), and transition ***C*** a $\Delta\lambda=1.0$ nm hypsochromic (blue−) shift, more pronounced in the C_3-symmetric complex [**Eu.L^3**]. In the $\Delta J=4$ manifold, the two stronger transitions ***D*** and ***E*** are well resolved in polar media (686.5 *vs* 690.0 nm in MeOH across the series, $\Delta\lambda=3.5$ nm difference) but coalesce as solvent polarity decreases, merging into a single unresolved band centred at 688.0 nm. The transition ***F*** displays a $\Delta\lambda=$ 1.0 nm bathochromic shift. The solvatochromic shifts in total emission are highly consistent across the series. The intensity ratio of selected transitions exhibits a modest 10–20% change with polarity.

CPL spectra for [**Eu.L**$^{1-2}$] have transitions in the $\Delta J=2$ manifold that undergo very small shifts of around 0.5 nm (Figure 4 and Figure SI 2). The intensity of transition ***A***, however, displays a tenfold increase with respect to the intensity of either ***B*** or ***C*** as polarity is decreased. This increase in CPL intensity is consistent with the decrease in the magnitude of the electric dipole moment in less polar solvents, highlighting the potential of this system as a more sensitive polarity probe. In the $\Delta J=4$ manifold, the ***D*** and ***E*** transitions are always resolved as they are of opposite sign in CPL. All the transitions display very small shifts (order of $\Delta\lambda=0.5$ nm) as the polarity of the medium is varied. Only transition ***E*** shows a more substantial 2.0 nm

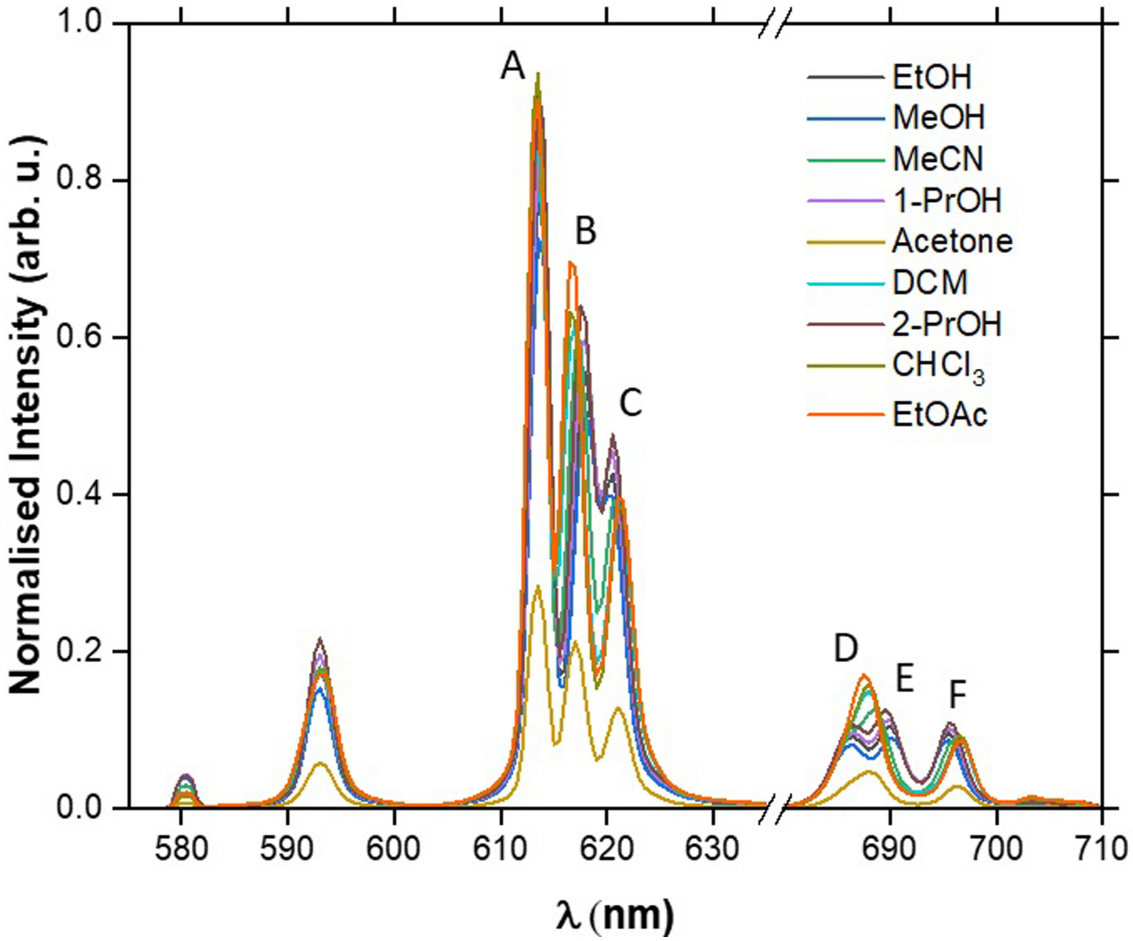

Figure 3. Total emission spectra of [**Eu.L**^{1}] in solvents of varying polarity with the six relevant transitions labelled. λ_{exc} = 336 nm, scanning step = 0.5 nm, integration time = 500 ms/step.

bathochromic shift, consistent with the trend observed in total emission spectra, where ***D*** and ***E*** coalesce as solvent polarity is decreased.

The changes in intensity of transitions within the $\Delta J = 4$ manifold are much smaller than those observed in the $\Delta J = 2$ manifold. The stability of sign and intensity with respect to the nature of the solvent parallels the behaviour observed in previous studies, where it was shown that the sign sequence of transitions within the $\Delta J = 4$ manifold correlates with the propeller chirality of each enantiomer, *e.g.* the Λ enantiomer has a $-/+/-/-/+$ sequence. The complex absolute configuration has been independently determined via X-ray crystallography[22,23] The simultaneous presence within the same emitting species of transitions that are highly sensitive towards solvent polarity ($\Delta J = 2$) and comparatively insensitive ($\Delta J = 4$) allows internally referenced ratiometric measurements of medium polarity to be undertaken, with greatly enhanced sensitivity. To exemplify this point, the intensity ratio between the CPL transitions ***A*** (belonging to the $\Delta J = 2$ manifold) and ***H*** (belonging to the $\Delta J = 4$ manifold) can be considered (Figure 5 and Figure SI 3). The intensity of transition ***A*** undergoes a 20-fold increase with respect to the intensity of transition ***H*** as solvent polarity decreases from MeOH to EtOAc.

Racemisation kinetics

The kinetic plots for enantiomer interconversion of [**Eu.L**^{1}] at 60 °C in various solvents are shown in Figure 6. The slopes of the kinetic plots for [**Eu.L**$^{1-3}$] (Figure SI 4) were used to calculate the racemisation half-lives at 60 °C according to the mathematical model, (Table 1). To further elucidate the strikingly large values obtained, especially in low-polarity solvents, half-lives at room temperature (25 °C) were estimated under the crude assumption that kinetic rates double upon a ten-degree temperature increase.

No evidence for racemisation was found for [**EuL**^{2}] and [**EuL**^{3}] within the limit of detection (1 % enantiomeric excess, as measured by integrating the two peaks in the analytical chiral HPLC chromatogram) after two weeks in solution at 60 °C for both of the aprotic solvents NMP and EtOAc. The complex [**EuL**^{1}] is the only one in the series showing slow, but unequivocable racemisation.

A lower limit to the racemisation half-life was estimated by assuming a racemisation rate equal to the instrumental error occurring between the first and last measured points in time. Half-lives in non-polar media at room temperature ranged therefore from centuries to millennia, highlighting the remark-

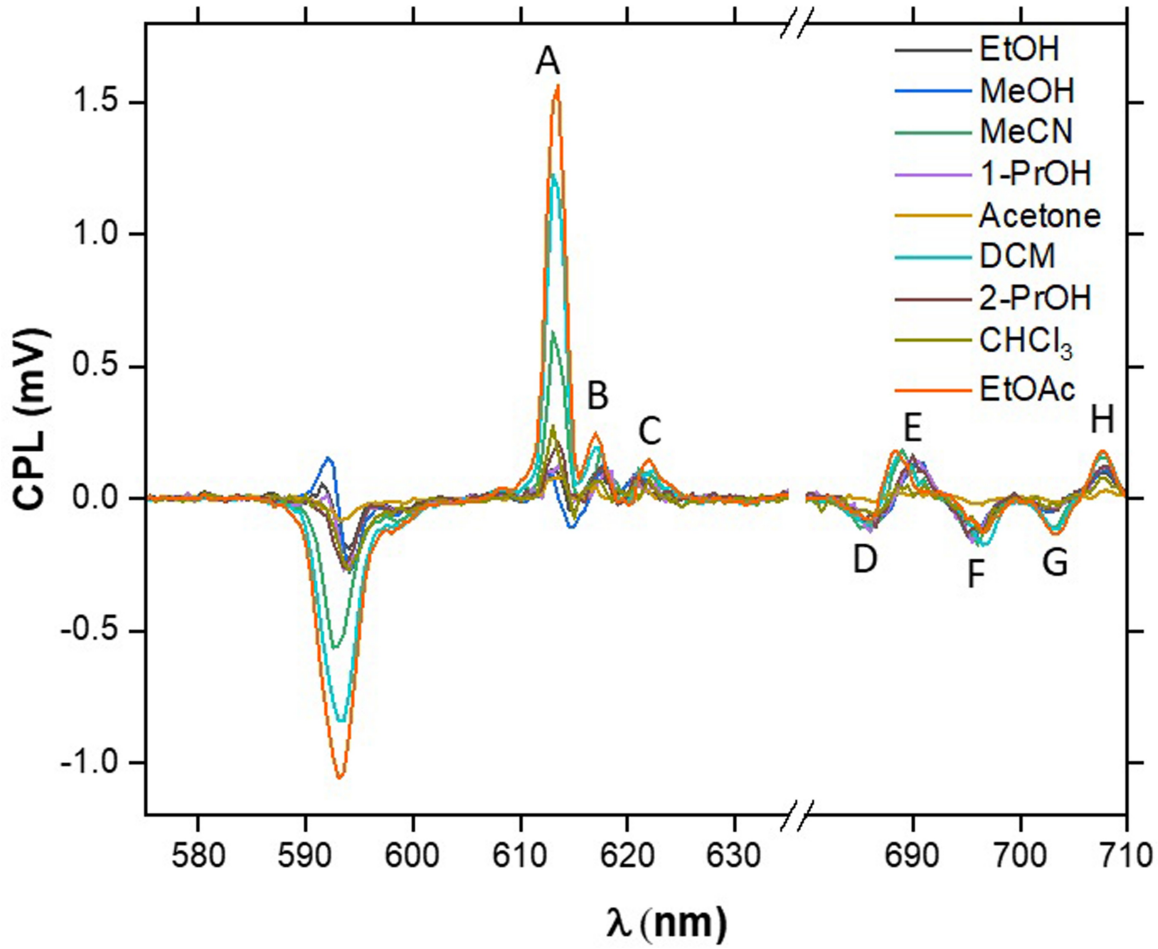

Figure 4. CPL spectra of Λ-[**Eu.L^2**] in solvents with varying polarity with the eight relevant transitions labelled. λ_{exc} = 336 nm, scanning step = 0.5 nm, integration time = 500 ms/step.

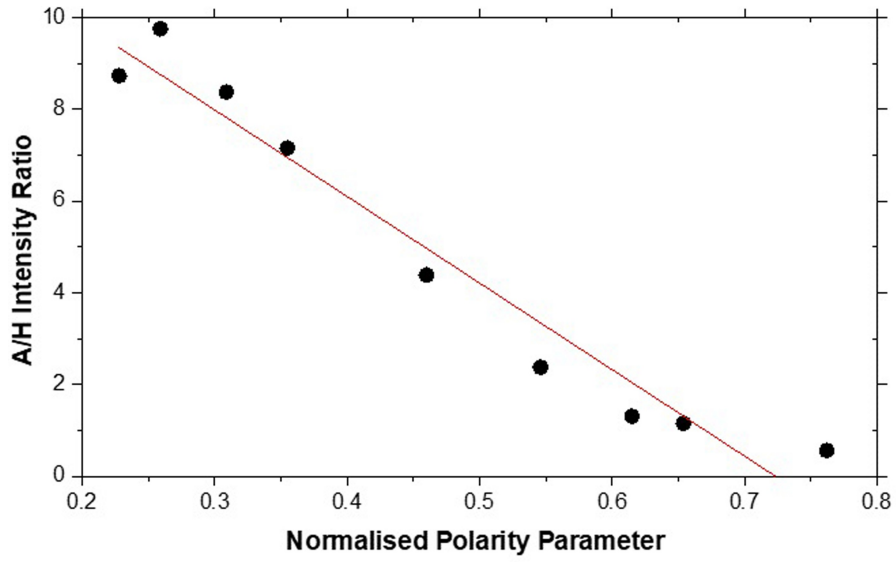

Figure 5. Intensity ratio for the CPL ***A*** and ***H*** transitions of [**Eu.L^1**] as a function of Reichardt's polarity parameter.[24]

able stability imparted by the phenyl phosphinate donor groups.

The solvents NMP and EtOAc respectively possess the same polar groups as the monomers in polyvinylpyrrolidone (PVP)

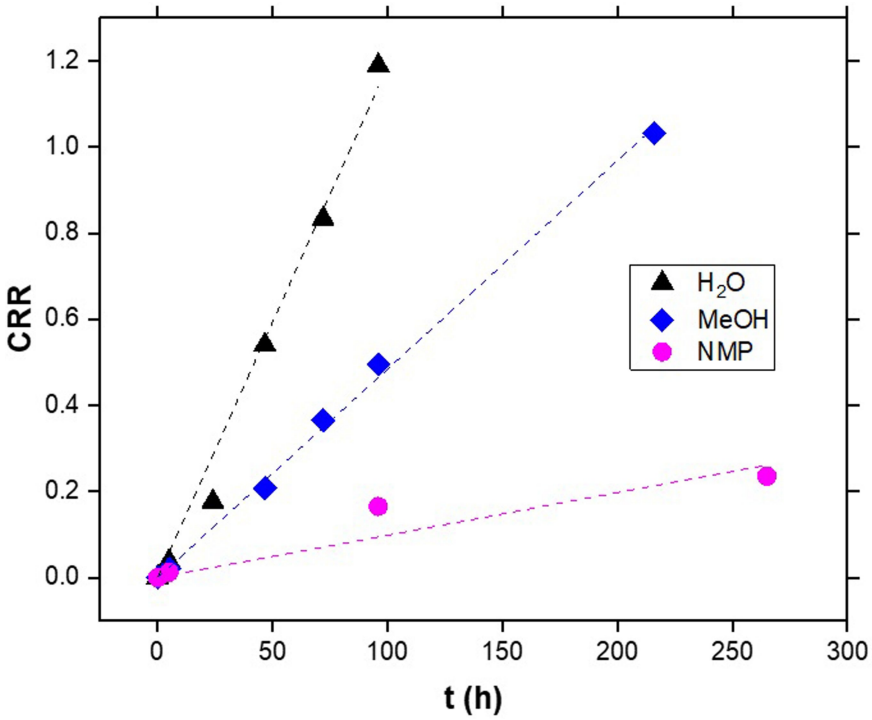

Figure 6. Kinetic plots for the corrected enantiomer interconversion rate (adjusted for a starting enantiomeric excess of 90:10, see eq. 12) for **[Eu.L^1]** at 60 °C in various solvents (*black triangle* = water; *blue square* = methanol; *magenta circle* = NMP). Ethyl acetate is not shown as no enantiomer interconversion was detected over a period of 300 h.

Table 1. Summary of half-lives for racemisation, $t_{1/2}$, for **[Eu.L$^{1-3}$]** in solvents of decreasing polarity (Reichardt's polarity parameters in parentheses). Half-lives measured at 60 °C are reported in days and estimated lifetimes at room temperature (25 °C) are expressed in years (in parentheses).

	Water (1.000)	**MeOH** (0.762)	**NMP** (0.355)	**EtOAc** (0.228)
[Eu.L^1]	2.4 d (22 y)	6.0 d (56 y)	36 d (340 y)	>110 d (1000 y)[a]
[Eu.L^2]	5.3 d (50 y)	8.5 d (79 y)	>400 d (3800 y)	>1900 d (18,000 y)[a]
[Eu.L^3]	6.1 d (58 y)	4.5 d (42 y)	>220 d (2000 y)	>1900 d (18,000 y)[a]

(a) No evidence of racemisation within experiment error over a period of two weeks. The estimate given corresponds to the lower limit calculated for the racemisation half-time.

and polymethylmethacrylate (PMMA). These complexes are therefore expected to be kinetically stable towards racemisation in such a polymeric matrix. Such devices could be used, for instance, in thin films to calibrate CPL spectrophotometric devices and microscopes. We hypothesise that in a more viscous medium, such as a polymeric matrix, the racemisation half-lives with respect to the solution state would tend to increase, as the arm rotation motion required for enantiomer interconversion is likely to be disfavoured.

The enantiomer interconversion process requires sequential breaking of each bond between the phosphinate oxygen and the europium ion. The complex must pass through a short-lived charged intermediate, where the europium ion is bound to seven or less ligand donor atoms, with additional coordination sites taken up by the solvent. For instance, water and MeOH are polar protic solvents capable of stabilising such a charged intermediate that arises from breaking a Eu–O and a Eu–N_{py} bond, facilitating the arm rotation step necessary for enantiomer interconversion.

Both NMP and EtOAc are aprotic solvents that are less effective at solvating the putative ionic intermediate (particularly local anionic charge centres), and hence are associated with a higher activation energy barrier and much longer racemisation half-lives. It is reasonable to assume that the cleavage of the ionic Eu–O bond is involved in the rate-limiting step, as it is thermodynamically stronger than the Eu–N_{py} bond. The complex with two extended chromophores (three in the case of water) exhibited the highest stability towards racemisation. This result is interesting for applications, as it allows the structure of the complex to be tailored more easily, *e.g.* by late-stage functionalisation of the simpler, single arm pyridyl donor moiety.[25]

In particular, we found that low-polarity aprotic solvents such as NMP and ethyl acetate give rise to a more intense CPL signal in the $\Delta J = 2$ manifold and seem to have a tendency to

promote same sign transitions. It is important to note that EtOAc and NMP bear a strong resemblance to the monomers of polymethylmethacrylate (PMMA) and polyvinylpyrrolidone (PVP) respectively. We have already conducted a brief investigation of the spectral properties of closely related parent europium(III) complexes in such polymers in conjunction with these solvents, as part of our recent work to develop a novel CPL photography equipment, and such a premise was supported by the near identical CPL fingerprints observed, (Figure 7–8).[18]

Discussion

This study draws attention to the crucial, albeit often neglected, relationship between the choice of solvent and the nature of the CPL active Eu(III) complex. The nature of the solvent can affect both the magnitude and sign of the emitted CPL signal, especially in the electric dipole allowed $\Delta J=2$ and $\Delta J=4$ transitions. For the sake of specific CPL applications, the complex and the solvent should be considered as an inseparable pair. Although these conclusions are only qualitative, and not yet predictive, the present study represents a first step in the ambition to engineer bright, high g_{lum} and monosignate Eu(III) complexes by controlling their photophysical parameters. We are poised to continue this investigation with particular emphasis on varying the nature and polarisability of the ligand donor atoms and the overall symmetry and stereochemistry at the Ln(III) centre.

In particular, we found that low-polarity aprotic solvents such as NMP and ethyl acetate give rise to a more intense CPL signal in the $\Delta J=2$ manifold and seem to have a tendency to promote same sign transitions. Moreover, the structural resemblance of NMP and EtOAc to the monomers of polyvinylpyrrolidone (PVP) and polymethylmethacrylate (PMMA) suggests that similar behaviour can be expected in solid state matrices fabricated with such polymers. We have already reported CPL spectra of structurally related Eu(III) complexes in those solvents and corresponding polymers showing complete CPL spectrum recovery, (Figure SI 6–7).[10,18] Pairing our mono-signate CPL emitters reported herein with our ambition to optimise the properties of CPL-active thin films, these parent systems will serve as a test-bed for future generations of purposely engineered Eu(III) complexes for applications where broad mono-signate CPL emission is needed.

A deeper insight into racemisation kinetics and environmental factors has been gained. The comparatively lower racemisation half-lives in water and methanol, while still long enough for most applications, were interpreted in terms of assistance of the dissociative process by these small polar solvent molecules, via stabilisation of the transient ion pair in the transition state through hydrogen bonding or specific

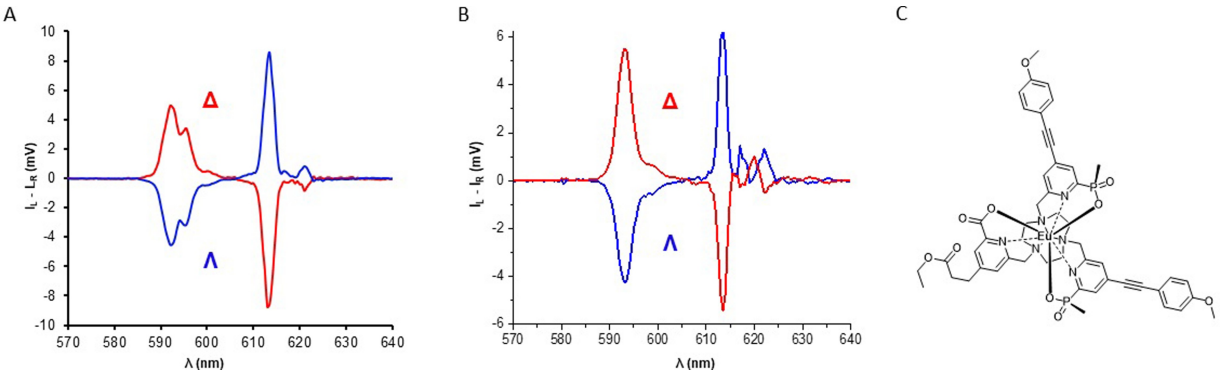

Figure 7. CPL spectra of the Λ- and Δ enantiomers of a structurally related parent complex [**Eu.L^4**] in (A) EtOAc and in (B) drop cast PMMA matrix, 100 μm thickness, C = 5×10^{-5} M, (C) structure of [**Eu.L^4**] for comparison.[18]

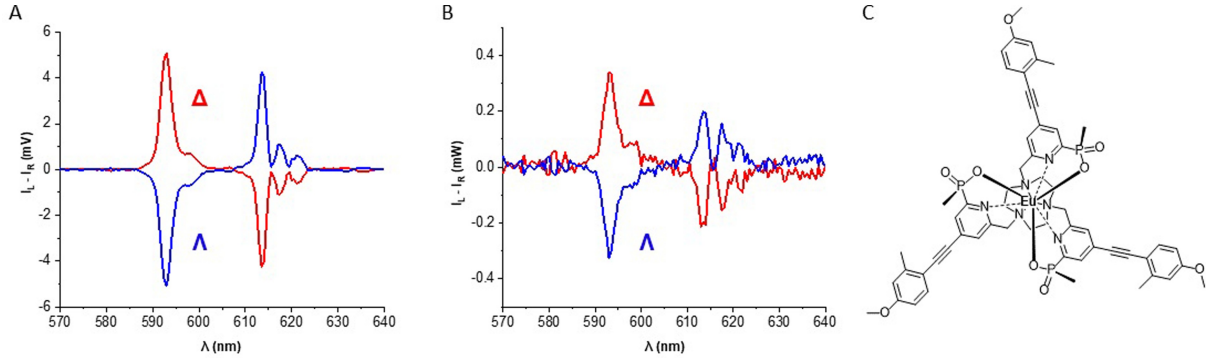

Figure 8. CPL spectra of the Λ- and Δ enantiomers of a structurally related complex [**Eu.L^1**] in (A) NMP and in (B) spin coated PVP matrix, 15 μm thickness, C = 5×10^{-5} M, (C) structure of [**Eu.L^1**] for comparison.[10]

solvation effects. The water molecule is especially efficient at coordinating to europium(III) due to its high oxophilicity, thereby lowering the energy of the transition state leading to its formation.[21,26] Indeed, the smallest racemisation half-life values were consistently obtained in water, followed by methanol. The abrupt increase in the racemisation half-life for low polarity solvents NMP and ethyl acetate can be ascribed to the absence of this H-bonding stabilisation effect.

Extended chromophore antennae are expected to increase the structural stability of the complex by increasing the overall steric bulk of the system and the magnitude of the electric dipole moment. The enhanced polarisability of the pyridyl nitrogen atom and the pyridyl moiety itself can be associated with increased Eu–N_{py} bond strength and is expected to inhibit dissociation of the Eu–N_{py} bond, and hence increase the energy barrier to formation of a partly dissociated intermediate, thereby limiting the rate of enantiomer interconversion.

The complexes with two extended chromophores showed the highest stability towards racemisation. Coincidentally, these systems have one pyridyl moiety available for applications such as functionalisation with a unique recognition motif that can be used as a recognition element for host-guest bio-imaging.[25,27] The enhanced stability towards racemisation of this structure is a desirable property for the development of responsive chiral bio-probes.[28]

The series of solvent chosen was based on two factors, *i.e.*, observing the changes in emission properties as a function of solvent polarity and studying the effects of hydrogen bond formation. Therefore, we examined some polar protic solvents with varying nucleophilicity. A handful of recent studies has observed changes in both the luminescence and paramagnetic NMR properties of Ln(III)-complexes. These studies showed that hydrogen bonding has a profound effect on the polarizability of the donor groups coordinated to the metal centre, determining the local ligand field and hence the NMR shift/relaxation and luminescence behaviour.[29–31]

In **[EuL$^{1-3}$]** the Ln–O–P and O=P bonds are likely hydrogen bond acceptors. This assertion is evidenced by the observation of significant changes in both the total and CPL emission (Figures 3 and 4) profiles of these complexes in H bond donor solvents.[32,33] The intensity and most importantly the dominance of monosignate CPL emission in the magnetically allowed $\Delta J=1$ transition diminished when protic solvents of increased hydrogen bond forming nature were used. These observations were most apparent when MeOH was used. The decreased polarisability due to protic solvent mediated hydrogen bond formation involving the P=O bond may effectively weaken the electrostatic Ln-O–P interaction. Moreover, in the racemisation pathway, where bond dissociation must occur, the polar protic solvent is more likely to stabilise better the putative charge-separated intermediate and/or the transition state leading to its formation, compared to a less polar or poorer H-bond donor solvent.

Conclusions

The present study has examined a selection of Eu(III) complexes and the conclusions can be extrapolated to the behaviour of isostructural series of lanthanide complexes. For instance, to terbium(III) complexes that display more intricate CPL spectra owing to the greater multiplicity of the emissive states.[4,23] For this reason, further work is necessary to verify if it is possible to exploit solvent effects to obtain mono-signate CPL emission for chiral terbium(III) systems, e.g. over a narrowly defined emission range.

The unique photophysical phenomenon of circularly polarised emission can be used to monitor medium polarity with enhanced sensitivity. The solvation-induced changes in the shape of the CPL were found to be an order of magnitude larger and were more informative than the analysis of total emission variations. This study highlights the importance of the solvent in CPL fingerprint engineering of a CPL active Eu(III) complex. In addition, it highlights that the stability towards thermally promoted racemisation is also solvent sensitive to the point where complex design and solvent choice cannot be decoupled. Ultimately, by understanding the effect and influence of these vital external parameters a new generation of CPL active Eu(III) probes can be developed that display broad, bright monosignate CPL emission when paired with an adequate solvent.

Additionally, examination of the effect of photo-irradiation on racemisation kinetics may be of interest to preserve both the observed CPL sign and brightness. Previous work has discussed the impact of photo-irradiation on the integrity of the coordinating bonds within europium(III) complexes, e.g. in labilising the Eu–N_{py} bond.[34] With the rapid uptake of CPL active Eu(III) complexes in material and life sciences and the recent expansion of CPL instrumental capabilities we foresee that more research groups will embark on creating new CPL active entities and will need to adopt a 'back to basics' approach, exploring the importance of key physical and environmental factors on the shape, sign and magnitude of CPL active luminescent transitions.

Author Contributions

DFDR: Executed all solvatochromism and racemisation kinetics experiments, data analysis and mathematical modelling, and drafted/edited the manuscript. MS: Synthesized all precursors and complexes used in this work. DP and RP: Secured project funding, devised the project, and edited the manuscript.

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Conflict of Interests

The authors declare no competing interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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