Excitation modulation of Eu:BPEPC based complexes as low-energy reference standards for circularly polarised luminescence (CPL).

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The enantiomers of [EuL$_3$].3Cl, an analogue of Eu:BPEPC with a lowered energy excitation wavelength, serve as effective reference complexes for the calibration of circularly polarised luminescence (CPL) spectrometers.

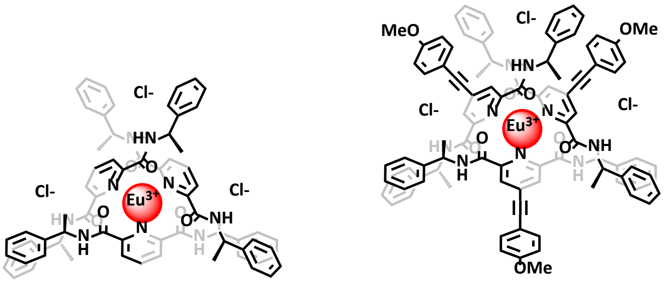
Circularly Polarised Luminescence (CPL) spectroscopy is the emission analogues of Circular Dichroism.[1-3] Whilst the latter allows the detection of the differential absorption of left and right circularly polarised light, CPL quantifies the intensity of the left (I_L) and right (I_R) circularly polarised light emitted by chiral molecules, with the differential between I_L and I_R maximised for electronic transitions that are magnetic dipole allowed/electric dipole forbidden.[4] CPL activity is quantified in absolute terms by the emission dissymmetry factor, $g_{lum}(\lambda)$, defined as :

$$g_{lum}(\lambda) = 2\Delta I/I = 2(I_L-I_R)/(I_L+I_R)$$

Therefore, CPL is a powerful tool for studying the intrinsic properties of emissive chiral molecules,[5] and is ideal for chiral emissive lanthanide complexes due to their singular photophysical properties.[6]

Despite the growing interest in CPL spectroscopy, many CPL spectrometers are one-off custom-built instruments.[3] There has been a long-standing need for a reliable, robust and accessible CPL standard to enable calibration of CPL spectrometers and to confirm the accuracy and inter-system comparability of CPL spectrometers.

Europium (N,N-bis(1-phenylethyl)-2,6-pyridinecarboxamide Eu:**BPEPC**, depicted in Figure 1, has emerged as a promising CPL standard[7, 8] with many favourable properties including good thermodynamic and kinetic stabilities, easily accessible enantiomers and large pseudo Stokes' shift and emission dissymmetry factors (Figure 2). More recently, some other examples of CPL active europium complexes have been described in the literature.[9, 10] However, these sensitising ligands (or antennas)[11] require a high-energy excitation at around 290 nm, as observed for Eu:**BPEPC** complexes (figure 3), to permit europium centred emission that is not compatible



Λ-[Eu((R,R)-BPEPC)$_3$].3Cl

Λ-[Eu((R,R)-L)$_3$].3Cl

Fig. 1. Schematic molecular structures of the *Λ*- enantiomers of Eu:**BPEPC** and [Eu**L**$_3$] complexes.

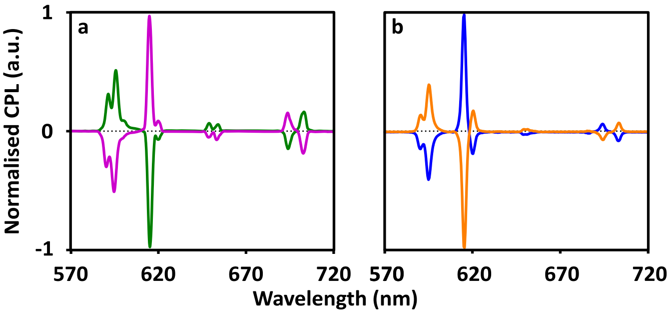


Fig. 2. Comparison of the CPL spectra of the *Λ*- (purple) and *Δ*- (green) isomers of Eu:**BPEPC** (**a**, λ_{exc} = 290 nm, *c* = 5.40×10^{-5} M in acetonitrile) and of the CPL spectra of the *Λ*- (blue) and *Δ*- (orange) isomers of [Eu**L**$_3$]$^{3+}$ (**b**, λ_{exc} = 365 nm, *c* = 18×10^{-6} M in acetonitrile).

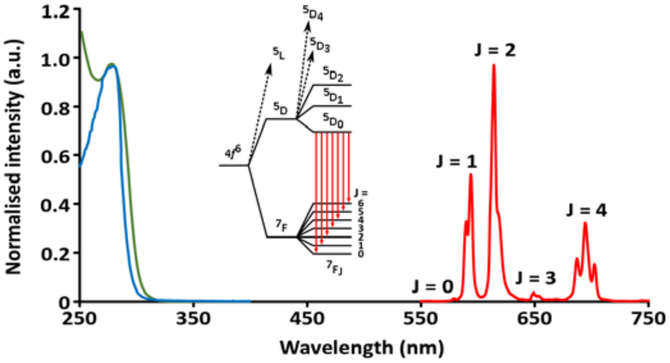


Fig. 3. Absorption (green), excitation (blue, λ_{em} = 614 nm) and total emission spectra (red, λ_{exc} = 290 nm) of Eu:**BPEPC** complexes (c = 5.40×10^{-5} M) in acetonitrile.

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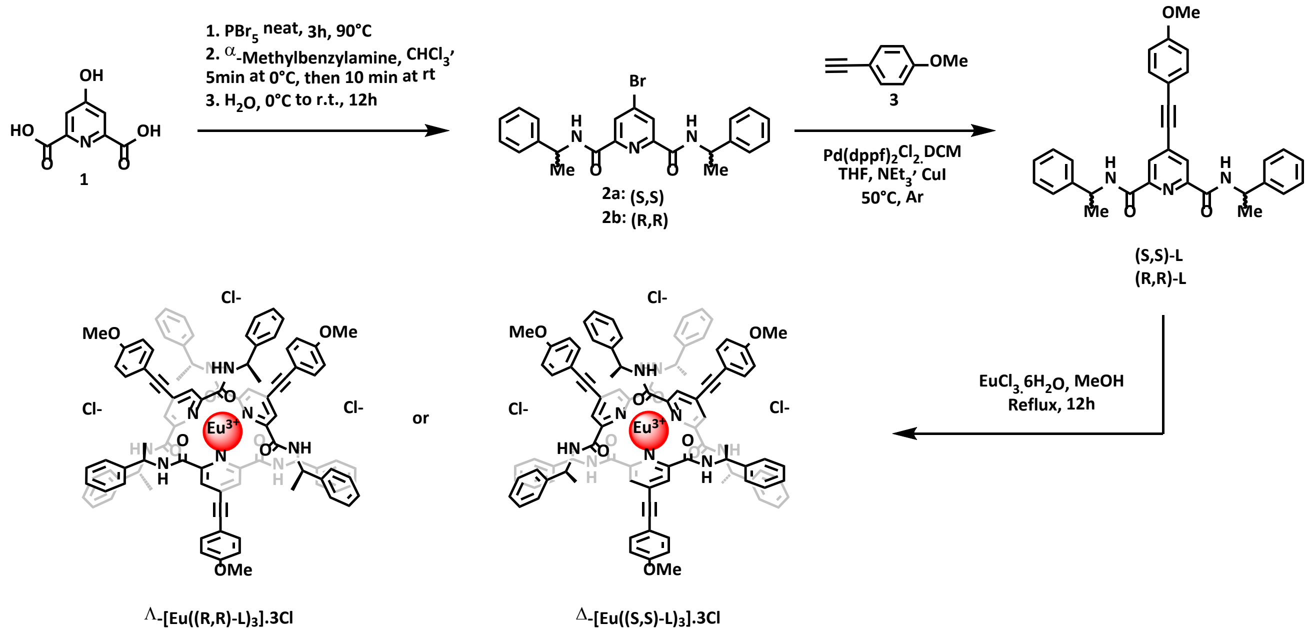

Scheme 1. Synthesis of *Λ* and *Δ*-[Eu**L**$_3$].3Cl.

with many conventional off-the-shelf light sources. Therefore, previous studies have employed inefficient ~300 nm excitation wavelength using cumbersome and bulky Xenon arc lamps.

To address this issue, we report the preparation of analogues of Eu:**BPEPC**, containing a conjugated antenna that can be excited at a readily available lower-energy wavelength, whilst retaining favourable CPL emission properties to serve as a CPL standard. This standard can be used for the calibration a new CPL spectrometer[12] which requires an excitation waveband compatible with a 365 nm LED used as a cost-effective primary excitation source.

The synthesis of the two isomers of the complex [EuL$_3$].3Cl is depicted in Scheme 1. 4-Bromo-2,6-diacyl bromide, a derivative of chelidamic acid,[13] was directly converted to the 4-bromo-2,6-diamide stereoisomers, **2a** or **2b,** via a Schotten-Baumann reaction using the appropriate α-methylbenzylamine enantiomer. Compound **2** is a versatile intermediate: the bromine atom in the para position of the pyridine ring can be involved in various conventional metal-assisted coupling reactions, allowing the extension of the electronic delocalisation with concomitant modulation of the absorption wavelength of the ligand.[14-16] The introduction of 1-ethynyl-4-methoxybenzene **3** using the palladium-assisted Sonogashira cross coupling reaction onto the aromatic framework afforded the (*S,S*) or (*R,R*) isomers of the ligand **L** with a maximum absorption wavelength at 365 nm.[17, 18] After complexation, the pure enantiomers were isolated by crystallisation following the described procedure[8] and were isolated as their trichloride salts *Λ*– and *Δ*- [Eu**L**$_3$]Cl$_3$, characterised by single-crystal X-ray diffraction (see table S1). The asymmetric unit of either enantiomer comprises two [Eu**L**$_3$]$^{3+}$ cations (Figure 4), six Cl$^-$ anions, two MeOBu^t molecules and variable amount of methanol and water, partly disordered. The Eu atom coordination environment is a slightly (ca. 13°) twisted trigonal prism O6 with side-faces capped by N atoms.

The electronic absorption spectrum of the ligand **L** was recorded in acetonitrile (c = 5.5×10^{-5} M). Compared to the absorption spectra of the ligand **BPEPC**, which shows only one strong absorption band at 280 nm corresponding to its $n, \pi \rightarrow \pi^*$ electronic transitions (Figure 1), ligand **L** displays two strong and distinct absorption bands at 248 nm (ε_{248nm} = 65000 M^{-1}.cm^{-1}) and at 324 nm (ε_{324nm} = 58000 M^{-1}.cm^{-1}) corresponding to the electronic transition $n, \pi \rightarrow \pi^*$ of the benzyl groups and para-substituted pyridinyl group respectively (Figure 5). Upon addition of europium(III) salts, the first absorption band became narrower and shifted to 252 nm and a

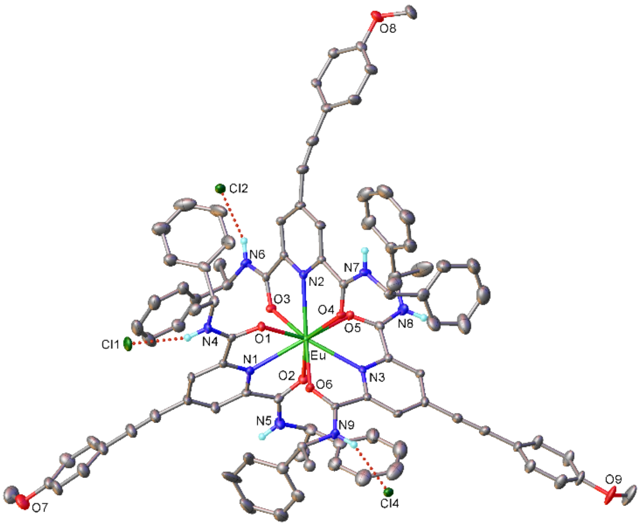

Fig. 4. X-ray structure of *Λ*-[Eu((*R,R*)-**L**)$_3$].3Cl (CCDC 1946560), omitting the disorder, solvent molecules and non-amino H atoms.

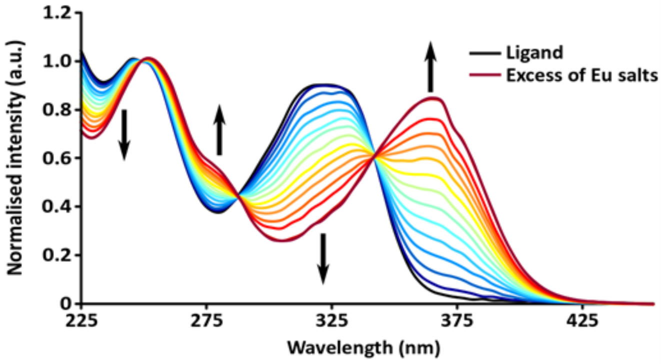

Fig. 5. Variation of the UV/Vis absorption spectra of ligand **L** (c = 5.55×10^{-5} M) in acetonitrile upon addition of a solution of Eu(OTf)$_3$ in acetonitrile (c = 5.61×10^{-4} M).

band at 280 nm appeared ($\varepsilon_{280\text{nm}}$ = 39400 M^{-1}.cm^{-1}). The band at 324 nm was significantly bathochromically shifted to 365 nm ($\varepsilon_{365\text{ nm}}$ = 55000 M^{-1}.cm^{-1}). The variation of the absorption is consistent with stepwise complex formation, confirmed by the presence of well-defined isosbestic points. The absorption intensity reached a maximum at 1:3 metal to ligand stoichiometry, consistent with formation of [Eu**L**$_3$]$^{3+}$.

The evolution of luminescence spectra and lifetime upon addition of europium salt was also monitored. The luminescence emission lifetime fitted well to a mono-exponential lifetime decay but did not show a significant change upon addition of europium(III) salts (see Figure S3), with a lifetime decrease from 1.23 ms to 1.10 ms. Emission intensity at 615 nm, given in Figure 6, showed a rapid increase of the luminescence intensity up to 0.33 equivalent of europium(III) salts added, corresponding to the formation of the 1:3 metal to ligand ratio complex [Eu**L**$_3$]$^{3+}$. From 0.3 to 1.0 equivalent, the emission intensity decreased before plateauing at 1 equivalents of added salt. Such behaviour is consistent with establishment of the dissociative equilibrium involving Eu**L**$_3$, Eu**L**$_2$ and Eu**L**$_1$**,** as reported for related tris chelate complexes.[1]

The photophysical spectra, displayed in Figure 7, were recorded using solutions of complexes prepared by dissolving the desired crystallised isomers in acetonitrile with a minimum concentration of 12×10^{-6} M corresponding to the concentration

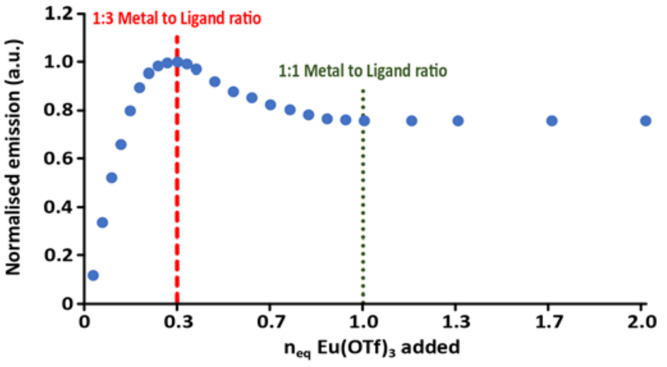

Fig. 6 Variation of the emission intensity at 615 nm of ligand **L** (c = 5.55×10^{-5} M) in acetonitrile upon addition of a solution of Eu(OTf)$_3$ in acetonitrile (c = 5.61×10^{-4} M)

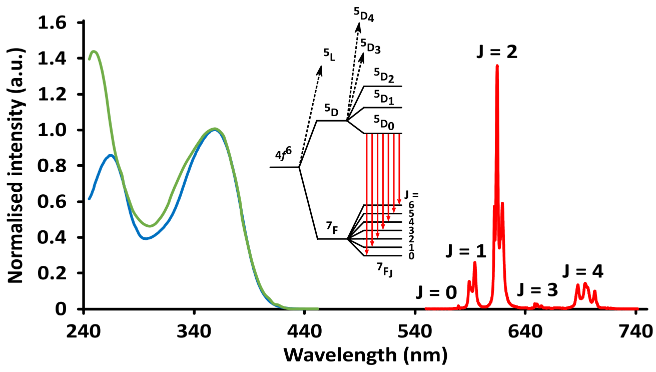

Fig. 7. Absorption (green) and excitation (blue, λ_{em} =615 nm) normalised at 365 nm and emission (red, λ_{exc} = 365 nm) spectra of [Eu**L**$_3$]$^{3+}$ complexes (c = 16×10^{-6} M) in acetonitrile.

where [EuL$_3$]$^{3+}$ is present as the major emissive species in solution. At lower concentrations, emission was observed to immediately diminish owing to ligand dissociation[19] (Figure S4).

Excitation spectra recorded from the hypersensitive europium emission line at 615 nm matched with the absorption spectra of the complexes, consistent with a good ligand to metal energy transfer,[11] i.e an effective antenna effect.[20] Each isomer has a quantum yield of 11% in acetonitrile, with a luminescence lifetime of 1.23 ms. sharp line-like europium emission spectra corresponding to the transitions $^5D_0 \rightarrow {}^7F_J$ (J = 0 to 4),[21] with a weak emission band at ca. 580 nm for the non-degenerate $\Delta J = 0$ forbidden transition. Two distinct bands ranging from 585 to 600 nm were observed for the $\Delta J=1$ transition, and an intense emission between 605 nm and 630 nm for the hypersensitive $\Delta J=2$ transition. Weak emission from 645 nm to 660 nm for $\Delta J=3$; and a broad emission of medium intensity from 680 nm to 710 nm corresponding to $\Delta J=4$.

CPL spectra of [Eu**L**$_3$]$^{3+}$, shown in Figure 2b, were measured on a custom-built spectrometer with standard scan settings described in the literature.[22] When excited at 365 nm, [Eu**L**$_3$]$^{3+}$ exhibited strong CPL features across the $^5D_0 \rightarrow {}^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$ transitions, with distinct sign reversals in the $\Delta J=2$ and 4 manifolds. Whilst similar to the CPL spectra of Eu:**BPEPC** (Figure 2a), the CPL spectra of [Eu**L**$_3$]$^{3+}$ is distinct, with a notable sign reversal in the ΔJ = 2 band. The g_{lum} values for [Eu**L**$_3$]$^{3+}$ are summarised in Table 1.

Table 1 CPL results for [Eu**L**$_3$]$^{3+}$ solutions in acetonitrile (c = 15×10^{-6} M, λ_{exc} = 365 nm). *Values from Figure S5.*

Electronic transition	Wavelength	g$_{\text{lum}}$ (± 0.01)		
		(R,R)-**L**	(S,S)-**L**	(R,R)-**L**^{a}
$^5D_0 \rightarrow {}^7F_1$	590.2 nm	-0.16	0.16	-0.16
	595.0 nm	-0.26	0.25	-0.26
$^5D_0 \rightarrow {}^7F_2$	615.7 nm	0.11	-0.10	0.11
	620.2 nm	-0.05	0.05	-0.05
$^5D_0 \rightarrow {}^7F_3$	649.5 nm	-0.25	0.23	-0.24
$^5D_0 \rightarrow {}^7F_4$	694.5 nm	0.06	-0.05	0.06
	703.5nm	-0.20	0.19	-0.20

a. *g_{lum} values measured for Λ-[Eu((R,R)-**L**)$_3$]$^{3+}$ after 4 months.*

A sample of Λ-[Eu((*R,R*)-**L**)$_3$]$^{3+}$ (c = 15×10^{-6} M) was left in for 4 months at room temperature. The g_{lum} values matched theinitial g_{lum} values, which is consistent with excellent stability in solution; ideal behaviour for a CPL reference complex.

In conclusion, we present a new chiroptical complex, bands (max g_{lum} = 0.26) which is stable in solution at room temperature, with intermittent light exposure over several months. The synthesis of [Eu**L**$_3$].3Cl is achieved in 3 steps with an overall yield of 32 %. [Eu**L**$_3$].3Cl possesses a decent quantum yield of 11 % and a long lifetime decay of 1.23 ms in acetonitrile. This complex [Eu**L**$_3$].3Cl is excited at 365 nm, and is compatible with cost-effective commercially available light sources, such as ultraviolet LEDs, and may serve as a useful reference complex to calibrate CPL spectrometers.

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