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VIP *Circularly Polarized Luminescence* *Very Important Paper*

Efficient 1400–1600 nm Circularly Polarized Luminescence from a Tuned Chiral Erbium Complex

Oliver G. Willis[+], Filippo Petri[+], Gennaro Pescitelli, Andrea Pucci, Enrico Cavalli, Alessandro Mandoli, Francesco Zinna, and Lorenzo Di Bari**

Abstract: Novel chiral Er complexes based on both enantiomers of extended ^{i}PrPyBox (2,6-Bis[4-isopropyl-4,5-dihydrooxazol-2-yl)]pyridine) show strong near-infrared circularly polarized luminescence (CPL) within the 1400 to 1600 nm spectral region under 450 nm irradiation. CPL activity in this region, despite being particularly rare, would open the way to potential applications in the domain, e.g., of fiber-optic telecommunications and free-space long-distance optical communications employing circularly polarized light. Moreover, the long wavelength excitation is advantageous for applications in the field of (circularly polarized) microscopy and bioimaging.

In the last few years, circularly polarized luminescence (CPL) has shown its potential. Numerous CPL-active materials have been prepared, giving rise to sizeable polarization.[1] This, in turn, is opening the way to various applications of CPL emitters in circularly polarized (CP) OLEDs,[2] CP microscopy,[3] security inks,[4] as well as in the field of CP electrochemiluminescence.[5,6] Thanks to their peculiar photo-physics and the possibility to attain extremely high degrees of circular polarization, chiral lanthanide complexes are at the forefront in the field of CPL.[1,3,7–14]

Despite the significant surge in CPL reports, most examples remain confined in the visible region.[1] Lanthanide complexes would allow for intense CPL in the near-infrared (NIR). Despite the potentialities of NIR-CPL in bioassays, telecommunications, etc., this field is still in its infancy and, until now, mostly limited to Yb-based systems, which emit around 1000 nm.[15–21] This may be due to the fact that instrumentation with extended NIR-CPL capability is still rare, and, at the same time, efficient NIR-CPL active compounds are yet to be developed. These two issues represent a deadlock which needs to be broken to advance the field and open new possibilities in the extended NIR region. In particular, wavelengths around 1550 nm are widely employed for fiber optical communications (the so-called C-band) and promising for free-space long-distance optical transmission.[22,23] In this field, a potential application for CPL emitters in the NIR involves active sensing systems, such as Light Detection and Ranging (LIDAR) in autonomous vehicles and active imaging.[24] Besides being orientation insensitive, circularly polarized light shows superior persistence of the degree of polarization in fog environments compared to its linear counterpart due to decreased depolarization. Thus, it allows for a greater sensing range and increased efficiency in detecting the location of a point source in scattering media, such as detecting the light from a beacon in a misty atmosphere.[24]

Within this exciting context, chiral Er complexes offer interesting features. Er displays a term-to-term transition ($^4I_{15/2}\rightarrow{}^4I_{13/2}$) falling in the 1400–1600 nm region which can be sensitized through suitable antenna ligands. Recently, we showed that when Er is encapsulated in suitable chiral ligands, it shows remarkable circular dichroism (CD) activity associated with the above-mentioned transition.[16] Subsequently, Ung et al.[25] reported the first, and so far only, example of CPL activity beyond 1200 nm by investigating a binaphthol-based heterobimetallic Er complex. These two works provide experimental evidence to Richardson's theoretical predictions concerning the selection rules needed for strong chiroptical activity associated with *f–f* transitions.[26] The Er $^4I_{15/2}\rightarrow{}^4I_{13/2}$ term-to-term transition is zero-order magnetic dipole allowed and gains electric dipole strength from the *ungerade* crystal field interaction term, and therefore intense CD and CPL are expected, provided suitable ligands are employed.[26] Despite these encouraging preliminary results and their promising implications, the field of NIR-CPL in the 1400–1600 nm region is yet to be explored.

Herein, thanks to a novel ligand design, we report a chiral Er complex, emitting in the 1400–1600 nm region and featuring highly circularly polarized emission. The strategy followed in this work was the preparation of a homoleptic complex where the ligand could act both as an efficient sensitizer for Er NIR luminescence and as a chiral inducer.

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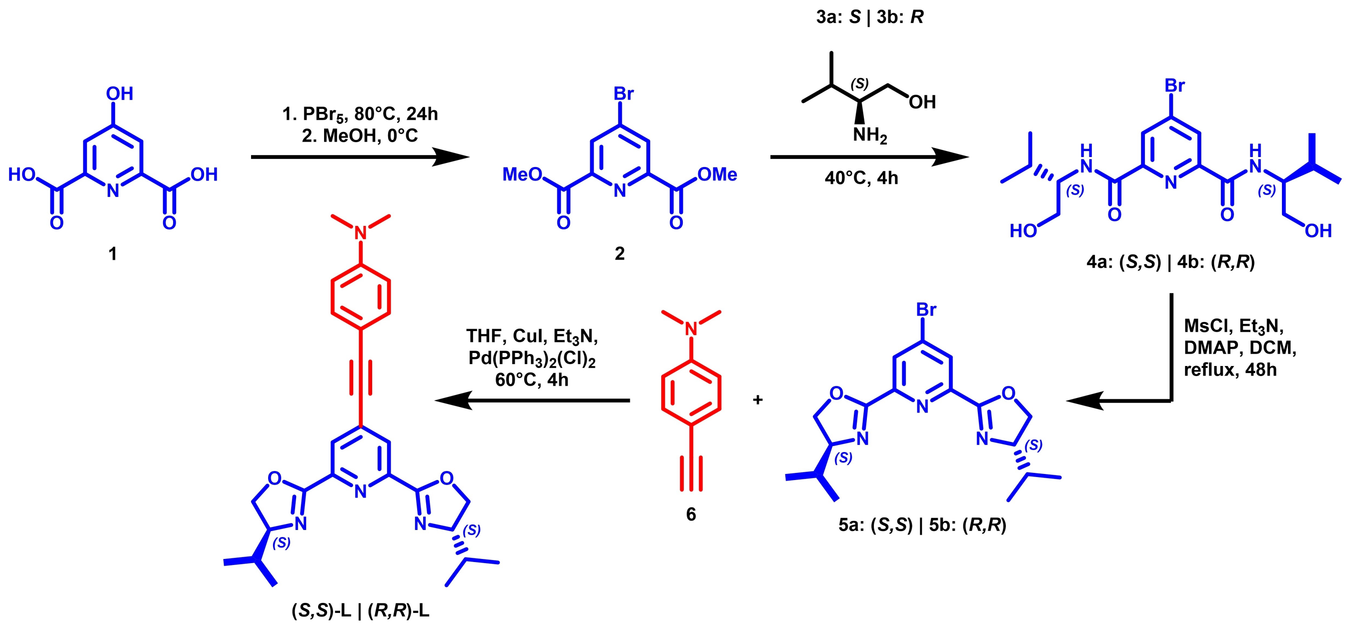

Scheme 1. Synthesis of the chiral ligands (*S*,*S*)-**L** and (*R*,*R*)-**L**.

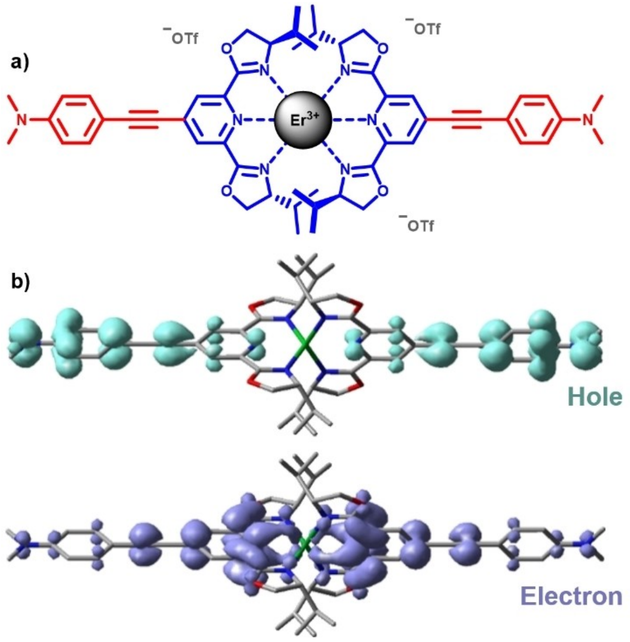

Figure 1. a) Structure of [Er(*R*,*R*)-**L**$_2$]·3OTf. b) Hole and electron distributions for the first excited state calculated for [Lu(*R*,*R*)-**L**$_2$]$^{3+}$ at CAM-B3LYP/def2-SVP/DZP[Lu]//B3LYP-D3BJ/def2-SVP/DZP[Lu] level; isovalue 0.0008.

Pyridine bis-oxazolines (PyBox) are excellent chiral inducers for lanthanides, and several heteroleptic Ln complexes, in particular Eu and Sm, bearing a PyBox and diketonate units have been reported to show significant CPL in the red region.[15,27–29] PyBox-based homoleptic complexes of Eu and Tb are also CPL-active.[30] On the other hand, regular PyBox ligands are not efficient sensitizers for red-emitting lanthanides, and even less for NIR-emitting ones, whose acceptor levels lay lower in energy. To overcome this issue, we designed and synthesized a ligand where the PyBox scaffold is conjugated through the pyridine 4-position with a *N*,*N*-dimethyl-*p*-ethynylaniline moiety (Scheme 1). A similar strategy applied to picolinic acid derivatives has been employed by Maury and other groups to sensitize Eu and Yb emission.[9,20,31] In our case, such modification allows us to increase PyBox conjugation significantly, without tampering with its ability to take a stereochemically effective arrangement around the metal centre.

The two enantiomers of the ligand 4-((2,6-bis(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridin-4-yl)ethynyl)-*N*,*N*-dimethylaniline (^{i}Pr-PyBox-NMe$_2$, **L**) were synthesized from the common reactant chelidamic acid (**1**), via dimethyl 4-bromo-pyridine-2,6-dicarboxylate (**2**). Reaction of **2** with enantiopure valinol (**3**) and subsequent cyclization afforded the 4-bromo-PyBox derivative (**5**). Finally, **L** was obtained by a Sonogashira coupling between **5** and alkyne **6** (Scheme 1). The ligand readily undergoes complexation with Er(OTf)$_3$ in acetonitrile, yielding [ErL$_2$]·3OTf (Figure 1a). The complexation is signalled by a 70 nm red shift of the first absorption band (from 380 nm to 450 nm) in the UV/Vis spectrum (Figure 2). Such red-shifted absorption indicates the presence of a low-energy charge transfer (CT) state, with the transition dipole oriented parallel to the conjugated chromophore's long axis, whose nature is clearly highlighted by transition density and hole/electron distribution plots (Figure 1b and Figures S9 and S10) obtained by time-dependent DFT calculations on the analogous closed-shell Lu compound (as diamagnetic reference). Such low-energy transition is likely responsible for the sensitization of Er NIR luminescence. This is supported by the excitation spectrum ($\lambda_{em}=1530$ nm), which closely retraces the absorption profile of the complex (Figure 2). The red-shifted absorption and CD bands for the complex (Figure S8) are

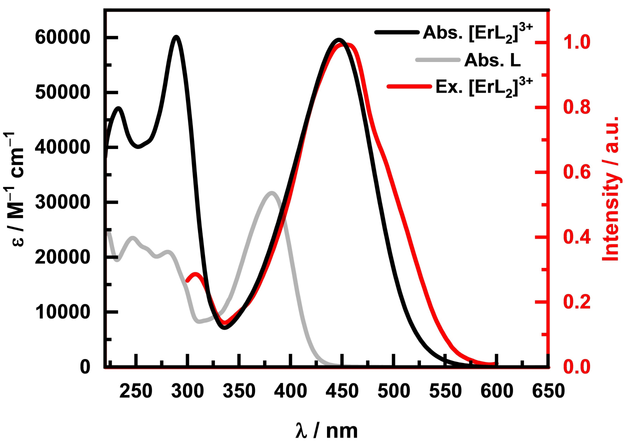

Figure 2. Absorption spectra of both the free ligand (grey) and complex (black), with the normalized complex excitation spectrum (red) superimposed ($\lambda_{em}=1530$ nm). All measurements were carried out in 0.01 mM anhydrous $CDCl_3$ solutions at room temperature.

due to the exciton coupling between the ligand CT transitions.[32] However, only the in-phase (head-to-tail) combination is UV-active and associated with a relatively weak monosignated CD band, indicating that an almost linear arrangement between the conjugated chromophores is maintained on average in solution. For a bent arrangement, both combinations would be UV-active and an exciton CD couplet would be expected. The 2:1 (**L**:Er) stoichiometry was confirmed by elemental analysis and absorption titrations (Figure S2) and it is in agreement with the literature.[30,33]

In $CDCl_3$ solution, upon ligand excitation at 450 nm, the complex gave an easily measurable emission with two maxima at 1510 and 1532 nm, associated with the $^4I_{15/2}\rightarrow{}^4I_{13/2}$ manifold (Figure 3). The overall quantum yield (Q^{L}_{Er}), measured using $Yb(TTA)_3(H_2O)_2$ (TTA = thenoyltrifluoroacetone, $Q^{L}_{Yb}=0.35\,\%$ in toluene)[34] as the reference, was determined to be around 0.03 %, in line with the values reported for other molecular Er complexes.[35,36] The emission decay is largely dominated by a time constant (τ_{obs}) of around 4 µsec (Figure S3), 3 to 4 times higher than those reported for, e.g., diketonate-based Er complexes.[37] Assuming a radiative lifetime (τ_{rad}) of 10 msec,[35,38,39] we can estimate an internal quantum yield ($Q^{Er}_{Er}=\tau_{obs}/\tau_{rad}$) of 0.04 %. These values make it possible to estimate a sensitization efficiency ($\eta=Q^{L}_{Er}/Q^{Er}_{Er}$) around 75 %. Such a high value indicates that the ligand-to-metal energy transfer process is rather efficient and confirms the suitability of our molecular design for Er sensitization. Moreover, the low excitation energy makes the luminescence of the complex easily achievable with commercially available LASER sources, like those available in scanning optical microscopes. We remark that, given the low energy emission, a significant part of the energy is non-radiatively lost through vibrational relaxation. In particular, the first overtone of CH vibrations plays a detrimental role in the quenching of Er luminescence and, in principle, extensive ligand fluorination could lead to higher internal quantum yields.

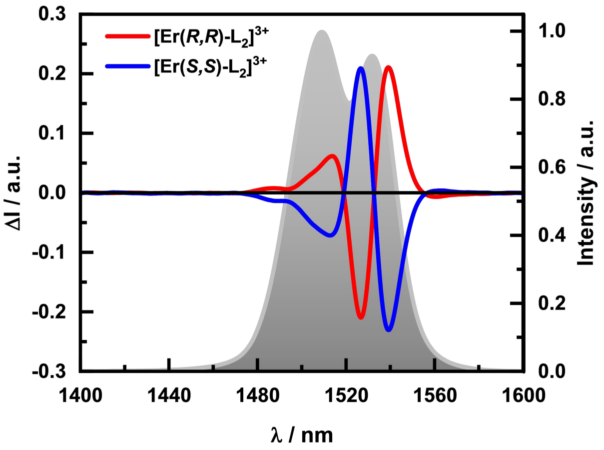

Figure 3. NIR-CPL spectra of enantiomers of [Er**L**$_2$]·3OTf (0.01 mM) with normalized average total emission traced in the background. Spectra recorded in anhydrous $CDCl_3$ at room temperature. $\lambda_{ex}=450$ nm.

Given these encouraging preliminary results, care was taken to investigate the CPL emission of the complex in the 1400–1600 nm region. To this end, a commercial standard fluorimeter equipped with a liquid nitrogen cooled InGaAs detector was employed. The circular polarization discrimination was achieved by means of a quarter wave plate (QWP) retarder followed by a linear polarizer, whose axes were reciprocally oriented at ±45°.[11,40] A 3D-printed holder for the optics was built for the purpose (Figure S1). By 90° rotation of the QWP, it was possible to recover the two circular polarization components of the NIR emission (Figure S4). In this way, a very strong CPL activity associated with the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ manifold was clearly observed under 450 nm excitation (Figure 3). At least 5 bands with alternating signs, corresponding to transitions between various Stark levels of the emitting and ground state, can be resolved. The main bands are found at 1514, 1527 and 1539 nm, with +/−/+ sign for the [Er(*R*,*R*)-$\mathbf{L}_2$]. As expected, a perfect mirror image CPL spectrum was obtained for [Er(*S*,*S*)-$\mathbf{L}_2$]. The absolute dissymmetry factors, $|g_{lum}|$, calculated for the three main bands were 0.07, 0.25 and 0.33 at 1514, 1527 and 1539 nm, respectively (Figure S7). The CPL bands centred at 1527 and 1539 nm are associated with B_{CPL} factors[1] of around 0.5 and 0.7 $M^{-1}cm^{-1}$ respectively. Such remarkably high g_{lum} values indicate an effective chiral environment provided by the modified PyBox ligands around the metal centre. Moreover, it confirms the favourable nature of the Er $^4I_{13/2}\rightarrow{}^4I_{15/2}$ term-to-term transition for intense chiroptical activity and in particular CPL. It could be stressed that these polarization features, together with the low excitation energy, makes such system comply with the needs of circularly polarized optical microscopy.[3]

To complete the set of chiroptical measurements, NIR-CD spectra of solutions of the two enantiomers were recorded. The spectra showed a strong signal corresponding to the manifold associated with the $^4I_{15/2}\rightarrow{}^4I_{13/2}$ term-to-term transition (Figure 4). The NIR-CD spectra are almost superimposable to the NIR-CPL, indicating that the same

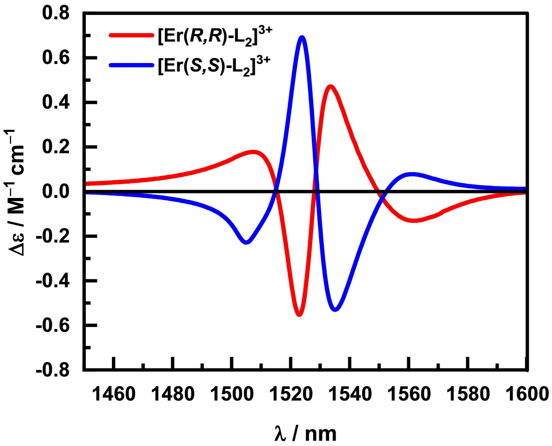

Figure 4. NIR-CD spectra of enantiomers of [Er**L**$_2$]·3OTf (4 mM). Spectra recorded in anhydrous CDCl$_3$ at room temperature.

transitions among Stark levels are observed in both absorption and emission. This behaviour contrasts with what is commonly observed for Yb compounds, where usually only the 1↔1′ transition (1 and 1′ refer to the lowest energy sublevels of ground and excited state) is in common in absorption (CD) and emission (CPL). This suggests that for [Er**L**$_2$]·3 OTf, the thermal energy available at room temperature (k_BT at 300 K is 209 cm^{-1}) is high enough to allow for a significant population of higher energy levels in both the ground and excited states. This is supported by the fact that the whole NIR-CD spectrum spans only ca. 240 cm^{-1} (the main bands, from 1506 to 1562, are spaced by 76, 47 and 115 cm^{-1}, respectively). The NIR absorption spectrum (Figure S5) showed a single main band with a molar extinction coefficient ≈1 M^{-1}cm^{-1}. This gave g_{abs} values (Figure S6) around 10^{-1}, which are comparable to the related g_{lum} values and are of the same order of magnitude as binaphthol or camphorate-based Er complexes.[16] We note that despite the overlap between NIR absorption/CD and emission/CPL, no significant self-absorption can occur (<10^{-5} absorbance units), given the low concentration of the solution used to record luminescence spectra (0.01 mM) and the very low extinction coefficient (≈1 M^{-1}cm^{-1}).

In this work, we have shown efficient CPL emission in the 1400–1600 nm window under 450 nm irradiation. This result was achieved by designing a chiral PyBox-based ligand with extended conjugation, which can efficiently sensitize the low energy NIR emission of Er^{III}, while also inducing the chiral coordination environment necessary for the emission of circularly polarized light. Moreover, we offer a simple protocol to carry out such measurements using a commercial fluorimeter and relatively inexpensive optics. These concepts could contribute to extend the scope and applications of CPL and establish new research avenues in the field of NIR-CPL, where exciting potential applications, ranging from telecommunications and LIDAR systems to bioassays and bioimaging, can be envisaged.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Circularly Polarized Luminescence · Lanthanides · Near Infrared (NIR) · PyBox

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