Supporting Information

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

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SUPPORTING INFORMATION

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Experimental Procedures

Reagents and general procedures

TLC analyses were carried out with Merck 60 F254 (0.2 mm) plates: a UV lamp (254 and 365 nm) was used for the detection of UV-detectable organic compounds. The chromatographic purifications were performed with Macherey-Nagel flash grade silica gel (230-400 mesh) or using an Automated Chromatography system Isolera One 3.0™ with Biotage Sfär D-silica and Snap KP-Si columns. The $^1$H NMR and $^{13}$C NMR spectra were recorded with a JEOL 400 MHz or with a JEOL 500 MHz. Chemical shifts are reported in ppm, with frequency referencing made by setting the signal of the residual non deuterated solvent ($^1$H) or that of the deuterated solvent ($^{13}$C) to their recommended values.[1]

Unless otherwise specified, all the chemicals were used as obtained from the supplier (Sigma Aldrich, Tokio Chemical Industries, Carlo Erba Reagent). Triethylamine (TEA) was refluxed over CaH$_2$ for two hours, under an atmospheric pressure of dry N$_2$, and then distilled in a dry Schlenk tube. MeCl$_2$ was refluxed over P$_2$O$_5$ at 80-90 mmHg for 2 hours and then distilled, at the same pressure, in Schlenk tube containing molecular sieves (MS) 4 Å; the product was stored under dry N$_2$. THF, DCM and Et$_2$O were obtained from a SPS 5/7 solvent purification system (Mbraun GmbH) and stored under an atmosphere of dry N$_2$. All the glassware used for the reactions under inert atmosphere were dried by heating under vacuum and then subjected to three vacuum-N$_2$ cycles. Unless otherwise specified, all the reactions were conducted under an atmosphere of dry N$_2$. Deuterated solvents were purchased from Deutero. The CDCl$_3$ used for chiroptical studies was filtered over basic Al$_2$O$_3$, previously dried in an oven at ca. 130 °C for 24 h and stored in the dark, over activated MS 4 Å, under an atmosphere of dry N$_2$. Elemental analysis of CHNS were performed with a Vario MICRO cube CHNOS Analyzer (Elemental GmbH).

Dimethyl 4-bromo-2,6-pyridinedicarboxylate (2)

Following a literature procedure,[2] with modifications, chelidamic acid (1, 5.00 g, 27.3 mmol, 1 equiv.) and PBrs (29.4 g, 68.3 mmol, 2.5 equiv.) were heated for 24 hours at 80°C. The mixture was then cooled to 0°C and MeOH (50 mL) was added dropwise. The solution was concentrated under reduced pressure, then dissolved in CHCl$_3$ and washed with a saturated aqueous solution of NH$_3$Cl. The organic phase was dried (Na$_2$SO$_4$) and concentrated at reduced pressure to give 2 (6.5 g, 87%) of. The NMR data were in agreement with those reported in the literature.[2] m.p. 159 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.45 (s, 2H), 4.02 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.69, 149.71, 135.58, 127.74, 61.69, 57.71, 29.11, 19.79, 19.30.

4-Bromo-N,N$^\text{2}$,N$^\text{6}$-bis((S,S)-1-hydroxy-3-methylbutan-2-yl)pyridine-2,6-dicarboxamide (4a)

Following a literature procedure,[3] with modifications, in a 50 mL Carius tube, 2 (1.3 g, 4.7 mmol, 1 equiv.) and (S,S)-valinol (970 mg, 9.4 mmol, 2 equiv.) were heated to 40°C and stirred for 4 hours. The reaction was monitored by TLC (n-hexane/ACOEt). A white amorphous solid was obtained which was triturated with DCM and filtered to give 4a as a powdery white solid (1.7 g, 87% yield). The NMR data were in agreement with those reported in the literature.[4] $\rho_\text{R} = 0.61$ (n-hexane/ACOEt 3:7); m.p. 127 °C; [$\alpha$]$^\text{D}$ = +0.60 (c = 0.4 g/100 mL in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.46 (s, 2H), 8.00 (d, J = 8.7 Hz, 2H), 3.95-3.85 (m, 6H), 2.73 (s, 2H), 2.11 – 2.01 (m, 2H), 1.03 (d, J = 6.8 Hz, 6H), 1.01 (d, J = 6.8 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 162.40, 151.16, 135.58, 127.74, 61.69, 57.71, 29.11, 19.79, 19.30.

4-Bromo-N,N$^\text{2}$,N$^\text{6}$-bis((R,R)-1-hydroxy-3-methylbutan-2-yl)pyridine-2,6-dicarboxamide (4b)

Obtained by the same method used for 4a, by reacting 2 (650 mg, 2.35 mmol, 1 equiv.) and (R,R)-valinol (485 mg, 4.7 mmol, 2 equiv.). The yield of 4b was 791 mg (80%). The NMR data were in agreement with those reported in the literature.[4] $\rho_\text{R} = 0.61$ (n-hexane/ACOEt 3:7); m.p. 128 °C; [$\alpha$]$^\text{D}$ = +0.62 (c = 0.4 g/100 mL in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.45 (s, 2H), 7.95 (d, J = 8.7 Hz, 2H), 4.00-3.80 (m, 6H), 2.66 (s, 2H), 2.10 – 2.04 (m, 2H), 1.02 (d, J = 6.8 Hz, 6H), 0.99 (d, J = 6.8 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 162.40, 151.13, 135.56, 127.73, 61.69, 57.69, 29.10, 19.79, 19.31.
Following a literature procedure, with modifications, in a two-necked round bottom flask, 4a (980 mg, 2.35 mmol), DMAP (28 mg, 0.24 mmol, 10% mol), MsCl (0.40 mL, 1.48 g/mL, 5.2 mmol, 2.2 equiv.), TEA (1.3 mL, 9.4 mmol, 4 equiv.) and DCM (12 mL) were stirred for 1 hour. The solution was then refluxed for 48 hours and monitored via TLC (n-hexane/AcOEt). The solution was washed with 10% NaOH and extracted with DCM (3 x 15 mL). The combined organic phases were dried (Na2SO4) and concentrated at reduced pressure. After column chromatography, 5a was recovered as a colorless crystalline solid (820 mg, 92% yield). The NMR data were in agreement with those reported in the literature. R = 0.34 (n-hexane/AcOEt 5:6); m.p. 132 °C; [α]D20 = -0.42 (c = 0.4 g/100 mL in CHCl3); 1H NMR (400 MHz, CDCl3): δ 8.35 (s, 2H), 4.53 (dd, J = 9.6, 8.7 Hz, 2H), 4.25 (m, 2H), 4.19 (m, 2H), 1.90 (m, 2H), 1.05 (d, J = 6.7 Hz, 6H), 0.94 (d, J = 6.7 Hz, 6H); 13C NMR (101 MHz, CDCl3): δ 161.59, 148.09, 133.80, 128.81, 73.73, 71.68, 34.38, 19.62, 18.90.

Obtained by the same method used for 5a, by reacting 4b (490 mg, 1.18 mmol), DMAP (14 mg, 0.24 mmol,10% mol), MsCl (0.20 mL, 2.6 mmol, 2.2 equiv.), TEA (0.70 mL, 4.7 mmol, 4 equiv.) and DCM (8 mL). The yield of 5b was 350 mg (78%). The NMR data were in agreement with those reported in the literature. R = 0.34 (n-hexane/AcOEt 5:6); m.p. 135 °C; 1H NMR (400 MHz, CDCl3): δ 8.37 (s, 2H), 4.56-4.48 (dd, J = 9.6, 8.7 Hz, 2H), 4.25 (m, 2H), 4.10 (m, 2H), 1.85 (m, 2H), 1.03 (d, J = 6.7 Hz, 6H), 0.92 (d, J = 6.7 Hz, 6H); 13C NMR (101 MHz, CDCl3): δ 161.61, 148.09, 133.81, 128.81, 73.75, 71.68, 34.38, 19.59, 18.90.

4-((2,6-bis((S,S)-4-isopropyl-4,5-dihydroxazol-2-yl)pyridin-4-yl)ethynyl)-N,N-dimethylaniline ((S,S)-L)

Following a literature procedure, with modifications, a 50 mL two-necked round bottom flask, equipped with a magnetic stirrer and a condenser, was charged with 5a (100 mg, 0.26 mmol), N,N-dimethyl-p-ethynylaniline (6, 45.30 mg, 0.31 mmol, 12 equiv.), Cul (1.23 mg, 6.5 μmol, 2.5% mol) and Pd(PPh3)2Cl2 (4.6 mg, 6.5 μmol, 2.5% mol). After addition of TEA (1.33 mL, 9.62 mmol, 37 equiv.) and THF (5 mL), the solution was heated to 60°C and stirred for 4 hours. The reaction was monitored by TLC (n-hexane/AcOEt) and HPLC. Conc. NH4Cl was added to the solution, and the biphasic solution was vigorously stirred for an hour. The mixture was diluted with DCM, and the organic layer was separated and washed three times with a conc. NH4Cl solution.

After back-extraction of the aqueous phases with DCM, the combined organic extracts were dried (Na2SO4) and concentrated at reduced pressure. The resulting crude material was purified by column chromatography with an Isolera system. The product was purified further by washed with Et2O to give (S,S)-L as a yellow solid (74 mg, 65% yield). R = 0.39 (n-hexane/AcOEt 1:1); m.p. 164 °C; 1H NMR (400 MHz, CDCl3): δ 8.21 (s, 2H), 7.40 (d, J = 8.9 Hz, 1H), 6.65 (d, J = 8.9 Hz, 2H), 4.52 (dd, J = 9.6, 8.2 Hz, 2H), 4.22 (t, J = 8.3 Hz, 2H), 4.14 (ddd, J = 9.7, 8.4, 6.4 Hz, 2H), 3.01 (s, 6H), 1.87 (dq, J = 13.4, 6.7 Hz, 2H), 1.05 (d, J = 6.7 Hz, 6H), 0.94 (d, J = 6.7 Hz, 6H); 13C NMR (126 MHz, CDCl3): δ 162.23, 150.92, 146.96, 134.23, 133.53, 127.01, 111.78, 108.16, 98.23, 84.84, 72.98, 71.08, 40.21, 32.93, 19.17, 18.39; elemental analysis calcd (%) for C29H28N4O4: C 71.50, H 7.33, N 12.35; found: C 71.84, H 7.14, N 12.27.

4-((2,6-bis((R,R)-4-isopropyl-4,5-dihydroxazol-2-yl)pyridin-4-yl)ethynyl)-N,N-dimethylaniline ((R,R)-L)

Obtained by the same method used for (S,S)-L, by reacting 5b (100 mg, 0.26 mmol), N,N-dimethyl-p-ethynylaniline (6, 45.30 mg, 0.31 mmol, 12 equiv.), Cul (1.23 mg, 6.5 μmol, 2.5% mol), Pd(PPh3)2Cl2 (4.6 mg, 6.5 μmol, 2.5% mol), TEA (1.33 mL, 9.62 mmol, 37 equiv.) and THF (5 mL). After purification the yield of (R,R)-L was 66 mg (58%). R = 0.39 (n-hexane/AcOEt 1:1); m.p. 166 °C; 1H NMR (400 MHz, CDCl3): δ 8.18 (s, 2H), 7.41 – 7.39 (m, 2H), 6.66 – 6.64 (m, 2H), 4.52 (dd, J = 9.6, 8.2 Hz, 2H), 4.22 – 4.10 (m, 4H), 3.01 (s, 6H), 1.87 (h, J = 6.7 Hz, 2H), 1.05 (d, J = 6.7 Hz, 6H), 0.94 (d, J = 6.7 Hz, 6H); 13C NMR (126 MHz, CDCl3): δ 162.22, 150.87, 146.92, 134.17, 133.49, 127.02, 111.75, 108.15,

(4S,4'S)-2,2'-(4-bromopyridine-2,6-diy)bis(4-isopropyl-4,5-dihydroxazol) (5a)

(Supporting Information)
Supporting Information

98.22, 84.81, 72.96, 71.04, 40.18, 32.94, 19.14, 18.37; elemental analysis calcd (%) for C\textsubscript{27}H\textsubscript{4}O\textsubscript{13}S\textsubscript{2}: C 71.55, H 7.36, N 12.44.

General procedure: [\textit{Er}L\textsubscript{3}]\textsuperscript{3+}OTf

In a two-necked 10 mL round-bottom flask equipped with a magnetic stirrer, the appropriate ligand ((S,S)-L or (R,R)-L, 1 equiv.) and the lanthanide salt (0.5 equiv.) in ACN were stirred at room temperature for 24 hours. The reaction progress was followed by UV-Vis spectrophotometry. After complete complexation, the solution was concentrated at reduced pressure, leaving the desired product.

[\textit{Er}(S,S)-L\textsubscript{3}]\textsuperscript{3+}OTf

In accordance with the general method, reaction of (S,S)-L (30 mg, 0.07 mmol) and Er(OTf)\textsubscript{3} (20.7 mg, 0.03 mmol) in ACN (1.5 mL) yielded the complex as a ruby red solid. Complete conversion, 50 mg). Elemental analysis calcd (%) for C\textsubscript{27}H\textsubscript{6}O\textsubscript{13}S\textsubscript{2}: C 44.99, H 4.37, Er 10.99, F 11.24, N 7.36, O 14.72, S 6.32; found: C 45.38, H 4.53, N 7.12, S 5.98.

[\textit{Er}(R,R)-L\textsubscript{3}]\textsuperscript{3+}OTf

In accordance with the general method, reaction of (R,R)-L (30 mg, 0.07 mmol) and Er(OTf)\textsubscript{3} (20.7 mg, 0.03 mmol) in ACN (1.5 mL) yielded the complex as a ruby red solid. Complete conversion, 50 mg). Elemental analysis calcd (%) for C\textsubscript{27}H\textsubscript{6}O\textsubscript{13}S\textsubscript{2}: C 44.99, H 4.37, Er 10.99, F 11.24, N 7.36, O 14.72, S 6.32; found: C 45.53, H 4.29, N 7.45, S 6.40.

Computational details

Conformational searches were run with Spartan'20 (v. 20.1.3, Wavefunction, Inc., Irvine, CA, 2022). A geometry of Lu(R,R)-L\textsubscript{2} with +3 charge was built in Spartan'20 and optimized at PM6 level. Then, a conformational search was run at the same level by varying the relevant C(sp\textsuperscript{3})-C(sp\textsuperscript{3}) bonds. All DFT calculations were run with the Gaussian'16 package.\textsuperscript{[6]} First, the set of low-energy PM6 conformers was optimized with B3LYP functional, def2-SVP basis set for all atoms except Lu, SDD basis set and the Stuttgart/Dresden ECP MWB60 for Lu.\textsuperscript{[7]} The D\textsubscript{2h}-symmetric structure from this set was then optimized using B3LYP functional with D3BJ dispersion correction,\textsuperscript{[8]} the def2-SVP basis sets for all atoms except Lu, and the all-electron DZP basis set for Lu.\textsuperscript{[9]} Time dependent DFT calculations were run using several functionals (B3LYP, CAM-B3LYP, BH&HLYP, PBE0), with the same basis set mentioned above, either in vacuo or employing the polarizable continuum model for chloroform in its integral equation formalism,\textsuperscript{[10]} and including up to 36 excited states (root). Hole and electron distributions and transition densities were generated using Multwf v. 3.8,\textsuperscript{[11]} and plotted using Gaussview.

Instrumentation

NIR-CD/NIR-Abs measurements

NIR-CD measurements were performed using a Jasco J200 spectropolarimeter provided with an ADC system. All complexes were measured in CDCl\textsubscript{3} with concentrations ca. 6 mM in 1 cm optical glass cells with parameters as follows: Scan speed 50 nm/min, slit width 2-4 nm, integration time 4 sec, accumulations 16. The spectra were baseline corrected by subtraction of the solvent spectrum. Solutions of ca. 4 mM were used to measure the corresponding NIR absorption spectra using a Cary 5000 UV-Vis-NIR spectrophotometer.

UV-Vis/CD and Polarimetry measurements

UV-Vis spectra were recorded using a Jasco-V650 spectrophotometer in the spectral range of 220 to 600 nm. All samples were measured in 1 mM CDCl\textsubscript{3} solutions at room temperature. The same solutions were used to record CD spectra using a J1500 spectropolarimeter in 0.2 cm optical glass cells and averaging 16 accumulations. The optical rotation was measured with a Jasco DIP-360 digital polarimeter in a 10 cm polarimetric cell, using the Sodium lamp's D line.

Lifetime measurements

Lifetime measurements were carried out using an Edinburgh FLS1000 spectrophotometer equipped with a pulsed Xe lamp, a double excitation monochromator, a single emission monochromator and a N\textsubscript{2} cooled NIR extended photomultiplier. All the spectra were measured at room temperature in 0.1 mM CDCl\textsubscript{3} solutions and corrected for the spectral responsiveness of the setup. The decay time...
was evaluated after deconvolution of the experimental decay profile taking into account the Instrumental Response Function (IRF), using the routine implemented in the software of the spectrofluorometer.

Quantum yield measurements

Luminescence quantum yields (or External Quantum Efficiency, EQE, $Q_{\text{L}}^E$) were measured with a Horiba Jobin–Yvon Fluorolog®-3 spectrofluorometer equipped with a 450 W Xenon arc lamp, double-grating excitation and single-grating emission monochromators and with a liquid nitrogen-cooled InGaAs detector. The EQE and Internal Quantum Efficiency (IQE, $Q_E^r$) were calculated using Eqs. 3 and 4 respectively. The fluorescence quantum yields were measured in CDCl$_3$ relative to Yb(TTA)$_3$(H$_2$O)$_3$ ($Q_{\text{L}}^E = 0.35\%$ in toluene).\[6\]

$$Q_{\text{L}}^E = Q_r^E \cdot \frac{A_r(\lambda)}{D_r \cdot n_r^2} \cdot \frac{D_x \cdot n_x^2}{A_x(\lambda)} \quad (3)$$

$$Q_E^r = \eta_{\text{sens}} \times Q_E^r = \eta_{\text{sens}} \times \frac{\tau_{\text{obs}}}{\tau_{\text{rad}}} \quad (4)$$

In the previous two equations, A is the absorbance at the excitation wavelength ($\lambda = 380$ nm), n is the refractive index and D the luminescence integrated intensity. The indices r and x stand for reference and sample respectively. The observed lifetime is $\tau_{\text{obs}}$ and $\tau_{\text{rad}}$ is the radiative lifetime of the Ln(III). Finally, the efficiency of the ligand-to-erbium energy transfer process is given as $\eta_{\text{sens}}$.

NIR-CPL

Emission spectra were recorded using a Horiba Jobin–Yvon Fluorolog®-3 spectrofluorometer equipped with a 450 W Xenon arc lamp, double-grating excitation, and single-grating emission monochromators and with a liquid nitrogen-cooled InGaAs detector. Discrimination of left- and right-CP light, was achieved using a quarter waveplate and linear polarizer, suitable within the 1400 to 1600 nm spectral region, from Edmund Optics. The optics were placed into custom 3D-printed holders (Fig. S1b, 52 × 52 mm), which were placed between the sample and detector. Subsequent manual rotations of the QWP by 90° allowed for the measurements of the two states of polarization (Fig. S4, I$_L$ and I$_R$). The CPL (I$_L$ – I$_R$) and total emission (average of I$_L$ and I$_R$) were then extracted. Each fluorescence measurement utilized a 0.5 sec integration time over 201 points meaning each scan lasted ca. 1 min 40 sec. Two total repetitions of each of the four positions (Fig. S1a) were performed, meaning a spectrum of either I$_L$ or I$_R$ were an average of four total fluorescence measurements each. The overall measurement took around 14/15 min.

Figure S1. a) Each of the four QWP orientations in which each of the polarization states were measured. b) The 3D-printed holder for the QWP and LP, showing both the front view, each of the individual layers and finally the combined set-up.
Results and Discussion

Additional spectra

![UV/Vis absorption spectra](image1)

Figure S2. Left: UV/Vis absorption spectra of ligand L (2.20 × 10^{-4} M) in CDCl3 upon addition of Eu(OTf)3. Right: plot of the absorption read at 460 nm against Er equivalents added.

![Decay curve](image2)

Figure S3. Decay curve of the 4I_{13/2} excited state of Er^{3+} along with the reconvolution fitting. Measurements carried out in 0.1 mM CDCl3 solutions at room temperature.
Figure S4. Total luminescence intensity of the two circularly polarized component, where $I_L$ and $I_R$ are the left- and right-components respectively. Left: The emission spectra of each polarization for $[\text{Er}(R,R)-L_2]^{3+}$. Right: The emission spectra of each polarization for $[\text{Er}(S,S)-L_2]^{3+}$.

Figure S5. Raw NIR-CD spectra of the two enantiomers (solid lines) with the fittings shown (dashed lines).

Figure S6. NIR absorption spectrum of $[\text{ErL}_2]^{3+}$ measured in CDCl$_3$ (4 mM) at room temperature. The shaded area covers a strong CDCl$_3$ absorption.
Figure S7. Left: The $g_{\text{lum}}$-vs-wavelength plot for each enantiomer of [ErL$_2$]$^{3+}$. Right: The $g_{\text{abs}}$-vs-wavelength plot for each enantiomer of [ErL$_2$]$^{3+}$. Notice that $g_{\text{abs}}$ could not be calculated in the 1515-1535 nm interval, due to the strong CDCl$_3$ absorption.

Figure S8. Electronic circular dichroism (ECD) spectra of the two enantiomers of both the free ligand (dashed lines) and the complex (solid lines). All samples were measured in 1 mM CDCl$_3$ solutions at room temperature.
Computational results

Figure S9. Frontier Kohn-Sham orbitals calculated for [Lu(R,R-L)]^{3+} at CAM-B3LYP/def2-SVP/DZP[Lu]/B3LYP-D3BJ/def2-SVP/DZP[Lu] level; isovalue 0.02.

Figure S10. Transition densities of the first two excited states calculated for [Lu(R,R-L)]^{3+} at CAM-B3LYP/def2-SVP/DZP[Lu]/B3LYP-D3BJ/def2-SVP/DZP[Lu] level; isovalue 0.0008. The orbital contributions (see Figure S9) are: state #1 (top), 2.16 eV, 271 → 274, coefficient –0.45, 272 → 273, coefficient 0.51; state #2 (bottom), 2.16 eV, 271 → 273, coefficient 0.51, 272 → 274, coefficient –0.46. The two transitions arise from the in-phase (head-to-tail) and out-of-phase (head-to-head) combinations of π-π* transitions localized on the conjugated ligands, respectively.
Figure S11. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of (S,S)-L.

Figure S12. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of (S,S)-L.

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### Author Contributions

O.G.W. carried out spectroscopic measurements and data analysis; F.P. carried out the synthesis of ligand and complex; G.P. carried out calculations; A.P. gave instrumentation support; E.C. carried out lifetime measurements; A.M. supervised the synthesis; F.Z. and L.D.B. conceived the idea, supervised the whole work, and discussed the data regularly; O.G.W., F.Z. and G.P. wrote the manuscript. All authors read and approved the final manuscript.