Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Impact of the experimental bandwidth on Circularly Polarized Luminescence measurements of lanthanide complexes: the case of erbium(III).

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Contents

S 1. MATERIALS AND GENERAL CONSIDERATIONS

Solvents were purchased from Fisher Scientific, VWR Chemicals or Carlo Erba Reagents and used without further purification. Acetonitrile, tetrahydrofurane as well as the methanol/dichloromethane mixture used for the complex synthesis were stored over 3 Å molecular sieve. $CDCl_3$ and methanol-d_4 was supplied by Eurisotop. **Starting materials** were purchased from Sigma-Aldrich, TCI, Alfa Aesar or Acros Organics. **Centrifugation** was carried out on a Sigma 2-16P centrifuge (9000 rpm, 10 minutes).

S 2. ANALYTICAL METHODS AND TECHNIQUES

^{1}H, ^{13}C and the corresponding two-dimensional **nuclear magnetic resonance (NMR)** spectra were recorded at room temperature on a Bruker Avance III 300 or on a Bruker Ascend 400 spectrometer. The chemical shifts in ppm were referenced to the solvent residual proton signals ($CDCl_3$: 7.26 ppm; CD_3OD: 3.31 ppm).

Acquisition of **low-resolution mass spectra** was performed on a Agilent LCMS 6120, composed of a quadrupole multimode source (ESI + APCI) connected to a HPLC system with a UV/Vis detector, operating by an array of diodes. **High resolution mass spectra** were recorded at the Centre Commun de Spectrométrie de Masse (Villeurbanne, France). **Fourier-transform Infrared (FTIR) spectroscopy** was performed using a Perkin Elmer Spectrum 65 device, equipped with an Attenuated Total Reflectance (ATR) module.

Single crystal X-ray diffraction. Single crystals of [Er(*R,R*-L)$_3$](OTf)$_3$·4(MeOH) were obtained by overlayering of a concentrated complex solution in MeOH by methyl *tert*-butyl ether. Single crystal of [Er(*R,R*-L)$_3$](OTf)$_3$·4(MeOH) was mounted on a D8 VENTURE Bruker-AXS diffractometer for data collection (MoK_α radiation source, λ = 0.71073 Å), from the Centre de Diffractométrie X (CDIFX), Université de Rennes, France. Structure was solved with a direct method using the SHELXT program (and refined with a full matrix least-squares method on F^2 using the SHELXL-14/7 program.[1,2] SQUEEZE procedure of PLATON[3] was performed for structures containing large solvent accessible voids in which residual peak of diffraction were observed. Crystallographic data are summarized in Table S1. Complete crystal structure results as a CIF file (CCDC 2280053) including bond lengths, angles, and atomic coordinates is deposited as Supporting Information.

Absorption spectra were recorded on a JASCO V-650 spectrophotometer using complex solutions ($c \approx 10^{-5}$ to 10^{-6} M for absorption in the UV/Vis region, optical density < 1) in spectroscopic grade methanol or ethanol using 10x10 mm quartz glass cuvettes. Absorption in the NIR wavelength region was measured using solutions of higher concentrations ($c \approx 10^{-4}$).

Measurements of **circular dichroism (CD)** in the UV/Vis region were performed on a JASCO J-710 spectropolarimeter on complex solutions with concentrations around 10^{-5} M.

Luminescence spectra were recorded on a Horiba Jobin Yvon Fluorolog spectrofluorimeter, equipped with a three slit double grating excitation and emission monochromator, the former with a dispersion of

2100 grooves/mm. For the measurement of Er emission in the NIR wavelength region, an emission grating of 150 grooves/mm with a blaze wavelength of 1200 nm was chosen. The steady-state luminescence was excited by unpolarized light from a 450 W xenon continuous wave (CW) lamp and detected at an angle of 90 ° using a liquid nitrogen cooled Symphony II FIOE scientific CCD camera. Spectra were reference corrected for the emission spectral response (detector and grating). Luminescence measurements were conducted on EPR glass tubes containing the complex either as solid powder or dissolved in a mixture of ethanol/methanol in a 4/1 ratio. For measurements at 77 K the sample was cooled by immersion of the EPR tube in liquid nitrogen using a transparent Dewar-type glass tube.

For **luminescence lifetimes**, the sample in an EPR quartz tube was excited using a pulsed Nd:YAG laser (SpectraPhysics), operating at 10 Hz. Light emitted at right angles to the excitation beam was focused onto the slits of a monochromator (PTI120), which was used to select the appropriate wavelength. The growth and decay of the luminescence at selected wavelengths was detected using a Ge photodiode (Edinburgh Instruments, EI-P) and recorded using a digital oscilloscope (Tektronix TDS320) before being transferred for analysis. Luminescence lifetimes were obtained by iterative reconvolution of the detector response (obtained by using a scatterer) with exponential components for growth and decay of the metal-centred luminescence.

NIR Circularly polarized luminescence (CPL) spectra were recorded on a homemade apparatus displayed in Figure S1.[4] Solutions of the complex in MeOD-d_4 in quartz cuvette are excited by UV light from a diode (wavelength at 365 nm, power 2 mW, from Roithner), placed around 90 degrees of the collection angle. The luminescent light is collected with a lens and directs to the Photo-Elastic Modulator (PEM) and the following Glan polarizer (neutral axes at 45 degrees of that one of the PEM). A second lens focuses the light on the entrance slit of a monochromator (Cornerstone CS260 from Newport). A photomultiplier tube (H10330B-75 from Hamamatsu) is used as detector and the electric signal is measured by a Keythley multimeter for the DC signal UDC and a Standford SR830 LockIn amplifier for the 1f modulated signal U1F. The fluorescence signal is given by the DC part of the signal while the CPL is the modulated U1F signal. Because the usual value of phase retardance of 2.405 radians is in our case out of range, we reduce it to 1.287 radians. The second harmonic was checked to be close to zero to avoid any correction in the UDC signal through the J0 correction (where J0 is the first kind Bessel function of zero order) and the U1F is corrected by sqrt(2) (as we measure the effective voltage) and 2 times J1(1.287) (where J1 is the first kind Bessel function of first order, for a PEM phase retardation amplitude of 1.287). All the spectra have been obtained with steps of 1 nm and an integration time of 7 s/step.

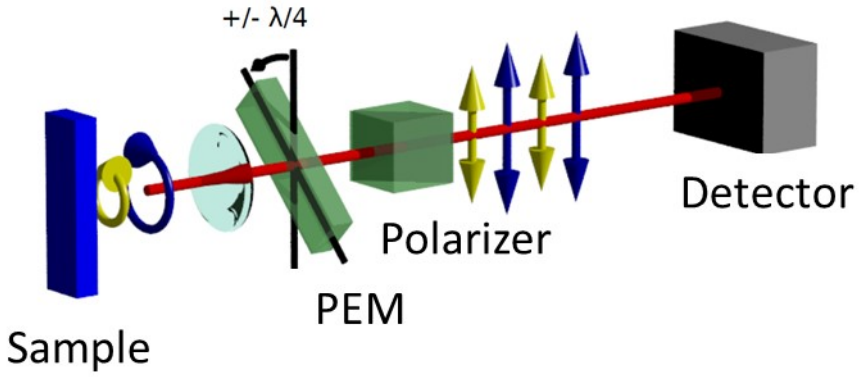
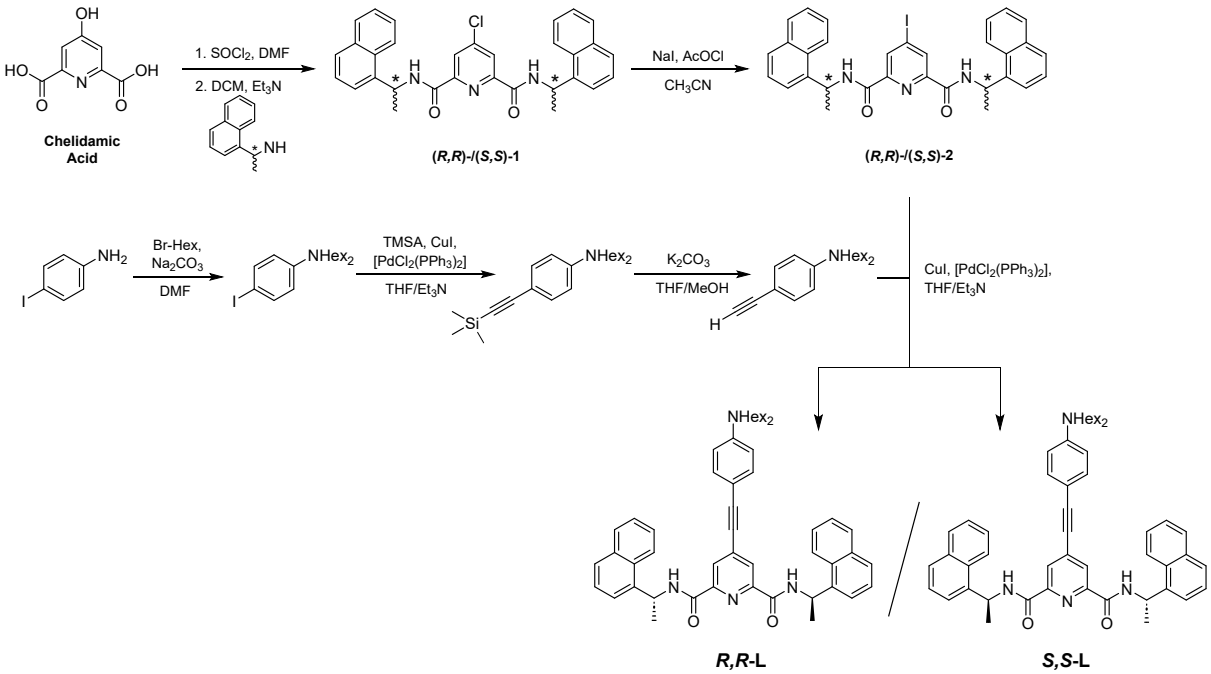


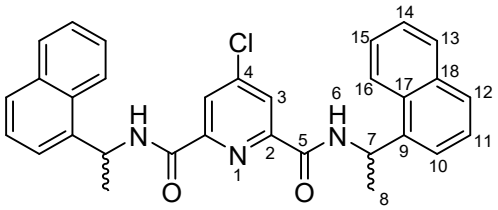
Figure S1. *Schematic representation of the NIR-CPL (PEM + Polarize + Detector) setup (λ/4: quarter waveplate).*

S 3. LIGAND SYNTHESES



Scheme S1: *Synthetic pathway towards the chiral ligands R,R-L and S,S-L bearing conjugated antenna functionalities, starting from chelidamic acid.*

SYNTHESIS OF (*R,R*)-1/(*S,S*)-1[5]



$C_{31}H_{26}ClN_3O_2$
508.02 g/mol

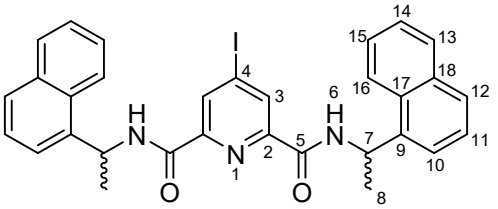
Under argon atmosphere, chelidamic acid (500 mg, 2.49 mmol, 1 equiv.) was suspended in thionyl chloride (50 mL) and the suspension was cooled to 0 °C using an ice/water bath. Anhydrous DMF (0.3 mL) was added and the mixture was at 80°C overnight. The solvent was co-evaporated with two portions of toluene (2 x 10 mL) and the remaining solid was dissolved in dichloromethane (10 mL) under argon atmosphere. The solution was cooled to 0 °C and the chiral enantiopure (*R*)-(+)- or (*S*)-(-)- 1-(1-naphthyl)ethylamine (1.06 g, 6.22 mmol, 2.5 equiv.), dissolved in Et_3N (1 mL, 7.97 mmol, 3.2 equiv.), was slowly added. The orange mixture was stirred at room temperature overnight. A 1 M aqueous solution of K_2CO_3 was added until pH = 10 and the organic phase was washed with water (twice) and with brine, dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (Al_2O_3 activity III, dichloromethane/ethyl acetate 98:2) to yield both the enantiomer products as white solid (0.88 g, 1.74 mmol, 70%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ [ppm] = 8.29 (s, 2H, H-3), 8.12-8.07 (m, 2H, H-16), 7.89-7.84 (m, 2H, H-13), 7.82-7.77 (m, 2H, H-12), 7.74 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H-6), 7.53-7.47 (m, 4H, H-14, H-15), 7.41-7.38 (m, 4H, H-10, H-11), 6.03-5.93 (m, 2H, H-7), 1.61 (d, $^3J_{HH}$ = 6.8 Hz, 6H, H-8).

^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ [ppm] = 161.52 (C-5), 150.19 (C-2), 147.84 (C-4), 137.95 (C-9), 134.09 (C-18), 131.06 (C-17), 129.10 (C-13), 128.70 (C-12), 126.85 (C-15), 126.13 (C-14), 125.68 (C-3), 125.35 (C-11), 123.31 (C-16), 122.86 (C-10), 45.52 (C-7), 20.96 (C-8).

HRMS (ESI): found 508.1783 m/z $[M+H]^+$, calculated for $C_{31}H_{26}ClN_3O_2$ 508.1786 m/z.

SYNTHESIS OF (*R,R*)-2/(*S,S*)-2[5]



$C_{31}H_{26}IN_3O_2$
599.47 g/mol

A suspension of **(*R,R*)-1** or **(*S,S*)-1** (400 mg, 0.77 mmol, 1 equiv.) and sodium iodide (1.20 g, 7.68 mmol, 10 equiv.) in acetonitrile (50 mL) was sonicated for 1 h in an ultrasound bath. Acetyl chloride (450 µL, 6.3 mmol, 8 equiv.) was added dropwise and the mixture was sonicated for further 2 h. Dichloromethane (50 mL) was added to the suspension and the organic phase was washed with an aqueous saturated

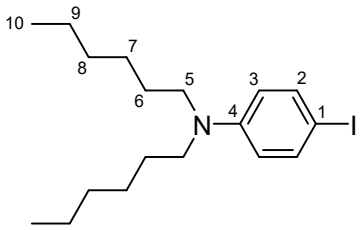
Na_2CO_3 solution, a 0.1 M aqueous solution of sodium thiosulfate, water (until pH = 7) and brine. The solution was dried with anhydrous Na_2SO_4 and the solvent was evaporated. After recrystallization of the crude product from hot methanol, the both product enantiomers **(*R,R*)-2** and **(*S,S*)-2** were obtained as white solids in yields of 70-75%.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ [ppm] = 8.70 (s, 2H, H-3), 8.14-8.08 (m, 2H, H-16), 7.92-7.86 (m, 2H, H-13), 7.83 (dd, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 2.4 Hz, 2H, H-12), 7.63 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-6), 7.54-7.48 (m, 4H, H-14, H-15), 7.45-7.39 (m, 4H, H-10, H-11), 6.05-5.95 (m, 2H, H-7), 1.64 (d, $^3J_{HH}$ = 6.7 Hz, 6H, H-8).

^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ [ppm] = 161.32 (C-5), 148.85 (C-2), 137.96 (C-9), 134.69 (C-3), 134.12 (C-18), 131.10 (C-17), 129.11 (C-13), 128.75 (C-12), 126.87 (C-15), 126.16 (C-14), 125.41 (C-11), 123.35 (C-16), 122.91 (C-10), 107.43 (C-4), 45.50 (C-7), 20.97 (C-8).

HMRS (ESI): found 600.1143 m/z $[M+H]^+$, calculated for $C_{31}H_{26}IN_3O_2$ 600.1142 m/z.

SYNTHESIS OF 4-IODO-*N,N*-DIHEXYLANILINE[6]

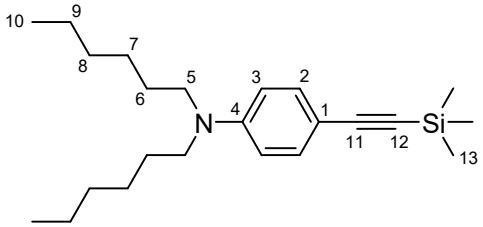


$C_{18}H_{30}IN$
387.35 g/mol

4-Iodoaniline (1.00 g, 4.57 mmol, 1 equiv.) and 1-bromohexane (2.2 mL, 15.54 mmol, 3.4 equiv.) were dissolved in DMF (25 mL) and sodium iodide (2.74 g, 18.28 mmol, 4 equiv.) and sodium carbonate (0.87 g, 8.23 mmol, 1.8 equiv.) were added. The mixture was stirred at 120 °C for 24 h. Deionized water was added and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography (SiO_2, pentane/DCM: 8/1) to yield 4-iodo-*N,N*-dihexylaniline as colorless oil (0.87 g, 2.23 mmol, 49%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ [ppm] = 7.43 (d, $^3J_{HH}$ = 9.1 Hz, 2H, H-2), 6.43 (d, $^3J_{HH}$ = 9.1 Hz, 2H, H-3), 3.24 (t, $^3J_{HH}$ = 7.6 Hz, 4H, H-5), 1.63-1.52 (m, 4H, H-6), 1.39-1.29 (m, 12H, H-7, H-8, H-9), 0.93 (t, $^3J_{HH}$ = 6.7 Hz, 6H, H-10).

SYNTHESIS OF 4-(TRIMETHYLSILYLETHYNYL)-*N,N*-DIHEXYLANILINE

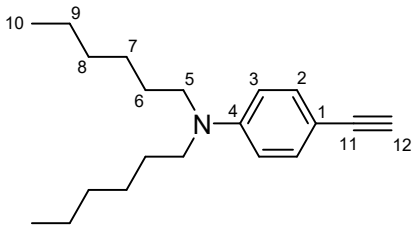


$C_{23}H_{39}NSi$
357.66 g/mol

Under argon atmosphere, 4-iodo-*N,N*-dihexylaniline (1.80 g, 4.65 mmol, 1 equiv.) was dissolved in a mixture of tetrahydrofuran (20 mL) and Et_3N (15 mL). The solution was degassed by sparging with argon for 30 min, followed by the addition of copper iodide (0.17 g, 0.93 mmol, 0.2 equiv.), [$PdCl_2(PPh_3)_2$] (0.32 g, 0.46 mmol, 0.1 equiv.) and ethynyltrimethylsilane (1.3 mL, 9.30 mmol, 2 equiv.). The mixture was stirred overnight at room temperature. Dichloromethane and deionized water were added, the aqueous phase was extracted with dichloromethane and the combined organic layers were washed with water and brine and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography (SiO_2, pentane/DCM: 8/1) to yield 4-(trimethylsilylethynyl)-*N,N*-dihexylaniline as yellow oil (1.37 g, 3.82 mmol, 82%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ [ppm] = 7.29 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H-2), 6.50 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H-3), 3.25 (t, $^3J_{HH}$ = 7.6 Hz, 4H, H-5), 1.60-1.50 (m, 4H, H-6), 1.36-1.26 (m, 12H, H-7, H-8, H-9), 0.90 (t, $^3J_{HH}$ = 6.7 Hz, 6H, H-10), 0.23 (s, 12H, H-13).

SYNTHESIS OF 4-ETHYNYL-*N,N*-DIHEXYLANILINE

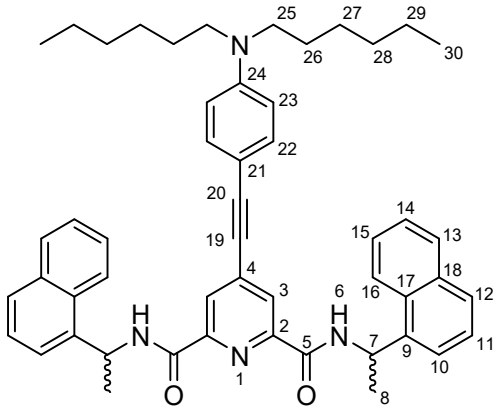


$C_{20}H_{31}N$
285.48 g/mol

4-(Trimethylsilylethynyl)-*N,N*-dihexylaniline (0.50 g, 1.40 mmol, 1 equiv.) was dissolved in a mixture of THF (10 mL) and methanol (10 mL). K_2CO_3 (0.38 g, 2.80 mmol, 2 equiv.) was added and the suspension was stirred for 1 h at room temperature, before it was diluted with dichloromethane, filtered and concentrated under reduced pressure. The remaining solid was purified by filtration over a silica plug with dichloromethane as eluent. After solvent removal, 4-ethynyl-*N,N*-dihexylaniline was obtained as a yellow oil in quantitative yields.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ [ppm] = 7.32 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H-2) 6.53 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H-3), 3.26 (t, $^3J_{HH}$ = 7.8 Hz, 4H, H-5), 2.96 (s, 1H, H-12), 1.62-1.52 (m, 4H, H-6), 1.36-1.28 (m, 12H, H-7, H-8, H-9), 0.91 (t, $^3J_{HH}$ = 6.5 Hz, 6H, H-10).

SYNTHESIS OF LIGANDS *R,R*-L and *S,S*-L



$C_{51}H_{56}N_4O_2$
757.04 g/mol

Under argon atmosphere, a solution of **(*R,R*)-2** or **(*S,S*)-2** (200 mg, 333 mmol, 1 equiv.) in dry tetrahydrofuran was degassed by sparging with argon for 30 min. Copper iodide (13 mg, 66 µmol, 0.2 equiv.), $[PdCl_2(PPh_3)_2]$ (23 mg, 33 µmol, 0.1 equiv.) and a solution of 4-ethynyl-*N,N*-dihexylaniline (143 mg, 500 µmol, 1.5 equiv.) in Et_3N (8 mL) was added. The mixture was stirred for 24 h at room temperature, before it was diluted with dichloromethane. The organic solution was washed with saturated, aqueous NH_4Cl solution, water and brine, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, DCM) to yield the desired ligands as orange solid.

***R,R*-L: 74% yield**

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] = 8.32 (s, 2H, H-3), 8.17-8.15 (m, 2H, H-16), 7.91-7.88 (m, 2H, H-13), 7.83 (dd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 2.7 Hz, 2H, H-12), 7.73 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-6), 7.53-7.50 (m, 4H, H-14, H-15), 7.45-7.42 (m, 4H, H-10, H-11), 7.39 (d, $^3J_{HH}$ = 8.6 Hz, 2H, H-22), 6.59 (d, $^3J_{HH}$ = 8.8 Hz, 2H, 23), 6.04 (quint, $^3J_{HH}$ = 7.5 Hz, 2H, H-7), 3.29 (t, $^3J_{HH}$ = 7.7 Hz, 4H, H-25), 1.65 (d, $^3J_{HH}$ = 6.8 Hz, 6H, H-8), 1.63-1.56 (m, 4H, H-26), 1.36-1.30 (m, 12H, H-27, H-28, H-29), 0.93-0.89 (m, 6H, H-30).

^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C): δ [ppm] = 162. 45 (C-5), 149.09 (C-24), 148.81 (C-2), 138.34 (C-9), 136.24 (C-4), 134.16 (C-18), 133.95 (C-22), 131.15 (C-17), 129.07 (C-13), 128.63 (C-12), 126.81 (C-14), 126.38 (C-3), 126.10 (C-15), 125.44 (C-11), 123.50 (C-16), 122.85 (C-10), 111.34 (C-23), 106.82 (C-21), 99.90 (C-20), 85.22 (C-19), 51.14 (C-25), 45.41 (C-7), 31.84 (C-28), 27.31 (C-26), 26.93 (C-27), 22.82 (C-29), 21.15 (C-8), 14.18 (C-30).

HRMS (ESI): found 757.4457 m/z $[M+H]^+$, calculated for $C_{51}H_{57}N_4O_2$ 757.4476 m/z.

***S,S*-L: 72% yield**

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] = 8.32 (s, 2H, H-3), 8.18-8.15 (m, 2H, H-16), 7.91-7.87 (m, 2H, H-13), 7.83 (dd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 2.8 Hz, 2H, H-12), 7.74 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-6), 7.54-7.49 (m, 4H, H-14, H-15), 7.44-7.42 (m, 4H, H-10, H-11), 7.39 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H-22), 6.59 (d,

$^3J_{HH}$ = 8.8 Hz, 2H, 23), 6.03 (quint, $^3J_{HH}$ = 7.3 Hz, 2H, H-7), 3.29 (t, $^3J_{HH}$ = 7.7 Hz, 4H, H-25), 1.65 (d, $^3J_{HH}$ = 6.7 Hz, 6H, H-8), 1.63-1.56 (m, 4H, H-26), 1.36-1.30 (m, 12H, H-27, H-28, H-29), 0.94-0.88 (m, 6H, H-30).

^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C): δ [ppm] = 162. 45 (C-5), 149.09 (C-24), 148.80 (C-2), 138.33 (C-9), 136.23 (C-4), 134.15 (C-18), 133.94 (C-22), 131.14 (C-17), 129.06 (C-13), 128.62 (C-12), 126.80 (C-14), 126.38 (C-3), 126.09 (C-15), 125.43 (C-11), 123.49 (C-16), 122.85 (C-10), 111.33 (C-23), 106.81 (C-21), 99.89 (C-20), 85.21 (C-19), 51.14 (C-25), 45.40 (C-7), 31.84 (C-28), 27.31 (C-26), 26.93 (C-27), 22.82 (C-29), 21.14 (C-8), 14.18 (C-30).

HRMS (ESI): found 757.4463 m/z $[M+H]^+$, calculated for $C_{51}H_{57}N_4O_2$ 757.4476 m/z.

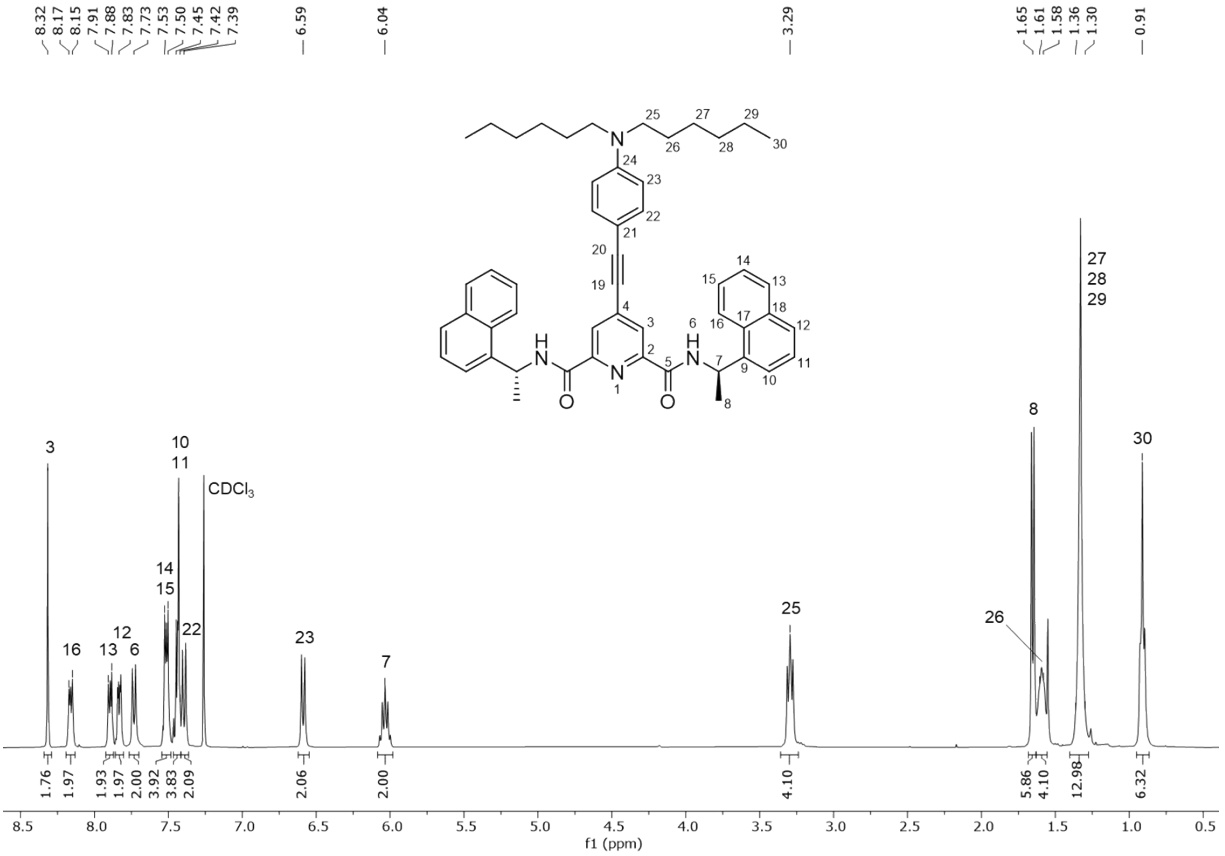


Figure S2: *^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of ligand* ***R,R-L*** *with assigned signals.*

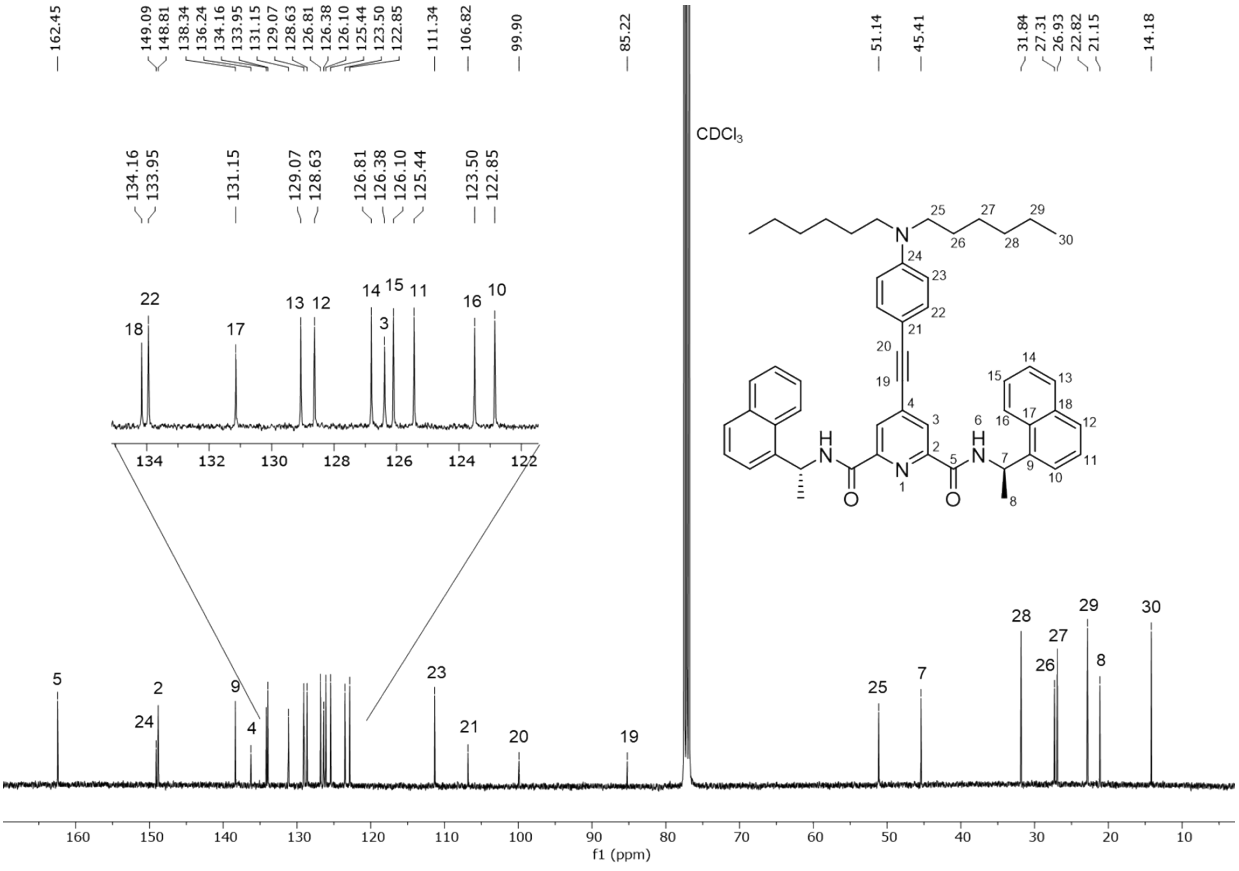


Figure S3: *^{13}C-NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of ligand* ***R,R-L*** *with assigned signals.*

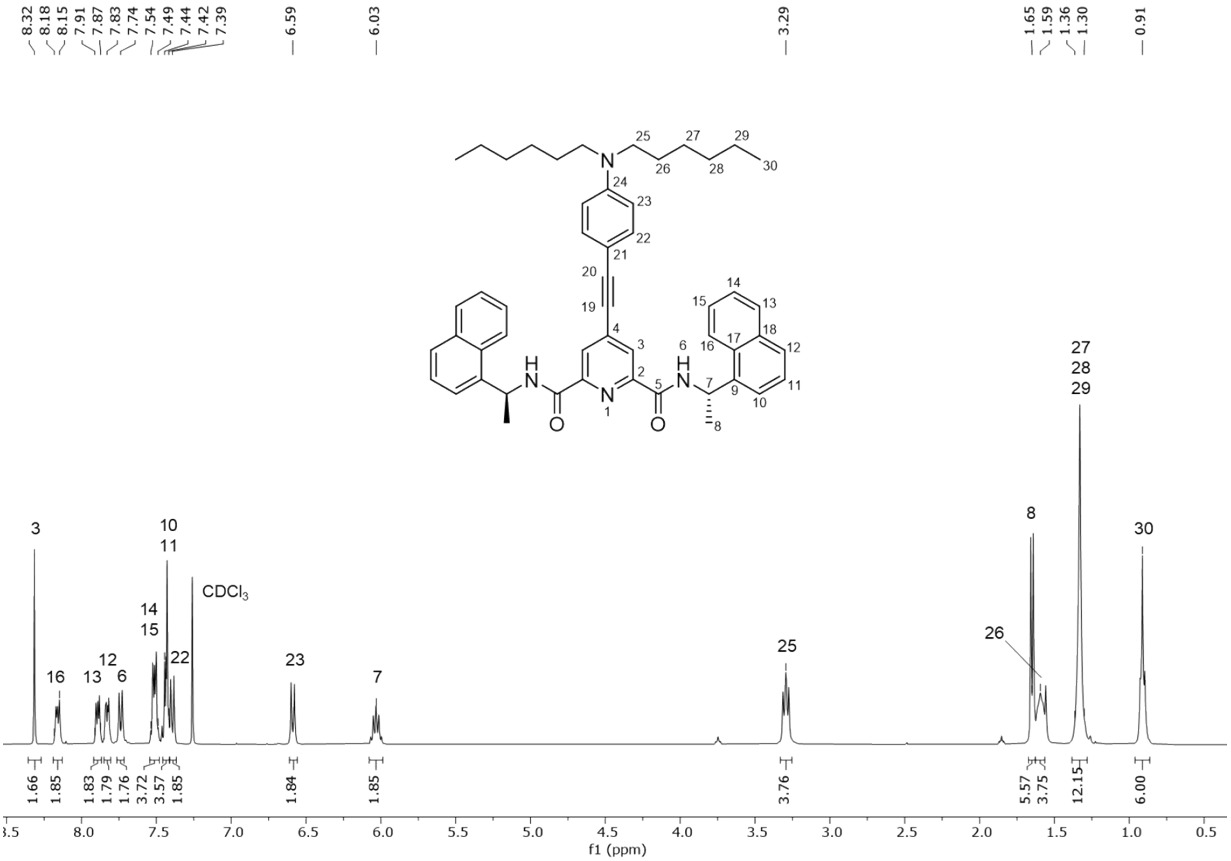


Figure S4: *^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of ligand* ***S,S-L*** *with assigned signals.*

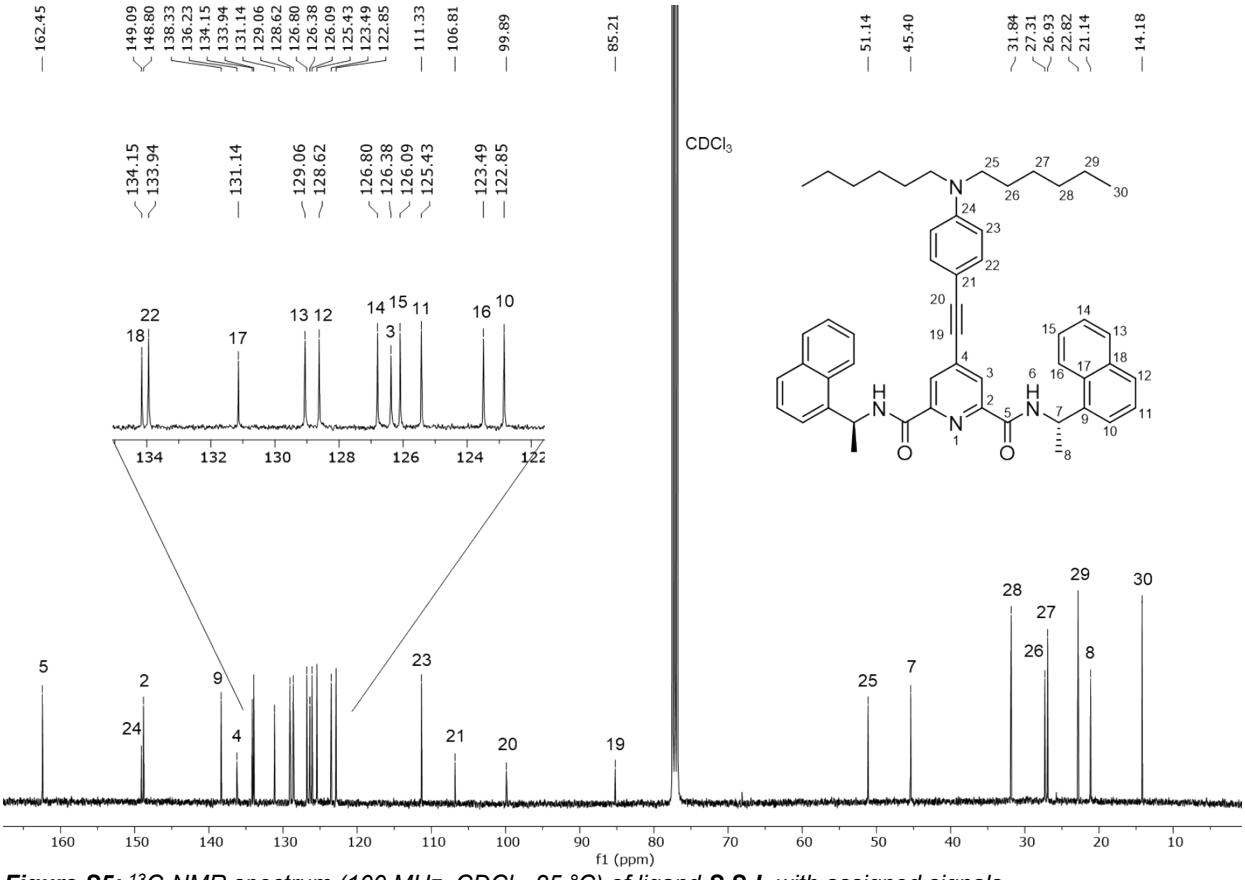
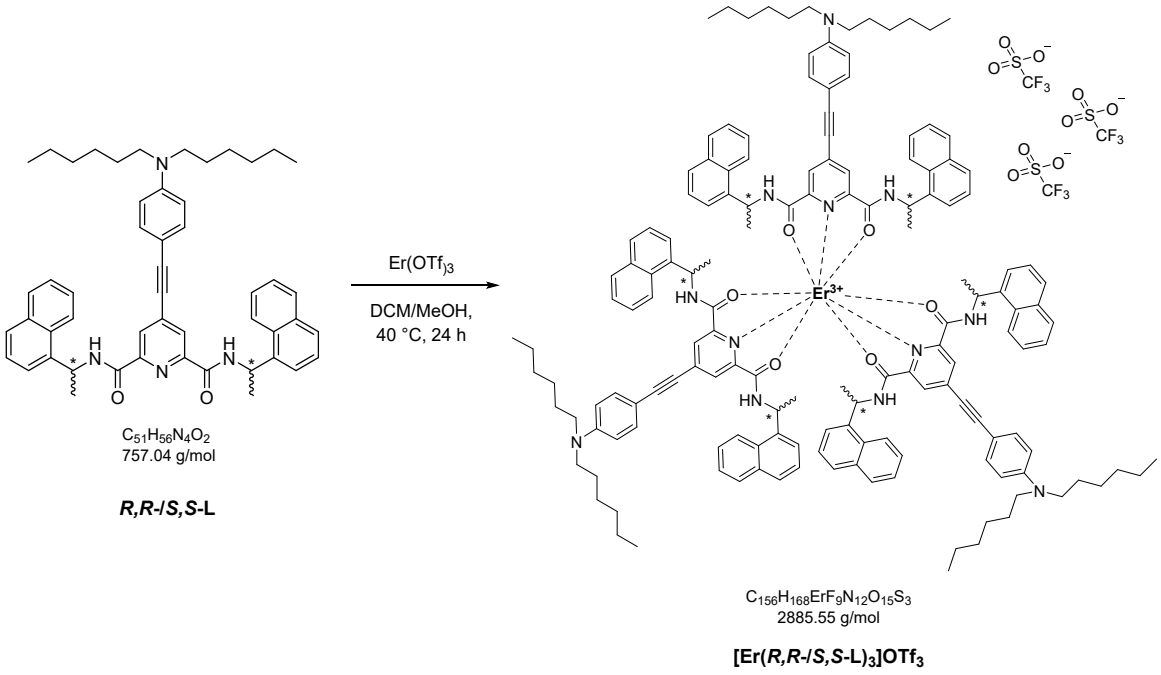


Figure S5: *^{13}C-NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of ligand* ***S,S-L*** *with assigned signals.*

S 4. COMPLEX SYNTHESES



Scheme S2: *Formation of the chiral Er complexes starting from either the R,R- or S,S-type ligand.*

Complexation

The ligand of interest (3 equiv.) was dissolved in 40 mL of a 1/1 mixture of methanol and dichloromethane under argon atmosphere. The respective lanthanide triflate salt (1 equiv.) was added and the solution was stirred overnight at 40 °C. After solvent removal under reduced pressure, the crude product was purified by washing with diethyl ether, centrifugation (4000 rpm, 10 min) and decantation of the supernatant solution. This procedure was repeated three times and the complex was dried under vacuum prior to further analysis. Due to the presence of a paramagnetic metal center the signals in the ^{1}H-NMR spectra are very broad and a certain assignment of peaks was not possible. Proton signals are indicated according to their respective functional group: phenyl of the antenna moiety (H_{Ph}), hexyl chains of the antenna moiety (H_{Hex}), picolinic acid ester group (H_{PA}).

[Er(*R,R*-L)$_3$](OTf)$_3$

The complex was synthesized according to the general procedure, using *R,R*-L (37.3 mg, 49.3 µmol, 3 equiv.) and Er(OTf)$_3$ (10.1 mg, 16.4 µmol, 1 equiv.) to yield the desired complex as orange powder (45.9 mg, 15.9 µmol, 96%).

^{1}H-NMR (300 MHz, CD$_3$OD, 25 °C): δ [ppm] = 25.13 (br, 2H, H_{PA}), 17.74 (br, 2H, H_{PA}), 10.85 (br, 2H, H_{PA}), 7.03 (br, 2H, H_{PA}), 6.01 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H_{Ph}), 5.92 (m, 2H, H_{Ph}), 5.44 (br, 2H, H_{PA}), 4.97 (br,

4H, H_{PA}), 3.68 (br, 2H, H_{PA}), 2.98 (t, $^3J_{HH}$ = 6.8 Hz, 4H, H_{Hex}), 1.85 (br, 2H, H_{PA}), 1.29 (br, 2H, H_{PA}), 1.23-0.98 (m, 16H, H_{Hex}), 0.69 (t, $^3J_{HH}$ = 6.7 Hz, 6H, H_{Hex}), -1.50 (br, 2H, H_{PA}).

HRMS (ESI): Found 609.0654 m/z [2L, 1L+H$^+$, Er^{3+}]$^{4+}$, calculated for $C_{153}H_{169}ErN_{12}O_6^{4+}$ 609.0643 m/z. Found 811.7512 m/z [3L, Er^{3+}]$^{3+}$, calculated for $C_{153}H_{168}ErN_{12}O_6^{3+}$ 811.7500 m/z.

[Er(*S,S*-L)$_3$](OTf)$_3$

The complex was synthesized according to the general procedure, using *S,S*-L (35.3 mg, 46.6 µmol, 3 equiv.) and Er(OTf)$_3$ (9.6 mg, 15.5 µmol, 1 equiv.) to yield the desired complex as orange powder (44.8 mg, quantitative yield).

^{1}H-NMR (300 MHz, CD_3OD, 25 °C): δ [ppm] = 24.79 (br, 2H, H_{PA}), 17.74 (br, 2H, H_{PA}), 10.85 (br, 2H, H_{PA}), 7.03 (br, 2H, H_{PA}), 6.01 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H_{Ph}), 5.91 (m, 2H, H_{Ph}), 5.44 (br, 2H, H_{PA}), 4.96 (br, 4H, H_{PA}), 3.67 (br, 2H, H_{PA}), 2.97 (t, $^3J_{HH}$ = 6.9 Hz, 4H, H_{Hex}), 1.84 (br, 2H, H_{PA}), 1.28 (br, 2H, H_{PA}), 1.22-0.99 (m, 16H, H_{Hex}), 0.69 (t, $^3J_{HH}$ = 6.5 Hz, 6H, H_{Hex}), -1.53 (br, 2H, H_{PA}).

HRMS (ESI): Found 609.0654 m/z [2L, 1L+H$^+$, Er^{3+}]$^{4+}$, calculated for $C_{153}H_{169}ErN_{12}O_6^{4+}$ 609.0643 m/z. Found 811.7515 m/z [3L, Er^{3+}]$^{3+}$, calculated for $C_{153}H_{168}ErN_{12}O_6^{3+}$ 811.7500 m/z.

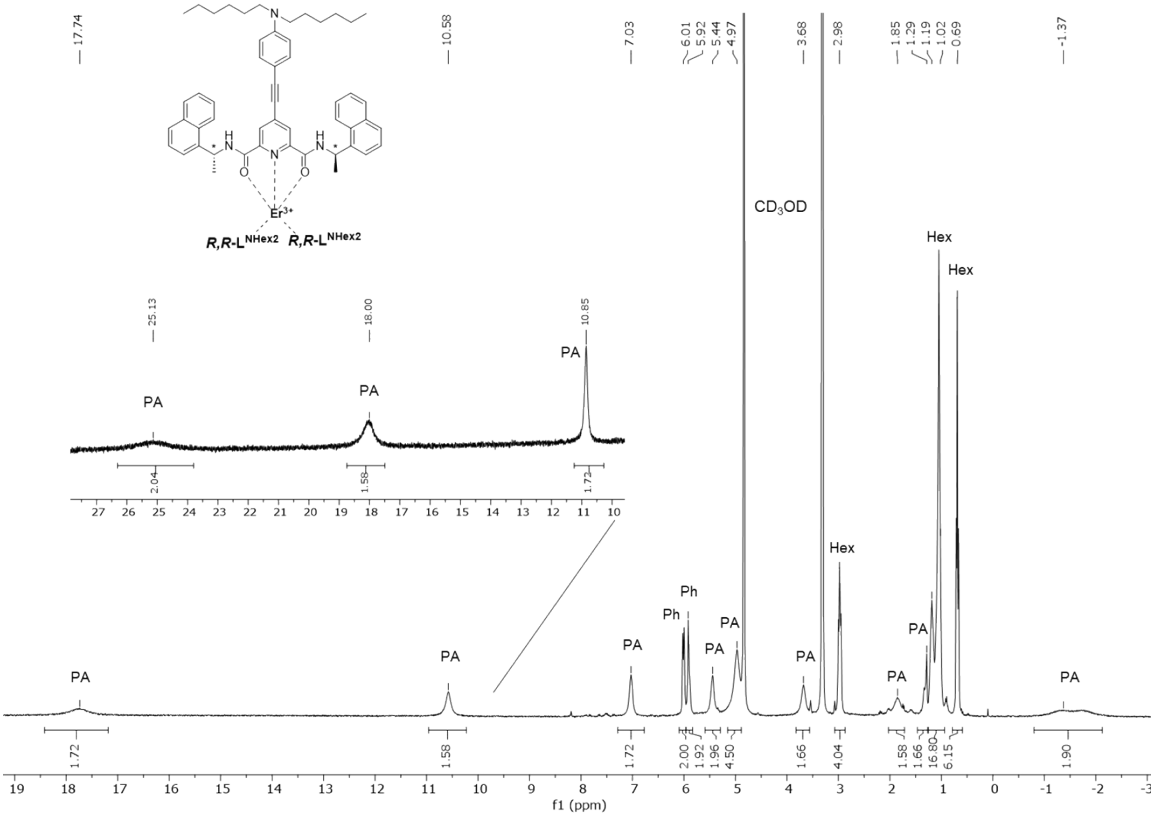


Figure S6. *^{1}H-NMR (300 MHz, CD_3OD, 289 K) spectra of [Er(R,R-L)$_3$](OTf)$_3$ with signals assigned according to their respective functional group.*

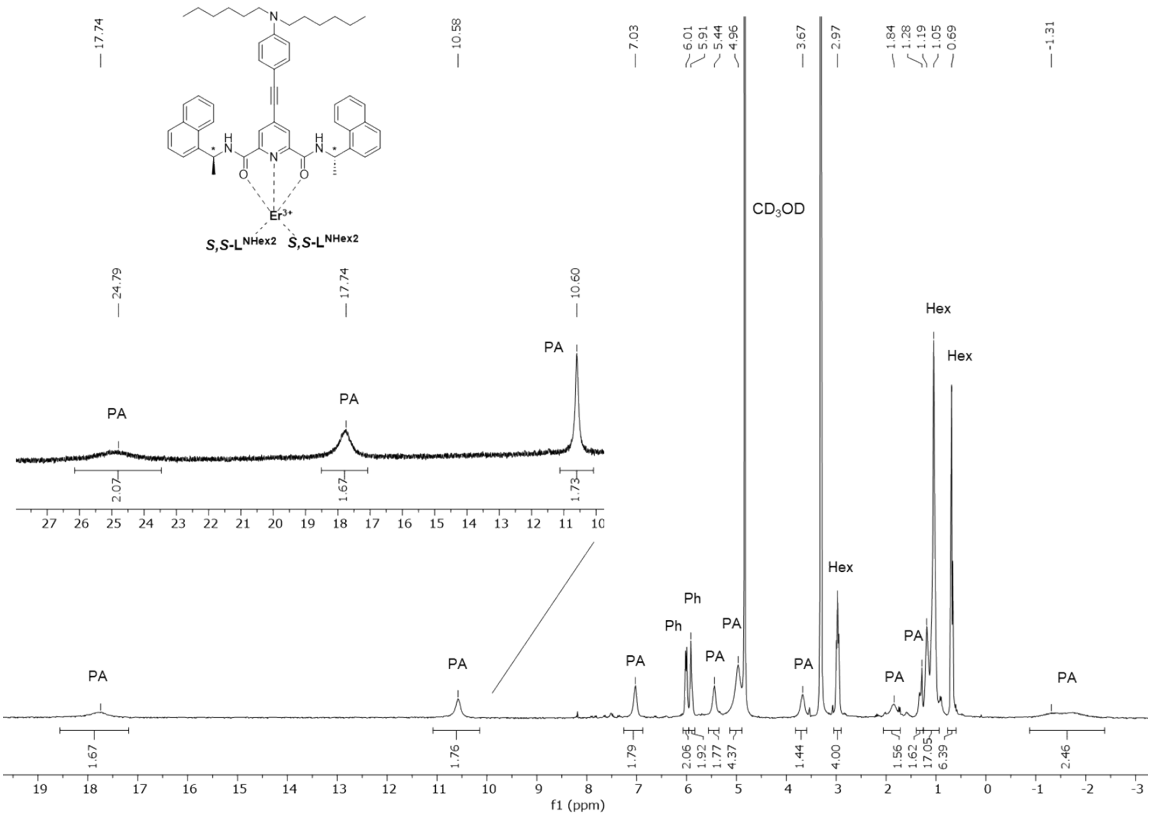


Figure S7. *^{1}H-NMR (300 MHz, CD_3OD, 289 K) spectra of $[Er(S,S\text{-}L)_3](OTf)_3$ with signals assigned according to their respective functional group.*

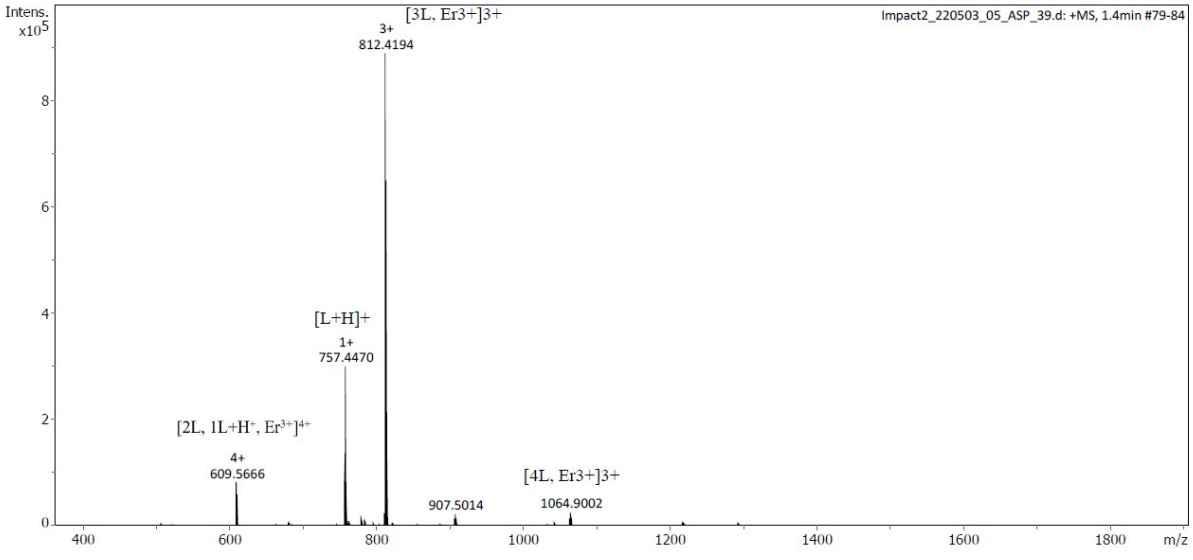


Figure S8: *High resolution mass spectrum of $[Er(R,R\text{-}L)_3](OTf)_3$ with assigned signals.*

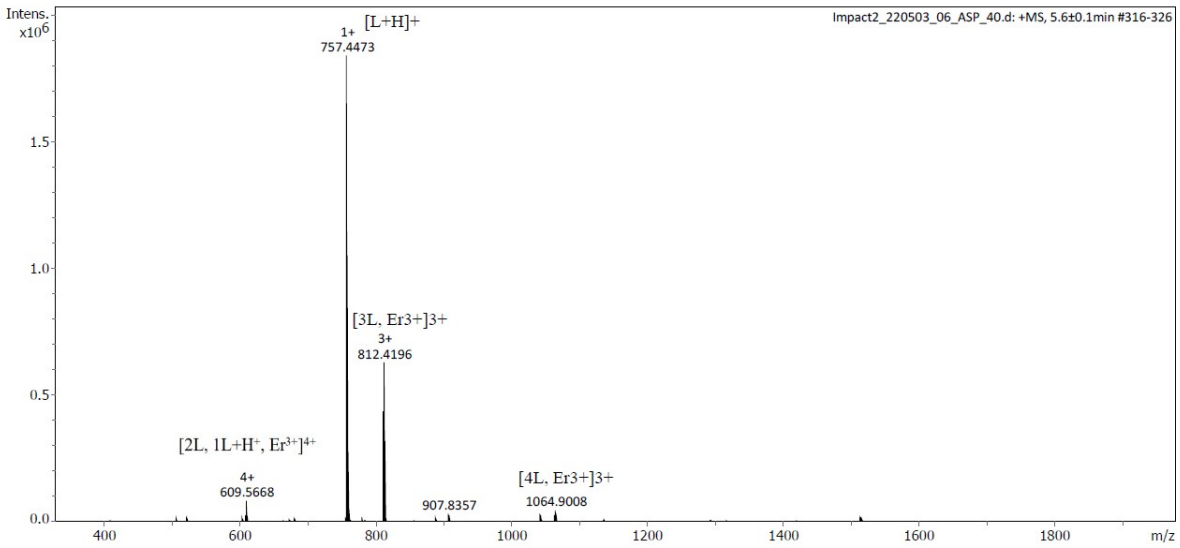


Figure S9: *High resolution mass spectrum of $[Er(S,S\text{-}L)_3](OTf)_3$ with assigned signals.*

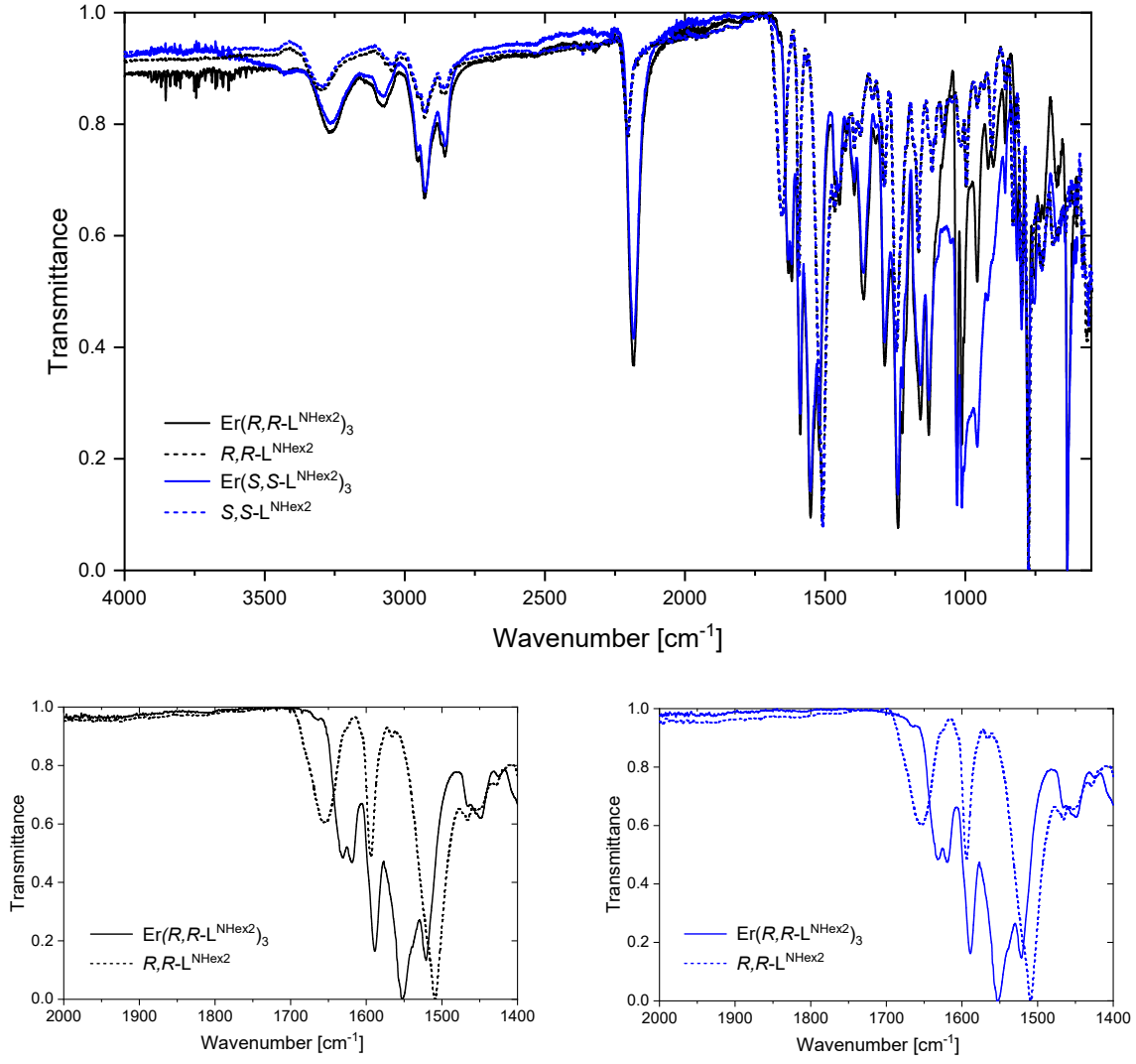


Figure S10: *FTIR spectra of the two Er(III) complexes (solid lines) and the corresponding ligands (dashes lines) with enlarged region of the ligands' carbonyl vibration.*

S 5. CRYSTAL STRUCTURE

Table S 1. *Summary of X-ray crystallographic data for [Er(R,R-L)$_3$](OTf)$_3$·4(MeOH).*

Compound	**[Er(*R,R*-L)$_3$](OTf)$_3$·4(MeOH).**
Formula	$C_{160}H_{174}ErF_9N_{12}O_{19}S_3$
M / g.mol^{-1}	3003.54
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (N°19)
Cell parameters	a = 22.065(3)Å b = 27.116(3)Å c = 30.111(4) Å
Volume / Å^3	18017(4)
Z	4
T / K	150 K
2θ range /°	3.76 ≤ 2θ ≤ 55.414
ρ_{calc} / g.cm^{-3}	1.107
μ / mm^{-1}	0.567
Number of reflections	144946
Independent reflections	41696
R_{int}	0.0988
$Fo^2 > 2\sigma(Fo)^2$	25069
Number of variables	1757
R_1, ωR_2	0.0723, 0.1837
Flack parameter	-0.023(4)

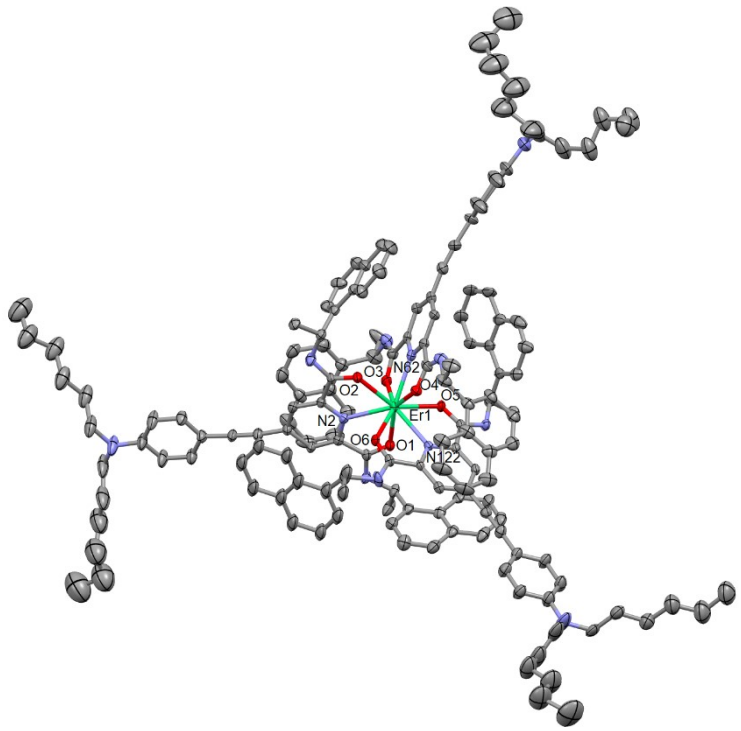


Figure S11. *Ortep view of the asymmetric unit for [Er(R,R-L)$_3$](OTf)$_3$·4(MeOH). Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms and MeOH molecules of crystallization are omitted for clarity.*

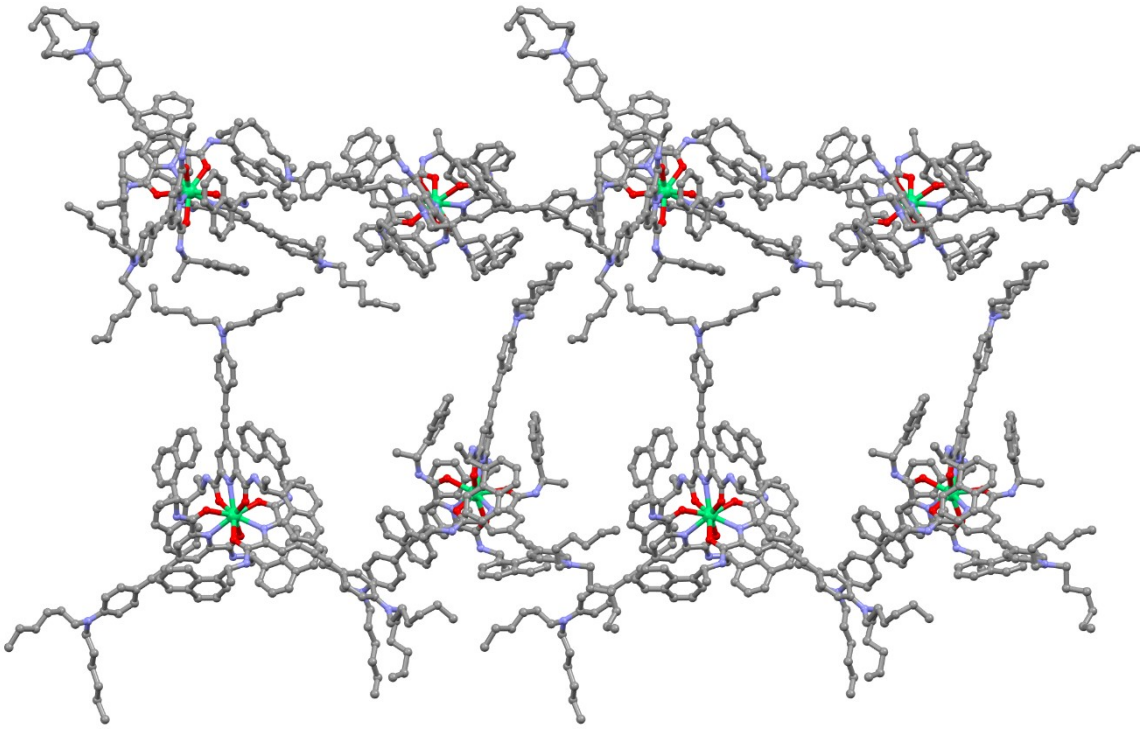


Figure S12. *Crystal packing of [Er(R,R-L)$_3$](OTf)$_3$·4(MeOH) showing the well-separated complexes.*

S 6. PHOTOPHYSICAL COMPLEX CHARACTERIZATION

Table S2: *Extinction coefficients of the complexes [Er(R,R-L)$_3$](OTf)$_3$ and [Er(S,S-L)$_3$](OTf)$_3$ calculated from optical densities of complex solutions in methanol at 293 nm and 455 nm.*

	[Er(*R,R*-L)$_3$](OTf)$_3$	**[Er(*S,S*-L)$_3$](OTf)$_3$**
ε [L/mol*cm] at λ = 293 nm	107000	120000
ε [L/mol*cm] at λ = 454 nm	105000	118000

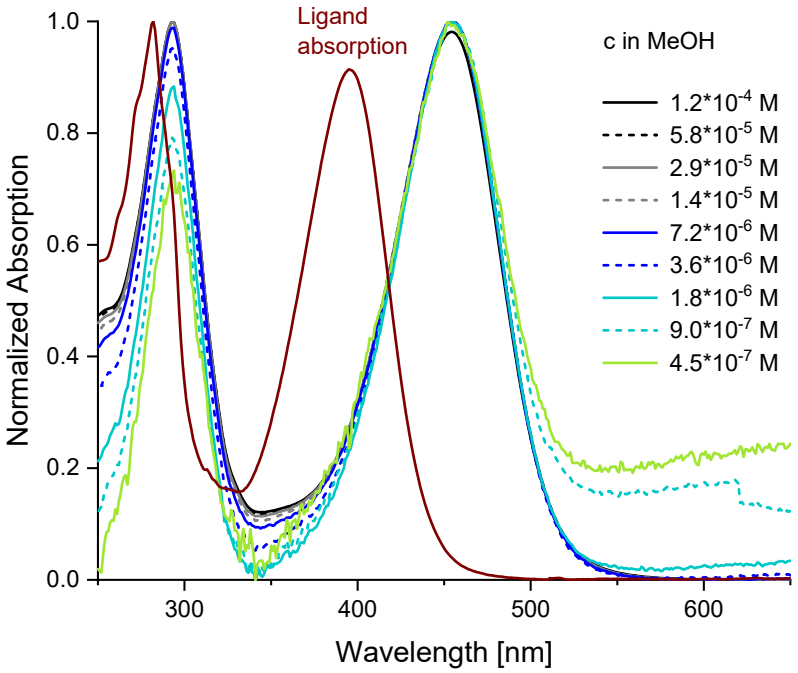


Figure S13: *Absorption spectra of the complex [Er(R,R-L)$_3$](OTf)$_3$ dissolved in methanol at various concentration with absorption spectrum of the respective ligand R,R-L(red line).*

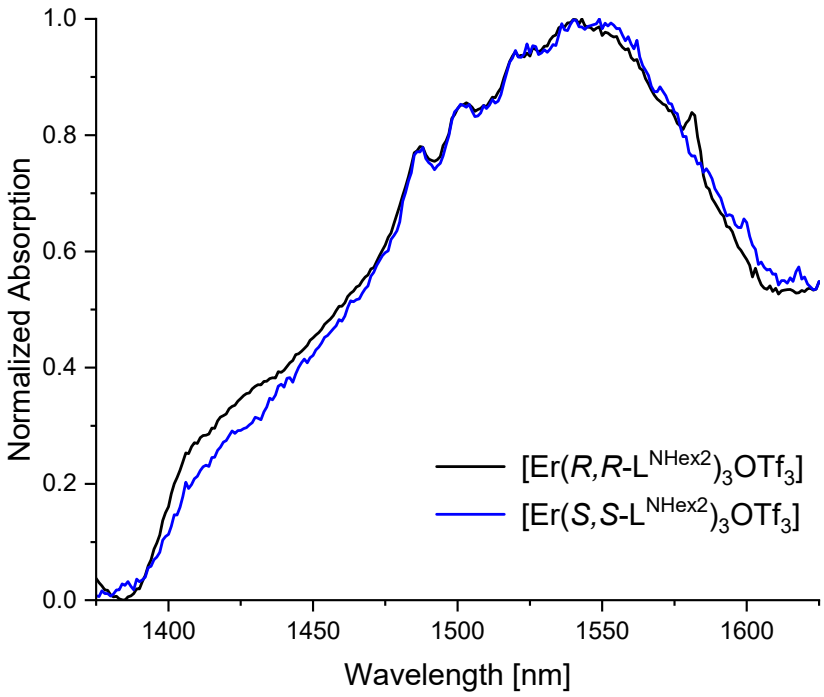


Figure S14: *NIR region absorption spectra of the complexes [Er(R,R-L)$_3$](OTf)$_3$ and [Er(S,S-L)$_3$](OTf)$_3$ in MeOD-d$_4$ at 298 K (c ≈ 3*10^{-4} M).*

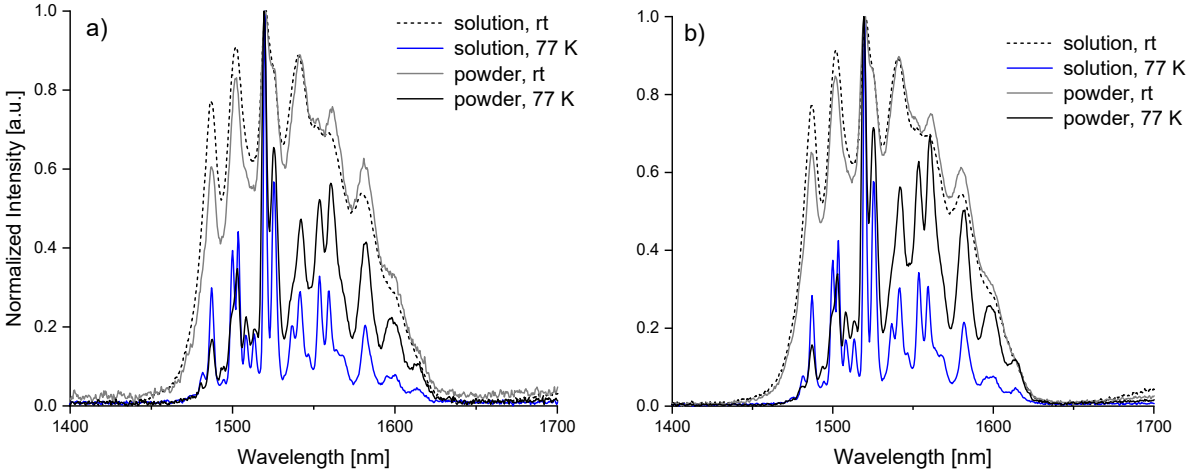


Figure S15. *Normalized luminescence spectra of the two enantiomers (a) [Er(R,R-L)$_3$](OTf)$_3$ and (b) [Er(S,S-L)$_3$](OTf)$_3$ in solution (4/1 ethanol/methanol mixture) and in solid state at 298 K and at 77 K.*

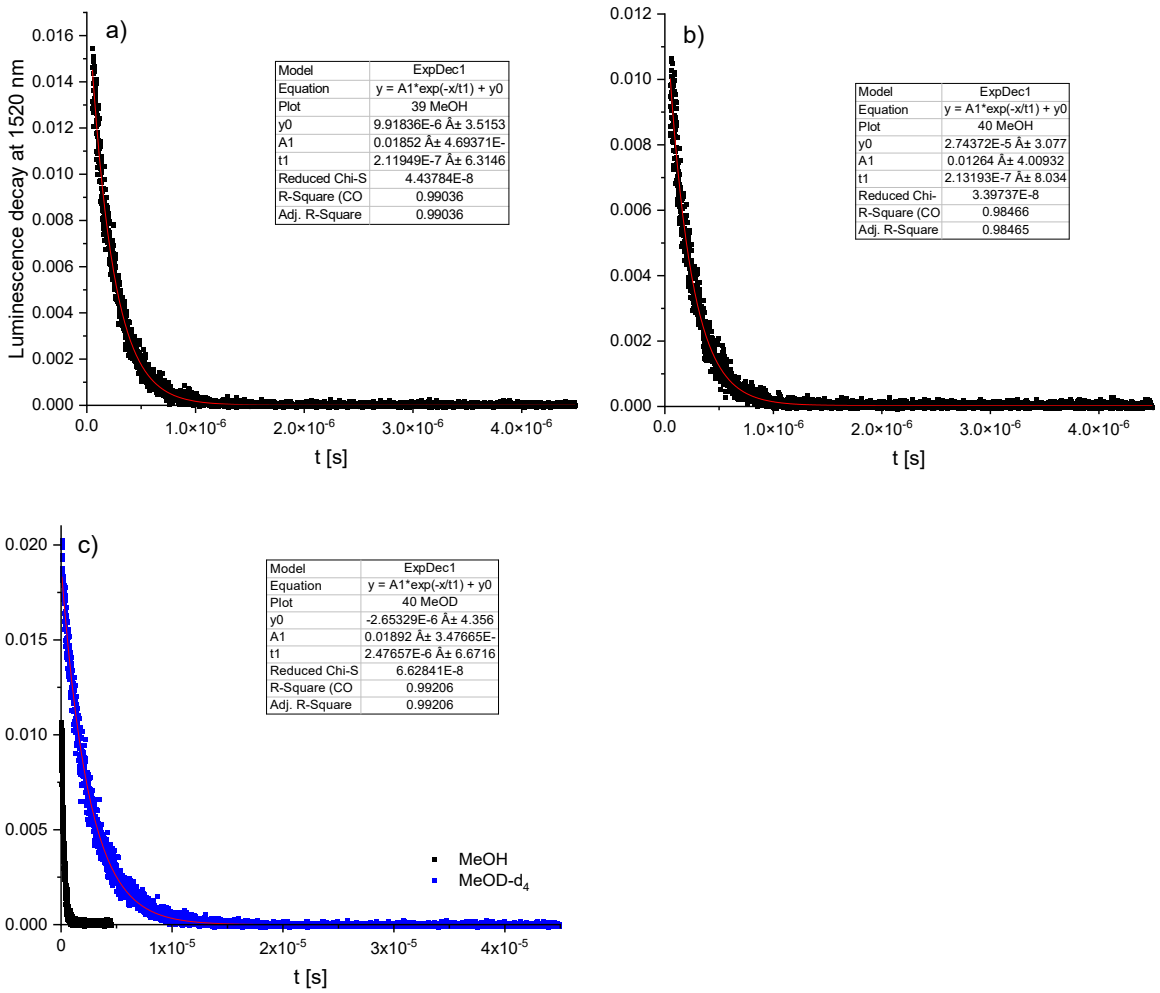


Figure S16. *Luminescence decays at 1520 nm and the corresponding monoexponential fits (red) recorded for the complexes [Er(R,R-L)$_3$](OTf)$_3$ (a) and [Er(S,S-L)$_3$](OTf)$_3$ (b, c) determined in solutions of methanol (a,b) and deuterated methanol (c).*

S 7. CHIROPTICAL MEASUREMENTS

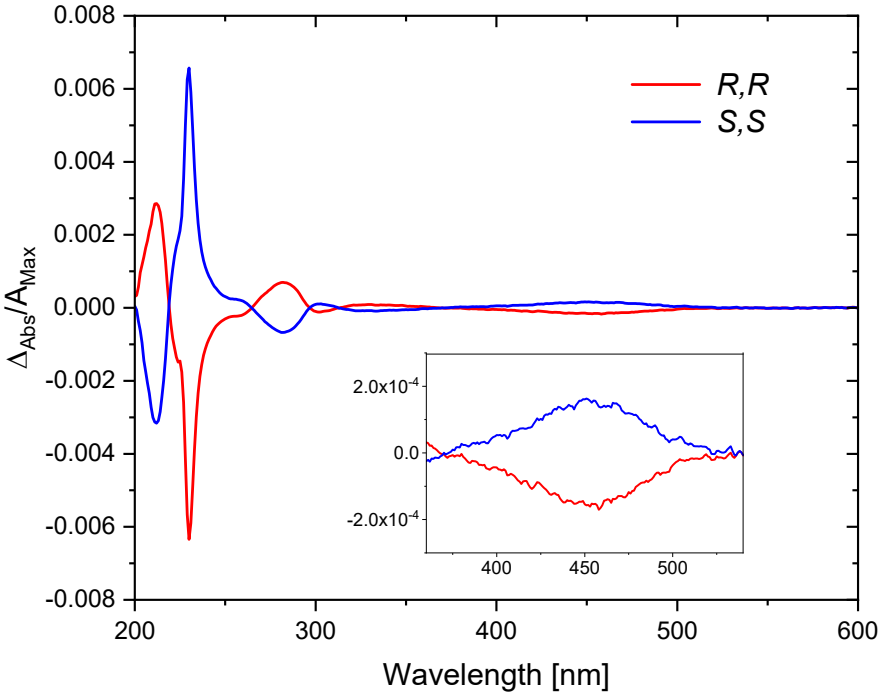


Figure S17. *Room temperature visible ECD of a diluted CD_3OD solution ($c \approx 10^{-5}$ M) of $[Er(R,R\text{-}L)_3](OTf)_3$ (red) and $[Er(S,S\text{-}L)_3](OTf)_3$ (blue).*

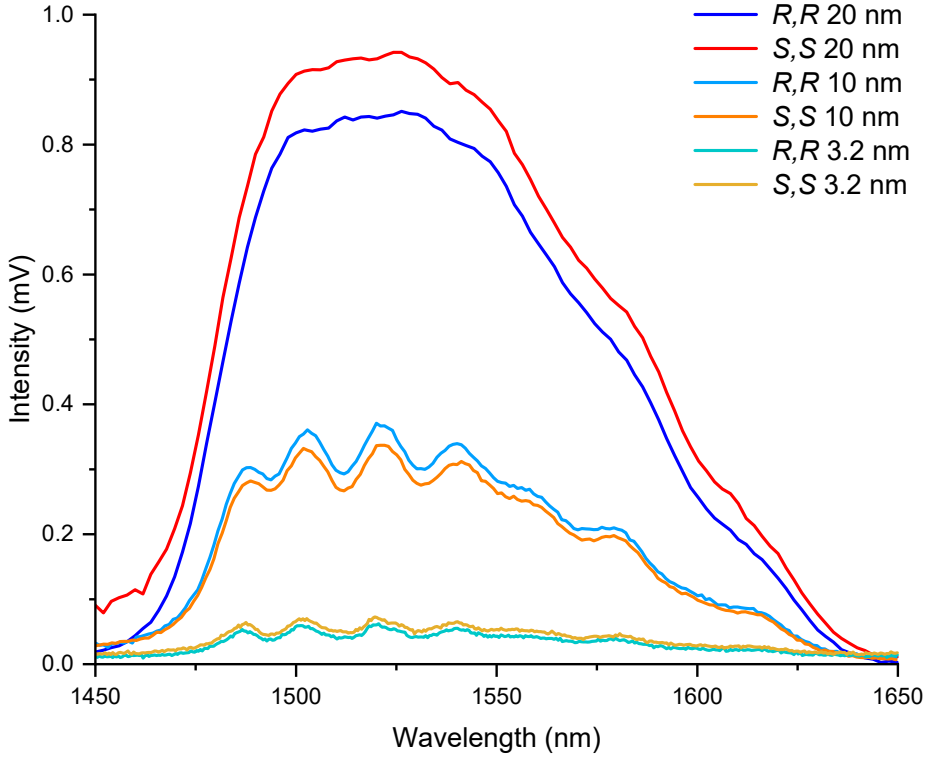


Figure S18. *Emission spectra of $[Er(S,S\text{-}L)_3](OTf)_3$ and $[Er(R,R\text{-}L)_3](OTf)_3$ recorded in parallel with the CPL measurements at different experimental bandwidth.*

S 8. ADDITIONAL SIMULATIONS

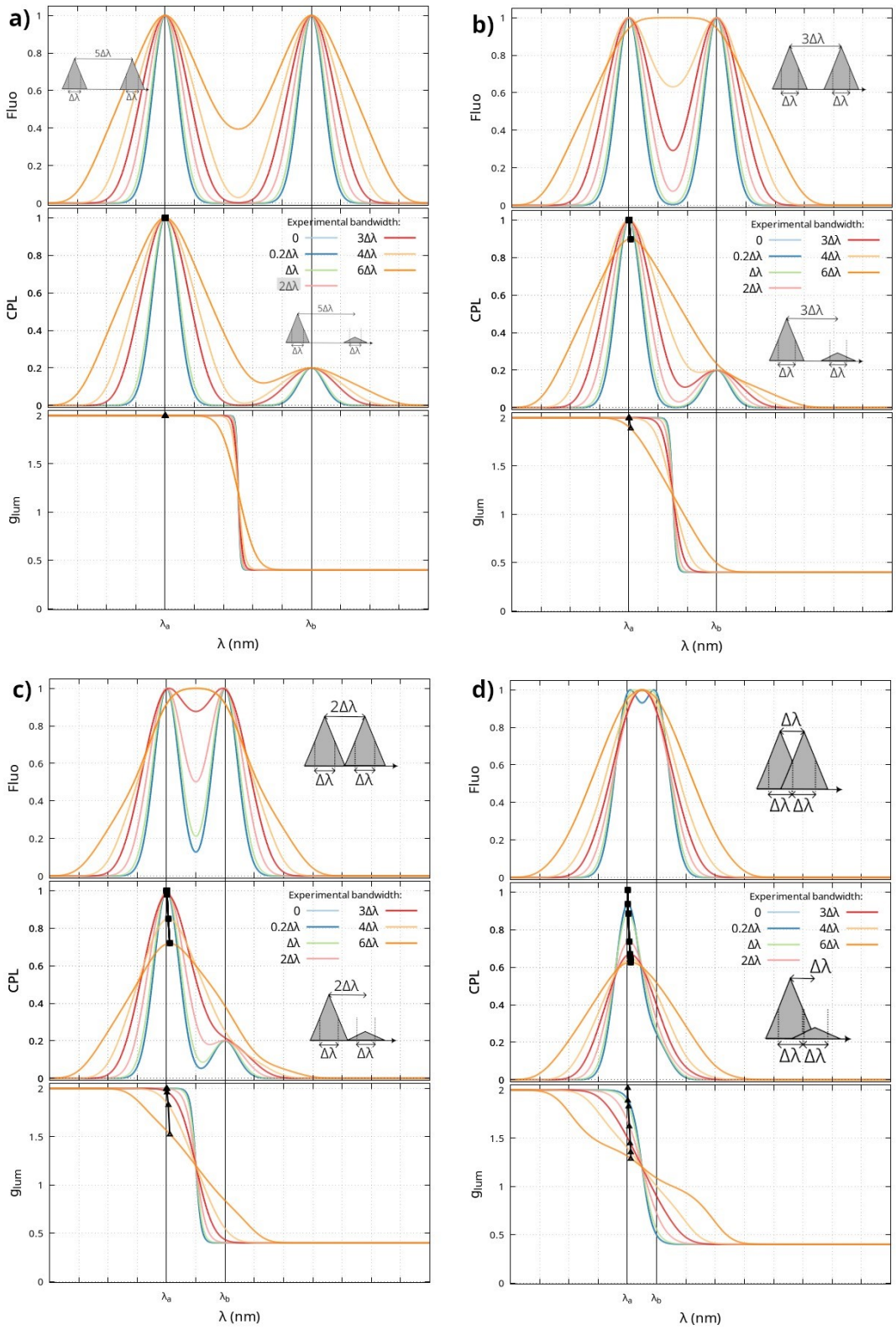


Figure S19: *Convolution of two gaussian bands (FWHM=Δλ) with triangle functions at various bandwidths from 0 to 6Δλ. Upper panels: evolution of the fluorescence spectra composed of two bands of same sign and intensity. Middle panels: evolution of the CPL spectra composed of two bands of same sign and two different intensities (1 and 0.2). Bottom panels: evolution of the g_{lum} values calculated as the ratio between the CPL and the fluorescence. Dotted black curves: evolution of the extrema of CPL intensity and g_{lum}. The distance between the two peaks is a) 5 Δλ, b) 3 Δλ, c) 2 Δλ, d) Δλ.*

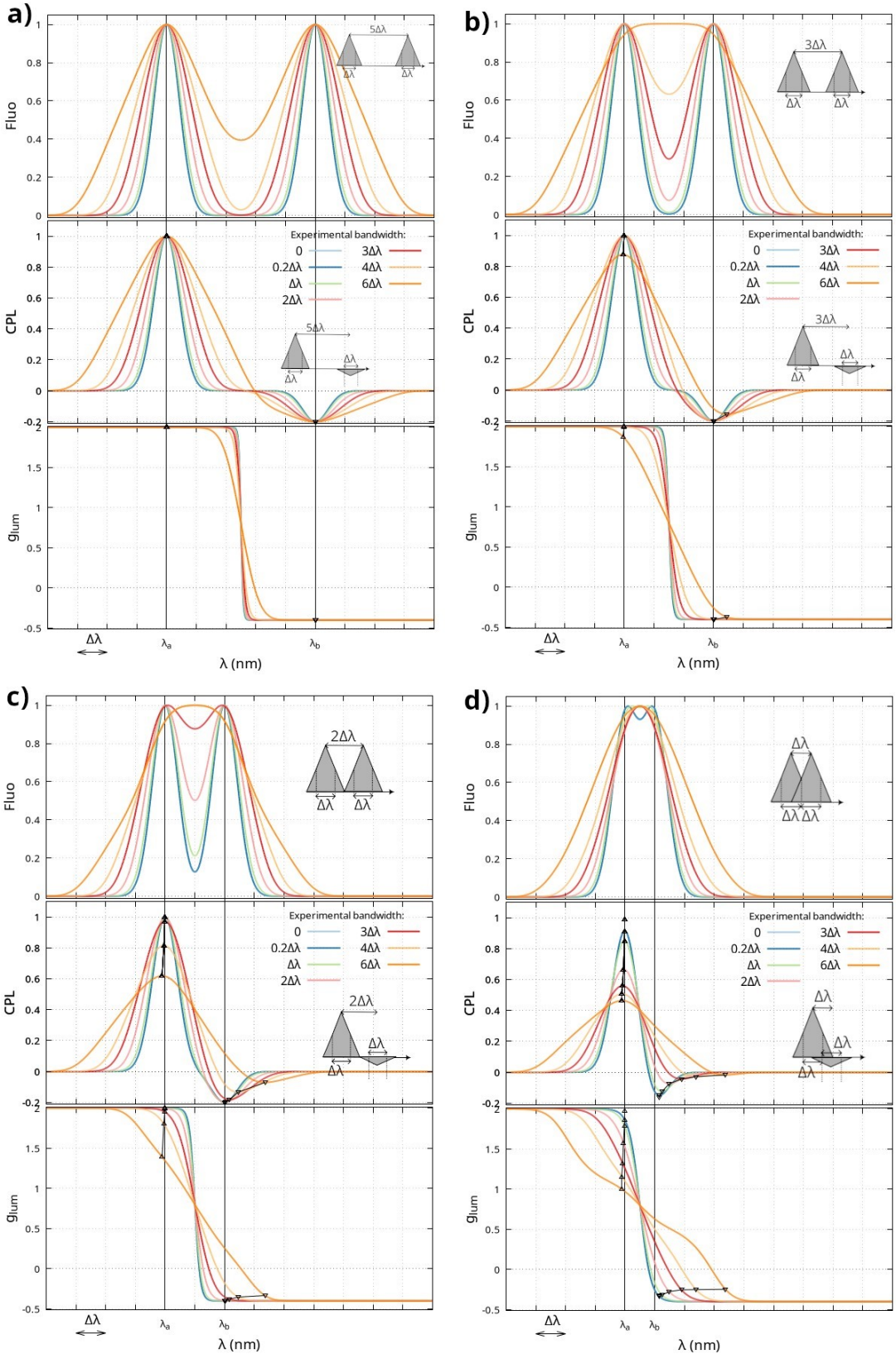


Figure S20: *Convolution of two gaussian bands (FWHM=Δλ) with triangle functions at various bandwidths from 0 to 6Δλ. Upper panels: evolution of the fluorescence spectra composed of two bands of same sign and intensity. Middle panels: evolution of the CPL spectra composed of two bands of opposite sign and two different intensities (1 and 0.2). Bottom panels: evolution of the g_{lum} values calculated as the ratio between the CPL and the fluorescence. Dotted black curves: evolution of the extrema of CPL intensity and g_{lum}. The distance between the two peaks is a) 5 Δλ, b) 3 Δλ, c) 2 Δλ, d) Δλ.*

REFERENCES

(1) Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst A* **2015**, *71*, 3–8.

(2) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst C* **2015**, *71*, 3–8.

(3) Spek, A. L. Single-crystal structure validation with the program PLATON. *J Appl Cryst* **2003**, *36*, 7–13.

(4) Baguenard, B.; Bensalah-Ledoux, A.; Guy, L.; Riobé, F.; Maury, O.; Guy, S. Theoretical and Experimental Analysis of Circularly Polarized Luminescence Spectrophotometers for Artifact-Free Measurements Using a Single CCD Camera. *Nat. Commun.* **2023**, *14*, 1065.

(5) Gendron, F.; Di Pietro, S.; Abad Galán, L.; Riobé, F.; Placide, V.; Guy, L.; Zinna, F.; Di Bari, L.; Bensalah-Ledoux, A.; Guyot, Y.*; et al.* Luminescence, Chiroptical, Magnetic and *ab initio* Crystal-Field Characterizations of an Enantiopure Helicoidal Yb(III) Complex. *Inorg. Chem. Front.* **2021**, *8*, 914–926.

(6) Vivas, M. G.; Silva, D. L.; Boni, L. de; Bretonniere, Y.; Andraud, C.; Laibe-Darbour, F.; Mulatier, J.-C.; Zaleśny, R.; Bartkowiak, W.; Canuto, S.*; et al.* Experimental and Theoretical Study on the One- and Two-Photon Absorption Properties of Novel Organic Molecules Based on Phenylacetylene and Azoaromatic Moieties. *J. Phys. Chem. B* **2012**, *116*, 14677–14688.