

Near-Infrared circularly polarized luminescence from chiral Yb(III)-diketonates

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Compound preparation

The reactions were performed under N₂ atmosphere, reactants and solvents were used as received from the supplier. CHNS analyses were performed with a vario MICRO cube CHNOS Elemental Analyzer GmbH.

Preparation of Yb(TTA)₃·2H₂O

KOH (224 mg, 4 mmol) was dissolved in 4 mL of ethanol and added to a solution of thenoyltrifluoroacetone (885 mg, 4 mmol) in ethanol (20 mL) under stirring. Then YbCl₃ hexahydrate (503 mg, 1.3 mmol) was dissolved in water (4 mL) and added dropwise to the reaction mixture. The solution was refluxed under stirring for 4 hours and then the solvent was removed under reduced pressure. The solid was dissolved in dichloromethane (30 mL) and extracted three times with water (10 mL). The organic phase was dried under Na₂SO₄, filtrate and the solvent removed under reduced pressure. Yb(TTA)₃·2H₂O was obtained as a yellow solid (920 mg, yield 81%) and used without any further purification.

Preparation of Yb(TTA)₃(*R,R*)-ⁱPrPyBox

Yb(TTA)₃·2H₂O (43 mg, 0.05 mmol) and (*R,R*)-ⁱPrPyBox (15 mg, 0.05 mmol) were dissolved in ethanol (4 mL) and heated under stirring at 60 °C for 4 h. The solution was let to cool down overnight and the precipitate collected by filtration, washed with cold ethanol and dried under vacuum. 31 mg of the compound were obtained (yield 55%). CHNS analysis: C 42.59, H 3.23, N 3.69, S 7.27 (calcd for C₄₁H₃₅F₉N₃O₈S₃Yb: C 43.27, H 3.10, N 3.69, S 8.45).

Preparation of Yb(TTA)₃(*S,S*)-ⁱPrPyBox

Same procedure as for Yb(TTA)₃(*R,R*)-ⁱPrPyBox was followed. 34 mg of the compound were obtained (yield 60%). CHNS analysis: C 42.56, H 3.18, N 3.29, S 7.62 (calcd for C₄₁H₃₅F₉N₃O₈S₃Yb: C 43.27, H 3.10, N 3.69, S 8.45).

Preparation of Yb(TTA)₃(*R,R*)-PhPyBox

Yb(TTA)₃·2H₂O (43 mg, 0.05 mmol) and (*R,R*)-PhPyBox (18 mg, 0.05 mmol) were dissolved in ethanol (4 mL) and heated under stirring at 60 °C for 4 h. The solvent was removed under reduced pressure. 55 mg of the compound were obtained (yield 90%). CHNS analysis: C 46.90, H 2.72, N 3.51, S 8.13 (calcd for C₄₇H₃₁F₉N₃O₈S₃Yb: C 46.81, H 2.59, N 3.48, S 7.98).

Preparation of Yb(TTA)₃(*S,S*)-PhPyBox

Same procedure as for Yb(TTA)₃(*R,R*)-PhPyBox. 58 mg of the compound were obtained (yield 95%). CHNS analysis: C 46.90, H 2.72, N 3.55, S 8.05 (calcd for C₄₇H₃₁F₉N₃O₈S₃Yb: C 46.81, H 2.59, N 3.48, S 7.98).

Spectroscopy details

Quantum yield measurements

Luminescence quantum yields (Φ) were measured with a Fluorolog-3 HORIBA Jobin Yvon fluorimeter equipped with a liquid nitrogen cooled InGaAs detector. The following equation was used:

$$\Phi_x = \Phi_r \frac{A_r(\lambda) D_x n_x^2}{A_x(\lambda) D_r n_r^2}$$

Where A is the absorbance at the excitation wavelength ($\lambda = 320$ nm), n the refractive index and D the luminescence integrated intensity. r and x indices stand for reference and sample respectively. The fluorescence quantum yields were measured in CH_2Cl_2 relative to $\text{Yb}(\text{TTA})_3(\text{H}_2\text{O})_2$ ($\Phi_r = 0.35\%$ in toluene).^{S1} Estimated error is $\pm 10\%$.

NIR-CPL measurements

NIR-CPL spectra were recorded using the home-built spectrofluoropolarimeter described in ref [S2], adapted for NIR measurement in the 900-1150 nm range (figure S1). In particular, left/right circular polarization discrimination was performed by a photoelastic modulator from a decommissioned Jasco J500C spectropolarimeter operating at 50 KHz coupled with an uncoated Glenn-Thompson polarizer. A Jasco CT-10 was used as the emission monochromator and the detection was performed by a Hamamatsu R316 photomultiplier tube. The spectra were collected under 365 nm irradiation from a commercial LED-source, using a 90° geometry between the excitation and detection direction. The set-up was calibrated in the red region using solution of $(\pm)\text{-CsEu}(\text{hfbc})_4$.^{S3} The extension of the calibration to the NIR region was checked by recording the NIR-CPL of a solution of $\text{Yb}(d\text{-facam})_3$ (tris[3-(trifluoromethylhydroxymethylene)-d-camphorato]ytterbium(III)) in dry DMSO^{S4} and verifying the qualitative (sign and spectral shape) and quantitative (g_{lum}) consistency of the spectrum obtained with the one reported in the literature (Figure S7).^{S4}

All the NIR-CPL spectra were recorded on 6 mM CH_2Cl_2 solution in 1 cm semi-micro (aperture 4 mm) optical glass cells using the following parameters: scan-speed 1 nm/sec, emission slit width ~ 8 nm, integration time 4 sec, accumulations 4, photomultiplier tube driving voltage 1100 V.

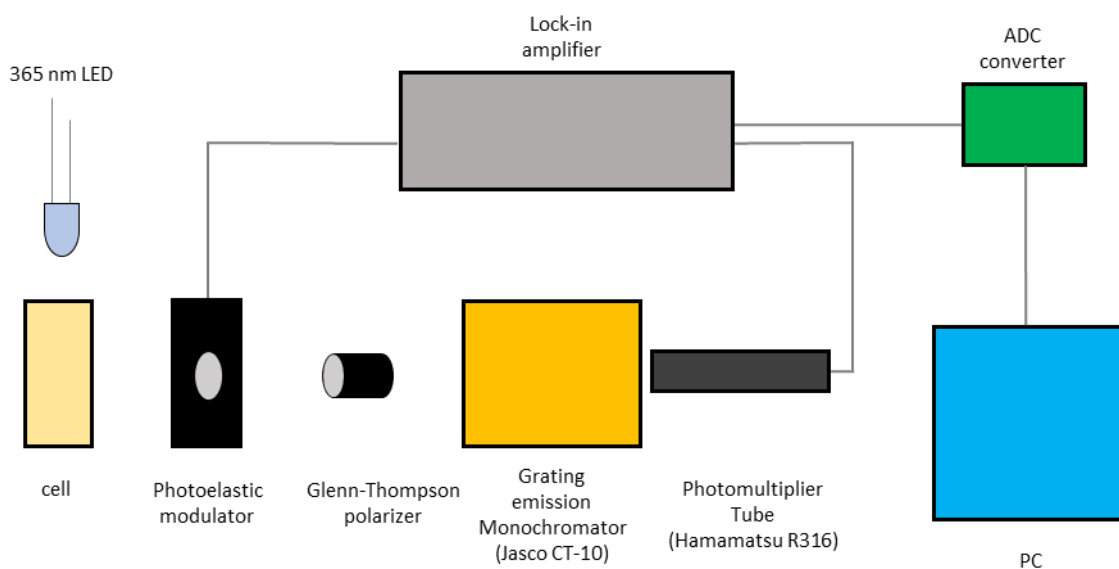


Figure S1. scheme of the experimental set-up employed for NIR-CPL measurements

NIR-CD measurements

NIR-CD measurements were performed using a Jasco J200 spectropolarimeter provided with an ADC system. The spectra were recorded on 7 mM CH_2Cl_2 solution in 1 cm optical glass cells using the following parameters: scan speed 20 nm/min, slit width 3 nm, integration time 1 sec.

The same solutions were used to record the corresponding NIR absorption spectra.

UV-ECD measurements

UV-ECD spectra were recorded using a Jasco J710 spectropolarimeter on 0.8 mM CH₂Cl₂ solution in 0.02 cm optical glass cells.

The same solutions were used to record the corresponding UV absorption spectra.

Additional spectra

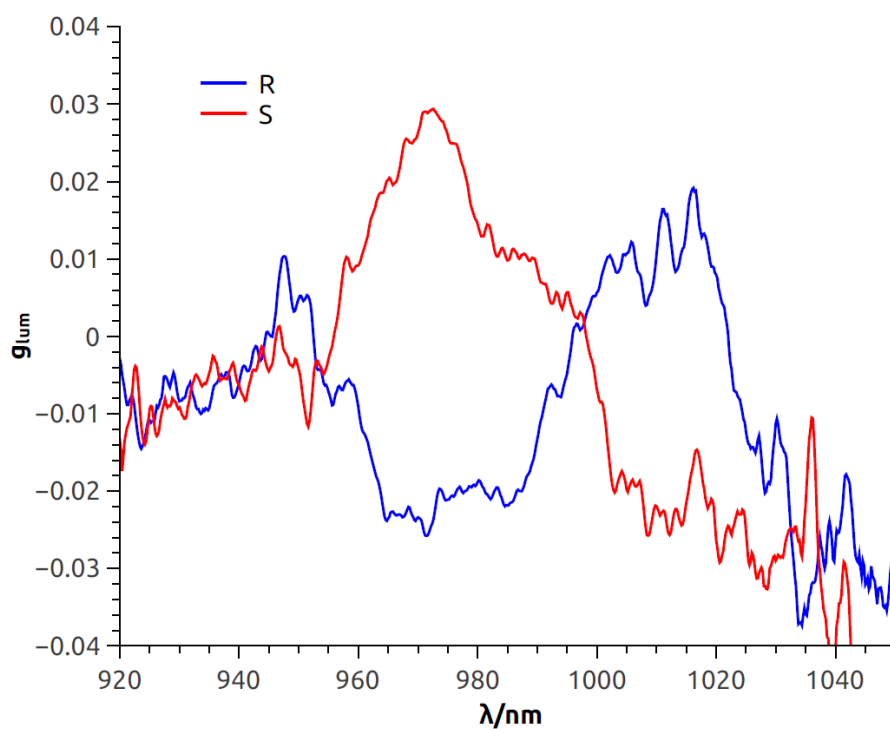


Figure S2. g_{lum} factor as a function of wavelength for the two enantiomers of Yb(TTA)₃PrPyBox.

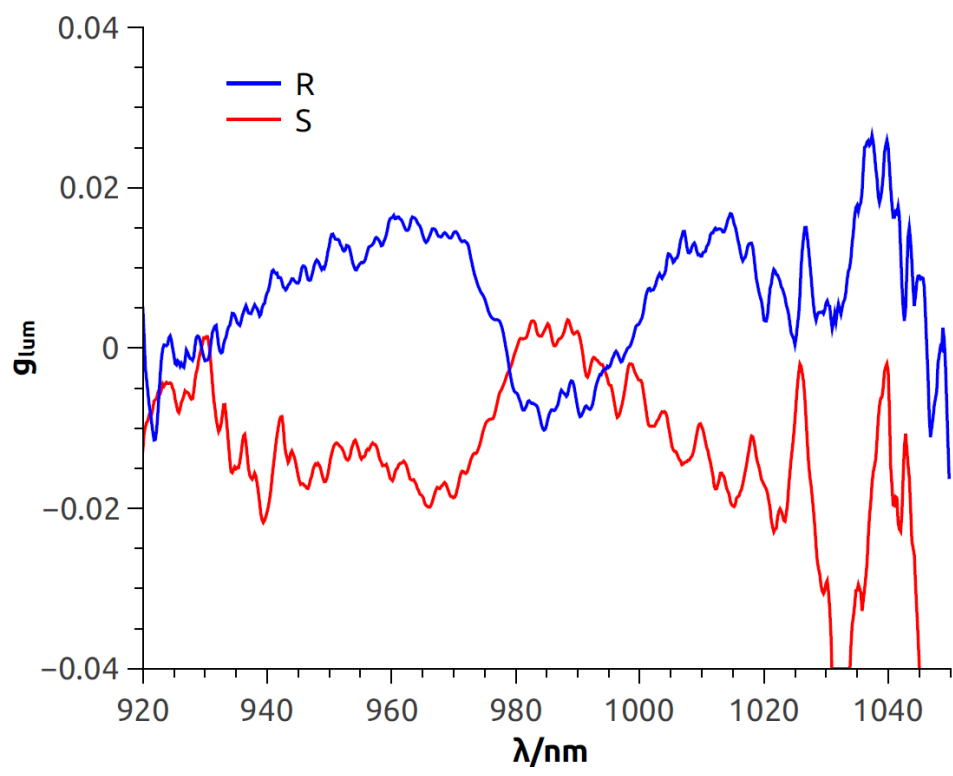


Figure S3. g_{lum} factor as a function of wavelength for the two enantiomers of $\text{Yb}(\text{TTA})_3\text{PhPyBox}$.

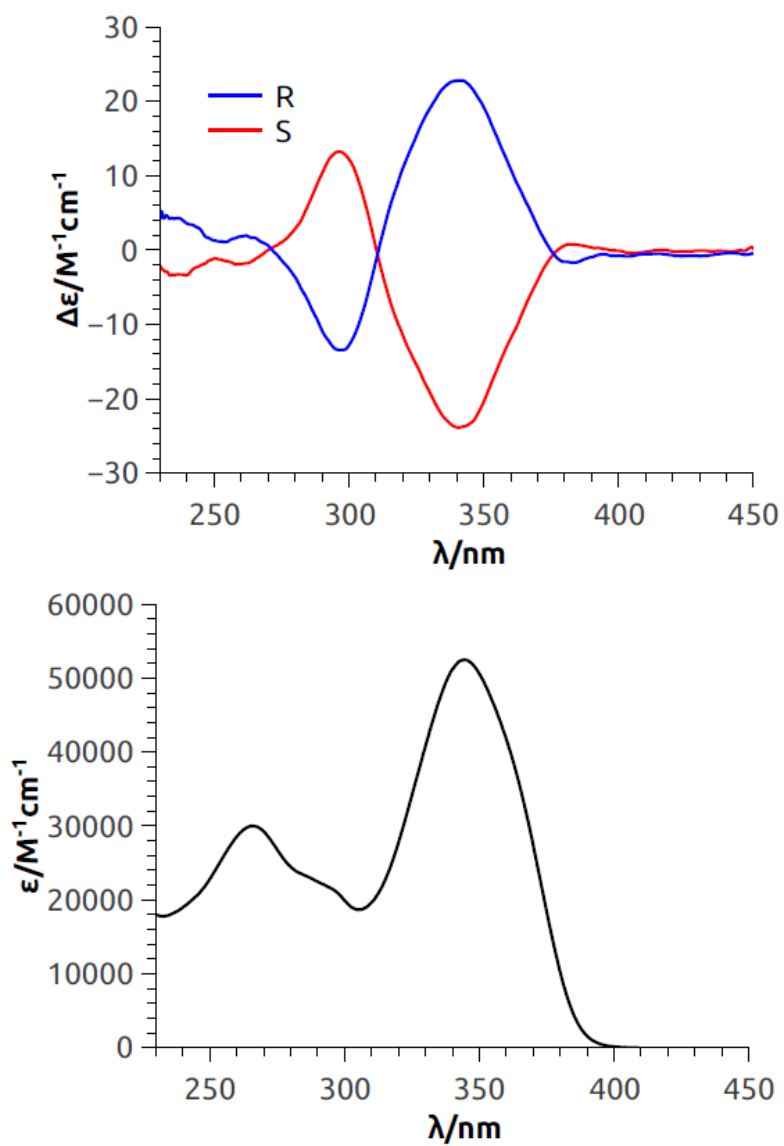


Figure S4. ECD (top) and absorption spectrum (bottom) for the two enantiomers of $Yb(TTA)_3PrPyBox$ in 0.8 mM CH_2Cl_2 solution (room temperature).

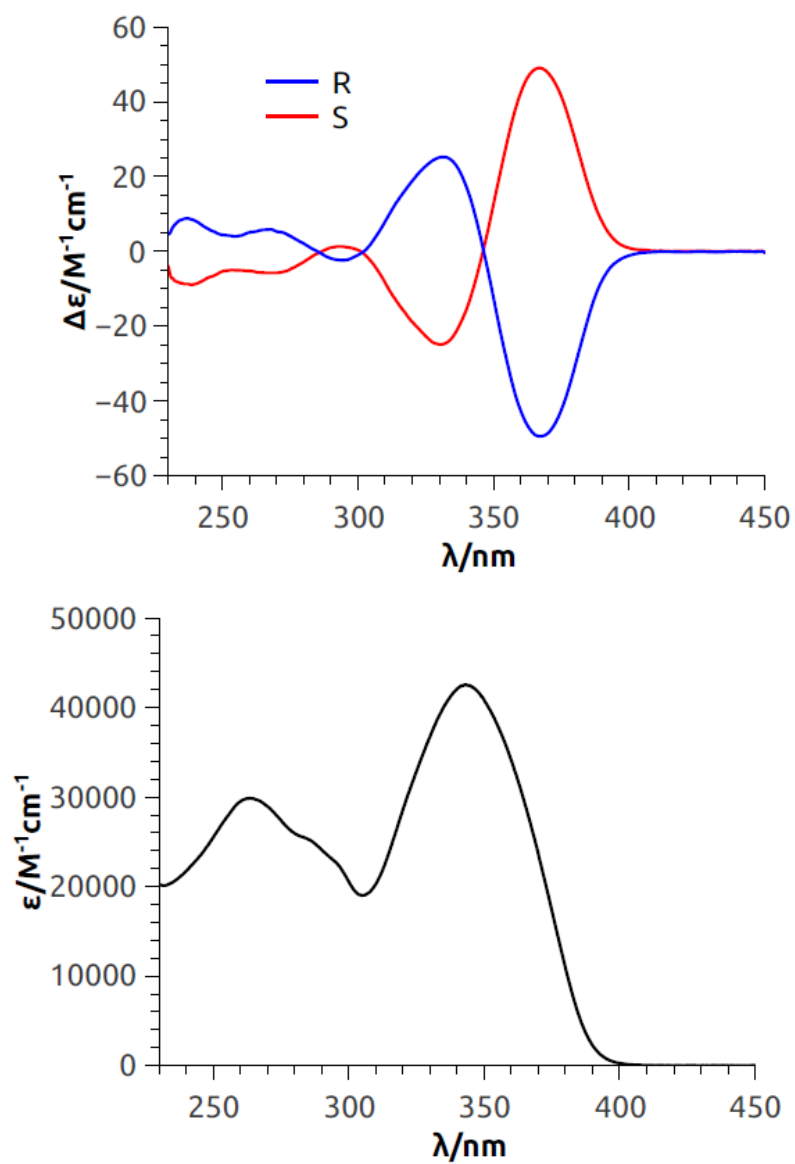


Figure S5. ECD (top) and absorption spectrum (bottom) for the two enantiomers of Yb(TTA)₃PhPyBox in 0.8 mM CH₂Cl₂ solution (room temperature).

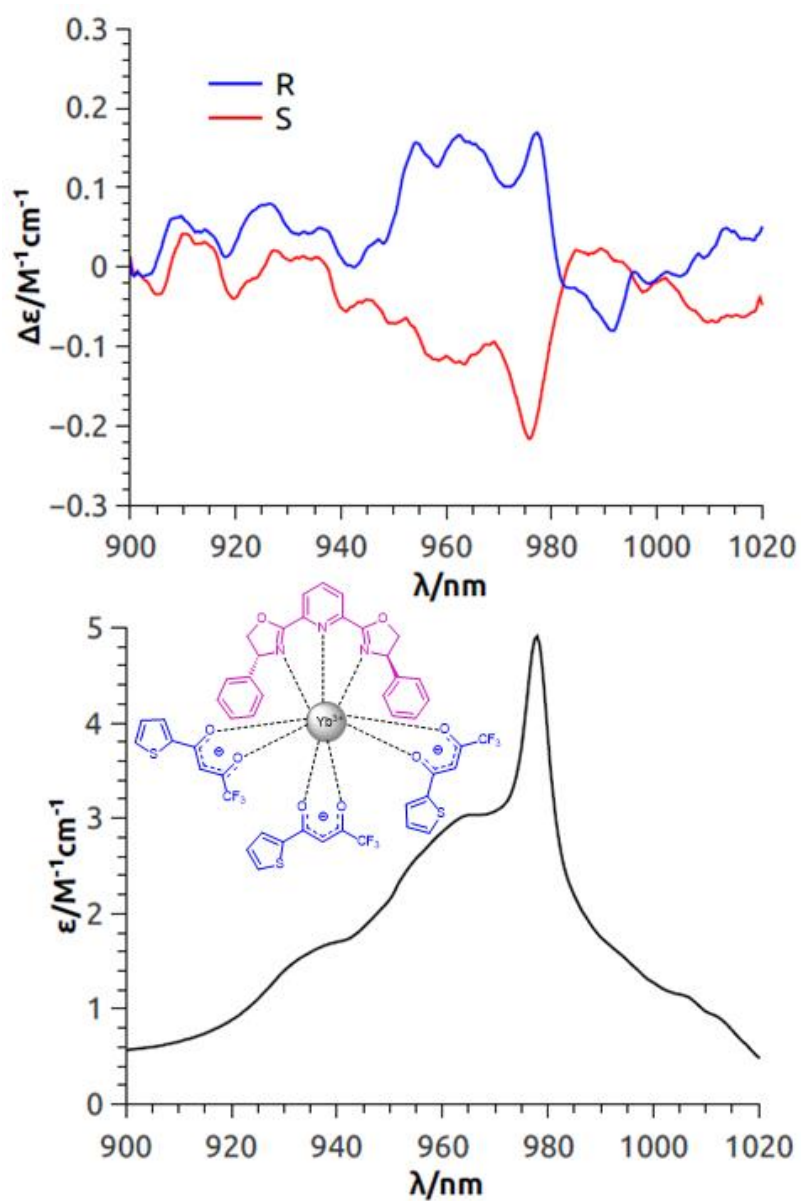


Figure S6. top: NIR-ECD spectra of both the enantiomers of $\text{Yb}(\text{TTA})_3\text{PhPybox}$; bottom: total NIR absorption. The spectra are measured in 7 mM CH_2Cl_2 solution (room temperature).

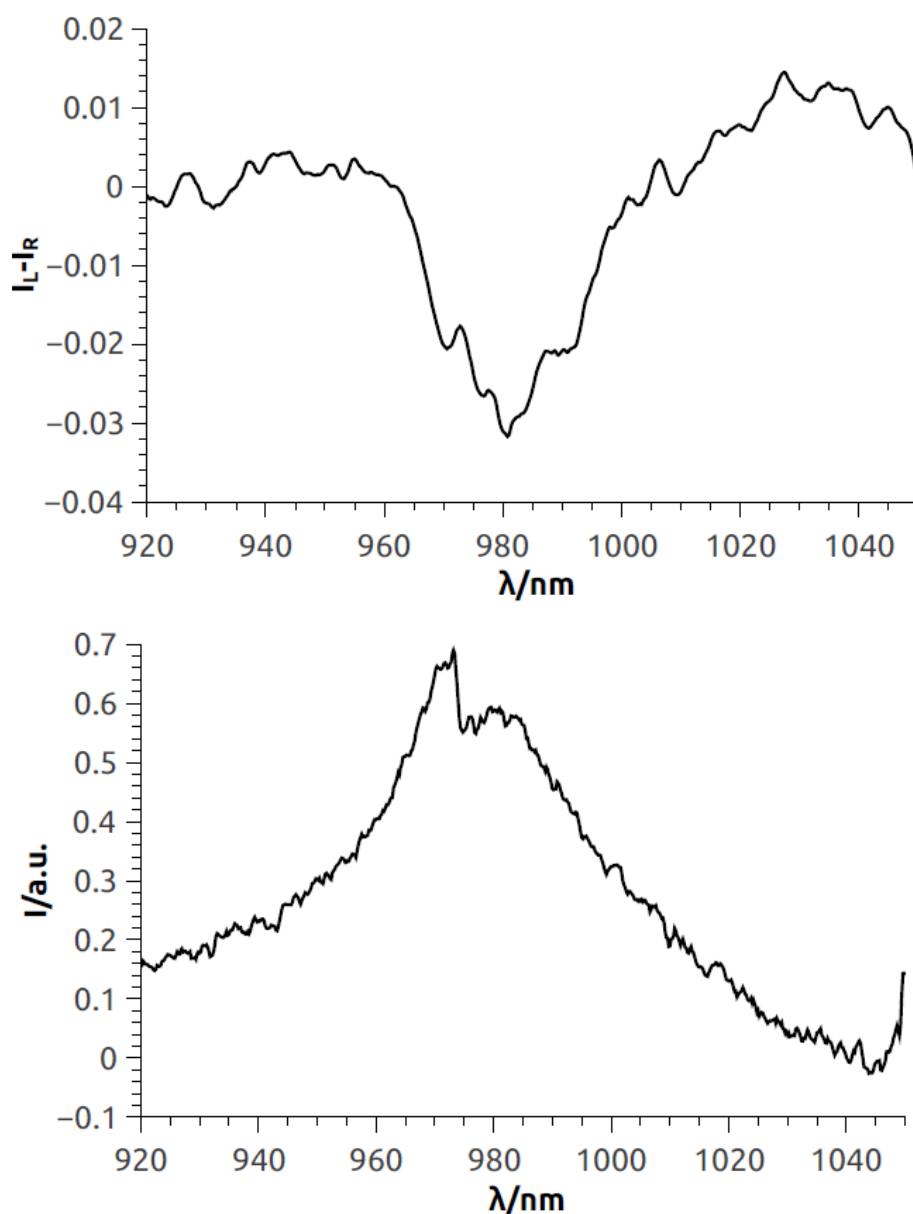


Figure S7. top: NIR-CPL spectra of $\text{Yb}(d\text{-facam})_3$; bottom: total NIR emission. The spectra are measured in 8 mM DMSO solution under 365 nm irradiation (room temperature).

References

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