Circularly polarized luminescence from Tb(III) interacting with chiral polyether macrocycles

Supporting Information

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1 General Information and Materials

1.1 CSP-HPLC

Enantiomers of ligand 1a were resolved by chiral stationary phase HPLC on an Agilent 1260 Infinity II apparatus (quaternary pump, auto sampler, column thermostat and diode array detector) using a semi-preparative CHIRALPAK® IG column (250 x 10 mm, 5 mic). Mixtures of HPLC grade CH₂Cl₂ and MeOH (99:1, with 0.1% diethanolamine as additive) were used as mobile phase.

1.2 Optical properties

Optical properties were recorded in analytical grade solvent (acetonitrile). UV-Vis absorption spectra were recorded on a JASCO V-650 spectrophotometer at 20 °C. Electronic circular dichroism (ECD) spectra were recorded on a Jasco J-815 spectropolarimeter at 20 °C in a 1 cm cuvette. Fluorescence spectra were measured using a Varian Cary 50 Eclipse spectrophotometer. All fluorescence spectra were corrected for the wavelength-dependent sensitivity of the detection. Fluorescence quantum yields \( \phi \) were measured in diluted solutions (at least 5 different concentrations for each sample) with an optical density lower than 0.1 using the following equation:

\[
\frac{\Phi_x}{\Phi_r} = \frac{A(R(\lambda))}{A_x(\lambda)} \left( \frac{n_x^2}{n_r^2} \right) \left( \frac{D_x}{D_r} \right)
\]

where A is the absorbance at the excitation wavelength (\( \lambda \)), n the refractive index and D the integrated intensity. “r” and “x” stand for reference and sample respectively. The fluorescence quantum yields were measured in acetonitrile relative to 9,10-diphenylnanthracene (\( \phi = 93\% \) in cyclohexane). Excitation of reference and sample was performed at the same wavelength.

Circularly polarized luminescence (CPL) spectra were recorded with the home-made spectrofluoropolarimeter previously described. The samples were excited with a 254 nm fluorescent mercury lamp, using a 90° geometry between excitation and detection.

Ba(ClO₄)₂ and Tb(OTf)₃ salts used for titration experiments were purchased from commercial sources and used without purification.

Lifetimes were determined using the phosphorescence mode of a Fluorolog 3 spectrophotometer (Horiba Jobin Yvon) in which the lamp of the instrument is flashed. Excitation was performed at 305 nm (1 nm slit) and detection with a visible photomultiplier.
tube (220-850 nm, R928P, Hamamatsu) at 545 nm (3 nm slit) at 545 nm, with an initial time gate of 50 μs.

1.3 $^1$H-NMR

The $^1$H NMR spectra were recorded in deuterated CDCl$_3$ using an Agilent Inova 600 ($^1$H: 600 MHz). $^1$H NMR chemical shifts are given in ppm relative to Me$_4$Si using solvent resonances as internal standards (CD$_3$CN δ = 1.94 ppm). Data were reported as follows: chemical shift (δ) in ppm, multiplicity (s = singulet, d = doublet, t = triplet, dd = doublet of doublet, q = quartet and m = multiplet), coupling constant (Hz) and integration.
2 Synthesis and characterization of organic compounds

2.1 Synthesis of unsaturated ester macrocycle 2

Unsaturated ester macrocycle 2 was synthetized according to previously reported procedure from the literature:\(^2\):

\[
\text{MeO}_2\text{C} \quad + \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \quad \xrightarrow{\text{Rh}_2(\text{TCPTCC})_4 (0.001 \text{ mol})} \quad \begin{array}{c}
\text{MeO}_2\text{C} \\
\text{O} \\
\text{O} \\
\text{CO}_2\text{Me}
\end{array} \]

60 °C, 4 days

3, 140 mmol as solvent (0.6 M)

2, 72%

2.2 Synthesis of ligands

Ligand 1a, 1b, 1c, 1d, S1, S2 and S3 were synthesized according to the previously reported procedure. See Figure S1:

Figure S1. Synthesis of ligands.
2.3 Resolution of ligand 1a<sup>6</sup>

Compound 1a were resolved by chiral stationary phase HPLC using a semi-preparative CHIRALPAK® IG column using a mixture of CH<sub>2</sub>Cl<sub>2</sub>-MeOH (99:1, with 0.1% diethanolamine as additive) as mobile phase at 20 °C. It is worth mentioning that it is necessary to remove traces of diethanolamine present in the separated compounds. The residue was thus dissolved in CH<sub>2</sub>Cl<sub>2</sub>, the organic phase was washed three times with H<sub>2</sub>O, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum to afford the pure products.

In the Figure S2 is shown the HPLC traces of ligand 1a on analytical CHIRALPAK® IG column (left, test run) and on semi preparative CHIRALPAK® IG column (right, run for resolution) with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (99:1, 0.1% diethanolamine) as mobile phase.

![HPLC traces of the racemic mixture on analytical CHIRALPAK® IG column (left) and semi preparative (right).](image)

**Figure S2.** HPLC traces of the racemic mixture on analytical CHIRALPAK® IG column (left) and semi preparative (right).

In the Figure S3 is shown the HPLC traces of ligand 1a on analytical CHIRALPAK® IG column of the separated enantiomers: 1<sup>st</sup> eluted enantiomer on the left and 2<sup>nd</sup> eluted enantiomer on the right with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (99:1, 0.1% diethanolamine) as mobile phase.
Figure S3. HPLC traces of the separated enantiomers. Left: 1st eluted enantiomer. Right: 2nd eluted enantiomer.

2.4 Key chirooptical properties of ligand 1a and complexes

**ECD description** for 1st eluted enantiomer of 1a in acetonitrile, \(\lambda/\text{nm} (\Delta\varepsilon/M\cdot\text{cm}^{-1})\): 279 (−2.4), 240 (+1.0).

**ECD description** for 1st eluted enantiomer of 1a complexed to Tb(III) in acetonitrile, \(\lambda/\text{nm} (\Delta\varepsilon/M\cdot\text{cm}^{-1})\): 274 (+7.7), 226 (−20). *See section 5 for further precision.*

**ECD description** for 1st eluted enantiomer of 1a complexed to Ba(II) in acetonitrile, \(\lambda/\text{nm} (\Delta\varepsilon/M\cdot\text{cm}^{-1})\): 274 (+4.4), 236 (−28.1). *See section 5 for further precision.*
3 Qualitative test of potential ligands

For the qualitative test, three solutions in three different vials (1 mL) were prepared and their emission was compared under UV irradiation (366 nm excitation wavelength). In the first one (reference 1), only the macrocycle of interest (<1 mg) is dissolved in acetonitrile. In the second one (reference 2), only terbium triflate (tip of a spatula) was dissolved in acetonitrile. In the third one, a mixture of the macrocycle of interest (<1 mg) and terbium triflate (tip of a spatula, excess) were dissolved in acetonitrile. In the reference 1 (1st vial), only the fluorescence of the macrocycle can be observed when visible. In the reference 2, no emission of the terbium salt was observed at this wavelength, but for the third vial (macrocycle/Tb mixture) resulted in the characteristic green terbium emission (see below). Combination of ligand 1a and terbium presents the most efficient luminescence and were selected for this study.

Figure S4. Ligand tested with terbium(III) and qualitative results of the mixture (picture under 366 nm irradiation).
4 Absorbance and fluorescence spectra and titrations

4.1 Procedure

In a typical experiment, UV-Vis absorbance and fluorescence spectra of a solution of interest compound (ca. 0.5·10^{-6} M) in acetonitrile were recorded in a 1 cm cell. For the complexation experiments, an excess of Tb(OTf)₃ (or Ba(ClO₄)₂) or an aliquot of a Tb(OTf)₃ (or Ba(ClO₄)₂) solution in acetonitrile (ca. 2·10^{-3} M) was added to the solution and the UV-Vis absorbance and fluorescence spectra were recorded again.

4.2 Ligand 1a and Tb(III)

Figure S5. Absorbance (red and blue lines) and fluorescence (pink and green lines) spectra of ligand 1a without (red and pink lines) or with 3.0 equivalents of Tb(III) (blue and green lines).
4.3 Titration of ligand 1a with Tb(III)

In a typical experiment, a known aliquot of a Tb(OTf)$_3$ solution in acetonitrile (ca. 2·10$^{-3}$ M) was added to a solution of the ligand (ca. 0.5·10$^{-6}$ M) in acetonitrile. Spectra were recorded from 0 equivalent of Tb(III) to 4.0 equivalents.

**Figure S6.** Titrations spectra in absorbance of ligand 1a with Tb(III): 0 to 4.0 equivalents. Left: absorbance spectra. Right: evolution of absorbance as function of the equivalents added at different relevant wavelength.

**Figure S7.** Titrations spectra in emission of ligand 1a with Tb(III): 0 to 4.0 equivalents. Left: normalized fluorescence spectra. Right: evolution of fluorescence as function of the equivalents added at different relevant wavelength.
4.4 Titration of ligand 1a with Ba(II)

In a typical experiment, a known aliquot of a Ba(ClO$_4$)$_2$ solution in acetonitrile (ca. 4·10$^{-3}$ M) was added to a solution of the ligand (ca. 0.5·10$^{-6}$ M) in acetonitrile. Spectra were recorded from 0 equivalent of Ba(II) to 4.0 equivalents.

![Figure S8](image)

**Figure S8.** Titrations spectra in absorbance of ligand 1a with Ba(II): 0 to 4.0 equivalents. Left: absorbance spectra. Right: evolution of absorbance as function of the equivalents added at 274 nm.

4.5 Titration of ligand 1b with Tb(III)

![Figure S9](image)

**Figure S9.** Titrations spectra of ligand 1b with Tb(III): 0 to 4.0 equivalents. Left: absorbance spectra. Right: normalized fluorescence spectra.
4.6 Titration of ligand 1c with Tb(III)

![Image of titration spectra for ligand 1c with Tb(III)]

Figure S10. Titrations spectra of ligand 1c with Tb(III): 0 to 5.0 equivalents. Left: absorbance spectra. Right: normalized fluorescence spectra.

4.7 Titration of ligand 1d with Tb(III)

![Image of titration spectra for ligand 1d with Tb(III)]

Figure S11. Titrations spectra of ligand 1d with Tb(III): 0 to 4.0 equivalents. Left: absorbance spectra. Right: normalized fluorescence spectra.
5 ECD and CPL spectra

5.1 Procedure

For **ECD**:

In a typical experiment, the ECD spectrum of a solution of enantiopure ligand (ca. 0.5·10⁻⁵ M) in acetonitrile was recorded in a 1 cm cell at 20 °C. For the complexation experiments, 3.0 equivalents of Tb(OTf)₃ or Ba(ClO₄)₂ (ca. 2·10⁻³ M stock solutions in acetonitrile) were added to the ligand solution and the ECD spectrum was recorded again.

The change in intensity in ECD is quantified using δΔε, which is the difference in normalized ECD intensity in presence and absence of tested metal ions:

$$\delta\Delta \varepsilon = |\Delta \varepsilon(\text{cation}) - \Delta \varepsilon(\text{without})|$$  \hspace{1cm} (S1)

For **CPL**:

The CPL spectrum of a solution containing the enantiopure ligand (ca. 2·10⁻⁵ M) in acetonitrile and 3.0 equivalents of Tb(OTf)₃ (from a ca. 10⁻³ M stock solution in acetonitrile) was recorded in a 1 cm cell.

The circular polarization degree of the emission is quantifying using the luminescence dissymmetry factor \(g_{\text{lum}}\) defined by equation S2 where \(I_L\) and \(I_R\) correspond to left and right circularly polarized component of the emission respectively:

$$g_{\text{lum}} = 2 \frac{I_L - I_R}{I_L + I_R}$$  \hspace{1cm} (S2)
5.2 Ligand 1a and Tb(III) - ECD

Figure S12. ECD (top) and absorbance (bottom) spectra ligand 1a (red) and [1a·Tb]$^{3+}$ complex (green). En1 and En2 corresponds to the 1st and 2nd eluted enantiomers on CHIRALPAK® IG column and a mixture of CH$_2$Cl$_2$-MeOH (99:1, 0.1% diethanolamine) as mobile phase.
5.3 Ligand 1a and Ba(II) - ECD

Figure S13. ECD (top) and absorbance (bottom) spectra ligand 1a (red) and [1a·Ba]^2+ complex (blue). En1 and En2 corresponds to the 1st and 2nd eluted enantiomers on CHIRALPAK® IG column and a mixture of CH₂Cl₂-MeOH (99:1, 0.1% diethanolamine) as mobile phase.
5.4 Ligand 1a, Tb(III) and Ba(II) - $g_{abs}$

*Figure S14*. $g_{abs}$ spectra of ligand 1a (red), [1a·Tb]$^{3+}$ (green) and [1a·Ba]$^{2+}$ (blue) complexes. En1 and En2 corresponds to the 1st and 2nd eluted enantiomers on CHIRALPAK® IG column and a mixture of CH$_3$Cl$_2$-MeOH (99:1, 0.1% diethanolamine) as mobile phase.
6 \textsuperscript{1}H-NMR titrations

6.1 Procedure

To an NMR tube, LuCl\textsubscript{3} was added (0, 0.5, 1 and 2 equivalents) as a solid. Just before the measurement 0.5 mL of a 15 mM solution of 1a was added and the tube was shaken, and the \textsuperscript{1}H spectrum was recorded.

6.2 \textsuperscript{1}H-NMR spectra

\textbf{Figure S15,} \textsuperscript{1}H NMR titration of 1a with LuCl\textsubscript{3} (0, 0.5, 1, 2 equivalents) c = 15 mM, 600 MHz
7 Solid state structure and crystallographic data

7.1 Procedure

About 5 mg of 1a were dissolved in 2 mL of MeCN and a large excess of La(ClO$_4$)$_3$ was added. The solution was filtered and the solvent allowed to slowly evaporate at room temperature over the course of one week.

7.2 Data complex [1e·La·(H$_2$O)$_2$](ClO$_4$)$_3$

![Figure S16. Crystal data and structure refinement for [1e·La·(H$_2$O)$_2$](ClO$_4$)$_3$](image-url)
CCDC number 2189306
Empirical formula C56 H58 Cl3 La N6 O22
Formula weight 1412.34
Temperature 120.00(11) K
Crystal system Monoclinic
Space group P21/c
Unit cell dimensions a = 23.5523(2) Å  α = 90°
  b = 11.12589(12) Å  β = 99.5672(10)°
  c = 23.3538(2) Å  γ = 90°
Volume 6034.52(11) Å³
Z 4
Density (calculated) 1.555 g/cm³
F(000) 2880.0
Crystal size 0.591 × 0.136 × 0.036 mm³
2Θ range for data collection 7.614 to 149.28°
Index ranges -29 ≤ h ≤ 29, -13 ≤ k ≤ 13, -29 ≤ l ≤ 29
Reflections collected 19051
Independent reflections 19051 [Rint = ?, Rsigma = 0.0100]
Data/restraints/parameters 19051/3/809
Goodness-of-fit on F² 1.034
Final R indexes [I>=2σ (I)] R1 = 0.0439, wR2 = 0.1169
Final R indexes [all data]  R 1 = 0.0465, wR2 = 0.1192
Largest diff. peak/hole 1.19/-1.26 e Å⁻³
8 Luminescence lifetime measurement

8.1 Procedure

A $10^{-5}$ M solution of 1a (S1) and a $10^{-3}$ M solution of Tb(OTf)$_3$ (S2) both in MeCN or MeCN-d3 were prepared. The samples were prepared by mixing the 2 solutions directly in a cuvette.

The lifetime of complex 1a in acetonitrile was determined using the phosphorescence mode of a Fluorolog 3 spectrophotometer (Horiba Jobin Yvon) in which the lamp of the instrument is flashed. Excitation was performed at 305 nm (1 nm slit) and detection with a visible photomultiplier tube (220-850 nm, R928P, Hamamatsu) at 545 nm (3 nm slit) at 545 nm, with an initial time gate of 50 $\mu$s.

8.2 Time trace

![Graph](image)

Figure S17. Luminescence decay of [1a·Tb][ClO$_4$]$_3$ at 545 nm upon 305 nm excitation in MeCN and MeCN-d3 solutions. Solid lines are exponential fits to the data points (open circles).
9 References

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