Electronic Supplementary Information for

A redox active switch for lanthanide luminescence in phenolate complexes

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1. Experimental part

1.1 Materials and methods

All chemicals were of reagent grade and were used without purification. Lanthanide triflate salts were purchased from Aldrich and titrated for metal content before use, in the presence of EDTA and xylene orange. High resolution mass spectra were recorded on a Waters Xevo G2-S QToF apparatus. The UV/Vis spectra were recorded on a Cary Varian 50 spectrophotometer equipped with a Hellma immersion probe (1.000 cm path length). The temperature in the cell was controlled using a Lauda M3 circulating bath.

Luminescence data of the lanthanide complexes were recorded using a modular Fluorolog FL3-22 spectrometer Horiba-Jobin Yvon-Spex equipped with a double grating excitation monochromator and an iHR320 imaging spectrometer. Hamamatsu R928P and Hamamatsu R5509 photomultipliers were used for visible and NIR measurements, respectively. All spectra were corrected for detection and optical spectral response (instrumental functions) of the spectrofluorimeters. Quartz capillaries 4 mm in diameter were used. For the acquisition of the excitation and emission spectra in the NIR, a long pass coloured filter was always used at 870 nm to block the signal of the 2nd harmonics. Phosphorescence lifetimes of the lanthanides were measured in time-resolved mode and are the averages of three independent measurements that were taken by monitoring the decay at the maxima of the emission spectra. The signals were analyzed with the OriginLab Origin Pro software. Lifetimes of singlet states were obtained using nanoled sources S-390 (FWHM 15 nm) from Horiba Scientific coupled to a Jobin Yvon NL-C2 Pulse Diode controller and a DH-HT TCSPC controller including a SpectraLED output. The output signal of the photomultiplier was fed to a PC and controlled and analyzed with the Data Station (v2.7) and Decay Analysis (v6.8) software from Horiba Scientific. Lifetimes are averages of 3 independent determinations with a calculated Chi-square < 2.

X-band EPR spectra were recorded on a Bruker EMX Plus spectrometer equipped with an Oxford helium cryostat and a dual mode cavity. Cyclic voltammetry curves as well as differential pulse voltammetry curves were recorded using a CHI 620 potentiostat. The measurements were performed in ca. 0.5 mM CH$_3$CN solutions containing 0.1 M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte for L-Tb. Complex L-Yb was not completely soluble in this medium, leading us to investigate its electrochemical properties in a CH$_3$CN:CH$_2$Cl$_2$ (4:1) mixture (+ 0.1 M TBAP). Experiments were performed in a standard three-electrode cell under argon atmosphere. A glassy carbon disc electrode (3 mm diameter), which was polished with 1 mm diamond paste, was used as the working electrode. The auxiliary electrode is a platinum wire, while an Ag/AgNO$_3$ 0.01 M electrode was used as reference. The electrolysis was carried out at 233 K on a PAR 273 instrument, by using a carbon foam working electrode.

1.2 Synthesis

H$_2$L was prepared according to literature procedures.

L-Tb. The ligand LH$_2$ (108.5 mg, 0.160 mmol) was dissolved in dichloromethane (1 mL) and then acetonitrile was added (8 mL). The salt Tb(NO$_3$)$_3$·2H$_2$O (79.9 mg, 0.160 mmol) was dissolved in acetonitrile (4 mL) and then added slowly to the solution of H$_2$L. After 10 min stirring NEt$_3$ (44.8 µl, 0.33 mmol) was added. Slow evaporation of the solvent affords pale yellow single crystals of 1-Tb,
0.65 CH$_3$CN. Yield: 0.035 g (53 %). HR-MS (Q-TOF): m/z calcd for C$_{44}$H$_{60}$N$_4$O$_2$Tb, 835.3970 [M-NO$_3$]$^+$; Found: 835.3968.

**L-Yb.** The complex **L-Yb** was prepared in a similar manner than **L-Tb.** Yield: 0.028 g (42 %). HR-MS (Q-TOF): m/z calcd for C$_{44}$H$_{60}$N$_5$O$_4$Yb, 913.4069 [M]$^+$, Found: 913.4079.

### 1.3 Crystal structure analysis

The collected reflections were corrected for absorption (SADABS)$[^3]$ and solved by direct methods and refined with Olex software.$[^4]$ All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generated in idealized positions, riding on the carrier atoms, with isotropic thermal parameters. CCDC-1449351 (**L-Yb**) and CCDC-1483265 (**L-Tb**) contain the supplementary crystallographic data for this paper; these data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.
2. Figures

**Figure S1.** Differential Pulse Voltammetry curves of **L-Tb** (blue) and **L-Yb** (black). Pulse Amp. 0.05 V, Pulse width 0.05 V. Ref: Fc⁺/Fc, T = 298 K. The conditions are **L-Tb**: 0.54 mM in CH₃CN + 0.1 M TBAP, **L-Yb**: 0.49 mM in CH₃CN:CH₂Cl₂ 8:2 + 0.1 M TBAP (insoluble in CH₃CN + 0.1 M TBAP).

**Figure S2.** Rotating Disc Electrode Voltammetry of **L-Tb** (blue) and **L-Yb** (black). v = 500 rpm, scan rate: 0.01 V/s. Ref: Fc⁺/Fc, T = 298 K. The conditions are **L-Tb**: 0.54 mM in CH₃CN + 0.1 M TBAP, **L-Yb**: 0.49 mM in CH₃CN:CH₂Cl₂ 8:2 + 0.1 M TBAP (insoluble in CH₃CN + 0.1 M TBAP).
Figure S3. Absorption spectra of L-Tb in CH$_3$CN:CH$_2$Cl$_2$ (4:1) (9.4 x 10$^{-5}$ M) upon the addition of (NH$_4$)$_2$Ce(NO$_3$)$_6$ (0.014 M) in CH$_3$CN. $T = 233$ K, $l = 1.000$ cm. The insert represents the absorbance at 412 nm as a function of the ratio [L-Tb]/[CAN]

Figure S4. Absorption spectra of L-Yb in CH$_3$CN:CH$_2$Cl$_2$ (4:1) (1 x 10$^{-4}$ M) upon the addition of (NH$_4$)$_2$Ce(NO$_3$)$_6$ (CAN) (0.014 M) in CH$_3$CN. $T = 233$ K, $l = 1.000$ cm. The insert represents the absorbance at 412 nm as a function of the ratio [L-Yb]/[CAN]
Figure S5. Absorption spectrum of L-Tb \( (8 \times 10^{-5} \text{ M}) \) in CH\(_3\)CN:CH\(_2\)Cl\(_2\) (4:1) after exhaustive electrolysis at a fixed potential of 0.6 V (identical spectra were obtained in CH\(_3\)CN).

Figure S6. Absorption spectrum of L-Yb \( (7 \times 10^{-5} \text{ M}) \) in CH\(_3\)CN:CH\(_2\)Cl\(_2\) (4:1) after exhaustive electrolysis at a fixed potential of 0.6 V.
Figure S7. Perpendicular mode X-Band EPR spectra of L-Tb: (black) before oxidation, (red) after two-electron electrochemical oxidation. Microwave freq. 9.63 GHz, power: 20 mW, Mod. Amp. 0.4 mT, Freq. 100 KHz. T = 8 K.

Figure S8. Parallel mode X-Band EPR spectra of L-Tb: (black) before oxidation, (red) after two-electron electrochemical oxidation. Microwave freq. 9.39 GHz, power: 2 mW, Mod. Amp. 0.7 mT, Freq. 100 KHz. T = 8 K. The star denotes a paramagnetic impurity present in the cavity.
Figure S9. Emission spectra of the free ligand LH$_2$, deprotonated ligand L$^2$- and its Ln$^{	ext{III}}$ complexes (Ln = Tb, Yb) at 298 K in acetonitrile. Fluorescence spectra (solid line) and phosphorescence spectra (dotted line).

Figure S10. Phosphorescence spectra of the free ligand LH$_2$, deprotonated ligand L$^2$- and its Ln$^{	ext{III}}$ complexes (Ln = Tb, Yb) at 77 K in acetonitrile in time resolved mode.
Figure S11. Emission and excitation spectra of the free ligand LH$_2$, deprotonated ligand L$^2$ and its Ln$^{	ext{III}}$ complexes (Ln = Tb, Yb) at 77 and 298K. The insert represents the excitation spectra of the Yb complexes.

Figure S12. X-Ray crystal structure of L-Tb. Only one position of the phenolates and amines, arbitrarily chosen, is depicted.
3. Table

**Table S1.** Lifetimes (ms) of the ligand and its Ln\(^{III}\) complexes measured at 298 and 77K with \(\lambda_{ex} = 280\) nm acetonitrile

<table>
<thead>
<tr>
<th>Compound</th>
<th>(77)K</th>
<th>(298)K</th>
<th>(\tau(\pi\pi^*)), (\lambda_{an}=430) nm ms</th>
<th>(\tau(\pi\pi^*)), (\lambda_{an}=311) nm ns</th>
<th>(\tau(5D_4), \lambda_{an}=545) nm ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH(_2)</td>
<td>18(1)</td>
<td>16(1)</td>
<td>3.1 (2)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>L(^2-)</td>
<td>77K</td>
<td>298K</td>
<td>508(23)</td>
<td>&lt; 0.5</td>
<td>1.51(2)</td>
</tr>
<tr>
<td>L-Tb</td>
<td>424(35)</td>
<td>301(30)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-Tb(^+)</td>
<td>77K</td>
<td>298K</td>
<td>2.15(10)</td>
<td>0.86(3)</td>
<td></td>
</tr>
<tr>
<td>L-Yb</td>
<td>185(53)</td>
<td>126(55)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-Yb(^+)</td>
<td>77K</td>
<td>298K</td>
<td>1.48(16)</td>
<td>[a]</td>
<td></td>
</tr>
<tr>
<td>L-Yb(^{2+})</td>
<td>77K</td>
<td>298K</td>
<td>1.49(32)</td>
<td>[a]</td>
<td></td>
</tr>
</tbody>
</table>

[a] very small signal ; [b] no residual signal
4. References


