Electronic supplementary information

Strong NIR Electrochemiluminescence from Lanthanide Ions Sensitized with a Carbon-Rich Ruthenium Chelate

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1. Synthetic procedures

All the lanthanide compounds used in this study were synthesized by the same procedure as those reported previously.^{1, 2}

2. Electrochemical characterization

Electrochemical studies were carried out under N_2 using a PGSTAT30 Autolab potentiostat (CH₂Cl₂, 0.2 M TBAPF₆). The working electrode, the pseudo-reference electrode and counter-electrode were a Pt disk (diameter: 2 mm), a Ag wire, and a platinum wire, respectively.

3. ECL and PL measurements

ECL spectra of all compounds with TPrA in CH_2Cl_2 were recorded using a Princeton Instruments Acton SpectraPro 2300i spectrometer. This photodetector is based on a silicon-based CCD spectrometer whose quantum efficiency vanishes drastically in the NIR. ECL intensity was recorded using a Hamamatsu photomultiplier tube R5070 (multialkali photocathode) with a Hamamatsu C9525 high voltage power supply. As for the spectrometer, its quantum efficiency vanishes drastically above 850 nm. The cell is built with a glass slide at the bottom in order to record the ECL signal. The optical fiber connected to the spectrometer was placed as close as possible to this glass slide in front of the working electrode.

PL spectra were recorded with a spectrometer equipped with an InGaAs dectector highly sensitive in the NIR range of interest.^{1,2}



4. Electrochemical, ECL and photochemical experiments

Figure S1. a) Voltammetric characterization of 0.5 mM **1Ru-Nd** (red line) or **3Ru** (black line) in a degassed CH_2Cl_2 solution with 0.2 M TBAPF₆ as supporting electrolyte. B) cyclic voltammetry of ferrocene recorded in the same conditions as **1Ru-Nd.** Scan rate: 0.05 V/s. A Pt disk and a Ag wire were used as the working electrode and pseudo-reference electrode, respectively.



Figure S2. Voltammetric characterization of 0.5 mM a) **1Ru-Yb** and b) **1Ru-Nd** in a degassed CH_2Cl_2 solution with 0.2 M TBAPF₆ as supporting electrolyte. Scan rate: 0.05 V/s. A Pt disk and a Ag wire were used as the working electrode and pseudo-reference electrode, respectively.



Figure S3. Voltammetric characterization of 0.5mM **2Yb** in a degassed CH_2Cl_2 solution with 0.2 M TBAPF₆ as supporting electrolyte. Scan rate: 0.05 V/s. A Pt disk and a Ag wire were used as the working electrode and pseudo-reference electrode, respectively.



Figure S4. Variations of the ECL spectra of 1Ru-Yb as a function of the imposed potential at very anodic values. ECL spectra were recorded in degassed CH₂Cl₂ solution containing 0.5 mM 1Ru-Yb, 100 mM TPrA and 0.2 M TBAPF₆.



Figure S5. a) ECL spectra of 1Ru-Yb recorded without (orange line) and with 0.1 M TPrA (black line) at 1.6 V. b) Comparison of the ECL spectra of 1Ru-Yb (black line), 2Yb (green line) and 3Ru (blue line) recorded at an imposed potential of 1.6 V in presence of 0.1 M TPA in the same experimental conditions. c) ECL emission spectrum of 3Ru. ECL spectra were recorded in degassed CH_2Cl_2 solution containing 0.5 mM complexes, 100 mM TPA and 0.2 M TBAPF₆ at an imposed potential of 1.6 V.



Figure S6. Electronic absorption spectrum of complex **1Ru-Yb** measured in dichloromethane (0.5 mM, optical path 0.1 cm), containing 0.1 M TPrA and 0.2 M TBAPF₆ and evidencing partial decoordination. The experimental data (orange dots) are well reproduced ((a)+(b)+(c)) assuming that one third of the complex is dissociated and summing the contribution of **3Ru** ((a), weight 33 %), **2Yb** ((c), weight 33 %) and **1Ru-Yb** ((b), weight 66 %) measured in dichloromethane (0.5 mM).



Figure S7. a) Evolution of the ECL spectra of 1Ru-Nd as a function of the imposed potential. Same experimental conditions as in Figure 2. b) Cyclic voltammetry of a degassed CH_2Cl_2 solution containing 0.5 mM 1Ru-Nd, 0.1 M TPrA and 0.2 M TBAPF₆. Scan rate: 0.1 V/s.

5. References

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