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Electronic Supporting Information

Chiroptical Detection of a Model Ruthenium Dye in Water by Circularly Polarized-Electrochemiluminescence

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Synthesis and characterizations

[Δ-Ru(dmbpy)$_3$][Δ-TRISPHAT]$_2$ and [Λ-Ru(dmbpy)$_3$][Δ-TRISPHAT]$_2$ were obtained according to literature procedures.[1]

The isolation of [Δ-Ru(bpy)$_3$]Cl$_2$ was performed in a two-step sequence:

First, following a recently reported protocol,[2] [Δ-Ru(dmbpy)$_3$][Δ-TRISPHAT]$_2$ (176 mg, 0.080 mmol, 1 equiv) and 60 ml of a 1:1 mixture water and CH_2Cl_2 were mixed together. Then, [^{n}Hex$_4$N]Br (70 mg, 0.16 mmol, 2 equiv) was added. After a few minutes, the migration of the orange Ru complex from the organic to the aqueous layer was observed. The layers were separated and the organic fraction was washed with water. To the collected aqueous layers, 20 ml of a saturated solution of KPF_6 was added to induce the precipitation of the complex. After Büchner filtration and washing the solid residue with water, [Δ-Ru(dmbpy)$_3$](PF$_6$)$_2$ (60 mg, 0.064 mmol) was afforded in 80% yield.

Second, salt [Δ-Ru(dmbpy)$_3$](PF$_6$)$_2$ (108 mg, 0.11 mmol) was dissolved in a minimum amount of acetone (1 ml). Then a saturated solution of [^{n}Bu$_4$N]Cl in acetone was added dropwise until precipitation of the desired compound[Δ-Ru(dmbpy)$_3$]Cl$_2$. Filtration afforded 82 mg of [Δ-Ru(dmbpy)$_3$]Cl$_2$ (0.11 mmol, 99% yield).

The isolation of [Λ-Ru(bpy)$_3$]Cl$_2$ was performed according the above procedure and yielded the [Λ-Ru(dmbpy)$_3$](PF$_6$)$_2$ and [Λ-Ru(dmbpy)$_3$]Cl$_2$ salts in 85% and 89% yields, respectively.

Enantiomerically pure [Ru(dmbpy)$_3$]Cl$_2$ salts have been previously characterized. [3]

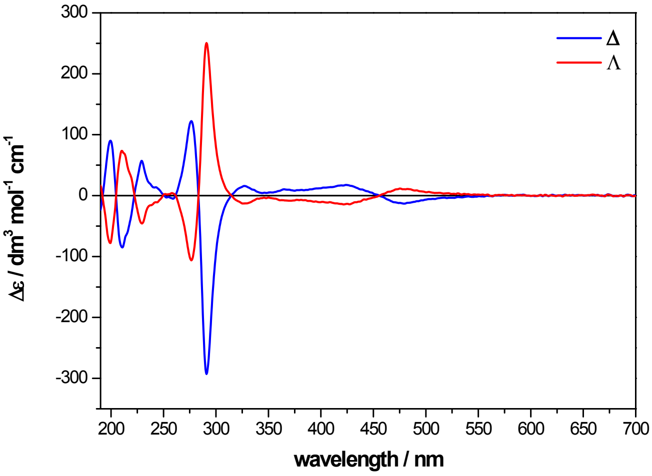

Figure S1. Electronic circular dichroism spectra of Δ- and Λ-[Ru(dmbpy)$_3$]Cl$_2$

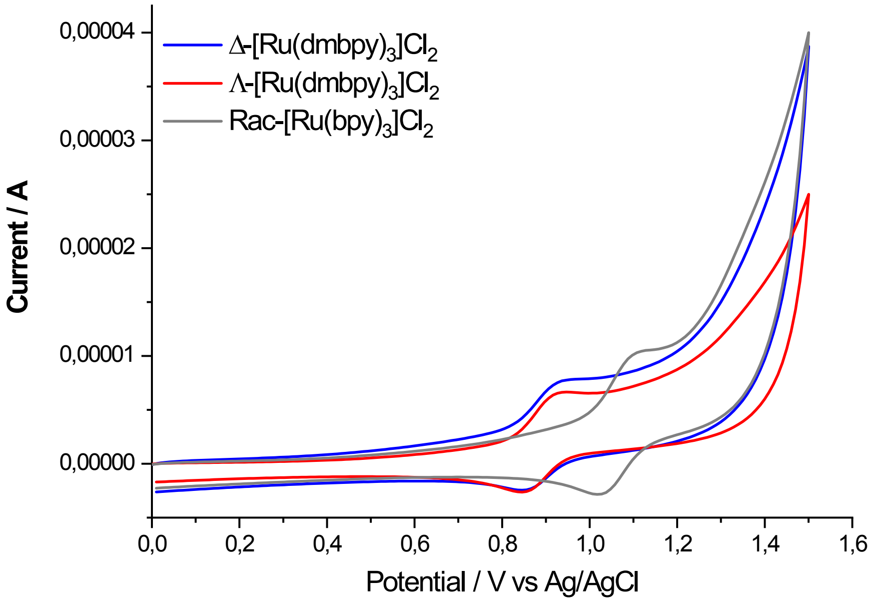

Figure S2. Cyclic voltammograms of 0.5 mM Δ-$[Ru(dmbpy)_3]Cl_2$, Λ-$[Ru(dmbpy)_3]Cl_2$ and of the racemic $[Ru(bpy)_3]Cl_2$ on glassy carbon working electrode in PBS. Scan rate 0.1 Vs^{-1}.

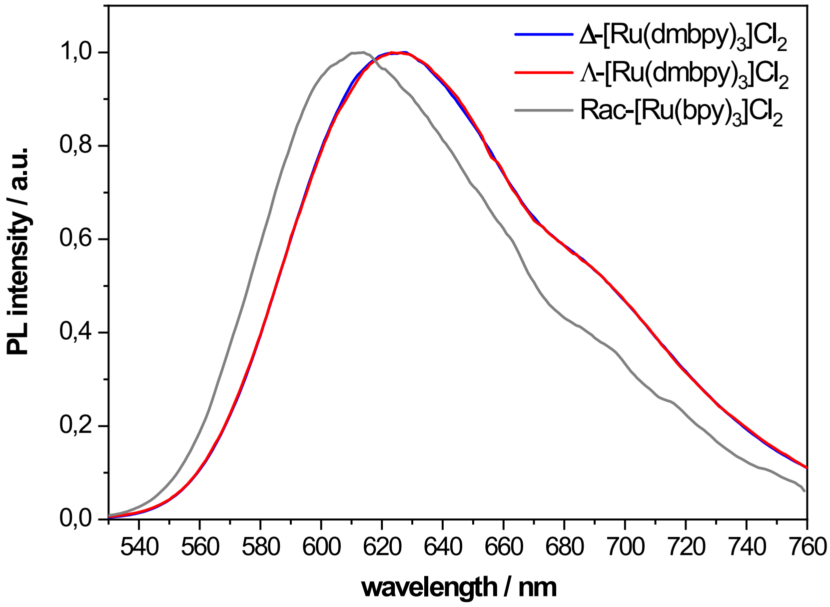

Figure S3. PL spectra of the two enantiomers Δ- and Λ-$[Ru(dmbpy)_3]Cl_2$ and of the racemic $[Ru(bpy)_3]Cl_2$ at a 10^{-5} M concentration in PBS. λ_{exc} = 365 nm.

CP-PL/ECL measurements

CP-PL/ECL measurements were carried out with a home-made spectrofluoropolarimeter.[4] CP-PL spectra were recorded under 365 nm 90° excitation. The following parameters were used: scan-speed 1 nm/sec, integration time 4 sec, slit width 4 mm (~10 nm), PMT-voltage 500 V.

Prior to voltammetric, ECL and CP-ECL measurements, the glassy carbon (GC) working electrodes (diameter: 3 mm) were polished with alumina slurry of different size, rinsed thoroughly with Milli-Q water between each polishing step, and sonicated in water and ethanol respectively, followed by a final rinse with acetonitrile and dried with N_2 stream. Voltammetric and ECL experiments were performed with a PGSTAT30 Autolab potentiostat connected to a conventional three-electrode cell, consisting in a Ag/AgCL/KCl 3M reference electrode, a platinum-wire auxiliary electrode, and a glassy carbon disk (GC) working electrode.

ECL spectra were recorded with a Princeton Instruments Acton SpectraPro 2300i after the CCD camera was cooled to -110°C with liquid N_2. The optical fiber connected to the device was located at a defined distance of few millimeters from the GC working electrode.

CP-ECL experiments were performed with a µ-Autolab potentiostat in a transparent home-made spectroelectrochemical cell. We used a three-electrode setup, consisting in a Ag pseudo-reference electrode, a platinum-wire auxiliary electrode and a GC working electrode. Since it was not possible to introduce a Ag/AgCl/KCl 3M reference electrode in the spectroelectrochemical cell, we had to use a Ag wire as the pseudo-reference electrode for the CP-ECL experiments. During the measurements, the following instrumental parameters were employed: integration time 4 sec, slit width 4 mm (~10 nm), PMT-voltage 800 V.

References

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