# **SUPPORTING INFORMATION**

# Understanding the ECL interaction of luminol and Ru(bpy)<sub>3</sub><sup>2+</sup> luminophores by spectroelectrochemiluminescence

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#### **Materials and Methods**

#### a. Reagents

Luminol sodium salt (Sigma-Aldrich), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (Rubpy<sub>3</sub>Cl<sub>2</sub>, Sigma-Aldrich), hydrogen peroxide solution (50 wt. %, Sigma-Aldrich), tripropylamine (TPrA, Sigma-Aldrich) and o-phosphoric acid (85%, Merck) were used as received. 0.1 M phosphate buffer solution pH 8 was prepared adjusting pH with sodium hydroxide (NaOH, Sigma-Aldrich) solution. All chemicals were analytical grade. Aqueous solutions were prepared using ultrapure water (Direct-Q<sup>TM</sup> 5 system, Millipore).

#### **b.** Instrumentation

Screen-printed carbon electrodes (DRP-110, Metrohm DropSens) were used to perform all experiments. Electrodic system consists of a flat ceramic card with a circular carbon working electrode (4 mm diameter), a carbon auxiliary electrode and a silver pseudo-reference electrode. ECL measurements were performed at room temperature using DRP-SpectroECL instrument (Metrohm DropSens) with a microspectrometer cell as detector. Additionally, DRP-SpectroECL was also used with a photodiode detector cell (DRP-ECLPHOTODIODCELL, Metrohm DropSens). Data acquisition as well as data treatment was done with DropView SPELEC software.

#### c. Methods

All ECL experiments were carried out at room temperature by cyclic voltammetry, scanning the potential from 0.00 V to  $\pm 1.50$  V and back to 0.00 V at 0.05 V.s<sup>-1</sup> in phosphate buffer solution (pH 8). Spectra were recorded using the microspectrometer cell and integration time of 1000 ms. ECL signals recorded with photodiode cell were obtained without amplification factor (x1).





**Figure S1.** (a) Electrochemical response and ECL signals obtained with (b) photodiode cell. (c) Evolution of emission band at 420 nm with potential. These signals have been obtained for a solution containing 1 mM of luminol and 50 mM of hydrogen peroxide in 0.1 M phosphate buffer pH 8.0.



**Figure S2.** (a) Electrochemical response obtained with 1 mM  $Ru(bpy)_{3}^{2+}$  and 50 mM TPrA in 0.1 M phosphate buffer pH 8 solution. (b) ECL signal obtained with 0.1 mM  $Ru(bpy)_{3}^{2+}$  and 50 mM TPrA in 0.1 M phosphate buffer pH 8 solution using the photodiode cell. (c) Evolution of emission band at 620 nm with potential obtained under the same experimental conditions than (a) using the microspectrometer cell.

## Figure S3



**Figure S3.** CIE color coordinates of 1 mM of luminol, 1 mM of  $Ru(bpy)_3^{2+}$ , 50 mM of hydrogen peroxide and 50 mM of TPrA in 0.1 M phosphate buffer pH 8.0.luminol at +0.20 V (red dot), +0.40 V (blue dot), +0.60 V (green dot), +0.80 V (grey dot) and +1.00 V (purple dot).





**Figure S4.** ECL spectra obtained in 1 mM luminol, 1 mM  $Ru(bpy)_3^{2+}$ , 50 mM hydrogen peroxide and 50 mM TPrA in 0.1 M phosphate buffer pH 8 with microspectrometer cell (a) from 0.00 V to +0.50 and (b) from +0.50 V to +1.50 V. fs: forward scan; bs: backward scan.

### Figure S5



**Figure S5.** Dependence of ECL intensity of 1 mM  $\text{Ru}(\text{bpy})_3^{2+}$  and 50 mM TPrA on the concentration of hydrogen peroxide from 1 to 50 mM in 0.1 M phosphate buffer pH 8. Maximum ECL signal was considered when potential was scanned from 0.50 V to +1.50 V.