## SUPPORTING INFORMATION

# Time-Resolved Luminescence Spectroelectrochemistry at Screen-Printed Electrodes. Following the Redox-Dependent Fluorescence of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>.

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#### DIGITAL SIMULATION STUDY

Digital simulation of the cyclic voltammetry of  $[Ru(bpy)_3]^{2+/3+}$  was performed by using a Python software (simEC) developed by D. Martín-Yerga and based on the work by Brown<sup>1</sup>, which makes the calculations by following Butler-Volmer kinetics. Some parameters for the digital simulation were: temperature (293.15 K), gas constant (8.31451 J/mol K), Faraday constant (96485 C/mol). Electrode area was 0.08 cm<sup>2</sup> as it was previously experimentally calculated for screen-printed carbon electrodes<sup>2</sup>, and the diffusion coefficient for  $[Ru(bpy)_3]^{2+/3+}$  was estimated by voltammetric measurements (5x10<sup>-6</sup> cm<sup>2</sup>/s) and a similar value was assumed for the oxidized and reduced species. **Figure S1** shows the digital simulation results in a graphical way and **Video S3** shows these results dynamically together with the evolution of the profile concentration of  $[Ru(bpy)_3]^{2+}$  (red line) and  $[Ru(bpy)_3]^{3+}$  (blue line). This demonstrates how the concentration of the species and the diffusion layer changed with the potential during the simulated cyclic voltammetry. As observed in the figures, the experimental results are well correlated with the simulation results obtaining a good fitting with a heterogeneous rate constant of  $5x10^{-2}$  cm/s, a value typically considered as a reversible electron transfer. Therefore, these studies suggest that the electrochemical reaction of the [Ru(bpy)<sub>3</sub>]<sup>2+/3+</sup> redox couple is fast(reversible) and it is controlled by the semi-infinite linear diffusion.



**Figure S1.** Results of the digital simulation of the cyclic voltammetry of  $[Ru(bpy)_3]^{2+/3+}$  compared to the experimental results obtained at different scan rates (10, 50, 100 and 250 mV/s).



**Figure S2.** Fluorescence spectra for a blank solution (0.1 M KNO<sub>3</sub>)(blue line) and for 1.5 mM  $[Ru(bpy)_3]^{2+}$  in 0.1 M KNO<sub>3</sub> (red line) using screen-printed carbon electrodes as substrate. Low background fluorescence was observed suggesting a low influence of the screen-printed electrodes and spectroelectrochemical cell materials.



**Figure S3.** Cyclic voltammograms of 0.1 M KNO<sub>3</sub> and 1.5 mM  $[Ru(bpy)_3]^{2+}$  in 0.1 M KNO<sub>3</sub> in normal and deareated solutions. Deareated solutions show the loss of the intense cathodic process at a potential near -0.80 V, which is attributed to the removal of O<sub>2</sub> from the solution.

#### VIDEOS

**Video S1.** Dynamic evolution of the normalized fluorescence and the derivative of the fluorescence at 610 nm for 1.5 mM of  $[Ru(bpy)_3]^{2+}$  in 0.1 M KNO<sub>3</sub> during the cyclic voltammetry experiment. Initial potential: 0 V, 1<sup>st</sup> vortex potential: +1.2 V, 2<sup>nd</sup> vortex potential: -1.2 V, scan rate: 10 mV/s.

**Video S2.** Dynamic evolution of the normalized fluorescence and the derivative of the fluorescence at 610 nm for 1.5 mM of  $[Ru(bpy)_3]^{2+}$  in 0.1 M KNO<sub>3</sub> during the multi-pulsed amperometric experiment (by applying consecutive pulses of +1.2 V and +0.3 V for 60 s each).

**Video S3.** Results of the digital simulation of the cyclic voltammetry of  $[Ru(bpy)_3]^{2+/3+}$  compared to the experimental results obtained at different scan rates (10, 50, 100 and 250 mV/s). Video also shows the evolution of the profile concentration with the distance to the electrode of  $[Ru(bpy)_3]^{2+}$  (red line) and  $[Ru(bpy)_3]^{3+}$  (blue line).

### REFERENCES

- (1) Brown, J. H. J. Chem. Educ. 2015, 92 (9), 1490–1496.
- (2) Martín-Yerga, D.; Costa Rama, E.; Costa García, A. J. Chem. Educ. 2016, 93 (7), 1270–1276.