Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

Quantification of Electrogenerated Chemiluminescence from Tris(bipyridine)ruthenium(II) and Hydroxyl Ions

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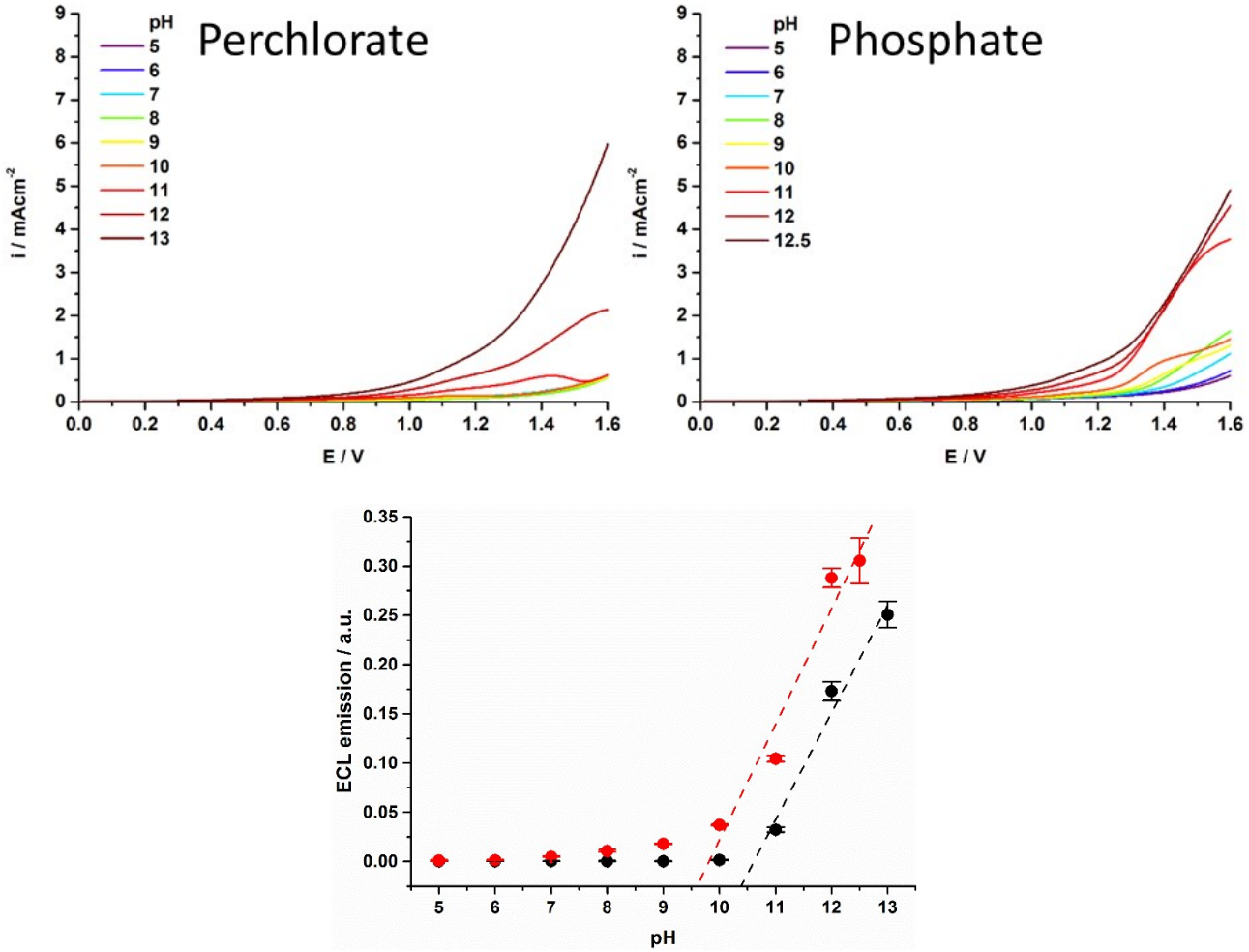

Figure S1. (Top) Current of forward scan of CV-ECL (for Fig. 1, main text) at different pH for the 100 mM electrolytes. Scan rate is 100 mVs^{-1}. Potential referred to Ag/AgCl (saturated KCl). (Bottom) Linear fitting of the ECL emission vs pH (from Fig. 2, main text).

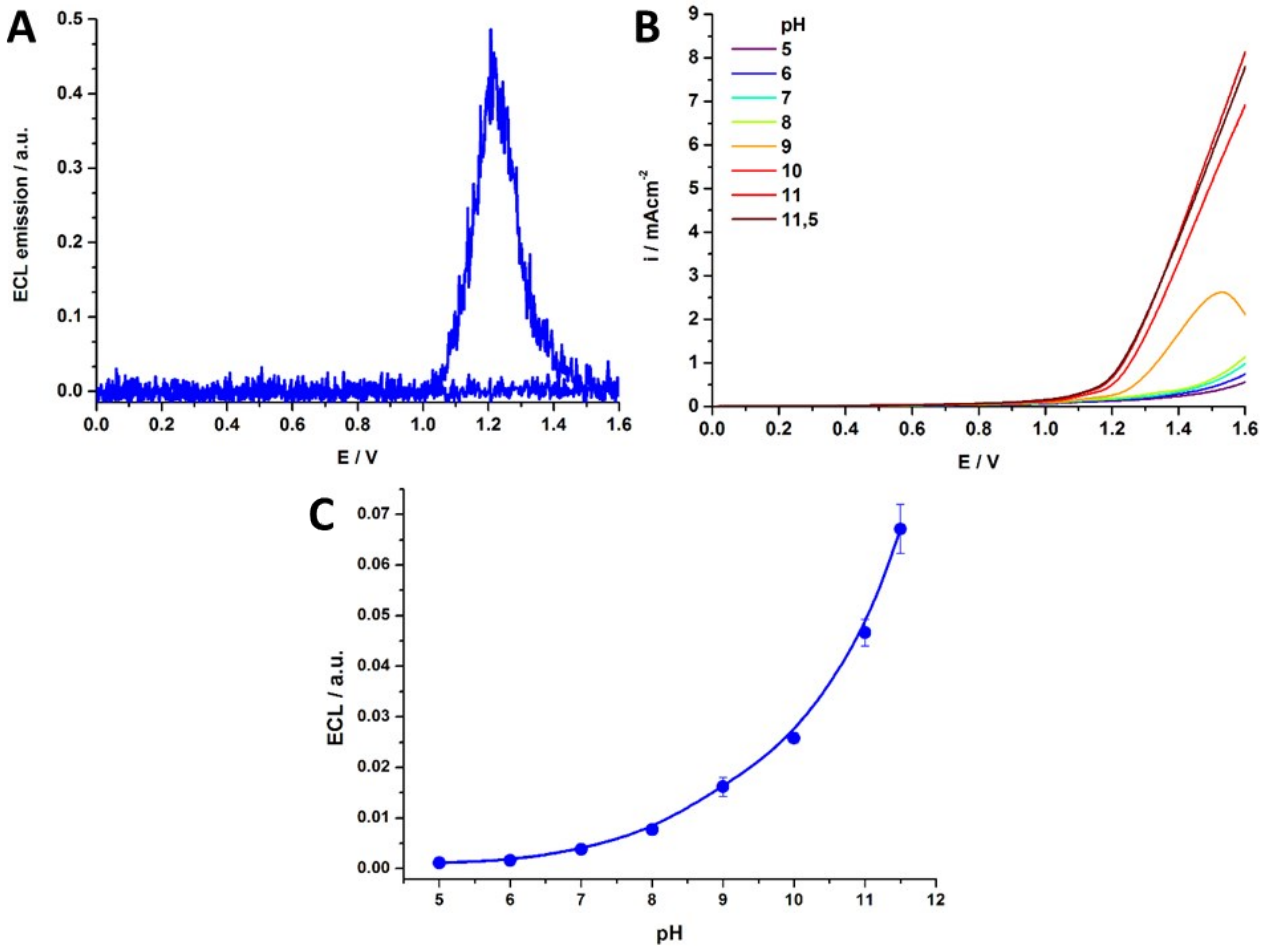

Figure S2. A) ECL emission of 100 μM $Ru(bpy)_3^{2+}$ in 100 mM carbonate pH 11.5 at 100 mVs^{-1}, and B) current of forward scan from CV-ECL at different pH. Scan rate is 100 mVs^{-1}. Potential referred to Ag/AgCl (saturated KCl). C) Integrated ECL emission from cyclic voltammetry at different pH. The line is drawn only as guide for the eye.

The ECL with carbonate differs from perchlorate and phosphate, its emission starts at the same time of others electrolytes, concurrently with $Ru(bpy)_3^{2+}$ oxidation, but it features only a single peak that gives a lower ECL emission (Figure S2-A).

Carbonate oxidation might hinder the ECL emission in competition with the oxidation process of $Ru(bpy)_3^{2+}$.

The current measured for carbonate is four and two times higher than perchlorate and phosphate, respectively (Figure S1 and S2-B).

Carbonate can be oxidized to percarbonate, which later decomposes in hydrogen peroxide.[1] This may lead to competition with Ru(II) oxidation or limiting the availability of hydroxide ions in the diffusion layer, since hydroxide enter the catalytic decomposition of hydrogen peroxide.[2] Moreover, hydrogen peroxide is a quencher of Ru(II) excited state.[3]

Another possible reaction pathway, involving hydroxyl radicals, is the extremely rapid addition to Ru(III) (k_{OH} = (0.6-2.0) $\times 10^{10}$ $M^{-1}s^{-1}$),[4] that will scavenge the Ru(III) preventing further reaction with OH^-.

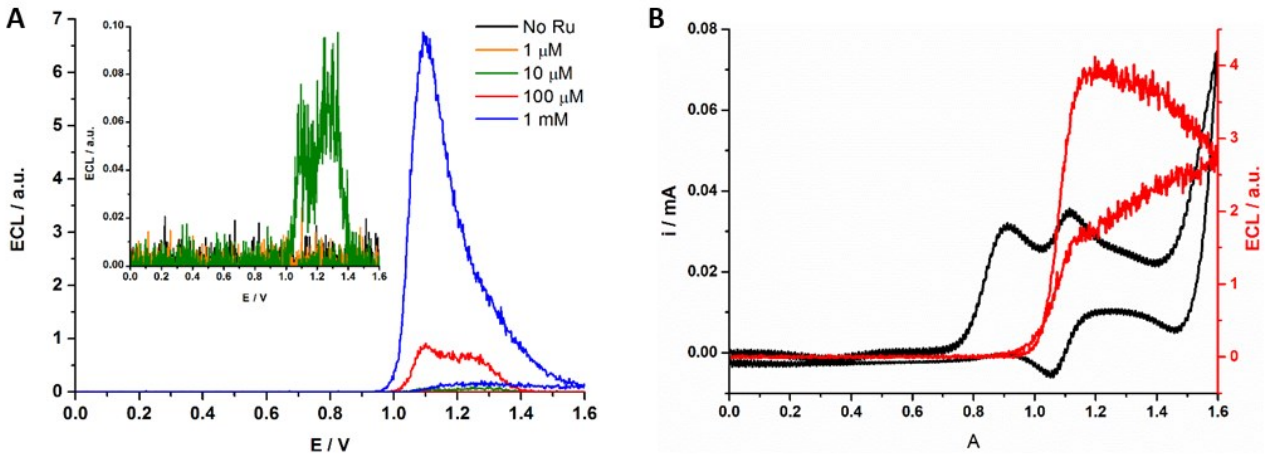

Figure S3. A) CV-ECL for different concentration of $Ru(bpy)_3^{2+}$ in 1 M NaOH at 100 mVs^{-1}. B) CV-ECL of 100 μM $Ru(bpy)_3^{2+}$ and 100 μM tri-*n*-propylamine in 0.2 M phosphate buffer (pH 7.5) at 100 mVs^{-1} (CV is background subtracted).

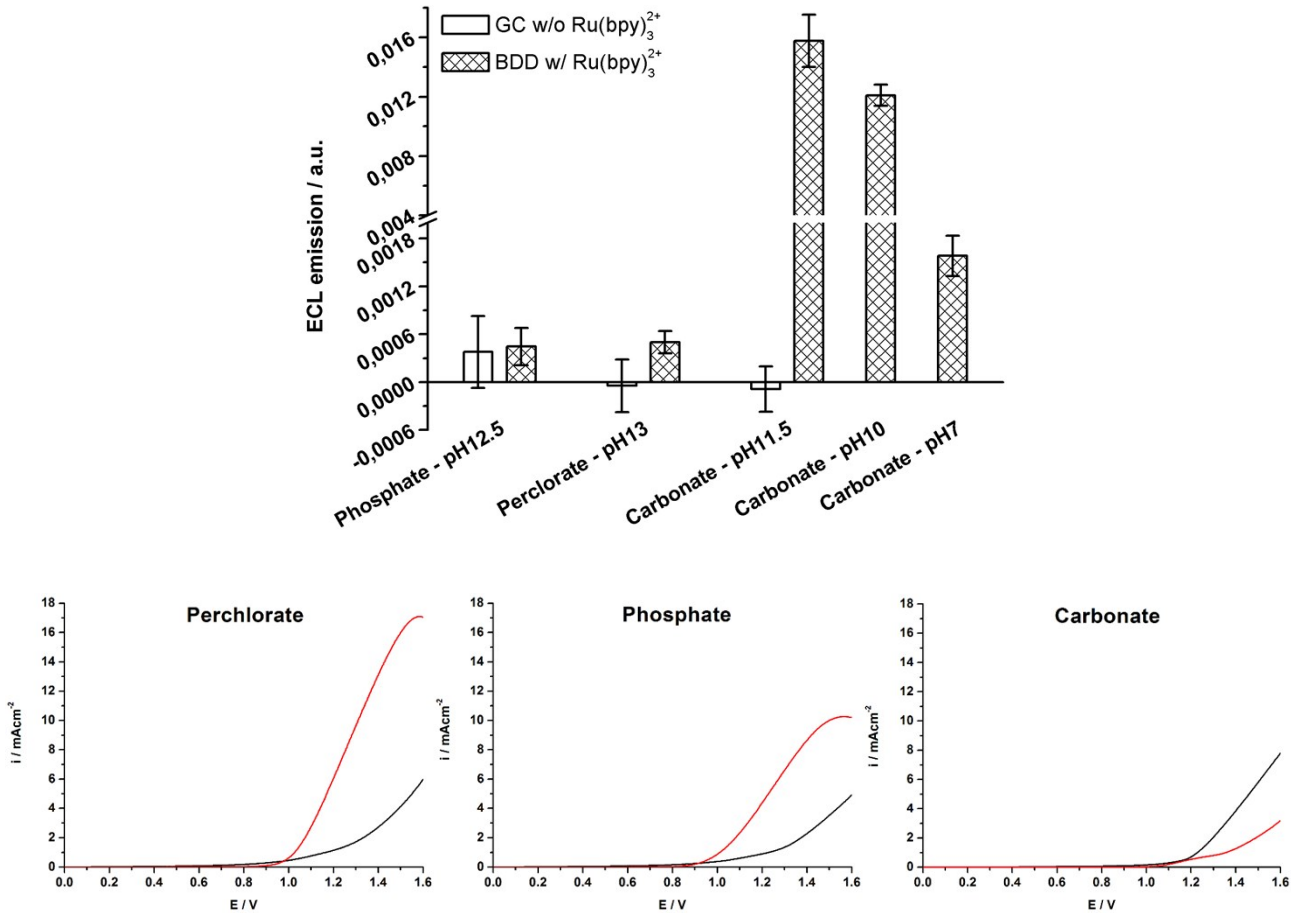

Figure S4. Top: integrated ECL signal from CV-ECL, GC without (GC w/o $Ru(bpy)_3^{2+}$) and BDD with (BDD w/ $Ru(bpy)_3^{2+}$) 100 μM $Ru(bpy)_3^{2+}$ in 100 mM supporting electrolyte at the specified pH. Bottom: current of forward scan from CV-ECL at 100 mM electrolytes with $Ru(bpy)_3^{2+}$ 100 μM (BDD, red line; GC, black line). Scan rate is 100 mVs^{-1}. Potential referred to Ag/AgCl (saturated KCl).

For perchlorate and phosphate electrolytes, the current measured with BDD electrode is oxidation of hydroxyl anions,[5,6] and it is higher than current measured for GC. This results in the depletion of hydroxyl ions at BDD and quenching of the ECL emission, while a detectable ECL emission is retained with carbonate that shows a lower current for BDD than GC.

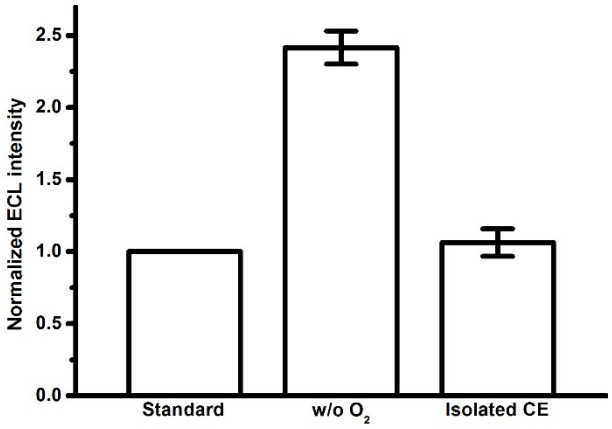

Figure S5. Normalized ECL intensity of the ECL system in the three electrode configuration (standard), without oxygen (10 ml of solution bubbled for 30 min with 20 ml/min nitrogen stream), and with isolated counter electrode (inside a glass tube closed with Vycor porous glass and filled with the electrolytic solution). $Ru(bpy)_3^{2+}$ 100 μM, phosphate 100 mM (pH 12.5); cyclic voltammetry from 0 V to 1.6 V at 100 mV/s. Error bar for the standard configuration is smaller than bar lines.

The increase of emission after nitrogen bubbling is ascribed to the quenching effect of oxygen on the excited state of $Ru(bpy)_3^{2+}$*.[7] The same emission obtained with isolated counter electrode rule out any parasitic reaction that may generate ECL at the counter electrode and might be wrongly associated with the main ECL system here investigated.[8]

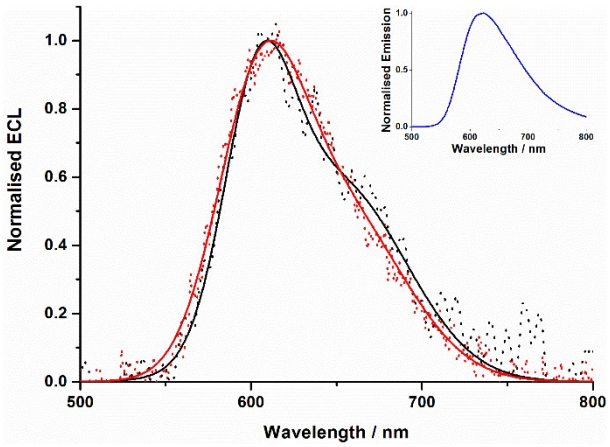

Figure S6. Normalised spectra: ECL emission for 1 mM $Ru(bpy)_3^{2+}$ with 1M NaOH (black, λ_{max} = 610 nm), and 100 µM $Ru(bpy)_3^{2+}$ with 100 µM TPrA in phosphate buffer at pH 7.5 (red, λ_{max} = 612 nm), obtained by chronoamperometry at 1.4 V on GC and 1.7 V on BDD, respectively; two peaks fitting, Gaussian function. Inset, photoluminescence emission for 50 µM $Ru(bpy)_3^{2+}$ in 100 mM Na_2SO_4 (λ_{max} = 623 nm). Spectra are uncorrected.

Part 1: The catalytic constant (k_{OH}) of reaction in Scheme 1 and TOF- η relationship

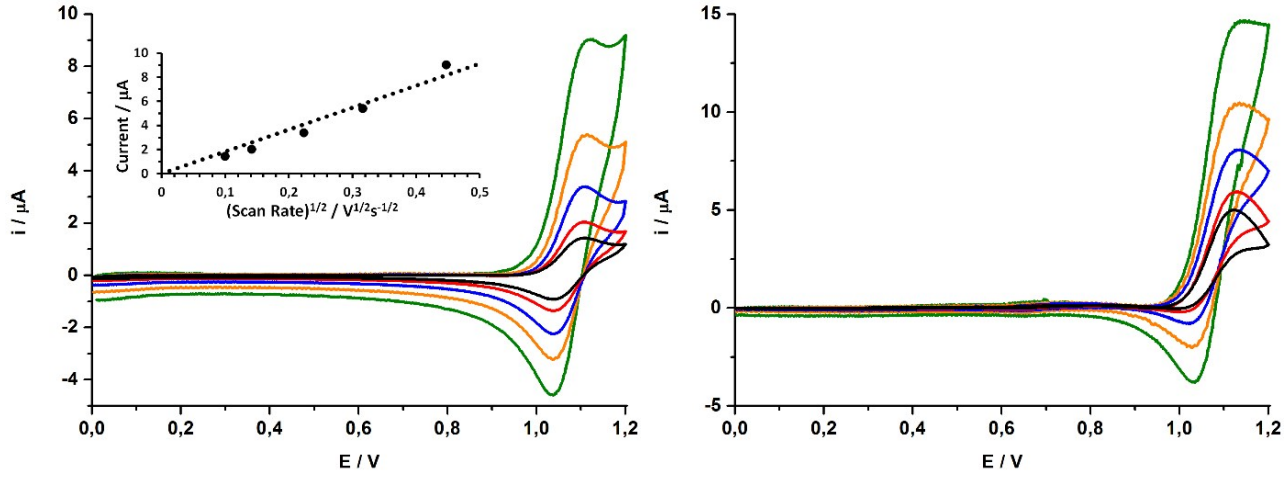

Figure S7. Background subtracted CVs of (left) 0.5 mM $Ru(bpy)_3^{2+}$ in 100 mM Na_2SO_4 (pH 6), and (right) 0.5 mM $Ru(bpy)_3^{2+}$ in 100 mM Na_2SO_4 and 1 mM NaOH. Scan rates at 10, 20, 50, 100 and 200 mV/s. Working electrode is glassy carbon ⌀ = 3 mm.

$E_{1/2}^{Ru3+/2+}$ = 1.07 V is used in the following foot of the wave analysis and measured from CV experiments (Figure S5, left), in agreement with previous results.[9]

The classical S-shaped catalytic wave follows the equation:

$$i = \frac{FAC_{Ru}^{0}\sqrt{D_{Ru}}\sqrt{k_1 C_{OH^-}^{0}}}{1 + exp\left[\frac{F}{RT}\left(E - E_{1/2}^{Ru3+/2+}\right)\right]}$$

The peak current of $Ru(bpy)_3^{2+}$ without NaOH is given by:

$$i_p = 0.446FAC_{Ru}^{0}\sqrt{D_{Ru}}\sqrt{\frac{Fv}{RT}}$$

Then, calibration of *i* for the electrode surface area (A), the catalyst concentration (C^0_{Ru}) and the diffusion coefficient (D_{Ru}) lead to:

$$\frac{i}{i_p} = \frac{2.24\sqrt{\frac{RT}{Fv}k_1 C_{OH^-}^{0}}}{1 + exp\left[\frac{F}{RT}\left(E - E_{1/2}^{Ru3+/2+}\right)\right]}$$

Plotting this against $1/\{1+\exp[F/RT(E-E_{1/2}^{Ru3/2+})]\}$ gives a straight line with slope $2.24(RT/Fv)^{1/2}(k_1C^0_{OH^-})^{1/2}$, to access $k_1C^0_{OH^-}$-[$M^{-1}s^{-1}$],

as the pseudo-first order rate constant k_{OH} [s^{-1}].[10,11]

$$TOF = \frac{k_{OH}}{1 + exp\left[\frac{F}{RT}\left(E_{1/2}^{Ru3+/2+} - E_{H_2O/O_2} - \eta\right)\right]}$$

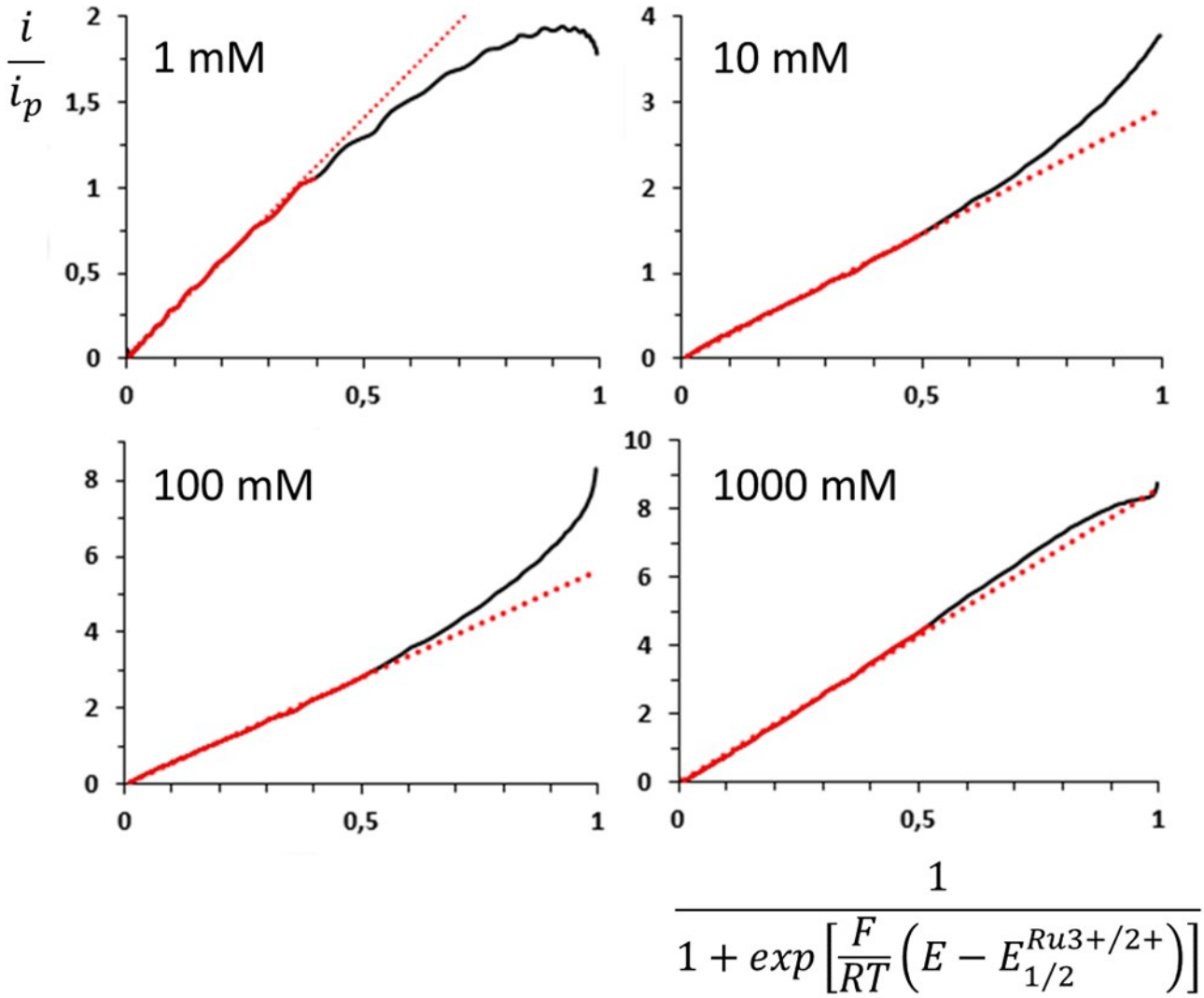

Figure S8. Foot of the wave analysis: CV of 0.5 mM $Ru(bpy)_3^{2+}$ in 100m M Na_2SO_4 and NaOH as specified. Scan rate is 100 mV/s. Glassy carbon ⌀ = 3 mm. The y-axis is i/i_p (i_p is the peak current of the CV at 100 mV/s in Figure S5, left), and the x-axis is $1/\{1+\exp[F/RT(E-E_{1/2}^{Ru3+/2+})]\}$.

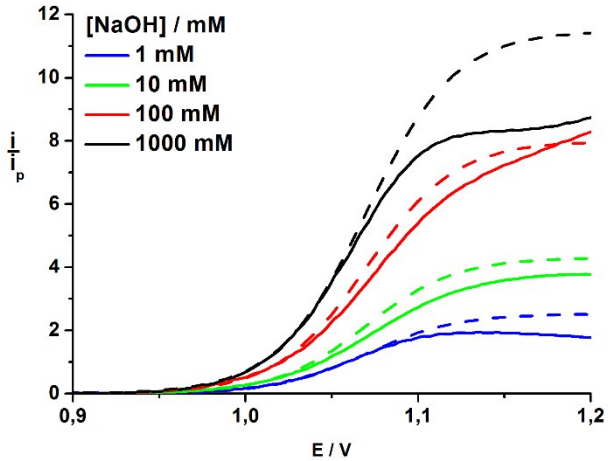

Figure S9. Forward scan CVs (background subtracted) with 0.5 mM $Ru(bpy)_3^{2+}$ and NaOH at specified concentrations in 100 mM Na_2SO_4 at 100 mVs^{-1} (full line). Fitting from foot of the wave analysis (dashed line).

Part 2: Mechanism and energetic considerations

Investigation of the undelaying mechanism involved in the ECL emissions is not the aim of this study, however we report some previous researches on the reaction mechanism of Ru(III) and OH^- to justify the assumptions used for the measurement of TOF. Ru(III) reduction by hydroxyl ions was first studied as potential application in a solar energy storage system, in photochemical water splitting.[4]

This mechanism, as described by Ghosh et al.,[12] and Lay et al.,[13] sees the first chemical step of this reaction as hydroxide addition on bpy ligand. Further reactions with Ru(III) are considered in the mentioned reaction mechanism, which may be involved in the ECL emission, for a second-order reaction in Ru(III). Furthermore, chemiluminescence from Ru(III) reduction may arise from hydroxyl ion attack at a coordinated bpy followed by intramolecular electron transfer from ligand to metal.[14]

Another mechanism, proposed by Serpone et al.,[15,16] concerns the formation of tight ion-pairs in an outer-sphere complex between the bpy ligands of Ru(III) and OH^-. This offers also a straightforward interpretation of the chemiluminescence reaction, since it predicts the formation of a MLCT excited stated ($d^5\pi^{*1} \rightarrow d^6$).

Concerning the ECL mechanism, we want to point out, the free Gibbs energy (ΔG_{es})[17] for the formation of the excited state (Ru^{2+}*, ^{3}MLCT = 2.12 eV)[18] is unfavourable, since the energy available from direct water oxidation is not sufficient.

$$\Delta G_{es} \simeq E^{0}_{O_2/H_2O(pH\ 12)} - E^{0}_{Ru(bpy)^{3+}_{3}/^{2+}_{3}} - {}^3MLCTRu(bpy)^{2+}_{3} = 1.37eV \quad (3)$$

Moreover, one electrode oxidation of OH^- to $OH^\bullet$ is not possible on energetic ground,[13] because the formation of ^{3}MLCT *Ru(II) and $OH^\bullet$ is endoergonic of about 3 eV.

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