Supplementary Information

Electrochemiluminescent swimmers for dynamic enzymatic sensing

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1. Materials

All chemicals were of analytical reagent grade and were used as received. Solutions were prepared using Milli-Q water (resistivity = 18.2 MΩ.cm^{-1}). Glucose dehydrogenase (EC1.1.1.47, from *Thermoplasma acidophilum*), β-nicotinamide adenine dinucleotide hydrate (NAD$^+$), β-nicotinamide adenine dinucleotide reduced dipotassium salt (NADH), D-(+)-Glucose, tris(2.2'-bipyridyl)dichlororuthenium(II)hexahydrate, sodium phosphate dibasic heptahydrate and sodium phosphate monobasic monohydrate were purchased from Sigma. Surfactant Gojo NXT was used. Glassy carbon beads (spherical powder 630–1000 mm, type 2) were purchased from Alfa Aesar.

2. Method

For the motion of the light-emitting GC bead, a U-shaped glass capillary (Figure S1) was used as an electrochemical cell. It was made by manual shaping of Pasteur pipettes (230 mm, VWR International) with a Bunsen burner. The electric field was applied using a DC generator (Fug MCN 140-350). The cell was filled with a PBS solution containing 1.5 mM tris(2,2'-bipyridyl) dichlororuthenium(II) hexahydrate, 10 mM NAD$^+$, various glucose concentrations (5 mM, 10 mM, and 40 mM) in 100 mM PBS solution (pH 7.4) and a few drops of surfactant. The cell was maintained in a vertical position and the glassy carbon bead was inserted into one arm of the cell. Due to the slightly conical shape of the capillary, the bead dropped until it was stopped by the surrounding capillary walls. The feeder electrodes (graphite rods) were inserted into the top part of the cell. The motion of the bead was recorded using a SLR commercial digital camera (Canon 60 D; Raw mode imaging in full frame resolution) equipped with a lens for macrophotography (Canon 100 mm-f:2.8).

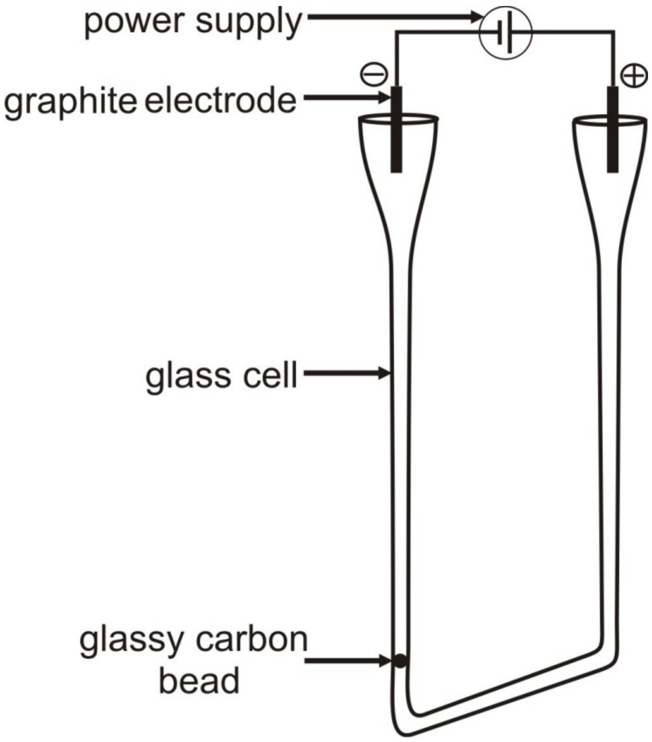

Figure S1. Scheme of the set-up used for the ECL experiments.

3. Electrochemical and ECL characterisation

Cyclic voltammetry experiments were performed with a μ-Autolab Type III or PGSTAT30 electrochemical stations. Electrochemical measurement was combined with a simultaneous monitoring of the ECL intensity by using a Hamamatsu photomultiplier tube (PMT) R4632. The three-electrode system consisted in a home-made glassy carbon (same material as the swimmer) electrode as working electrode, a Ag/AgCl/KCl 3 M saturated reference electrode and a platinum wire counter-electrode.

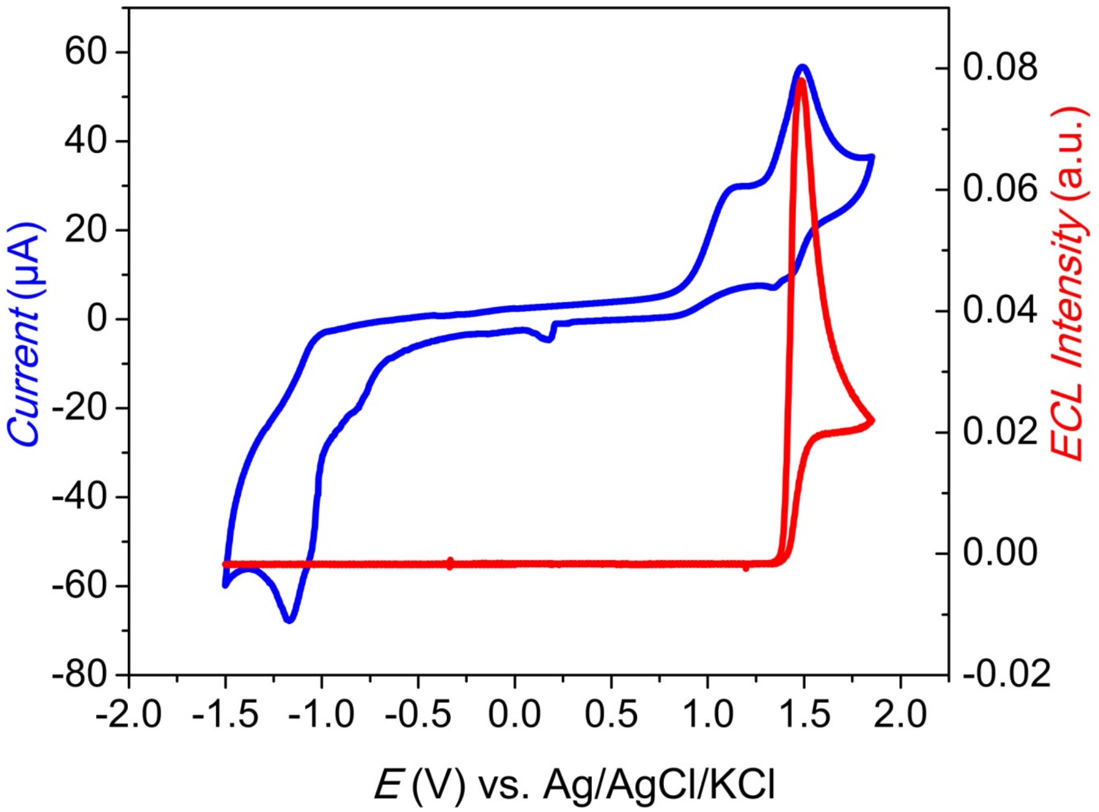

Figure S2. Cyclic voltammogram (blue) and ECL signal (red) of 100 mM PBS solution (pH=7.4) containing 10 U.mL^{-1} GDH, 1.5 mM $Ru(bpy)_3^{2+}$, 10 mM NAD$^+$, 10 mM glucose and a few drops of surfactant recorded on a home-made glassy carbon electrode at a scan rate of 0.05 V.s^{-1}.

From Fig. S2, the potential values for which the different redox reactions are occurring at the swimmer surface can be easily extracted. Water reduction takes place at $E_{red} = -0.75$ V *vs.* Ag/AgCl/KCl whereas ECL emission occurs at $E_{ox} = 1.55$ V *vs.* Ag/AgCl/KCl.

The polarization voltage ΔV induced on a conducting object is proportional to the external electric field E and the characteristic dimension of the object l,[1] as described by the simple relation (1):

$$\Delta V = E \times l \qquad (1)$$

Based on the values of E_{red} and E_{ox}, one can conclude that the coupling of water reduction and ECL emission at the reactive poles of a bipolar electrode (BE) is possible only if the polarization potential ΔV between both extremities of the BE is at least equal to $|E_{red} - E_{ox}| =$

2.3 V. Equation (1) thus states that for a BE having a diameter l of about 1 mm, the electric field E has to be, in a first order approximation, at least 21.7 V.cm^{-1}.

[1] G. Loget, D. Zigah, L. Bouffier, N. Sojic and A. Kuhn, *Acc. Chem. Res.* 2013, **46**, 2513.