Supporting Information for:

Electrogenerated Chemiluminescence Triggered by Electroseparation of $Ru(bpy)_3^{2+}$ Across a Supported Liquid Membrane

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Experimental section

Tris(2,2'-bipyridyl)-ruthenium(II) chloride ($Ru(bpy)_3Cl_2.6H_20$), 2-(dibutylamino)ethanol (DBAE), (potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate (KTFPB), o-nitrophenyloctylether (o-NPOE) and all salts were purchased from Sigma-Aldrich (Analytical grade). Microporous polypropylene membranes were obtained from Polypore (25 µm thickness, Celgard 2500).

Silver wires (Sigma-Aldrich) of 10 cm in length and 250 µm dia. were cleaned with acetone and water before chloridation. A 9 cm section of the cleaned wire was dipped in a 1M HCl solution. A potential of 200 mV against a double junction reference electrode was applied between the silver wire and the high surface area platinum counter electrode (CE). The process was carried out for 2 min. The silver/silver chloride wire was rinsed thoroughly with distilled water after chloridation. The Ag/AgCl wires were used as working electrode (W_1) and reference electrode (RE). Platinum counter electrode (10 cm, 500 µm diameter, Goodfellow) coil was used as CE. Gold electrode (3 mm dia. isolated with Teflon body, Metrohm) was used as W2 to generate the ECL. A gold electrode was carefully polished (1, 0.3 and 0.05 µm Alumina powder) and rinsed with ethanol between each step (an ultrasonic bath is required). Internal solution ISE bodies (Oesch Sensor Technology) were used to perform the potentiometric calibrations. The double-junction Ag/AgCl/3M KCl /1M LiOAc reference electrode was purchased from Mettler-Toledo AG, Schwerzenbach, Switzerland.

The cation-exchanger cocktail was prepared with 0.63 mg KTFPB and 136 mg o-NPOE as a solvent. 5 µL of the cocktail was deposited on the membrane. After 5 minutes the membrane became completely impregnated, as visualized by the membrane becoming transparent. After that, the membrane was conditioned for 2 hours in the chloride salt of 10 mM $Ru(bpy)_3^{2+}$. Potentiometric calibration and transport experiments were applied after fully conditioning.

Potentiometric calibration was performed using a 16-channel EMF monitor (Lawson Laboratories, Inc., Malvern,PA) connected to a personal computer. The transport experiments and ECL generation were performed with an Autolab PGSTAT302N (MULTI 16, module, Metrohm Autolab, Utrecht, The Netherlands) that permit one to apply subsequent pulses at two different working electrodes such as W1 and W2 (see Figure 1). Two ISMATEC peristaltic pumps (Glattbrugg, Switzerland) at a 100 μL min^{-1} flow rate were used to transport the fluids into the detection and sample compartment. A CCD camera (model 4100, Cohu) was used to record the ECL emission, whereas custom-made software was used to extract the information.

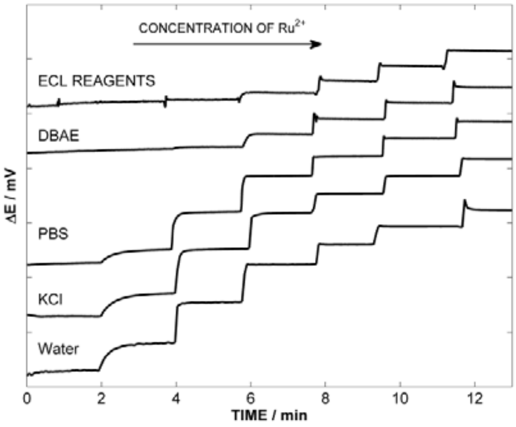

Fig 1S – Time response of Ru(bpy)$_3^{2+}$ calibration in different background solutions (Water; KCl 10 mM; PBS 100 mM pH 7.4, DBAE 20 mM) and ECL reagents (KCl 10mM; PBS 100 mM pH 7.4, DBAE 20 mM).

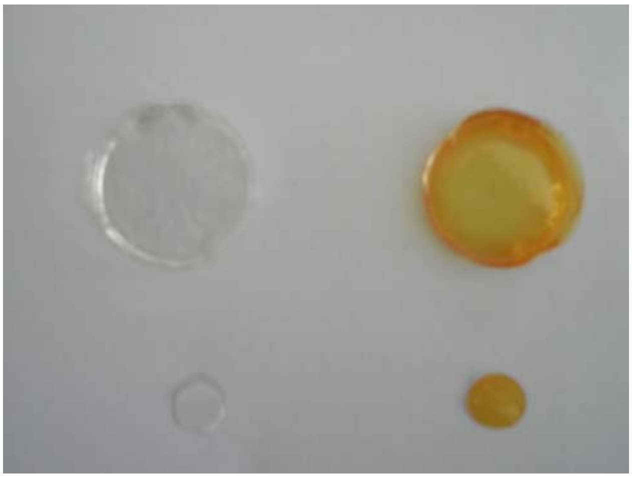

Fig 2S – Membranes photographs before and after conditioning in 10 mM of Ru(bpy)$_3^{2+}$ used for the tranport experiments (top, 10 mm diameter) and potentiometric measurements (bottom, 3 mm diameter).

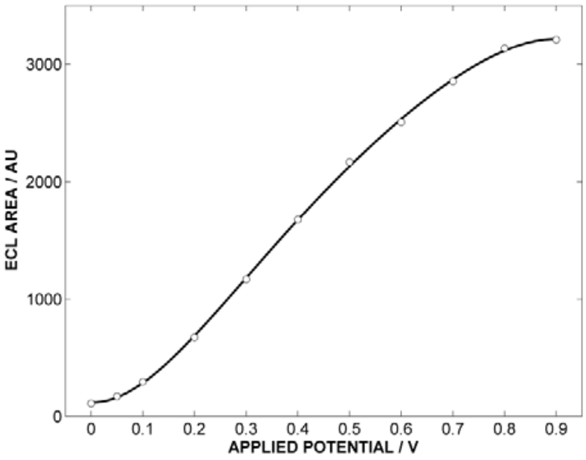

Fig 3S - Optimization of applied potential across the membrane at constant time (10 seconds). The external potential from 0 to 0.9 V was applied in steps of 0.1 V. The open circuit potential of the membrane is close to 0 V. Significant transport begins at 0.2 V. A value of 0.4 V was chosen to perform all subsequent transport experiments as a compromise between ECL sensitivity and adequate operational membrane selectivity. Even though 0.6 V offers larger ECL intensity, this goes at the expense of increasing interference from background ions.

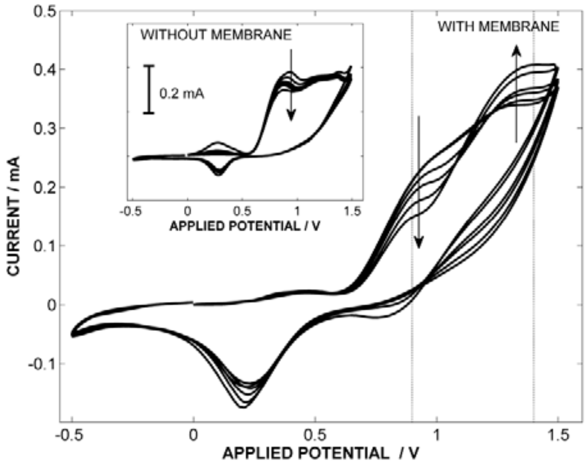

Fig 4S – ECL generation by cyclic voltammetry with/without (inset) membrane. The region marked by two vertical lines correspond to potentials where ECL emission was visible. Arrows indicate the increasing/decreasing shoulders at different concentrations of $Ru(bpy)_3^{2+}$

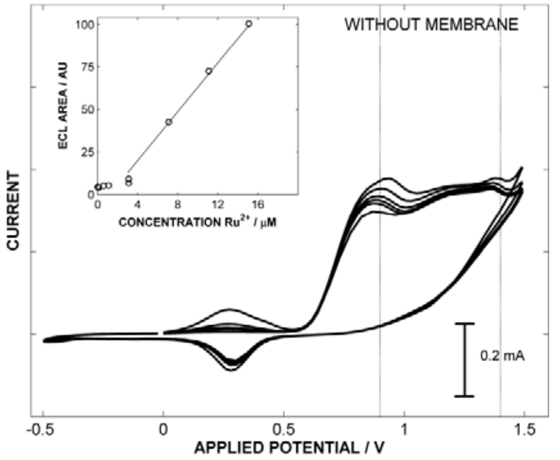

Fig 5S – ECL generation by cyclic voltammetry without membrane. The region marked by two vertical lines correspond to ECL emission. Inset, calibration curve for $Ru(bpy)_3^{2+}$ on a normalized scale. The equation of the calibration is: ECL area = 2 x 10^8 x $[Ru(bpy)_3^{2+}]$ – 290

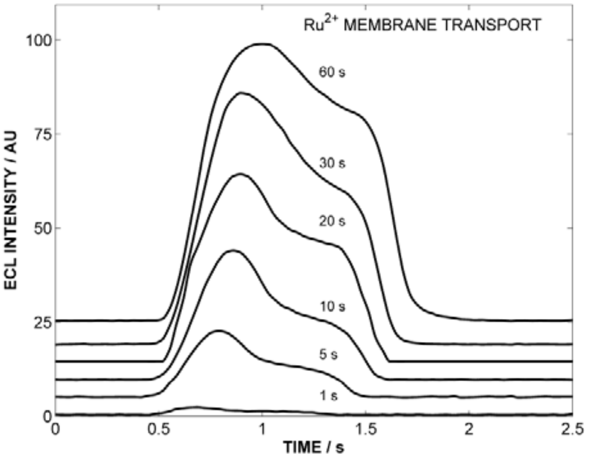

Fig 6S – ECL peaks at different $Ru(bpy)_3^{2+}$ membrane transport from 1 to 60s. ECL is generated by a fast CV at 1 V/s obtaining fast time of response around 1s. High reproducibly (less that 5%) is obtained by integrating each transient. The tailing peak is observed due to the fact that there are two potential emitting bands of ECL between 1-1.4V. Each curve is calculated from the convolution of thirty consecutive video frames.

Equation 1

Reference 1 gives the following equation for a constant potential thin layer current response (symmetrical case):

$$i(t) \simeq i(0)\exp(-pt) \text{ with } p = \frac{\pi^2 D_0}{l^2} \qquad (1)$$

where i(t) is the current as a function of time, i(0) is the initial current, D_o is the diffusion coefficient in aqueous solution (10^{-5} cm^2 s^{-1} was used); *l* is the distance of the thin layer gap (2 x 0.032 cm).

Note that equation (1) has been defined for a symmetrical thin layer[1]. The asymmetrical arrangement here was taken into account by multiplying *l* by a factor 2.

Reference

(1) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; 2nd edition, Wiley: New York, 2001, page 454, eq (11.7.8).