# Supporting Information for

# Electrogenerated Chemiluminescence for Potentiometric Sensors

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### Table of Contents

| Experimental section  | S3         |
|---|------------|
| Fig 1S Potentiometric characterization  | <b>S4</b>  |
| Fig 2S Potentiometric selective coefficient determination (Log $K_{ij}^{pot}$ ) | <b>S</b> 5 |
| Fig 3S Chronoamperometric pulses to generate ECL                                | <b>S6</b>  |

#### **Experimental section**

Tris(2,2'-bipyridyl)-ruthenium(II) chloride (Ru(bpy)<sub>3</sub>Cl<sub>2</sub>.6H<sub>2</sub>0), 2-(dibutylamino)ethanol (DBAE), (sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate (NaTFPB), dioctylsebacate (DOS), high molecular weight poly(vinyl chloride) (PVC) and all salts were purchased from Sigma-Aldrich (Analytical grade). Phosphate buffer saline (KH<sub>2</sub>PO<sub>4</sub>/K<sub>2</sub>HPO<sub>4</sub>, pH 7.5) was freshly prepared from the appropriate salts.

The solution placed in the detection compartment was always a mixture of Ru(bpy)<sub>3</sub>Cl<sub>2</sub>.6H<sub>2</sub>0 (0.01 mM), 2-(dibutylamino)ethanol (DBAE) (20 mM), LiCl (10 mM) and phosphate buffer solution (0.1M, pH 7.5).

Silver wires (Sigma-Aldrich) of 10 cm length and 250 µm diameter 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 at the silver wire, using a high surface area platinum counter electrode. 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 bridge and secondary reference electrode in the sample compartment. A platinum counter electrode coil (10 cm, 500 µm diameter, Goodfellow) was used as counter electrode. A gold electrode (3 mm diameter isolated with Teflon body, Metrohm) was used as working electrode to generate ECL. The 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 ion-selective electrode bodies (Oesch Sensor Technology) were used to mount the polymeric membranes. A double-junction Ag/AgCl/3M KCl /1 M LiOAc reference electrode was used in the determination of the selectivity coefficients of the ion-selective membranes (Mettler-Toledo AG, Schwerzenbach, Switzerland).

A cocktail was prepared with 0.58 mg NaTFPB (5 mmol kg<sup>-1</sup>), 1.46 mg of valinomycin (Potassium Ionophore I; 15 mmol kg<sup>-1</sup>), 5.1 mg of ETH 500 (30 mmol kg<sup>-1</sup>), 43.6 mg of PVC and 87.7 mg DOS was dissolved in 1 mL of THF and poured into a glass ring (10 mm ID) affixed onto a glass sheet. The solution was allowed to evaporate overnight. The thicknesses of the resulting membranes were ca. 0.15 mm. This mother membrane was cut with a hole puncher into small disks (3 mm diameter) and mounted into the electrode body. After that, the membranes were conditioned

either in 1 mM of LiCl or 1 mM of  $K_2SO_4$  for 24 h. Potentiometric calibration was performed using a 16-channel EMF monitor (Lawson Laboratories, Inc., Malvern,PA) connected to a personal computer. All the potentiometric calibrations were performed with 10 mM LiCl as background and inner electrolyte. The resistance of the membrane was tested by electrochemical impedance spectroscopy and found as 60 k $\Omega$ .

Both linear sweep voltammetry and ECL generation were performed with an Autolab PGSTAT302N (MULTI 16, module, Metrohm Autolab, Utrecht, The Netherlands). ECL light was collected with a photomultiplier tube at 600 V (Amplified PMT for 280-850 nm, PM002, Thorlabs Company). Two ISMATEC peristaltic pumps (Glattbrugg, Switzerland) at 0.100 mL min<sup>-1</sup> flow rate were used to transport the fluids into the detection and sample compartment.



Fig 1S – Potentiometric calibration curve measuring only the membrane potential in the sample compartment. Slope  $(59.7 \pm 0.2)$  mV.



**Fig 2S** – Potentiometric selectivity determined by the separate solutions method. All of the interference and the primary analyte exhibit a Nernstian response slope within the linear working range shown in the figure.  $\text{Log}_{K,Mg}^{\text{pot}} = -7.9 \pm 0.2$ ;  $\text{Log}_{K,Ca}^{\text{pot}} = -7.3 \pm 0.1$ ;  $\text{Log}_{K,Li}^{\text{pot}} = -6.6 \pm 0.1$ ;  $\text{Log}_{K,Na}^{\text{pot}} = -4.8 \pm 0.2$ 



**Fig 3S** – Observed ECL intensity for eight different potassium concentrations. Each standard solution was measured at least three times showing a relative standard deviation of less than 2%. The electrochemical pulse was performed at two potentials 0.8 V (top) and 0.9 V (bottom) for 0.1 s.