Electronic Supplementary Material

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Two-Channel Microelectrochemical Bipolar Electrode Sensor Array

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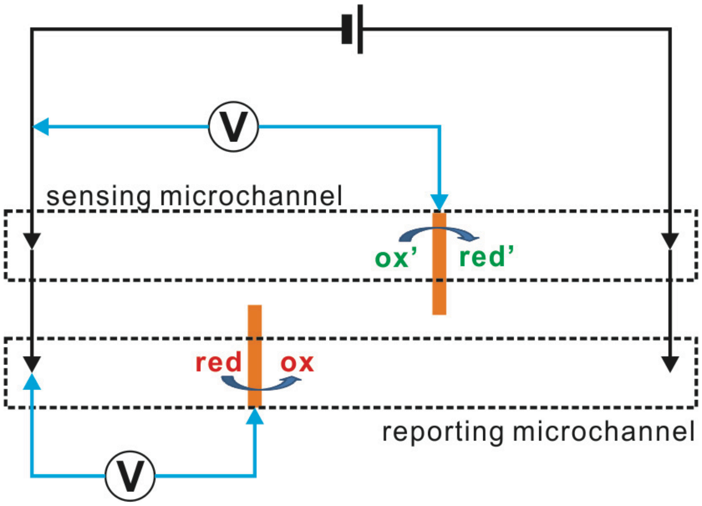
(7 pages)

Determination of the potential of the anodic and cathodic poles of a BPE as a function of the applied voltage (E_{tot}). Under ideal conditions, the electric field (V_0) in a microchannel is given as $V_0 = E_{tot}/l_{channel}$, where E_{tot} is the driving voltage and $l_{channel}$ is the total length of the channel. The potential at a given position, x, is $E(x) = V_0 \cdot x$. However, in a real situation, the actual values of $E(x)$ are somewhat lower, because a small portion of E_{tot} is lost at the driving electrodes (Mavré, F.; Chow, K.-F.; Sheridan, E.; Chang, B.-Y.; Crooks, J. A.; Crooks, R. M. A Theoretical and experimental framework for understanding ECL emission at bipolar electrodes *Anal. Chem.* **2009**, *81*, 6218-6225). To determine the effective potential profile in the microchannel under various electric field strengths, we experimentally measured the potential of microbands at x = 0.40 and 0.50 cm in the reporting and sensing microchannels, respectively. The experimental configuration is provided in Scheme S1.

Scheme S1



The results of the experiment, which are plots of the voltage difference between each pole of the interchannel BPE and a driving electrode vs. E_{tot}, are provided in Figure S1. The floating potential of the BPE was also measured by connecting the microbands externally. As shown in Figure S1, the resulting values are midway between the voltages of the individual microbands.

Using these data, we calculated the true potential difference between the anodic and cathodic poles of the BPEs (ΔE_{elec}), and plotted it vs. E_{tot} in Figure S2.

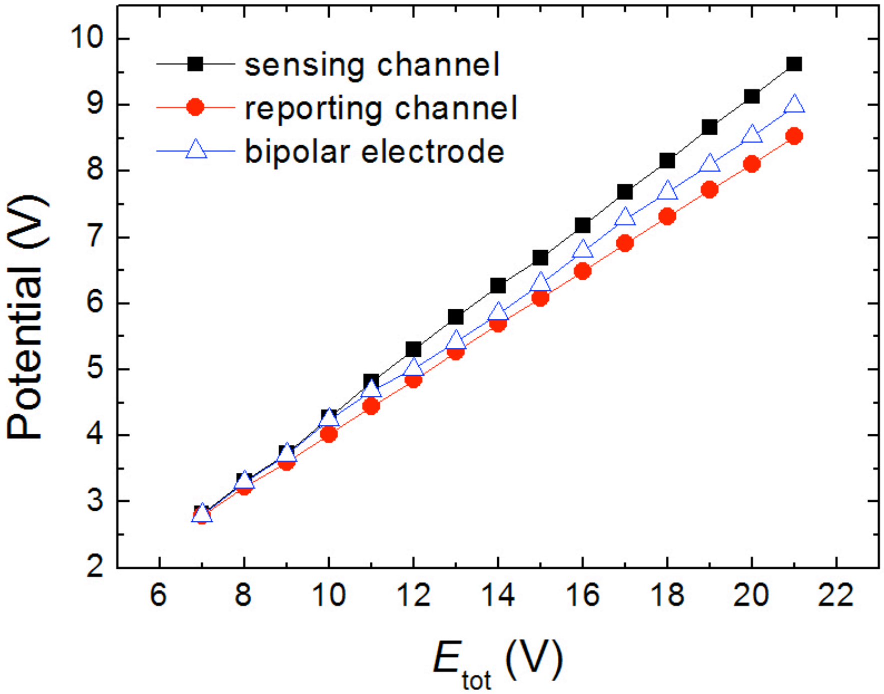


Figure S1. Potential profiles of microbands in the sensing (■) and the reporting channels (●), and the bipolar electrode (△) constructed by connecting the two separate microbands.

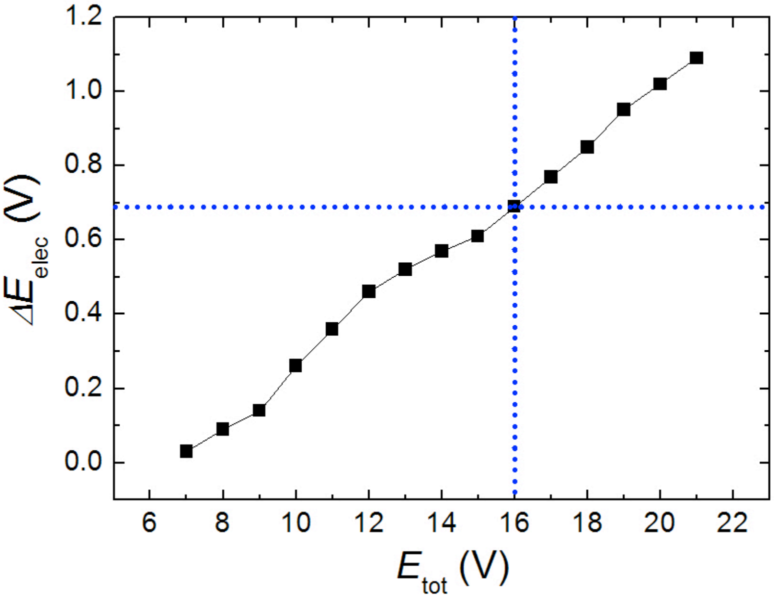


Figure S2. Plot of the potential difference (ΔE_{elec}) between cathodic and anodic poles of the BPE, calculated from the potential profiles plotted in Figure S1, as a function of the driving voltage (E_{tot}). ECL was observed with a minimum driving potential of E_{tot} = 16.0 V, which is equivalent to ΔE = 0.69 V (shown as blue dotted lines).

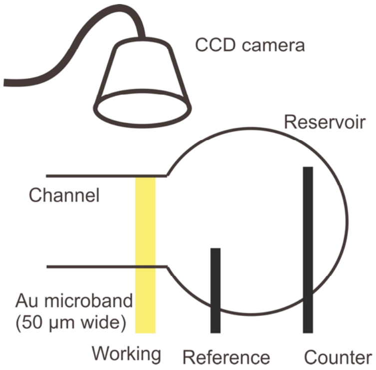
Estimation of the minimum ΔE_{elec} required for ECL emission.

We have previously demonstrated that when ΔE_{elec} is larger than the difference of the onset potentials for reduction and oxidation reactions, then the two reactions will occur simultaneously at the two poles of the BPE. [Mavré, F.; Chow, K.-F.; Sheridan, E.; Chang, B.-Y.; Crooks, J. A.; Crooks, R. M. A Theoretical and experimental framework for understanding ECL emission at bipolar electrodes *Anal. Chem.* **2009**, *81*, 6218-6225.] To find the minimum ΔE_{elec} required to observe ECL, we measured the onset potentials for the reduction of $Fe(CN)_6^{3-}$ and for the oxidation reactions of $Ru(bpy)_3^{2+}$ and TPrA that lead to light emission. This was done using traditional three electrode electrochemical cells

To determine the onset potential for the reduction of $Fe(CN)_6^{3-}$, a sampled-current voltammogram (SCV) was obtained using a 2.0 mm diameter Au disk electrode and an aqueous, deaerated solution containing 5.0 mM $Fe(CN)_6^{3-}$ and 0.10 M KCl. These data are presented on the right axis of Figure S3.

For the oxidation of $Ru(bpy)_3^{2+}$ and TPrA, we report ECL intensity vs. potential instead of current vs. potential because ECL intensity is the signal of interest in the BPE experiments. These measurements were made in the spectroelectrochemical cell shown in Scheme S2 and described previously [Mavré, F.; Chow, K.-F.; Sheridan, E.; Chang, B.-Y.; Crooks, J. A.; Crooks, R. M. <u>A Theoretical and experimental framework for understanding ECL emission at bipolar electrodes</u> *Anal. Chem.* **2009**, *81*, 6218-6225.]. Here, the working, counter, and reference electrodes are Au, Pt, Ag|AgCl, respectively. In this experiment, the microchannel and reservoir are filled with 1.0 mM $Ru(bpy)_3^{2+}$ and 25 mM TPrA in 0.10 M air-saturated, pH 6.9 phosphate buffer. Different potentials are then applied to the 50.0 μm-wide Au microband working electrode, and then the emission of ECL is monitored using a CCD camera (Cascade, Photometrics Ltd., Tucson, AZ) mounted on a microscope (Nikon AZ100, Nikon Co., Tokyo, Japan). The results are plotted on the left side of Figure S3.

Scheme S2



The double-sided arrow in Figure S3 indicates the difference between the onset potentials for the reduction of $Fe(CN)_6^{3-}$ and the ECL emission resulting from the oxidation of

$Ru(bpy)_3^{2+}$ and TPrA. This value of ~0.67 V. is the minimum value of ΔE_{elec} required to observed ECL. Therefore, when ΔE_{elec} is larger than 0.67 V, the two faradaic reactions will occur simultaneously at the two ends of the BPE. These data are consistent with those in Figure 1 of the main text, which indicate that ECL is not observed for values of E_{tot} < 16.0 V, which is equivalent to ΔE_{elec} = 0.69 V.

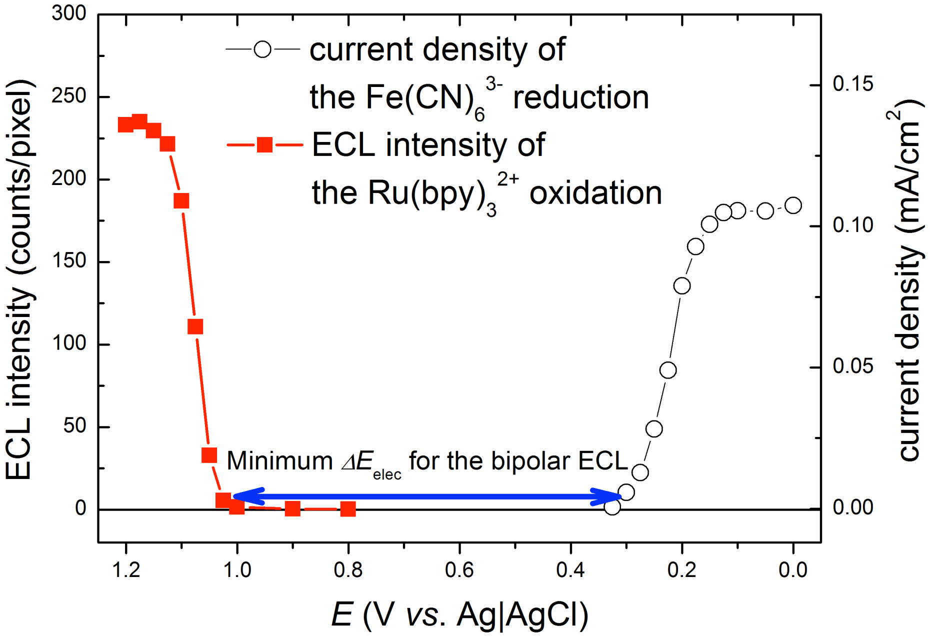


Figure S3. Plot of ECL intensity and current density as a function of electrochemical potential. The plots were obtained from separate experiments. The minimum ΔE_{elec} required for the ECL reporting is estimated to be 0.67 V based on the difference between the onset potentials for ECL and the reduction of $Fe(CN)_6^{3-}$.