# Supporting Information

## Visual voltammogram at an array of closed bipolar electrodes in a ladder configuration

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**Dependence of $i_{BPE}$ on fluid flow rate.** Eq. 3 (main text) indicates that the mass transfer limited current at a microband electrode embedded in a microfluidic channel will increase linearly with flow rate raised to the one third power. The data of **Figures 4a** and **4b** (main text) were further analyzed to determine whether this dependence is observed at the BPE ladder array. **Figure S1** shows the peak ECL intensity obtained when a solution of 5.0 mM $Fe(CN)_6^{3-}$ was flowed through the sensing channel at five distinct flow rates, plotted as a function of flow rate to the one third power. The plot is linear with an $R^2$ value of 0.94. This result is important because it indicates that the current at the BPE array is limited by mass transfer and not by the ECL reaction at the BPE anodes (reporting channel).

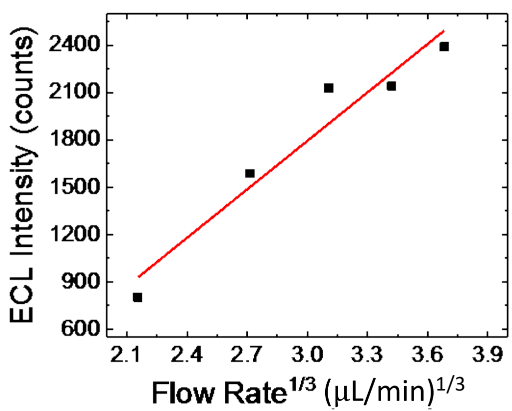


**Figure S1.** Dependence on flow rate to the one third power for the peak ECL intensity of Figure 3b, taken from Figure 3b (main text).

**Dependence of ECL intensity on current.** ECL emission has a linear dependence on current above a threshold for initiation of the luminescent reaction, and has been shown to maintain this feature when driven by a BPE.[1] Therefore, the ECL intensity (counts) obtained with our imaging system can be correlated to current. Such information allows $i_{BPE}$ at each BPE in the array to be deduced from the visual voltammogram.

**Figure S2** shows the ECL intensity (counts) obtained as a function of current density at a single ITO microband electrode in a microfluidic channel (device described in the Experimental section, main text). To obtain this result, first, the microchannel was filled with ECL solution and the flow stopped. Second, a potential step was applied to the ITO working electrode such that oxidative ECL was initiated. Finally, after apply the potential for 2 s, an image of the ECL intensity was acquired (2 s exposure time). The spatially averaged ECL intensity was obtained for a rectangular region of interest over the microband electrode, and then the background was subtracted. This procedure was repeated for a series of potentials along the ECL voltammetric wave to obtain seven distinct current densities. The ECL intensities were then plotted versus the average current density obtained during image acquisition. The results of **Figure S2** confirm the linear dependence of ECL intensity on current density. ECL intensities obtained at the BPE array (**Figures 2**, **3**, and **5**, main text) are about 4000 counts or less, indicating that the current density for $Fe(CN)_6^{3-}$ was below ~13 mA/cm$^2$.

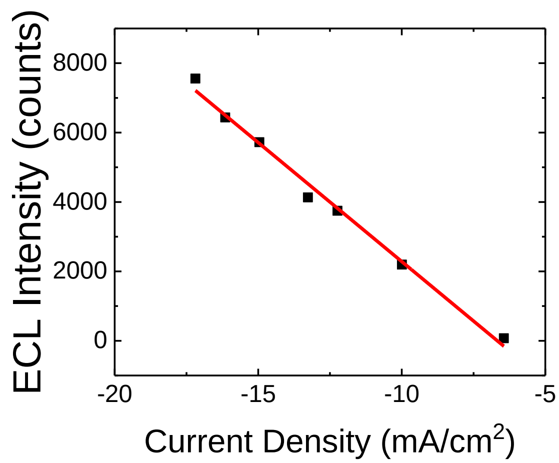


**Figure S2.** Plot of the background subtracted, spatially averaged ECL intensity at an ITO microband electrode as a function of current density. ECL solution composition matched that employed in the main text (5.0 mM $Ru(bpy)_3^{2+}$ and 25.0 mM TPrA in 0.2 M phosphate buffer, pH 6.9). The current density was averaged over the 2 s exposure time required for acquisition of the luminescence image.

**References**

1. Mavré F, Chow KF, Sheridan E, Chang BY, Crooks JA, Crooks RM. A Theoretical and Experimental Framework for Understanding Electrogenerated Chemiluminescence (ECL) Emission at Bipolar Electrodes. *Anal. Chem.* 2009;81:6218–25.