Supplementary Information

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Bipolar Electrode Focusing: Tuning the Electric Field Gradient

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Removal of peaks in the fluorescence profiles caused by reflection of light. For experiments in which fluorescence intensity and electric field profiles were monitored simultaneously, an electrode arrangement having 8 Au microband electrodes (~15 μm wide and 40 μm on center) adjacent to the BPE cathode was employed (see Figure 1a in the main text). Reflection of fluorescence from the microbands resulted in evenly space peaks in the fluorescence intensity profiles, as shown in the black curve in Figure S1. For all such experiments, these spikes were removed from the data to clarify the position and shape of the enriched tracer band (red curve, Figure S1). This was done by deleting the data points comprising the reflection peaks and then interpolating between the remaining data points using graphing software (Origin 8.0, OriginLab Corporation, Northampton, MA). Specifically, the deleted data points were replaced using a cubic spline function, which interpolated based on the trajectory of the data points preceding and following the spike.

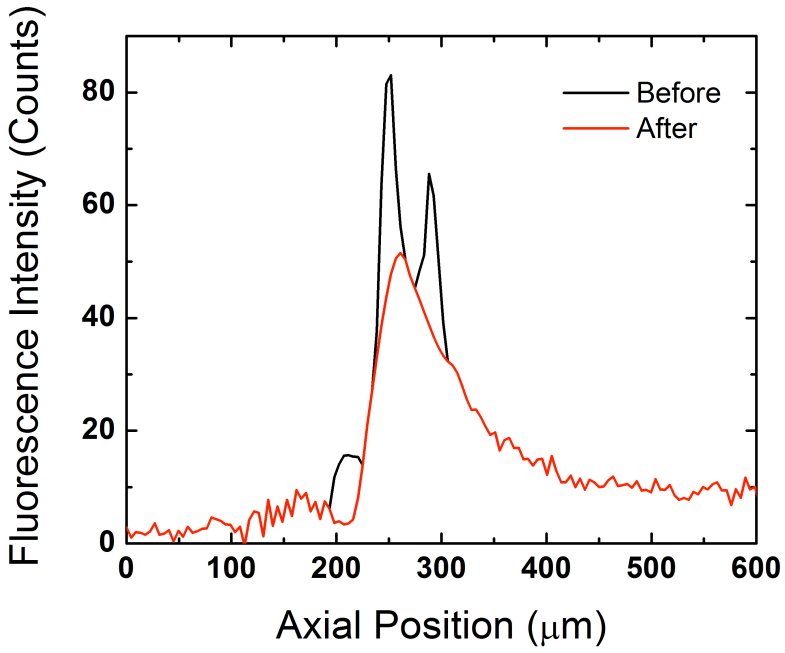

Figure S1. Background-subtracted fluorescence intensity as a function of position along the microfluidic channel (axial position = 0 at the cathodic edge of the BPE). The black spectrum was obtained before removing intensity spikes caused by reflection of fluorescence from the Au microband electrodes. The red spectrum was obtained after removal of the reflected intensity. The data shown here is taken from Figure 2c of the main text at t = 200 s.

Collapse of the electric field gradient with too much excess volume in the cathodic reservoir. Figure S2 shows the enrichment of 100 nM $BODIPY^{2-}$ in 10.0 mM Tris using the electrode configuration shown in Figure 1a of the main text. To obtain enrichment, the reservoirs were filled with the buffer/dye solution. Next, the two halves of the split BPE were connected via a conductive wire, and the SDMM started scanning the potential between the microband electrodes. Finally, E_{tot} = 35.0 V was applied to initiate enrichment. Excess buffer/dye solution was added to the cathodic reservoir in the volumes shown (Figure S2) in chronological order. Figure S2a shows the resulting fluorescence intensity profiles from the enriched band of fluorescent tracer, and Figure S2b shows the corresponding electric field profiles measured by the SDMM. The main text discusses the movement of the enriched tracer band and corresponding changes in the electric field gradient upon addition of excess solution to the cathodic reservoir of the microchannel. This excess volume induces pressure-driven flow which opposes the cathodic electroosmotic flow, reducing the net flow velocity in the channel. Typically, the reduction in flow velocity results in the enriched tracer band and the electric field gradient moving further toward the anodic reservoir (Figures S2a and S2b, respectively, at 2.0 and 2.5 μL). However, addition of too much excess volume to the cathodic reservoir results in the enriched band moving toward the BPE cathode and finally loss of the enriched band and collapse of the electric field gradient (Figures S2a and S2b at 3.0 and 3.5 μL).

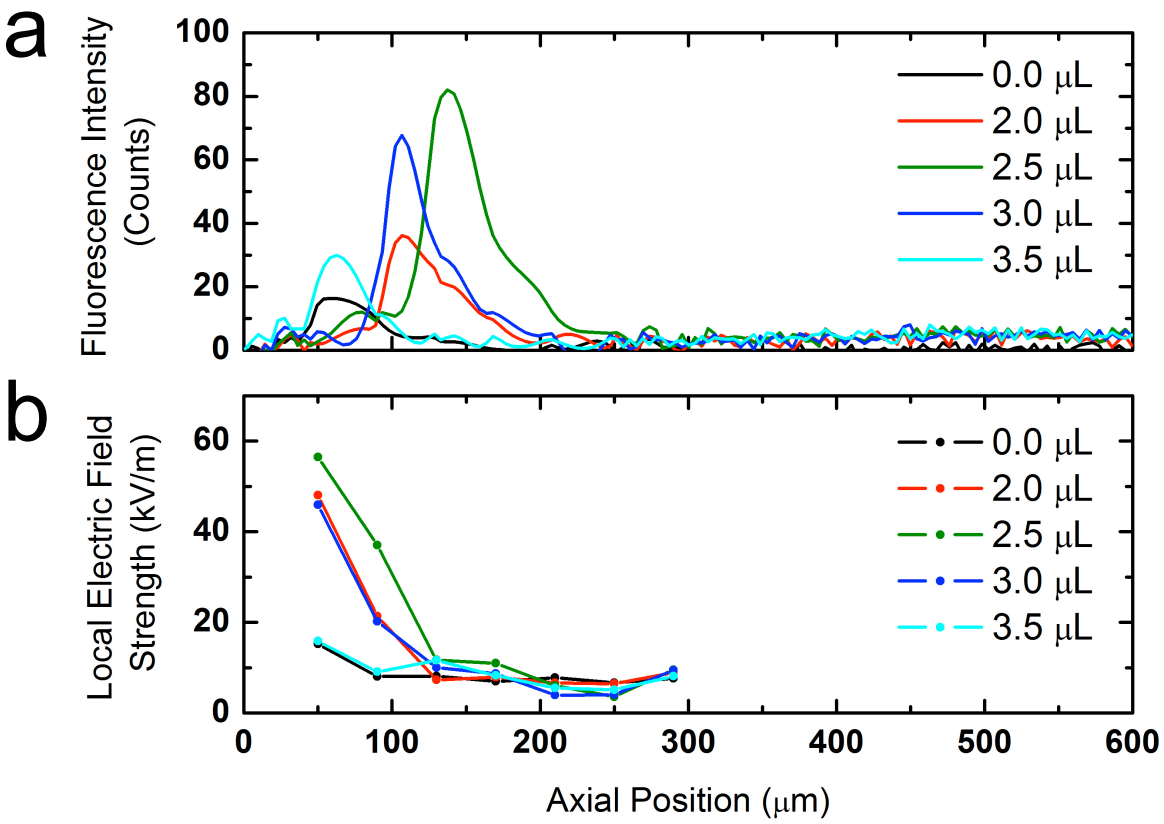

Figure S2. (a) Background-subtracted fluorescence intensity as a function of position along the microfluidic channel (axial position = 0 is at the cathodic edge of the BPE). (b) Local axial electric field strength as a function of axial position. The microchannel contained 100 nM $BODIPY^{2-}$ plus 10.0 mM Tris (pH 8.1). Pressure-driven flow was initiated by adding the indicated volumes of excess solution to the cathodic reservoir. The electrode arrangement shown in Figure 1a (main text) was used for these experiments. E_{tot} = 35.0 V.