Electronic Supplementary Information

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Electrochemically-gated delivery of analyte bands in microfluidic devices using bipolar electrodes

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**Movie S1.** BODIPY$^{2-}$ and MPTS$^{3-}$ enrichment, separation, and controlled delivery into secondary microchannels corresponding to Figure 3. The initial concentrations of the tracers were 1.0 µM and 15.0 µM, respectively, and the Tris-HCl buffer concentration was 5.0 mM (pH = 8.1). $E_{\text{tot}} = 30.0$ V. Each frame had an exposure time of 1.00 s and the frame rate of the movie is 4 frames/s. BODIPY$^{2-}$ was observed with an HQ:F filter and MPTS$^{3-}$ with a UV-2E/C filter (see below for a description of the filters).

**Movie S2.** BODIPY$^{2-}$ and MPTS$^{3-}$ enrichment, separation, and controlled delivery into secondary microchannels corresponding to Figure 5. The initial concentrations of the tracers were 1.0 µM and 15.0 µM, respectively, and the Tris-HCl buffer concentration was 5.0 mM (pH = 8.1). $E_{\text{tot}} = 30.0$ V. Each frame had an exposure time of 1.00 s and the frame rate of the movie is 4 frames/s. BODIPY$^{2-}$ was observed with an HQ:F filter and MPTS$^{3-}$ with a UV-2E/C filter (see below for a description of the filters).

**Fluorescence filters**
Throughout the experiments, two fluorescence filters were switched repeatedly so that the enriched bands of BODIPY$^{2-}$ and MPTS$^{3-}$ could be imaged individually. The MPTS$^{3-}$ filter (UV-2E/C, 96310M, C29632, Nikon, Japan) is not responsive to fluorescence from BODIPY$^{2-}$, but the BODIPY$^{2-}$ filter (HQ:F, 96320, C72455, Nikon, Japan) is also responsive to high concentrations of MPTS$^{3-}$ (50 µM or higher). By using these two filters it was possible to unambiguously identify the individual enriched bands.
Background fluorescence

The fluorescence observed outside the microchannels in Figures 3 and 5 is due to background fluorescence. Such background fluorescence is always present, and its presence in these figures reflects the low enrichment factors (EFs, the highest of which is 27±2). Figure S1 shows fluorescence micrographs, obtained using a single microdevice filled with 1.0 μM BODIPY\textsuperscript{2} in 5.0 mM Tris-HCl, after enriching for (a-c) 25 s and (d-f) 439 s at $E_{\text{tot}} = 30.0$ V. The background fluorescence observed at short enrichment times is considerably higher than at longer times. In addition, operation of the microdevices involves addition and removal of BODIPY\textsuperscript{2} and MPTS\textsuperscript{3} from the reservoirs, and slight spillage leads to staining of the outside walls of the PDMS and glass support. This, in turn, leads to the pixelated and out of focus fluorescence observed around the microchannels in Figures 3 and 5.

**Figure S1.** Fluorescence micrographs showing the contribution of background fluorescence after enriching BODIPY\textsuperscript{2} for (a-c) 25 s and (d-f) 439 s using a single microdevice. The evolution of the image processing used to construct Figures 3 and 5 in the main
text is also illustrated. (a) Un-edited fluorescence micrograph after 25 s of enrichment time. (b) After adjusting the brightness and contrast in (a). (c) After adding false color to (b). (d) Un-edited fluorescence micrograph after 439 s of enrichment time. (e) After adjusting the brightness and contrast in (d). (f) After adding false color to (e).

**Figure S2.** Un-edited fluorescence micrographs corresponding to Figure 3 in the main text. (a) BODIPY$^{2-}$ observed with the HQ:F filter during enrichment and separation. (b) MPTS$^{3-}$ observed with the UV-E/C filter during enrichment and separation. (c)
Electrochemically-gated delivery of BODIPY$^{2-}$ into SC1. (d)
Electrochemically-gated delivery of MPTS$^{3-}$ into SC2.
**Figure S3.** Un-edited fluorescence micrographs corresponding to Figure 5 in the main text. (a) BODIPY$^2^-$ observed with the HQ:F filter during enrichment and separation. (b) MPTS$^3^-$ observed with the UV-E/C filter during enrichment and separation. (c) Electrochemically-gated delivery of BODIPY$^2^-$ into SC2. (d) Electrochemically-gated delivery of MPTS$^3^-$ into SC1.
Figure S4: Frames used to measure the extent of leakage of BODIPY$^{2-}$ and MPTS$^{3-}$ into the gated (blocked) secondary microchannel using the microdevice corresponding to Figure 3 in the main text. The white dotted rectangles represent the regions of interest (ROI) used to measure the fluorescence intensity of the analyte inside that secondary microchannel. (a) Frame used to measure the fluorescence intensity in SC2 before delivery of BODIPY$^{2-}$ into SC1. (b) Frame used to measure the fluorescence intensity of SC2 during the delivery of BODIPY$^{2-}$ into SC1. (c) Frame used to measure the fluorescence intensity in SC1 before the delivery of MPTS$^{3-}$ into SC2. (d) Frame used to measure the fluorescence intensity in SC1 during the delivery of MPTS$^{3-}$ into SC2.
**Figure S5:** Frames used to measure the extent of leakage of BODIPY$^{2-}$ and MPTS$^{3-}$ into the gated (blocked) secondary microchannel using the microdevice corresponding to Figure 5 in the main text. The white dotted rectangles represent the regions of interest (ROI) used to measure the fluorescence intensity of the analyte inside the secondary microchannel. (a) Frame used to measure the fluorescence intensity in SC1 before the delivery of BODIPY$^{2-}$ into SC2. (b) Frame used to measure the fluorescence intensity of SC1 during the delivery of BODIPY$^{2-}$ into SC2. (c) Frame used to measure the fluorescence intensity in SC2 before the delivery of MPTS$^{3-}$ into SC1. (d) Frame used to measure the fluorescence intensity in SC2 during the delivery of MPTS$^{3-}$ into SC1.
**Figure S6**: Calibration curves used to calculate EFs for (a) BODIPY$^{2-}$ and (b) MPTS$^{3-}$.