SUPPORTING INFORMATION

(Almost) Stationary Isotachophoretic Concentration Boundary in a Nanofluidic Channel Using Charge Inversion

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Materials and Methods

Materials. Experiments were performed in, 5.6 mm × 6.2 μm × 100 nm straight nanofluidic channels, custom-fabricated in fused silica (Figure 1 of main text). These channel geometries were patterned onto fused silica wafers using conventional optical photolithography and then reactive-ion etched to a depth of 100 nm. Tolerances were 10 nm for the depth and 0.1 μm for the width. The channels were sealed by fusion bonding to a second fused silica wafer with 2 mm diameter predrilled wells. A schematic of channel geometry and experimental setup is shown in Fig. 1 of main the text. The fused silica chip was housed in a custom fabricated Delrin chip holder with 50 μL wells and sealed with a fluorosilicone gasket to prevent leakage and evaporation of samples. Platinum Iridium electrodes were used to apply the external potential.

Chemicals. Dry $Ru(bpy)_3Cl_2$ and $MgCl_2$ salts were purchased from Sigma Aldrich. Solutions were prepared with de-ionized filtered water at 18 MΩ/cm from Millipore Milli-Q water (EMD Millipore, Billierica, MA) and all stock solutions were measured to have a pH of 7.5. Stock solutions were prepared at 50 mM and were first filtered with 0.2 μm syringe filters (THERMO Scientific) before being diluted down to the concentrations reported in the results section.

Experimental Setup. Figure 1 of the main text shows a schematic of the experimental setup used for our experiments. We applied a voltage using a Keithley 2410 sourcemeter (Keithley, Inc.) and Platinum Iridium electrodes. Current was measured with a Keithley 6517a (Keithley, Inc.) electrometer for better precision. Fluorescence intensity measurements were performed on an IX71 Olympus microscope with an iXon Ultra 897 EMCCD with a 512 X 512 pixel array and 16-bit digitization. A frame rate of 20 fps was used for all experiments. We used a filter cube (MDFM-MF2, Thorlabs) with excitation filter (D405/90x, Chroma Technology Corp), emission filter (595AF60, Omega Optical), and dichroic mirror (470dcxr, Chroma Technology Corp) to excite the $Ru(bpy)_3^{2+}$ and measure the fluorescence. We collected data with LabVIEW and analyzed all resulting data in MATLAB. Relative intensity versus the measured intensity of a DI-filled channel was calculated.

Channel Preparation. Before use, all channels were baked at 400° C for ~2 hours then allowed to capillary fill. After use, all channel geometries were rinsed for 10 min with 100 mM HCl to fully protonate silanol groups on the glass surface, reducing the surface charge and freeing any ions that remained from the previous experiments[1] and stored in a 1:1 DI to EtOH mixture. To minimize carry-over upon changing solutions in the reservoirs during experiments, the wells were completely rinsed three times with the new solution before voltage was applied.

(1) Janssen, K. G. H.; Hoang, H. T.; Floris, J.; de Vries, J.; Tas, N. R.; Eijkel, J. C. T.; Hankemeier, T., *Anal. Chem.* **2008,** *80*, 8095-8101.