Supporting Information

Multiplexed DNA-Modified Electrodes

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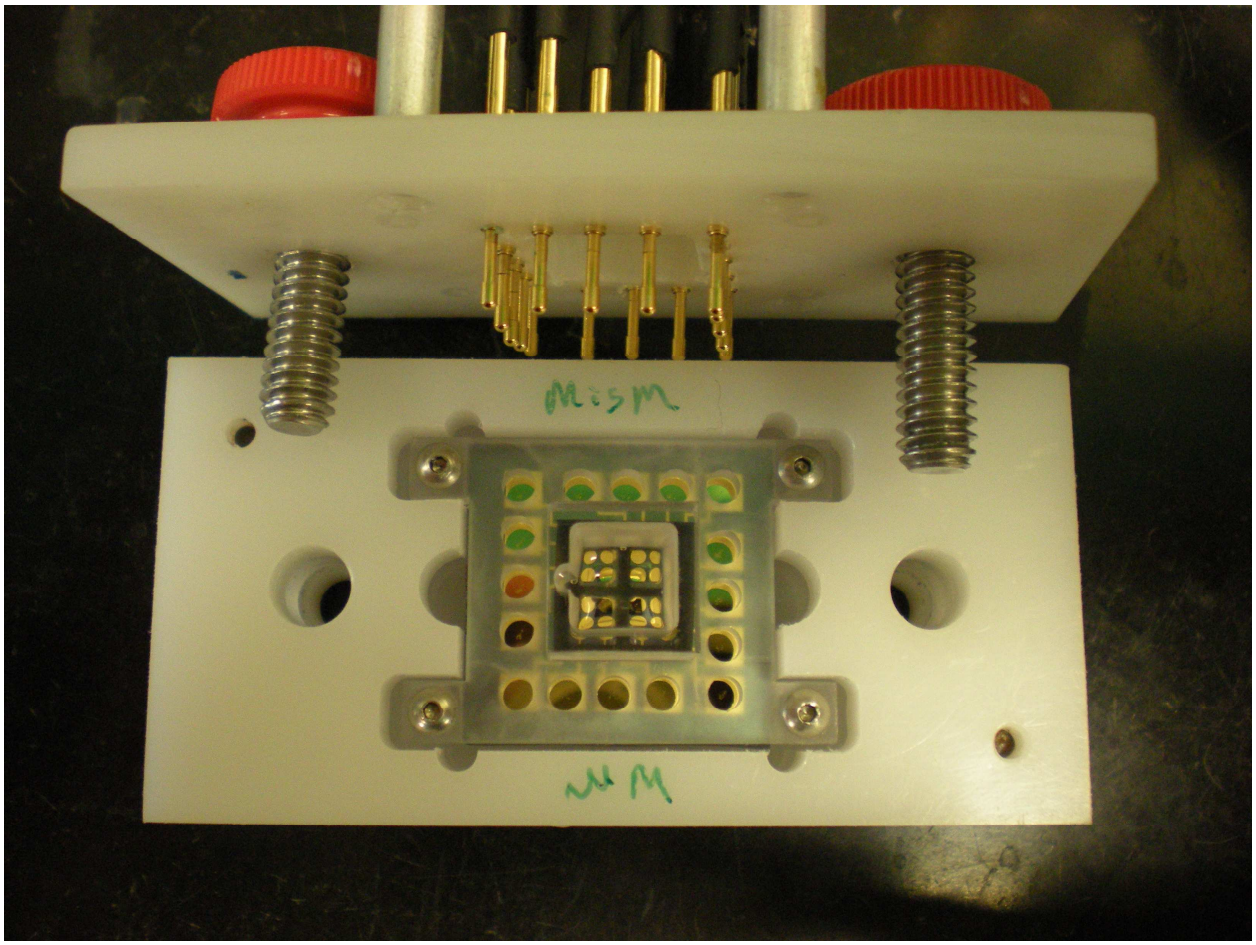
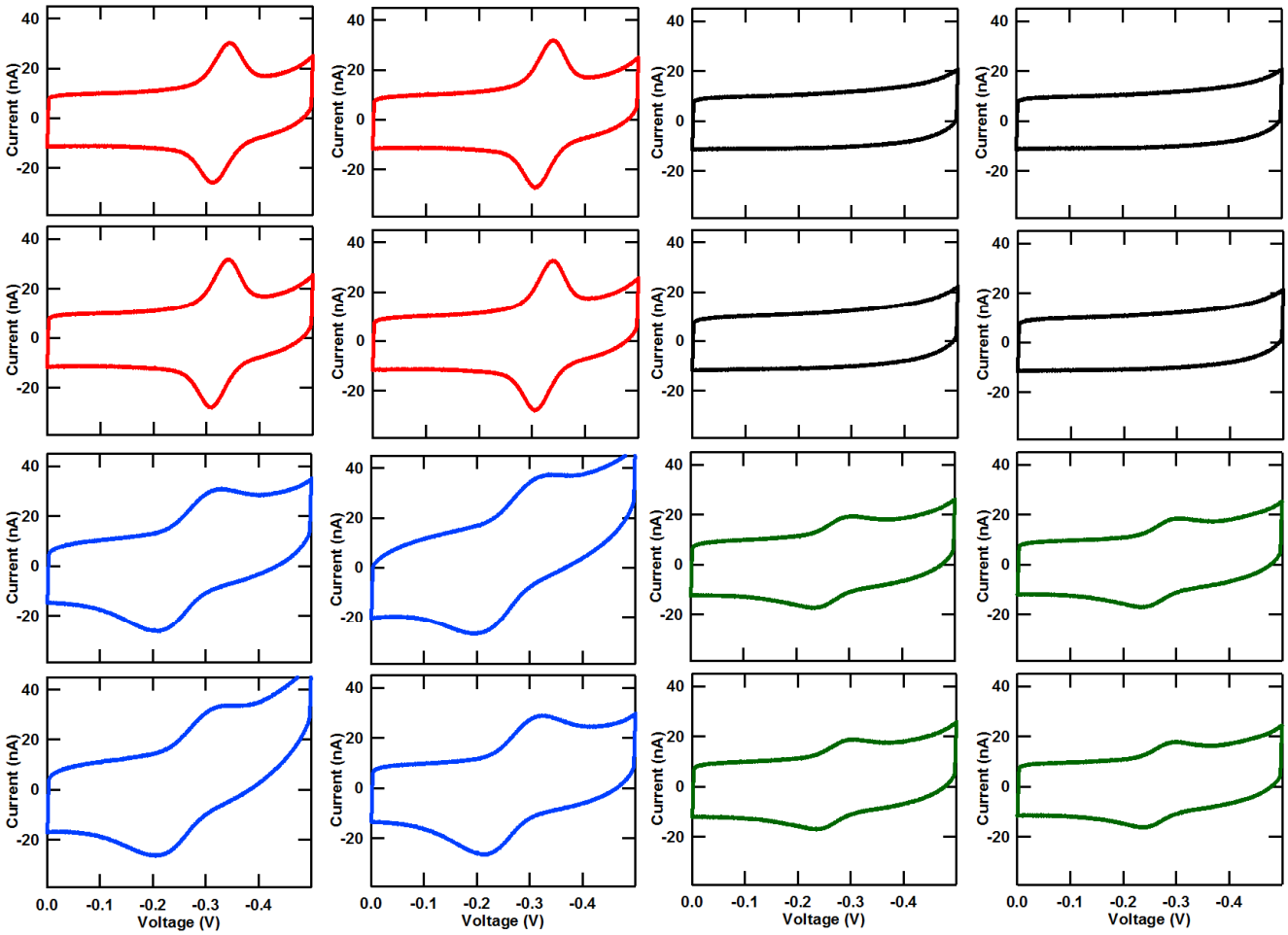


Supporting Figure 1. Close up picture of a DME chip with clamp well in the testing mount.

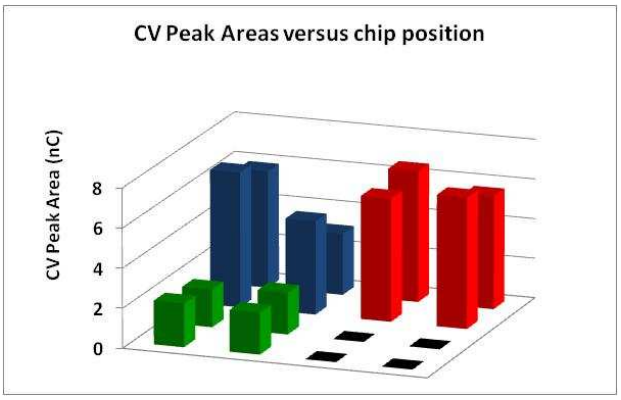
Supporting Table 1. DNA melting temperature data as obtained from UV-Vis spectrometry for the 17-mer sequences of Figure 2 of the main text.

DNA target	$T_{M,actual}$ (°C)	$T_{M,calculated}$ (°C)[a]
Well Matched 3′ Redmond Red	56.2	54.8
Well Matched 5′ Nile Blue	55.1	54.8
Mismatched 5′ Nile Blue	43.4	47.0
Well Matched No Probe	54.4	54.8

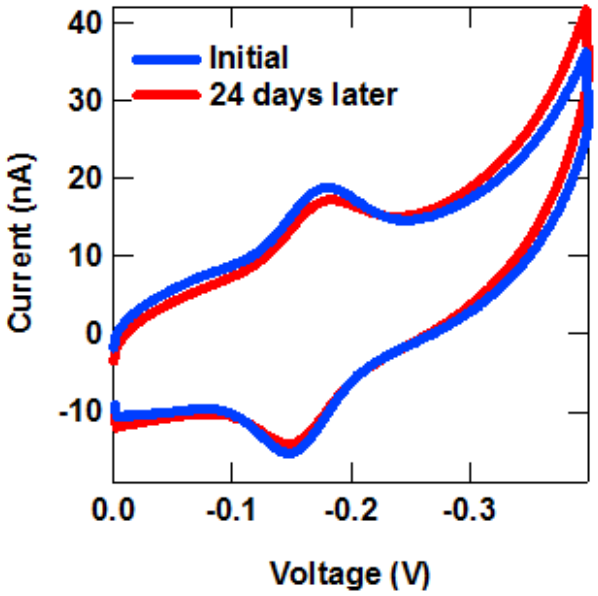
[a] Calculated values from Integrated DNA Technologies OligoAnalyzer software.



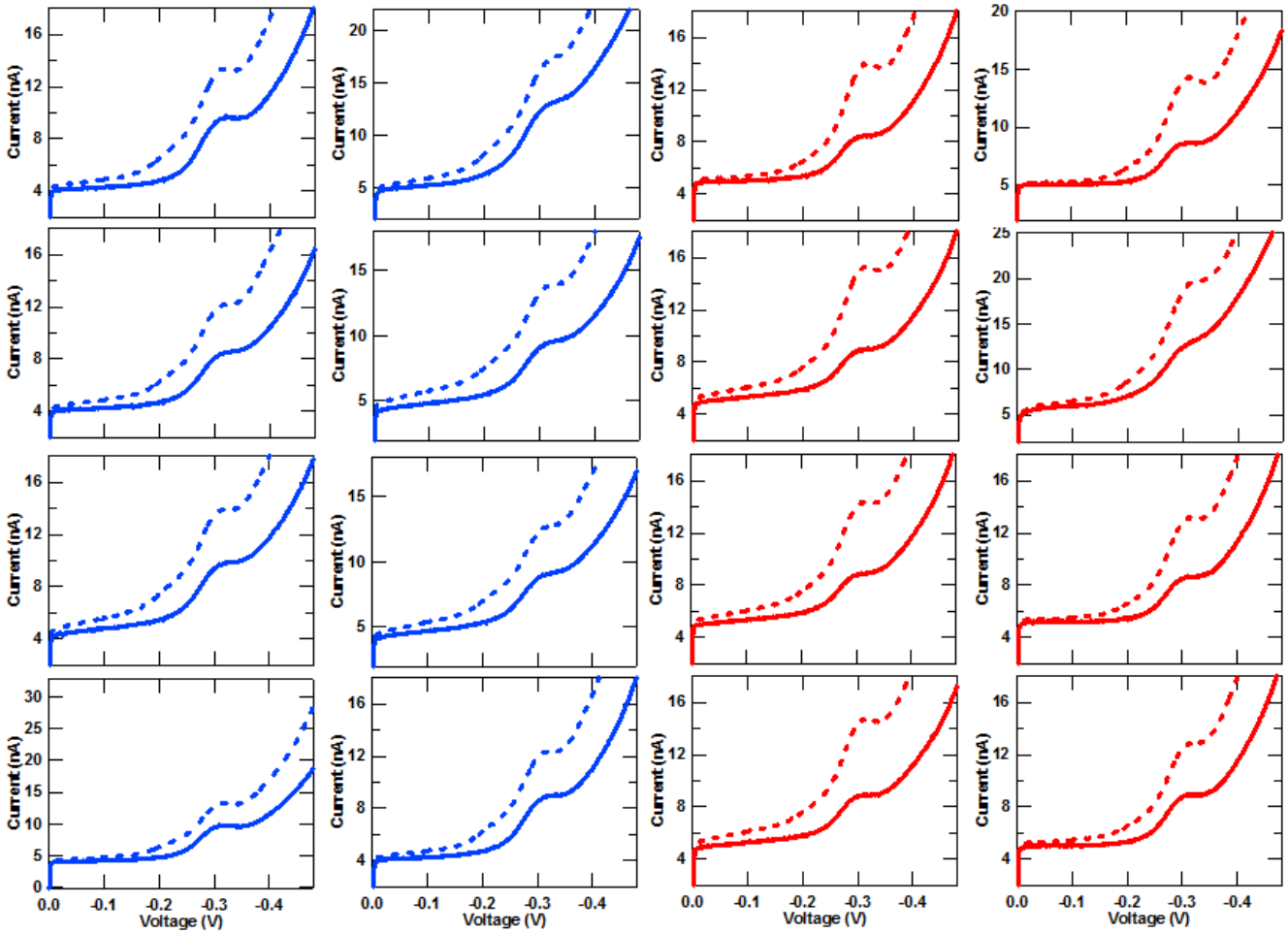
Supporting Figure 2. Cyclic voltammetry data showing all 16 electrode signals from the chip used in the experiment of Figure 2 of the main text. The chip was prepared with four different DNA sequences on four electrodes each. The four sequences consisted of (i) a well matched strand with a distal 5′ Nile Blue redox probe (5′-T_{NB}GC GTC TCA GCT GAA GT-3, blue), (ii) a well matched strand with a proximal 3′ Redmond Red probe (5′-TGC GTC TCA GCT GAA GT(RR)-3′, red), (iii) a well matched strand with no redox probe (5′-TGC GTC TCA GCT GAA GT-3′, black), and (iv) a 5′ Nile Blue-labeled strand containing a single base-pair (CA) mismatch (5′-T_{NB}GC GTC TCA GCT <u>A</u>AA GT-3, green). (T_{NB} is a thymine modified with a Nile Blue redox probe, <u>A</u> notes the location of a single CA mismatch, and RR denotes a Redmond Red redox probe.) The potentials are reported versus Ag/AgCl with a CV scan rate of 100 mV/s.



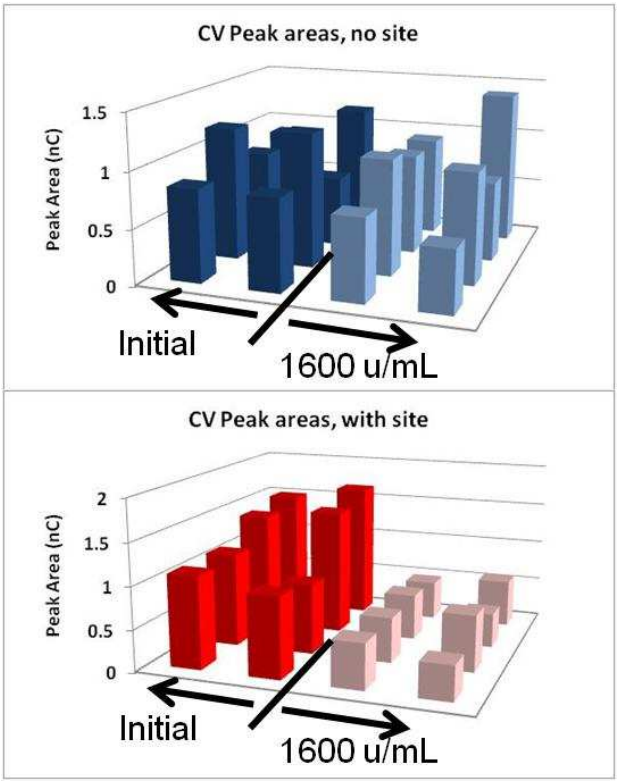
Supporting Figure 3. Integrated CV peak charge versus chip position for the chip used in the experiment of Figure 2 of the main text. The chip was prepared with four different DNA sequences on four electrodes each. The four sequences consisted of (i) a well matched strand with a distal 5′ Nile Blue redox probe (5′-T_{NB}GC GTC TCA GCT GAA GT-3, blue), (ii) a well matched strand with a proximal 3′ Redmond Red probe (5′-TGC GTC TCA GCT GAA GT(RR)-3′, red), (iii) a well matched strand with no redox probe (5′-TGC GTC TCA GCT GAA GT-3′, black), and (iv) a 5′ Nile Blue-labeled strand containing a single base-pair (CA) mismatch (5′-T_{NB}GC GTC TCA GCT AAA GT-3, green). (T_{NB} is a thymine modified with a Nile Blue redox probe, A notes the location of a single CA mismatch, and RR denotes a Redmond Red redox probe.)



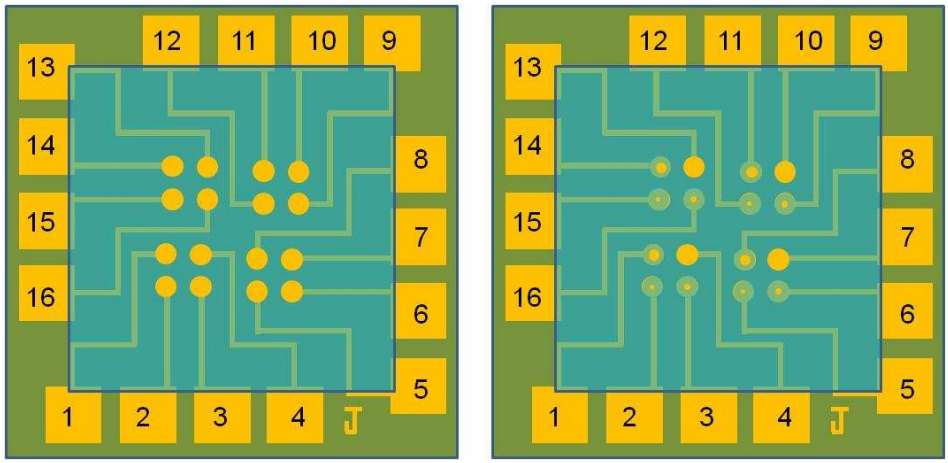
Supporting Figure 4. Cyclic voltammetry data of a chip measured initially (blue) and after 24 days of storage (red) at 4 °C. The DNA sequence was the well matched 17-mer 5′-T_{NB}GC GTG CTT TAT ATC TC-3′, where T_{NB} is a thymine modified with a Nile Blue redox probe. The curves are the average over all 16 electrodes on the chip. The potentials are reported versus Ag/AgCl with a CV scan rate of 50 mV/s.



Supporting Figure 5. Cyclic voltammetry data showing all 16 electrodes from the chip used in the *Alu*1 experiment of Figure 3 of the main text. The data shown is for the cathodic sweep at 50 mV/s for initial (dotted lines) and at 1600 units *Alu*1/mL (solid lines) for DNA with (red) and without (blue) the restriction site.



Supporting Figure 6. Integrated CV peak charge versus peak position for the chip used in the *Alu*1 experiment of Figure 3 of the main text. (Top) Integrated peak areas for the 8 electrodes modified with DNA monolayers without the restriction site before (left) and after (right) addition of 1600 units/mL *Alu*1. (Bottom) Integrated peak areas for the 8 electrodes modified with DNA monolayers bearing the restriction site before (left) and after (right) addition of 1600 units/mL *Alu*1.



Supporting Figure 7. (Not to scale) Illustration of the layout for a macroelectrode (left) and a microelectrode (right) DME chip. To create microelectrodes, the SU-8 is extended to expose smaller areas of the gold working electrodes. We used this scheme to create reduced electrode diameters of 300, 56, and 10 μm.