Supporting Information

Simulation-Based Approach to Determining Electron Transfer Rates Using Square-Wave Voltammetry

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ABBREVIATIONS

Fc, Ferrocene; MB, Methylene Blue; TCEP, tris(2-carboxyethyl)phosphine hydrochloride.

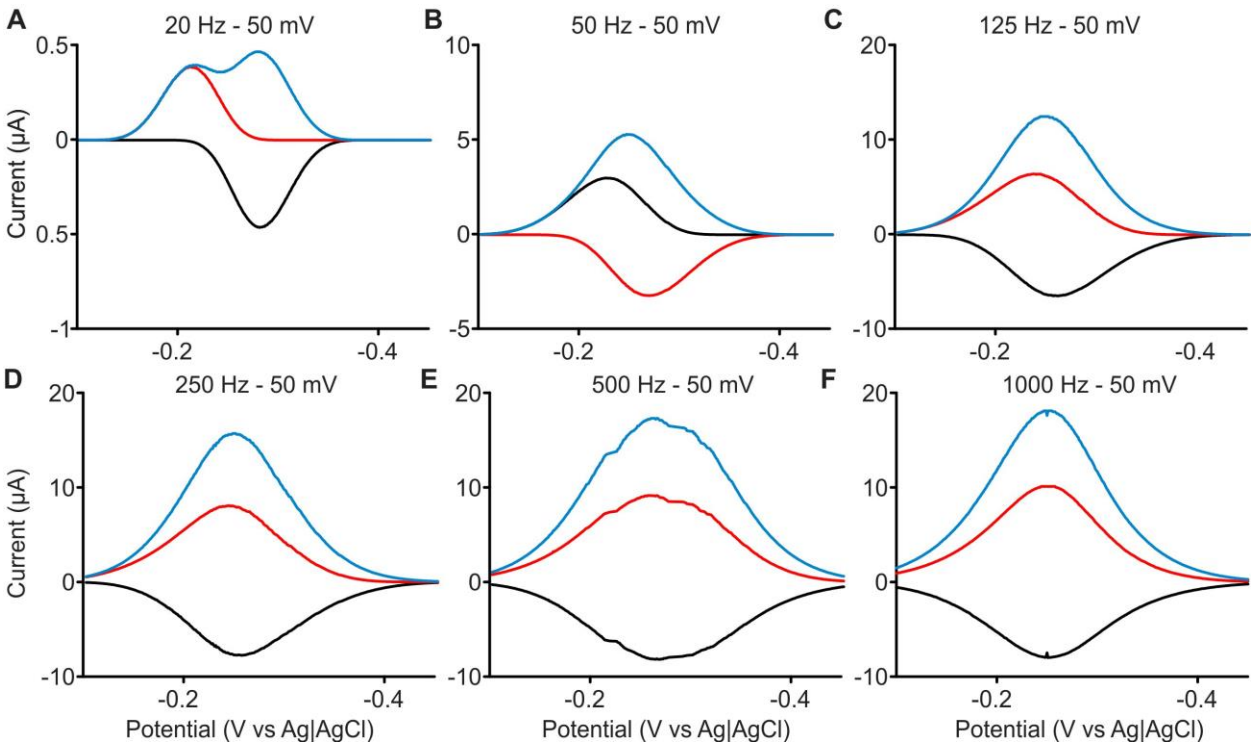

Figure S-1. Forward (red), backward (black) and net (blue) voltammograms of a reduction reaction simulated using increasing square-wave frequencies and a fixed amplitude of 50 mV, using k^0 and α of 1.0 cm s^{-1} and 0.5, respectively.

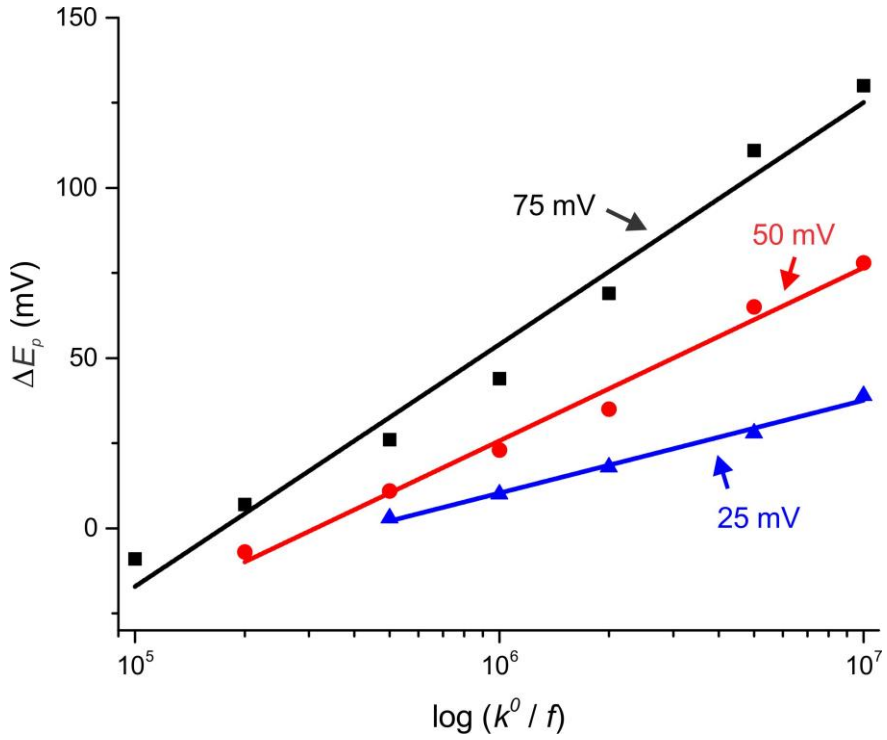

Figure S-2. The larger the separation between the forward and backward voltammograms, the greater the extent to which the shape of the net voltammogram carries kinetic information that is ignored when using approaches that only consider peak height. To see this we used our numerical model to characterize the separation (y-axis) between the forward and backward square-wave voltammogram peaks (ΔE_p) as a function of square-wave frequency and electron transfer rate (x-axis; shown as the unit-less ratio of the electron transfer rate over the square wave frequency) and the square-wave amplitude (indicated on the plot). As the kinetics become rapid relative to the square-wave frequency the peak splitting grows significantly, thus causing the peak split, reducing the information contained in peak height and increasing the information contained in peak shape.

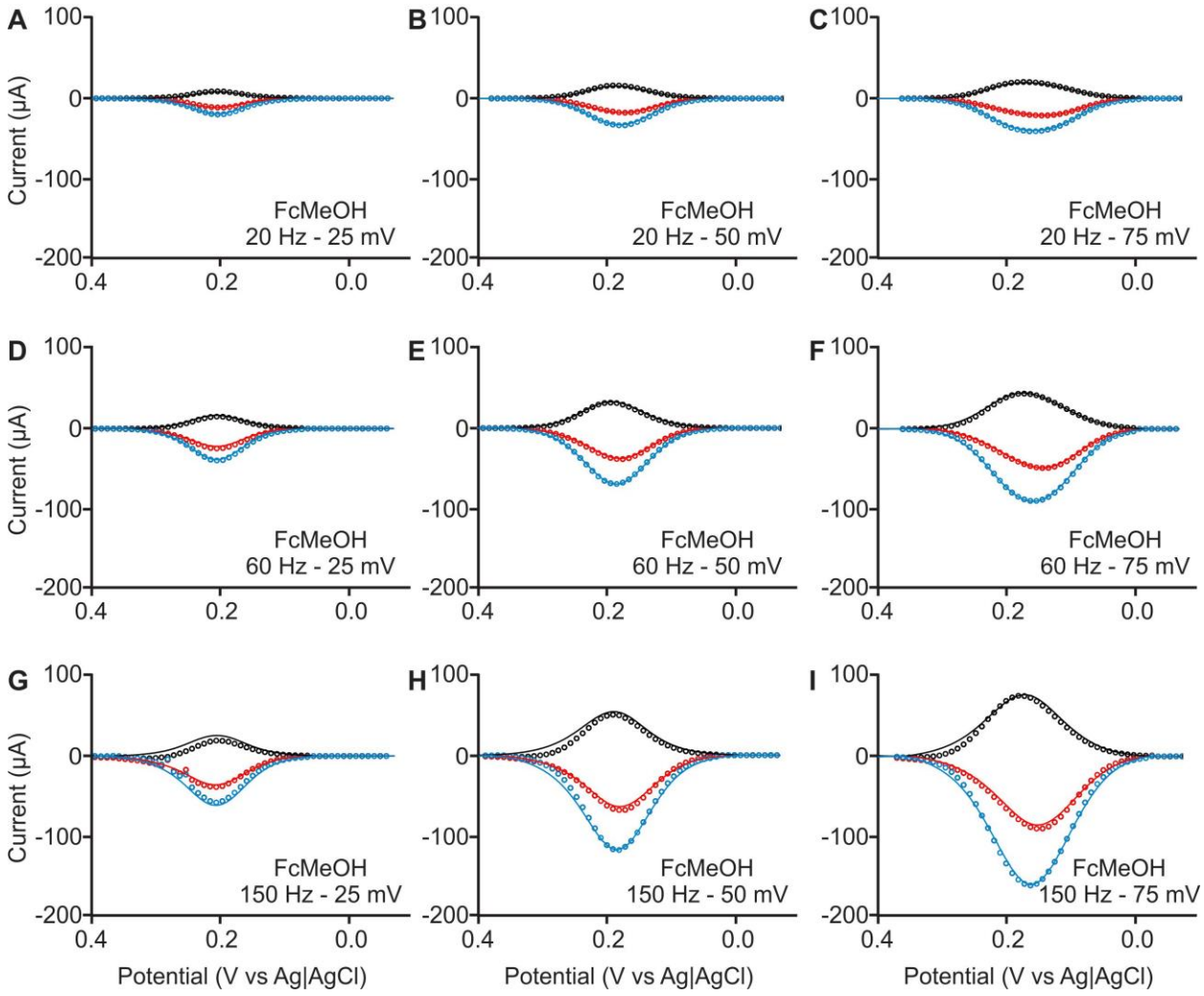

Figure S-3. Forward (red), backward (black) and net (blue) voltammograms (solid lines) recorded using a variety of square-wave frequency and amplitude combinations with a 2 mm gold electrode immersed in a solution of FcMeOH, with respective simulated voltammograms (open circles) superimposed. For the simulated voltammograms we used k^0 and α of 10 ± 1 cm s^{-1} and 0.50 ± 0.03, respectively. These values are in good agreement with a previously reported value of 8 ± 1 cm s^{-1} and 0.44 ± 0.03.

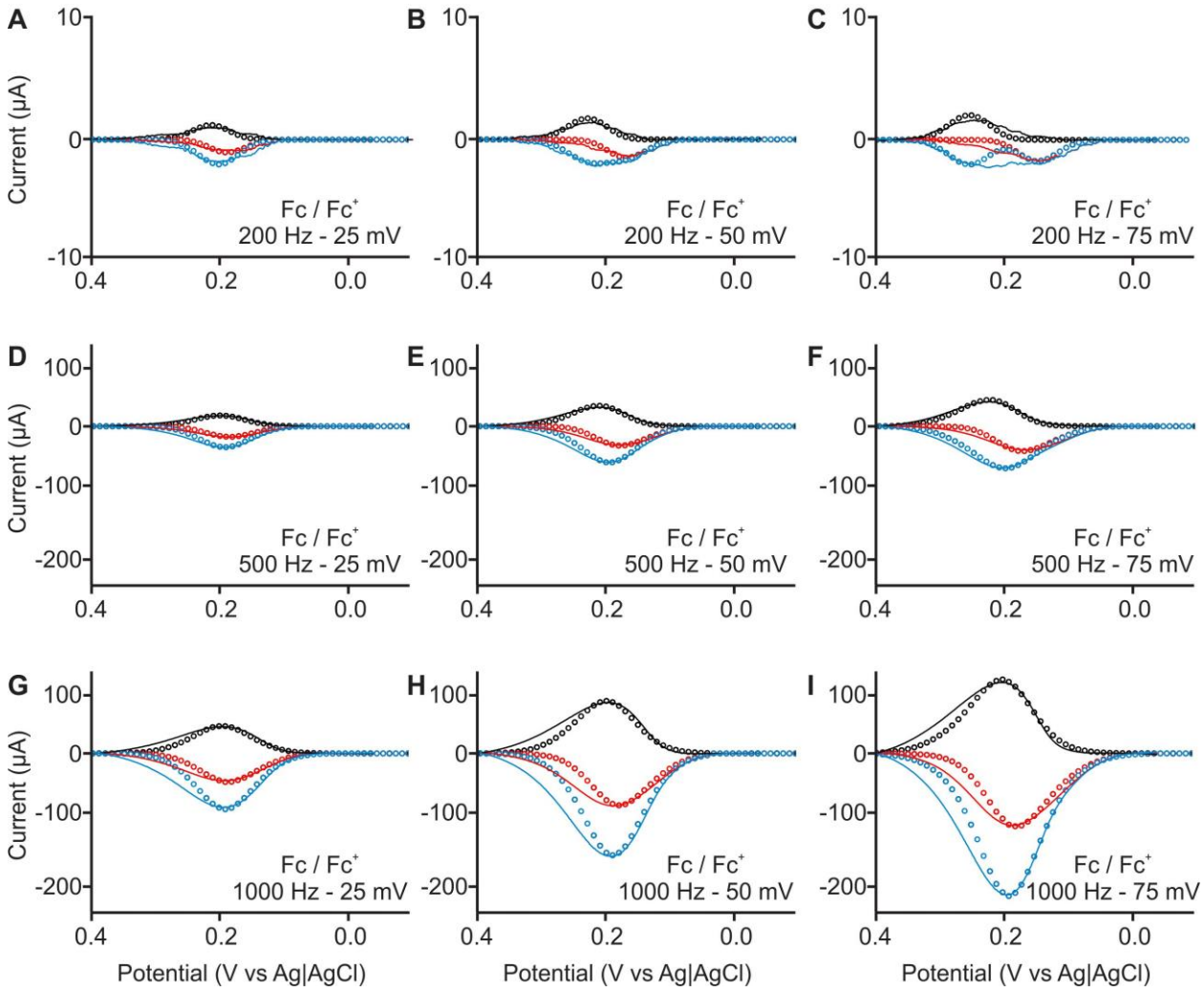

Figure S-4. Forward (red), backward (black) and net (blue) voltammograms (solid lines) recorded using a variety of square-wave frequency and amplitude combinations with ferrocene immobilized on a gold electrode using a hexanethiol chain, with respective simulated voltammograms (open circles) superimposed. For the simulated voltammograms we used k^0 and α of 8 ± 2 cm s^{-1} (or $k^0_{x=8Å}$ = 2.7 x 10^5 s^{-1}) and 0.50 ± 0.03, respectively. These are in good agreement with values previously reported for similar systems.

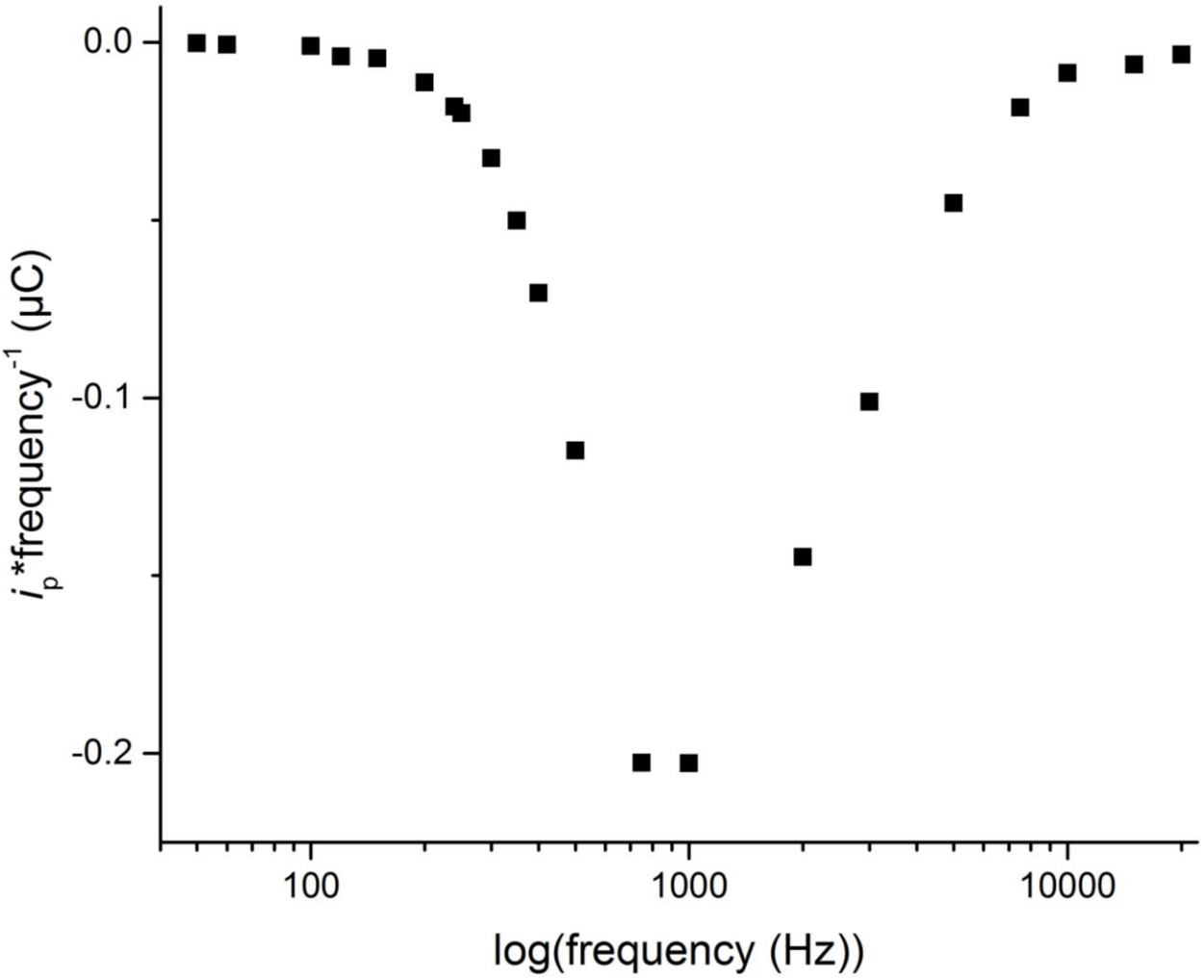

Figure S-5. Quasi-reversible maximum analysis of ferrocene immobilized on a gold electrode using a hexanethiol chain. This analysis produces an estimate of $k^0_{x=8Å}$ of ~ 880 s^{-1}, which is 2 orders of magnitude smaller than both value produced by our approach and by previous determinations via indirect laser induced temperature jump method.

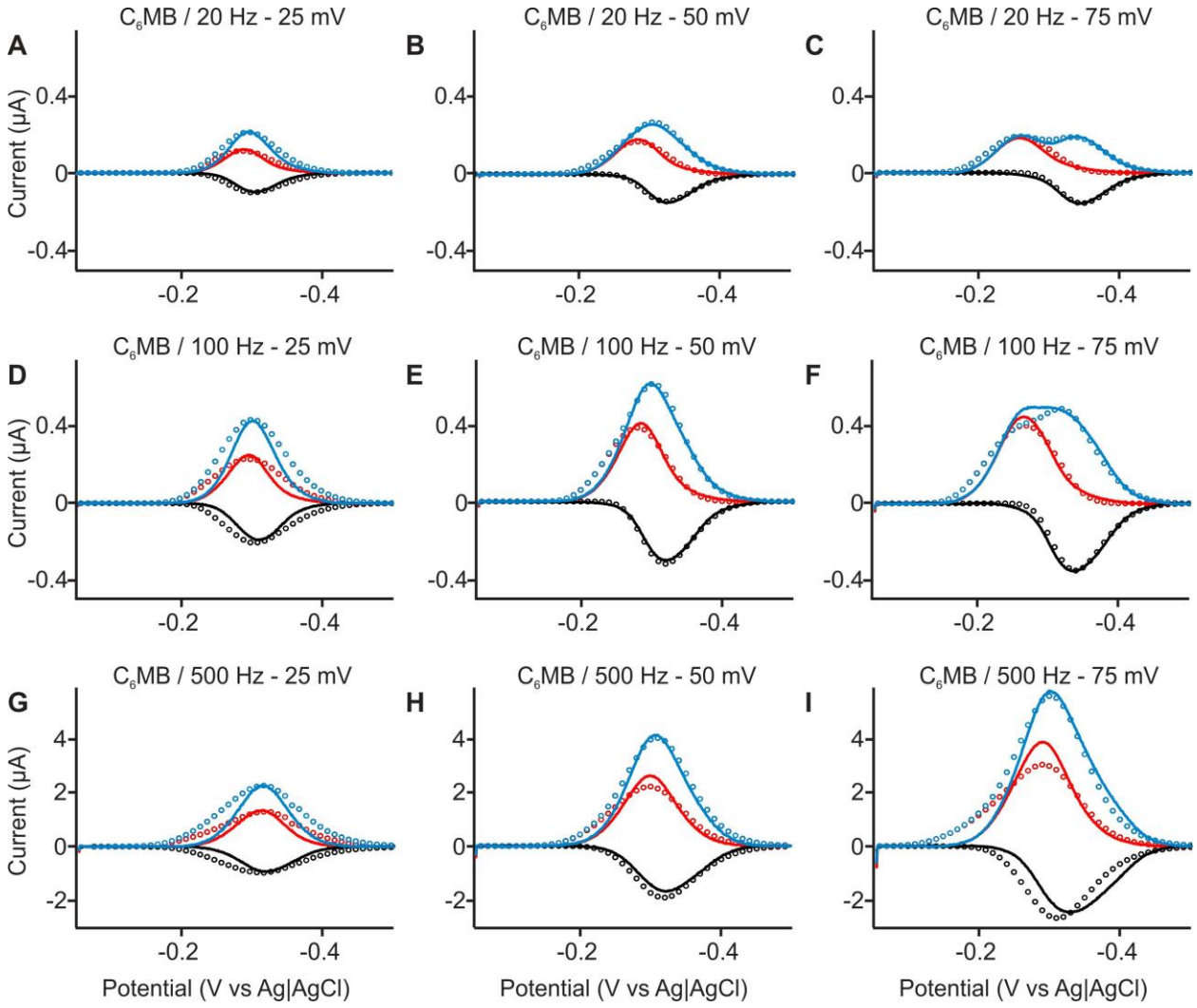

Figure S-6. Forward (red), backward (black) and net (blue) voltammograms (solid lines) recorded using a variety of square-wave frequency and amplitude combinations with methylene blue immobilized on gold electrode using maleimide chemistry to a hexanethiol chain incorporated in a 6-mercaptohexanol self-assembled monolayer, with respective simulated voltammograms (open circles) superimposed. For the numerical voltammograms we have used k^0 and α of 1.5 ± 0.5 cm s^{-1} ($k^0_{x=8Å}$ = 5.0 ± 1.7 x 10^4 s^{-1}) and 0.37 ± 0.02, respectively.

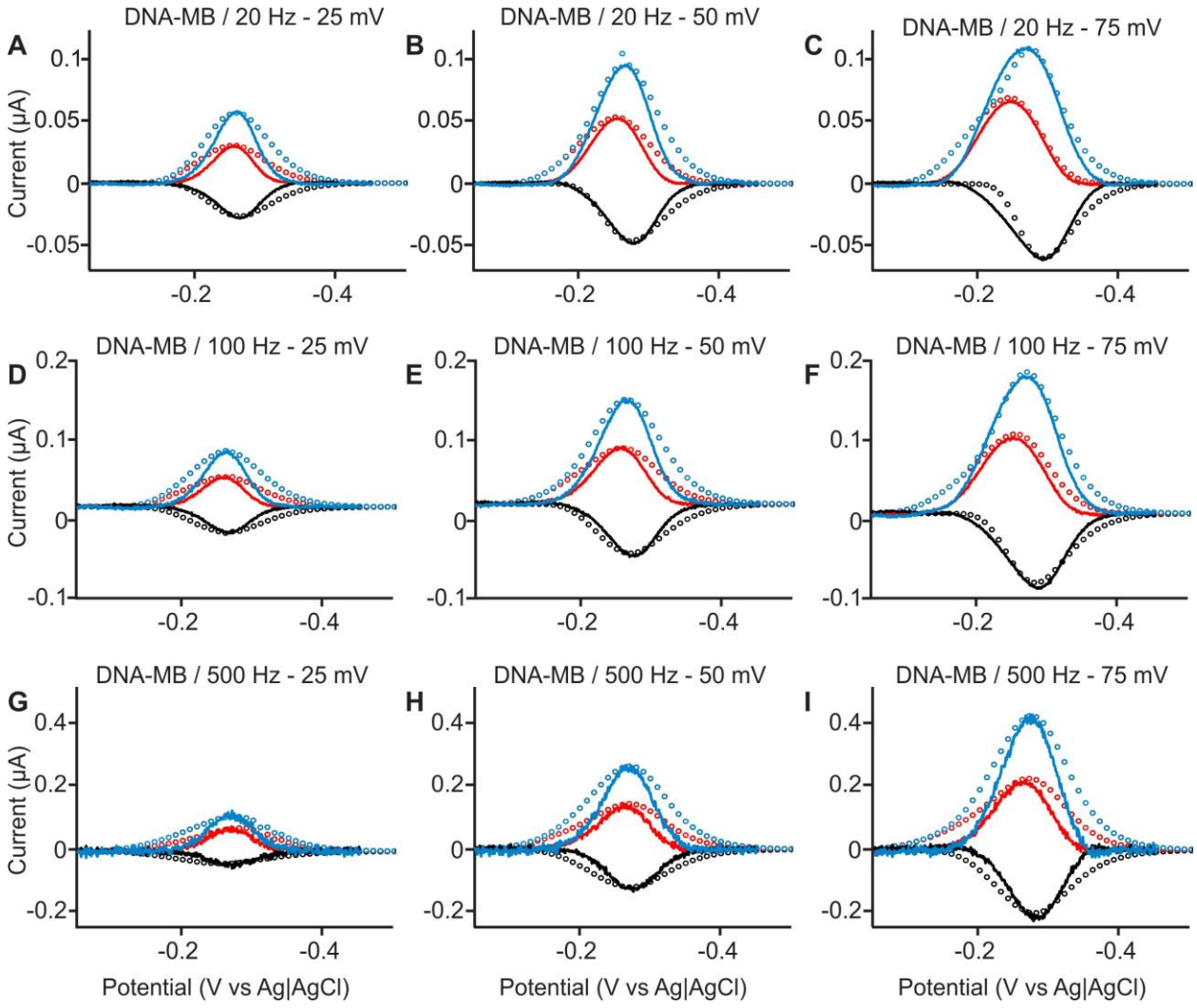

Figure S-7. Forward (red), backward (black) and net (blue) voltammograms (solid lines) recorded using a variety of square-wave frequency and amplitude combinations with a 20 base linear DNA modified with methylene blue on its distal end onto a gold electrode coated with a 6-mercapto-1-hexanol monolayer, with respective simulated voltammograms (open circles) superimposed. For the simulated voltammograms we used k^0 and α of 0.4 ± 0.1 cm s^{-1} and 0.37 ± 0.02, respectively.