

SUPPORTING INFORMATION

Scanning bipolar electrochemical microscopy

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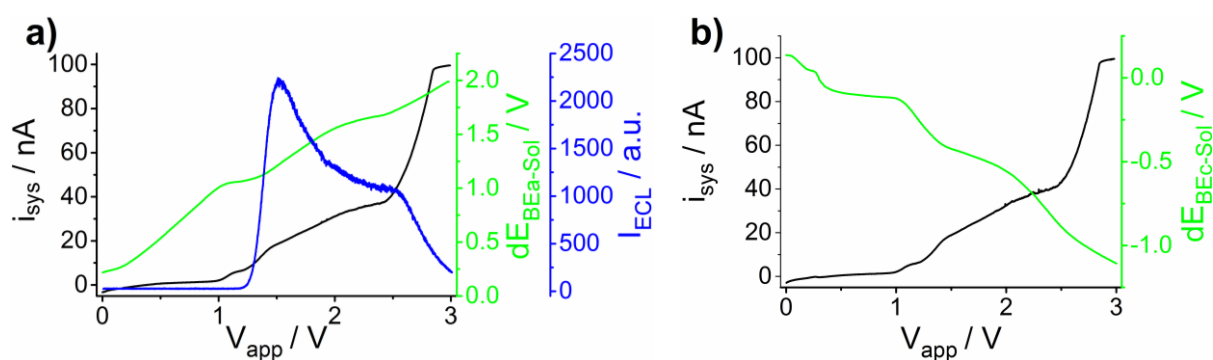


Figure S-1. Bipolar LSVs showing a) i_{sys} (black), I_{ECL} (blue), and $dE_{\text{BE}_a\text{-Sol}}$ (green) versus V_{app} and b) i_{sys} (black) and $dE_{\text{BE}_c\text{-Sol}}$ (green) versus V_{app} . For all measurements, a solution of 1 mM $[\text{Fc}(\text{MeOH})_2]$ and 1 mM $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ in 0.1 M KCl was used in the cathodic cell (BE_c: Ø 50 µm Pt-microelectrode), while a solution of 1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 50 mM TPrA in 0.1 M PBS (pH 7.4) was used in the anodic compartment (BE_a: Ø 25 µm Pt-microelectrode).

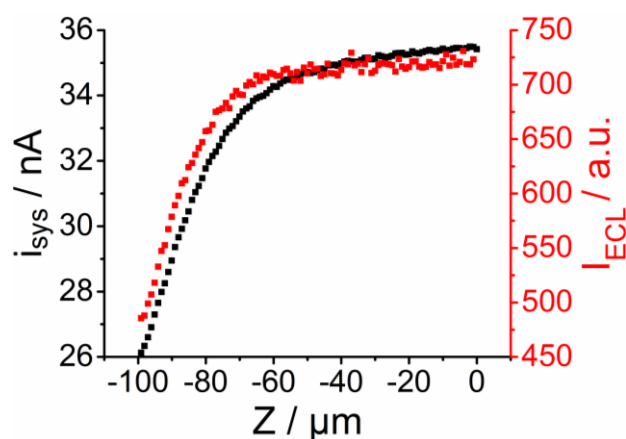


Figure S-2. Bipolar approach curve using 1 mM $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ in 0.1 M KCl solution in the cathodic compartment and a solution of 1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 50 mM TPrA in 0.1 M PBS (pH 7.4) in the anodic compartment. In the bipolar configuration, BE_c was approached to non-conducting bottom of the cathodic chamber while i_{sys} (black) and I_{ECL} (red) were recorded as indicators of the negative feedback upon approach. $V_{\text{app}} = 1.6$ V, EM gain = 250.

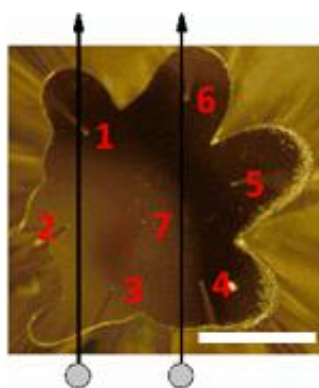


Figure S-3. Photograph taken with an optical microscope showing the cathodic poles of the seven BEs. Scale bar: 500 μm .

Video S-1. Video of the anodic BE poles of the array during the line scan shown in Figure 2b as recorded with the EMCCD camera (played back with 5 fps, one frame at each x, y-position). A solution of 1 mM $[\text{Fc}(\text{MeOH})_2]$ in 0.1 M KCl was used in the cathodic compartment, while a solution of 1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 50 mM TPrA in 0.1 M PBS (pH 7.4) was used in the anodic compartment. Increment: 50 μm , $d_{\text{tip-membrane}} = 50$ μm .