Supporting Information

Electrochemical Rectification of Redox Mediators Using Porphyrin-Based Molecular Multilayered Films on ITO Electrodes

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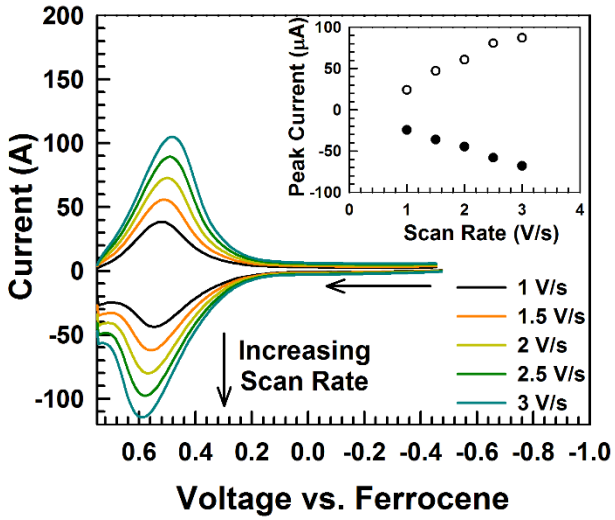
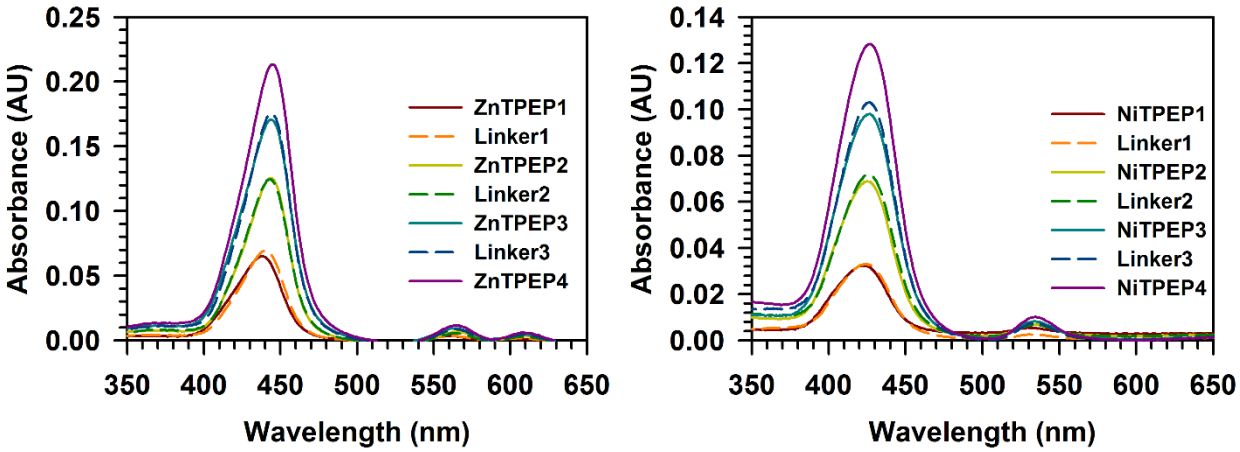


Figure S1. CVs of **ZnTPEP$_4$** film on ITO taken at a different scan rates. Inset includes peak current height as a function of scan rate for anodic (filled dots) and cathodic (unfilled dots) peaks of ZnTPEP's first oxidation.



Layer	molecules / cm^2	Layer	molecules / cm^2
ZnTPEP$_1$	5.74 x 10^{13}	**NiTPEP$_1$**	8.53 x 10^{13}
ZnTPEP$_2$	1.28 x 10^{14}	**NiTPEP$_2$**	2.01 x 10^{14}
ZnTPEP$_3$	2.10 x 10^{14}	**NiTPEP$_3$**	3.29 x 10^{14}
ZnTPEP$_4$	3.18 x 10^{14}	**NiTPEP$_4$**	4.12 x 10^{14}

Figure S2. *Top:* UV-visible absorption data obtained during the grown of **ZnTPEP** (left) and **NiTPEP** (right) multilayer films on ITO. *Bottom:* Table of surface coverages obtained from integration of **ZnTPEP** and **NiTPEP** CVs.

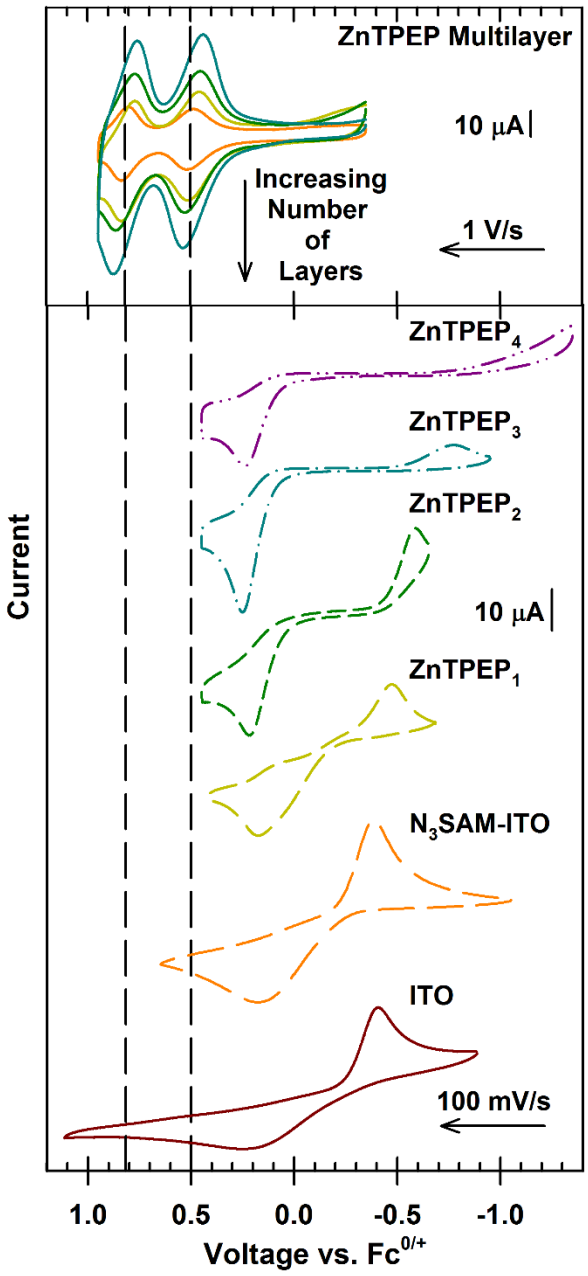


Figure S3. *Top:* CVs of one through four layers of **ZnTPEP** on ITO. *Bottom:* CVs of a 1 mM solution $[Co(dmb)_3]^{2+}$ at a clean ITO electrode (solid red line), SAM-functionalized ITO (long dashed orange), and one (dashed yellow), two (short dashed green), three (dash-dot cyan), and four (purple dash-dot-dot) layers of **ZnTPEP** on ITO. The vertical dashed black lines are located at the $\mathbf{ZnTPEP}^{0/+}$ and $\mathbf{ZnTPEP}^{+/2+}$ potentials.

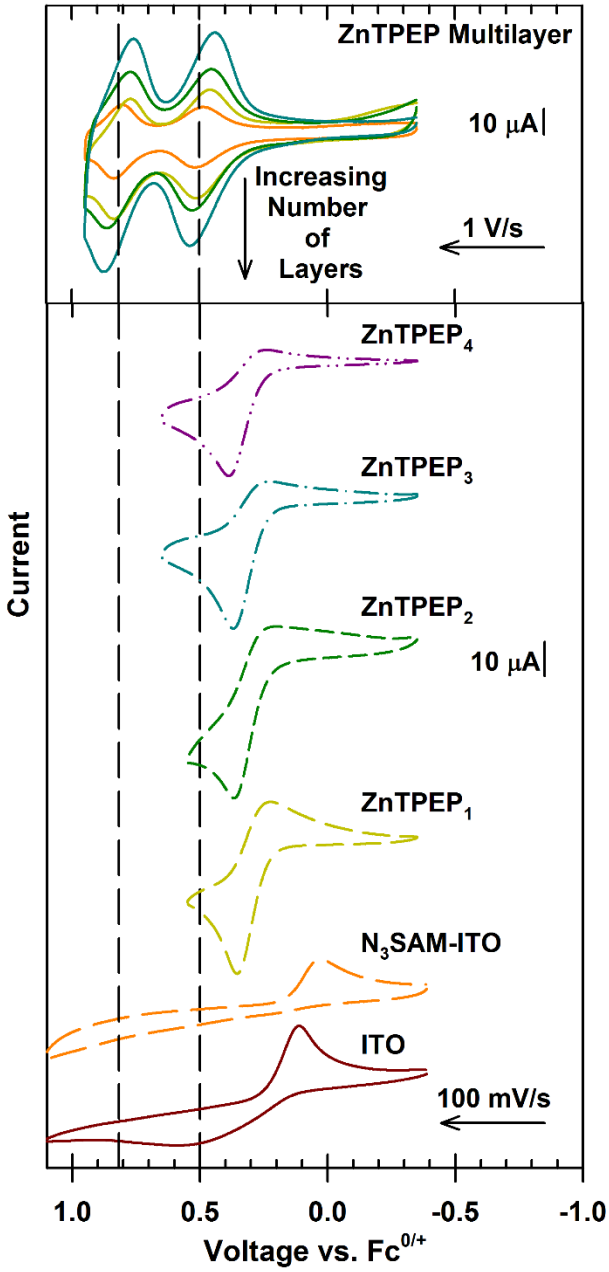


Figure S4. *Top:* CVs of one through four layers of **ZnTPEP** on ITO. *Bottom:* CVs of a 1 mM solution $[Co(NO_2\text{-phen})_3]^{2+}$ at a clean ITO electrode (solid red line), SAM-functionalized ITO (long dashed orange), and one (dashed yellow), two (short dashed green), three (dash-dot cyan), and four (purple dash-dot-dot) layers of **ZnTPEP** on ITO. The vertical dashed black lines are located at the $\mathbf{ZnTPEP}^{0/+}$ and $\mathbf{ZnTPEP}^{+/2+}$ potentials.

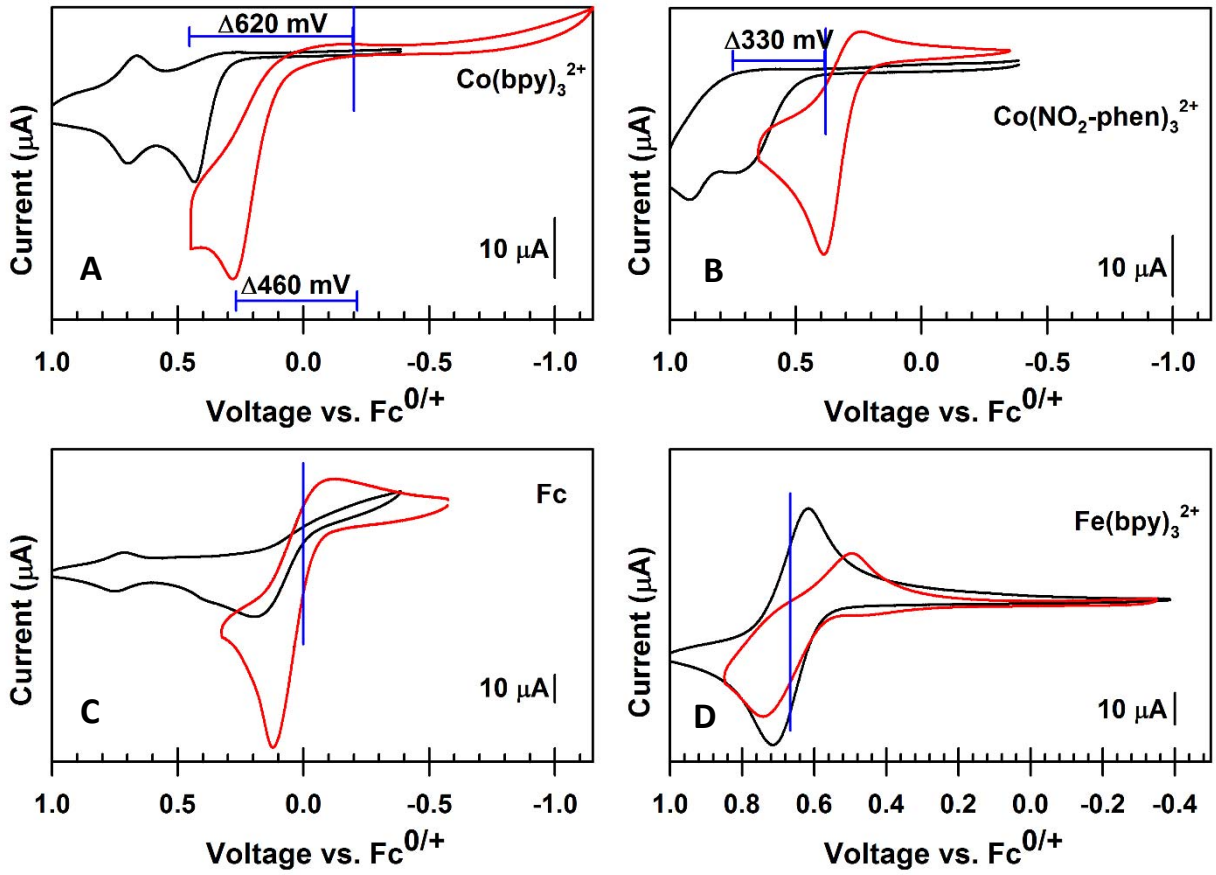


Figure S5. Comparison of redox mediator CVs over four layers of **ZnTPEP** (red lines) and **NiTPEP** (black lines) on an ITO electrode. All mediators are 1 mM: (A) $[Co(bpy)_3]^{2+}$, (B) $[Co(NO_2\text{-phen})_3]^{2+}$, (C) Fc, and (D) $[Fe(bpy)_3]^{2+}$.

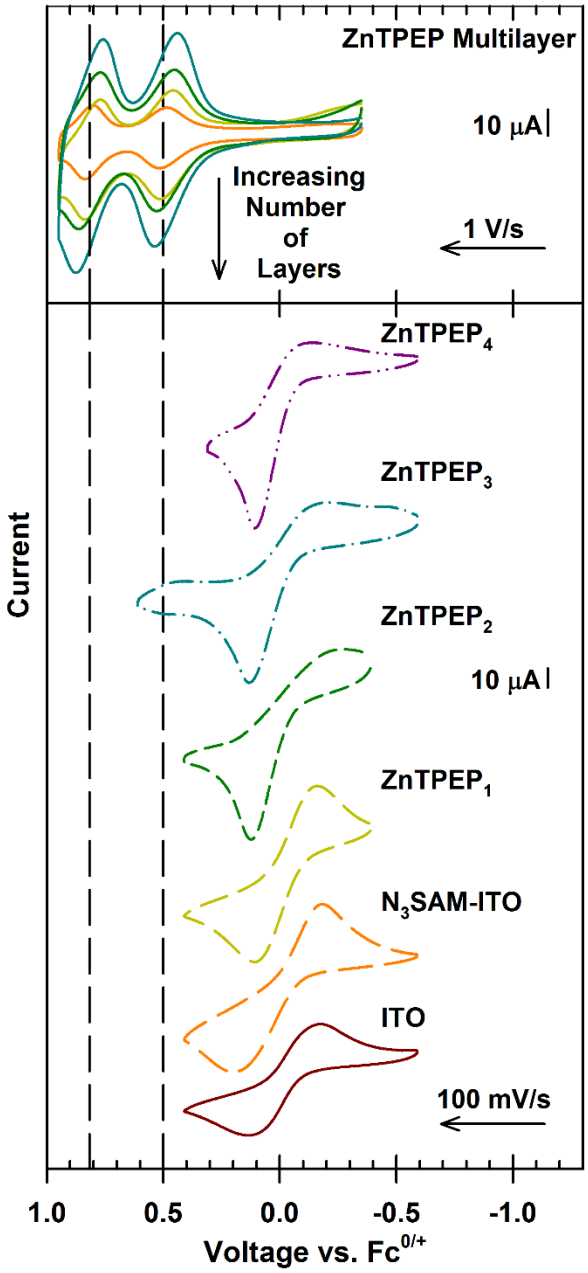


Figure S6. *Top:* CVs of one through four layers of **ZnTPEP** on ITO. *Bottom:* CVs of a 1 mM solution Fc at a clean ITO electrode (solid red line), SAM-functionalized ITO (long dashed orange), and one (dashed yellow), two (short dashed green), three (dash-dot cyan), and four (purple dash-dot-dot) layers of **ZnTPEP** on ITO. The vertical dashed black lines are located at the **ZnTPEP**$^{0/+}$ and **ZnTPEP**$^{+/2+}$ potentials.

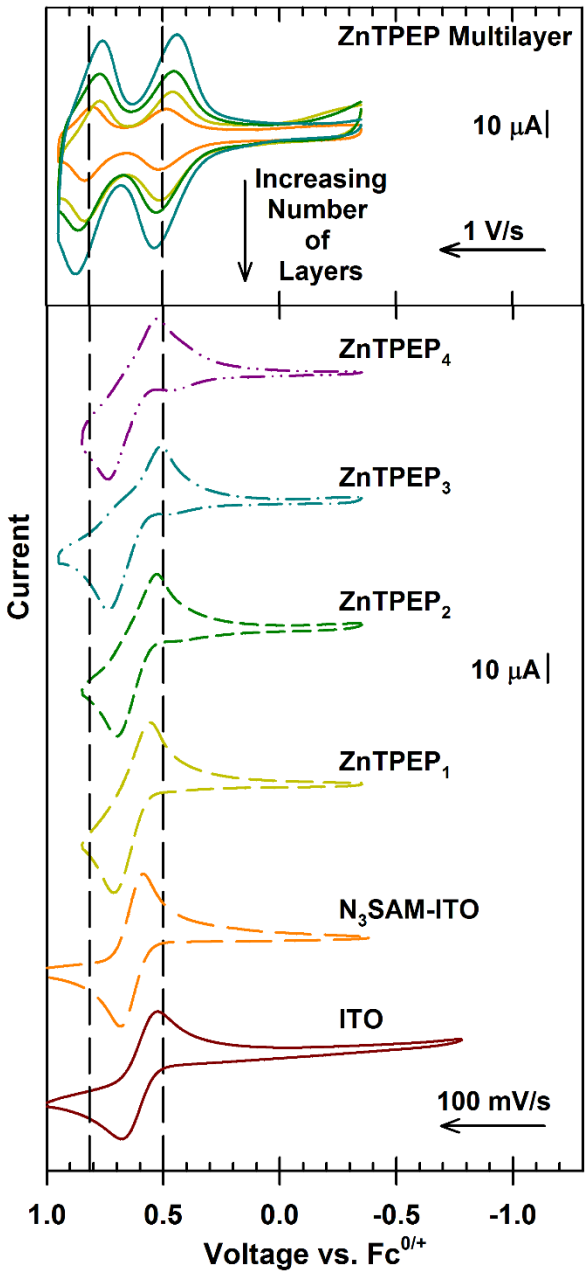


Figure S7. *Top:* CVs of one through four layers of **ZnTPEP** on ITO. *Bottom:* CVs of a 1 mM solution $[Fe(bpy)_3]^{2+}$ at a clean ITO electrode (solid red line), SAM-functionalized ITO (long dashed orange), and one (dashed yellow), two (short dashed green), three (dash-dot cyan), and four (purple dash-dot-dot) layers of **ZnTPEP** on ITO. The vertical dashed black lines are located at the $\mathbf{ZnTPEP}^{0/+}$ and $\mathbf{ZnTPEP}^{+/2+}$ potentials.

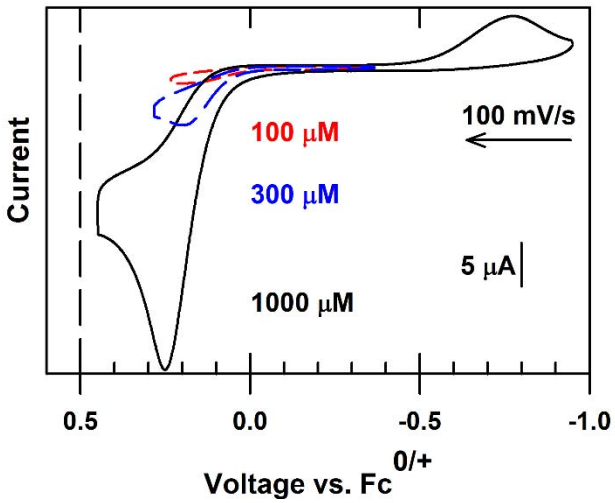


Figure S8. CVs of $[Co(dmb)_3]^{2+}$ over a film of three layers of **ZnTPEP** on ITO. Black solid line, blue long dash, and red medium dash are 1000, 300, and 100 μM respectively. The dashed black line at 0.5 V corresponds to the midpoint potential of $\mathbf{ZnTPEP}^{0/+}$.

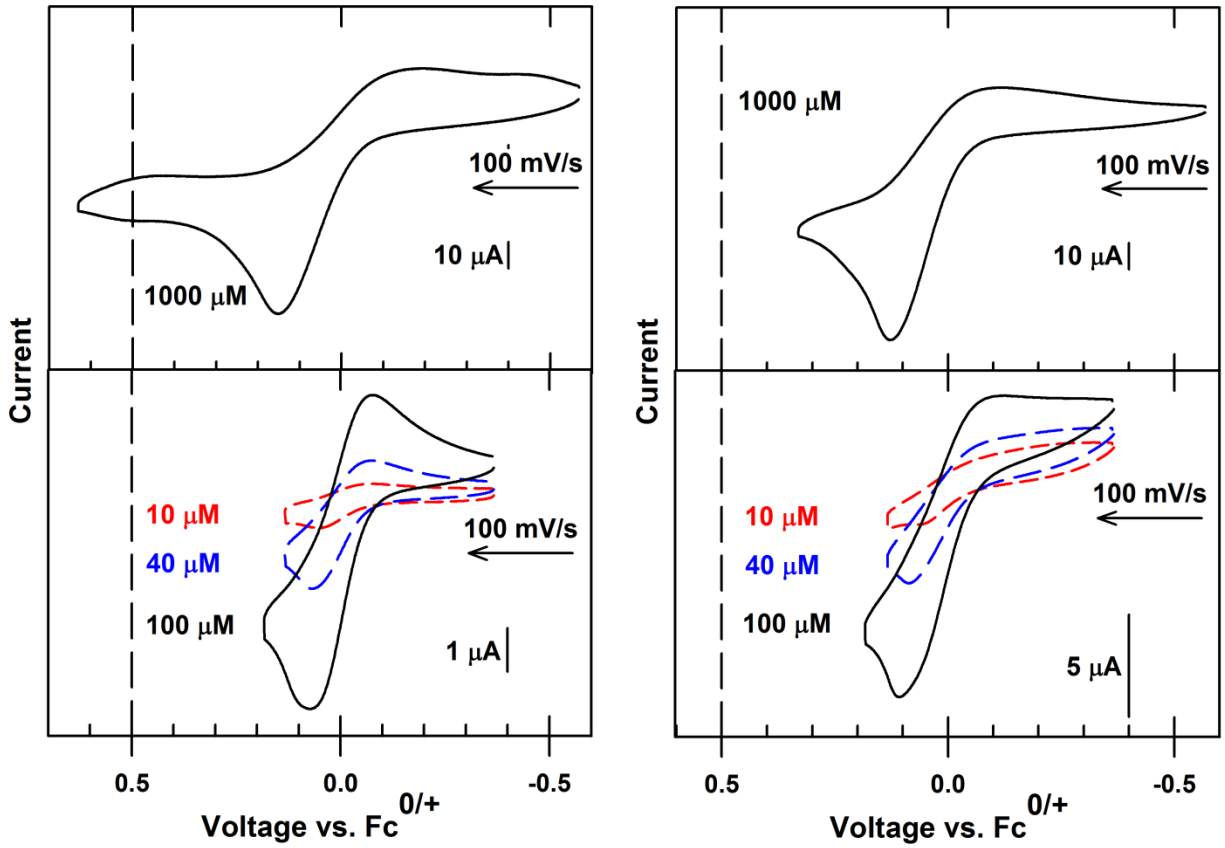


Figure S9. CVs of Fc over a film of three (left) and four (right) layers of **ZnTPEP** on ITO. The vertical dashed black line at 0.5 V corresponds to the midpoint potential of $\mathbf{ZnTPEP}^{0/+}$.

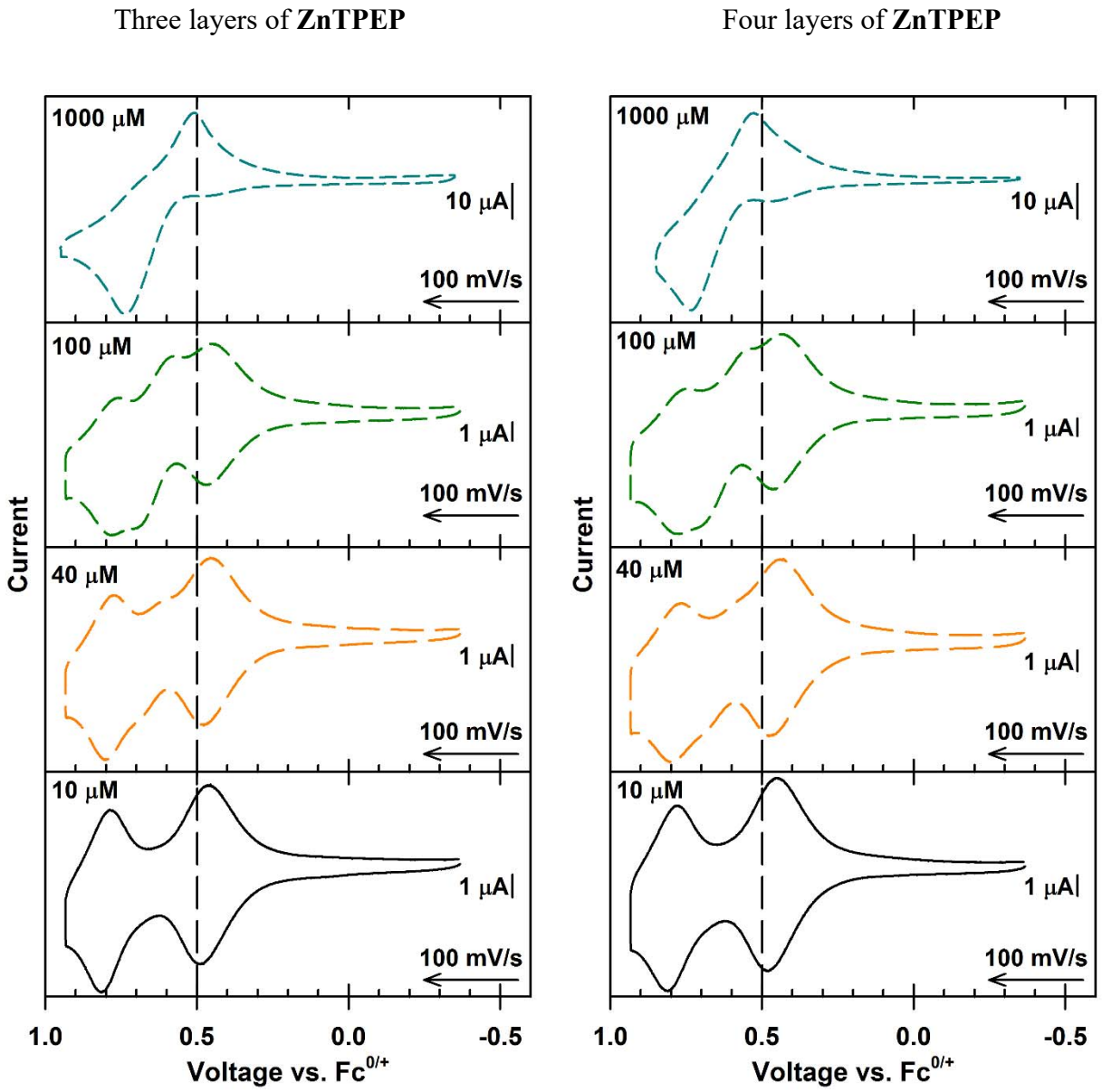


Figure S10. CVs of $[Fe(bpy)_3]^{2+}$ over a film of three (left) and four (right) layers of **ZnTPEP** on ITO. Black solid line, orange long dash, green medium dash, and cyan short dash are 10, 40, 100, and 1000 µM respectively. The vertical dashed black line at 0.5 V corresponds to the midpoint potential of $\mathbf{ZnTPEP}^{0/+}$.

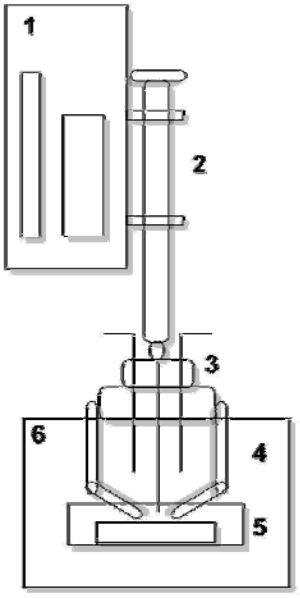


Figure S11. Schematic representation of wall-jet apparatus: 1) Syringe pump, 2) air-tight glass syringe, 3) Teflon cap, 4) Teflon cone, 5) electrode and 6) lexan cell holder.

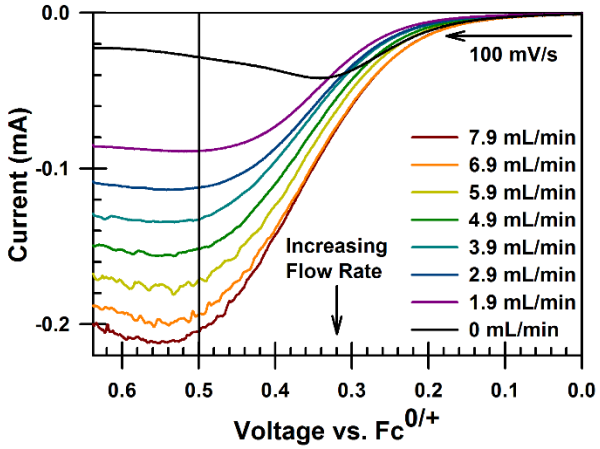


Figure S12. Linear sweep voltammograms of 1 mM $Co(bpy)_3^{2+}$ at varying flow rates. The solid black line at 0.5 V corresponds to the midpoint potential of **ZnTPEP**$^{0/+}$.

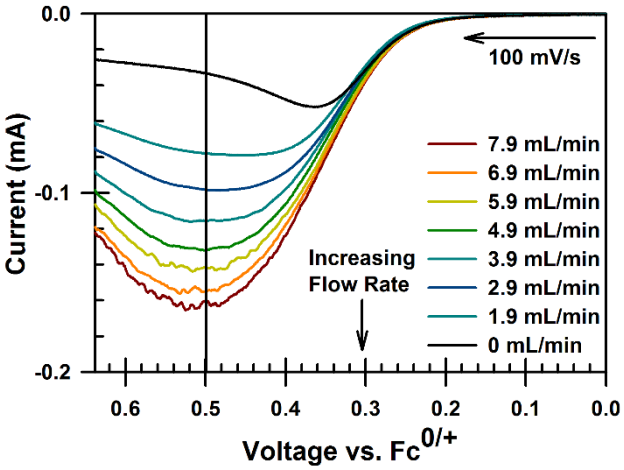


Figure S13. Linear sweep voltammograms of 1 mM $Co(NO_2\text{-phen})_3^{2+}$ at varying flow rates. The solid black line at 0.5 V corresponds to the midpoint potential of **ZnTPEP$^{0/+}$**.

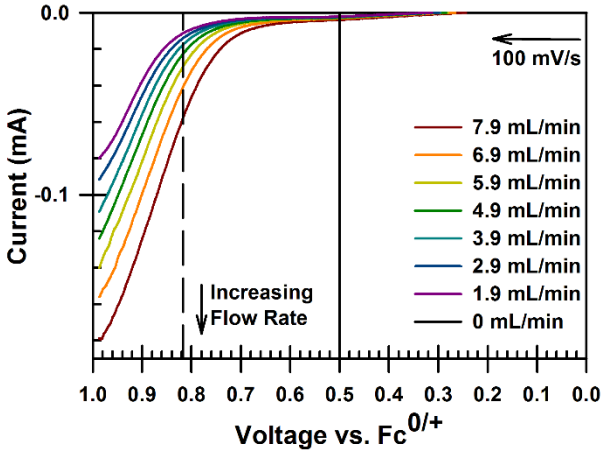


Figure S14. Linear sweep voltammograms of 1 mM $Fe(bpy)_3^{2+}$ at varying flow rates. The vertical solid and dashed black lines are located at the **ZnTPEP$^{0/+}$** and **ZnTPEP$^{+/2+}$** potentials, respectively.

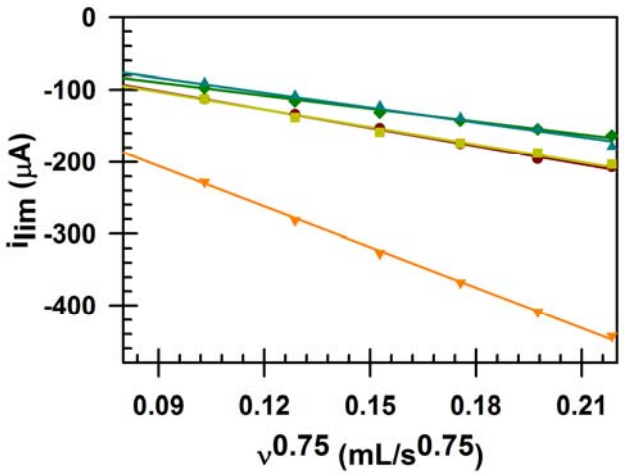


Figure S15. Levich analysis of each mediator: ferrocene is orange (down triangle); $[Co(bpy)_3]^{2+}$, red (circles); $[Co(dmb)_3]^{2+}$, yellow (squares); $[Co(NO_2\text{-phen})_3]^{2+}$, green (diamonds); and $[Fe(bpy)_3]^{2+}$, teal (upward triangle). Limiting current was taken at 0.50 V ($ZnTPEP^{0/+}$) for all mediators except $[Fe(bpy)_3]^{2+}$, which was taken 0.99 V.

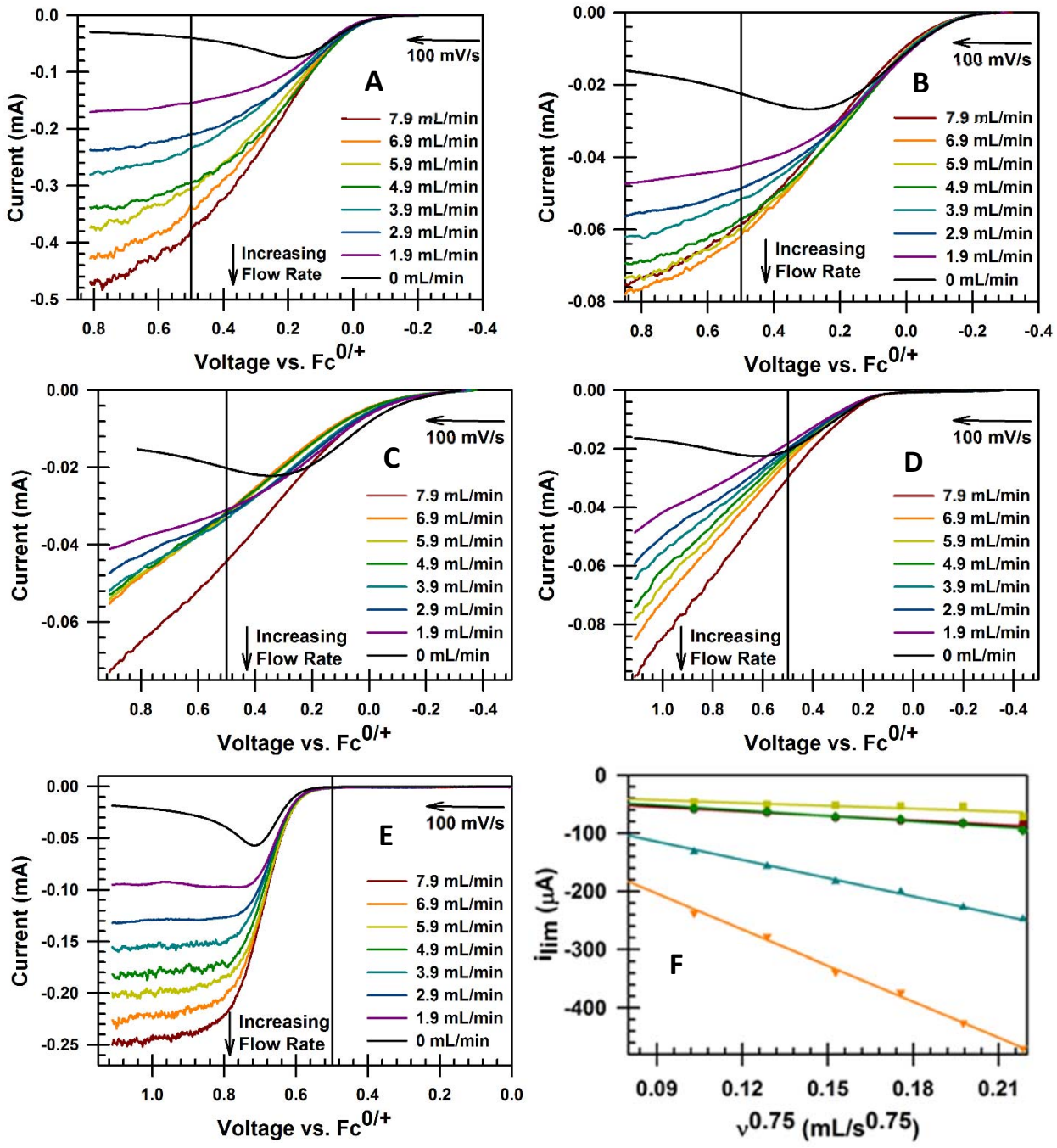


Figure S16. *Plots A-E:* Linear sweep voltammograms of 1 mM redox mediators at varying flow rates over ITO. The solid black line at 0.5 V corresponds to the midpoint potential of **ZnTPEP**$^{0/+}$. All mediators are 1 mM: (A) Fc, (B) $[Co(bpy)_3]^{2+}$, (C) $[Co(dmb)_3]^{2+}$, (D) $[Co(NO_2\text{-}phen)_3]^{2+}$, and (E) $[Fe(bpy)_3]^{2+}$. *Plot F:* Levich analysis of each mediator over ITO: ferrocene is orange (down triangle); $[Co(bpy)_3]^{2+}$, red (circles); $[Co(dmb)_3]^{2+}$, yellow (squares); $[Co(NO_2\text{-}phen)_3]^{2+}$, green (diamonds); and $[Fe(bpy)_3]^{2+}$, teal (upward triangle).