Supporting information available for:

Soft Coordination Suprapolymers: Novel Materials for Dual Electro-Catalysis

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Multilayers of Fe(III)-L_2EO_4, a polyanion, and PEI, a polycation, were made by alternately exposing GC electrode, or FTO slide to aqueous solutions of the polyelectrolytes. These films are designated $\{PEI/Fe(III)\text{-}L_2EO_4\}_n$, where *n* is the number of bilayer adsorption cycles. Figure S1A shows the UV-vis absorption spectra of the assembled $\{PEI/Fe(III)\text{-}L_2EO_4\}_n$ films on FTO slide with bilayer (layer pairs) numbers from 1 to 6. Since PEI solution has no apparent absorption in the wavelength range 330-440 nm, the maximum absorption observed at 380 nm is the characteristic band of Fe(III)-L_2EO_4 absorption. The peak intensities at 380 nm increase with the bilayer number. By plotting the absorption at 380 nm against the number of bilayers, good linear relationships can be obtained, as shown in the inset of Figure S1A, indicating that the $\{PEI/Fe(III)\text{-}L_2EO_4\}_n$ films are built up in a regular and reproducible fashion. The assembly of the $\{PEI/Fe(III)\text{-}L_2EO_4\}_n$ films on GC electrode was monitored using electrochemical impedance spectroscopy (EIS) in 0.1 M KCl solution containing 5.0 mM $[Fe(CN)_6]^{3-/4-}$. One can find in Figure S1B that the impedance encountered by $[Fe(CN)_6]^{3-/4-}$ increases dramatically when Fe(III)-L_2EO_4 was assembled as the outmost layer; the larger the number of assembled layers, the higher the impedance. In contrast, the impedance drops steeply when PEI is the outmost layer. These are indicatives of successful film growth on GC electrode, since the larger impedance was caused by the increased repulsion between cocharged Fe(III)-L_2EO_4 and $[Fe(CN)_6]^{3-/4-}$, whereas the small impedance was attributed to the electrostatic attraction between oppositely charged PEI and $[Fe(CN)_6]^{3-/4-}$.

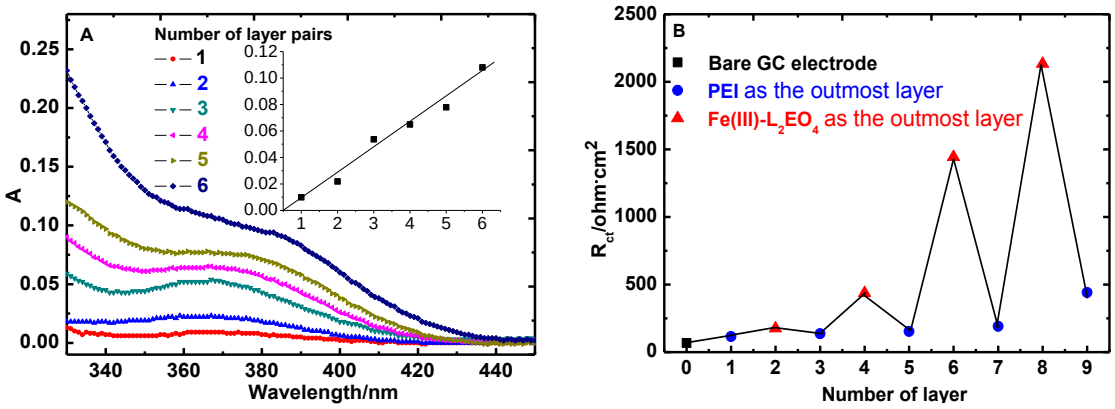

Figure S1. Increase UV-vis absorbance with increasing layer pairs (A) and variation of impedance with alternative layers (B). The inset in (A) shows the linear-relationship between the absorbance at 380 nm and the pair numbers.

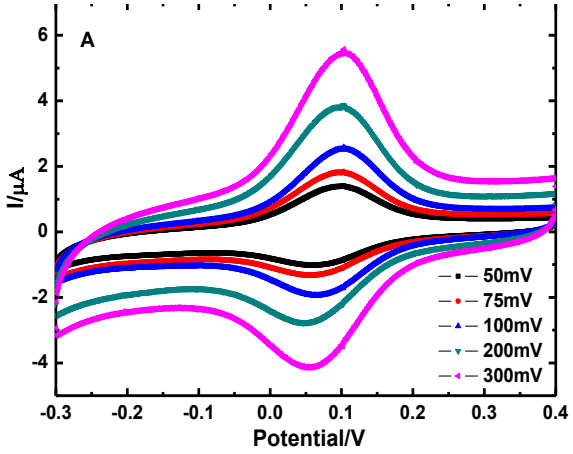

Figure S2. CV curves for {PEI/Fe(III)-L_2EO_4}$_5$ films on GC electrode at different scanning rates.

The current of the modified electrode was considerably influenced by the composition on the outmost layer. As demonstrated in Figure S3, the current drops by a factor of 2 when the outmost layer is PEI. Actually, with increasing the number of layers alternatively, the current drops significantly at each PEI layer. This is probably an indication that the extra PEI layer, which carries opposite charges to electrons, has

immobilized most electrons that released from the electrode so that they cannot access Fe^{3+} in the multilayers.

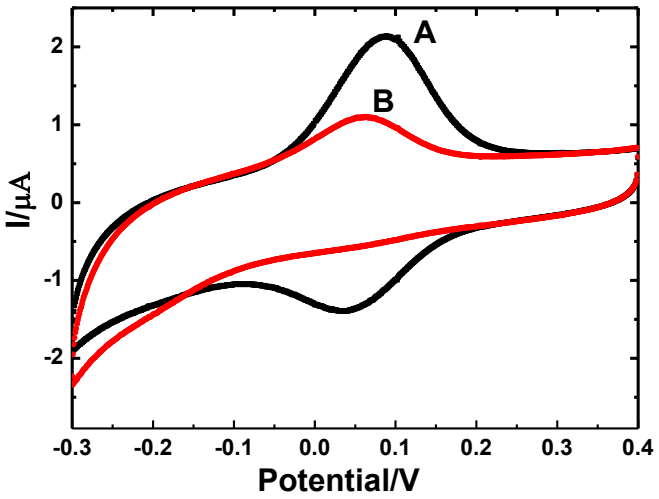

Figure S3. Comparison of CV curves at GC electrode modified with {PEI/ Fe(III)-L_2EO_4 }$_5$ (A) and {PEI/ Fe(III)-L2EO4}$_5$PEI (B).

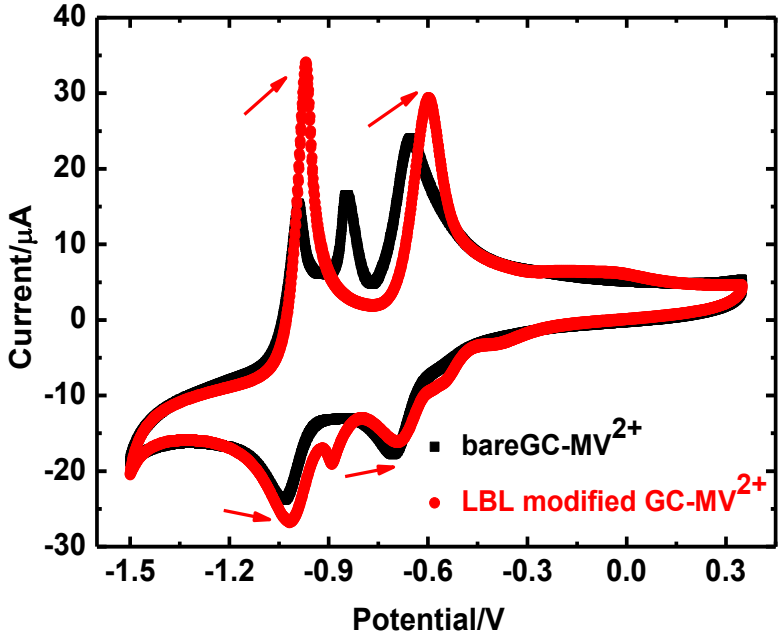

Figure S4. CV plot of MV^{2+} on GC electrode modified with {PEI/Fe(III)-L_2EO_4}$_6$.

It can be clearly observed the increase of current. The half-wave potentials for the two electron processes have been shifted by 35 mV and 21 mV.

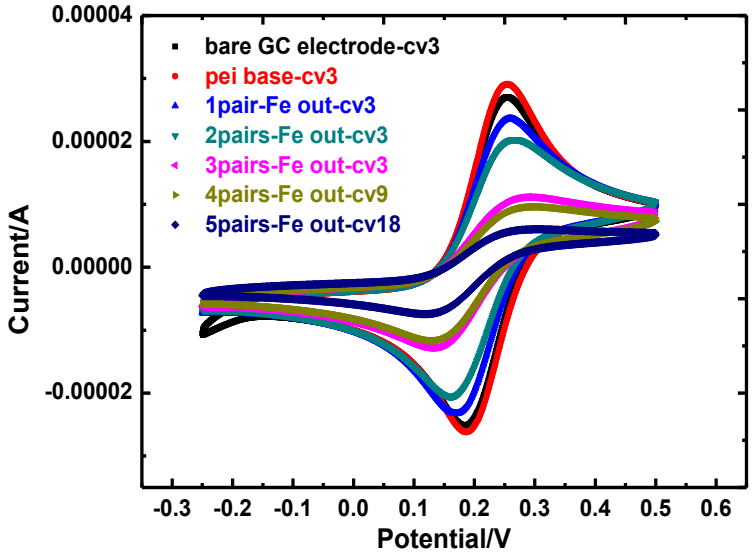

Figure S5. CV plots for $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ pairs on GC electrode modified with 1-5 pairs of PEI/Fe(III)-L_2EO_4.

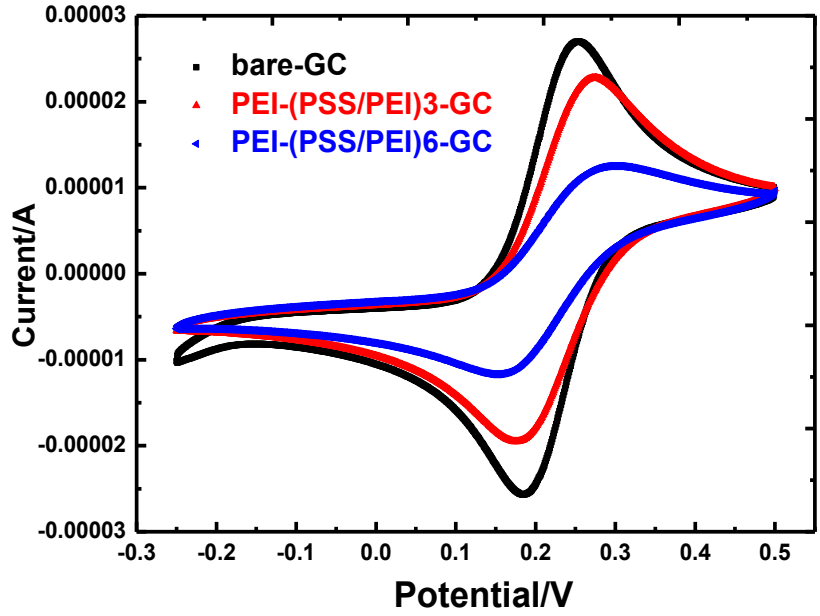

Figure S6. CV plots for $Fe(CN)_6^{3-/4-}$ pair on GCE modified with $(PEI/PSS)_{0-6}$.