

Fig. S1. UV-vis spectra of P_2W_{18} (1.2×10^{-5} M, black curve) and Rubpy (3.47×10^{-5} M, red curve) in the solutions (top), $\{(PEI/P_2W_{18})_2(PEI/P_2W_{18}/Rubpy/PSS)_2(PEI/P_2W_{18})_2\}$ thin-film on quartz as a function of the number of layers (middle) and the relationship of the absorbance at 200 nm as a function of the number of layers (bottom), confirming linear and uniform thin-film growth.

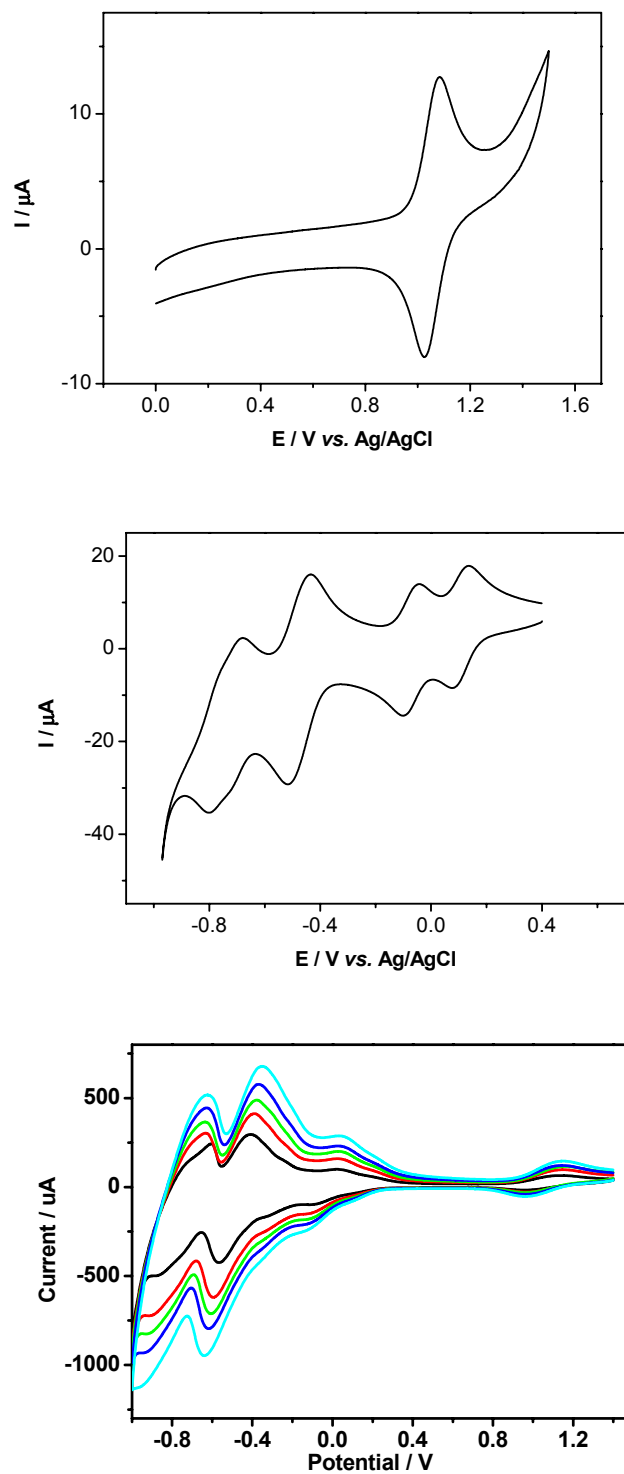


Fig. S2. CVs of 1mM Rubpy (top), 1mM P_2W_{18} (middle) and $\{(\text{PEI}/\text{P}_2\text{W}_{18})_8(\text{PEI}/\text{P}_2\text{W}_{18}/\text{Rubpy}/\text{PSS})_5(\text{PEI}/\text{P}_2\text{W}_{18})_7\}$ thin-film at different scan rates of 50, 80, 100, 120 and 150 $\text{mV}\cdot\text{s}^{-1}$ (bottom) in 0.5 M $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$ at pH 3.

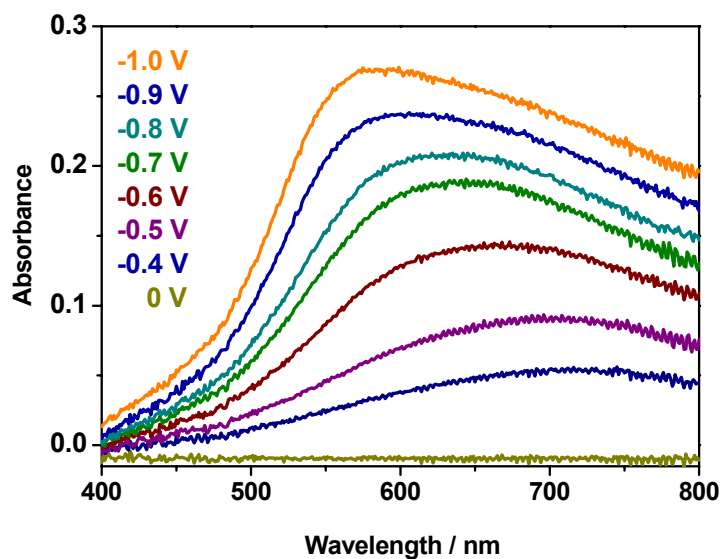


Fig. S3. UV-vis absorption spectra of a $\{(PEI/P_2W_{18})_8(PEI/P_2W_{18}/Rubpy/PSS)_5(PEI/P_2W_{18})_7\}$ thin-film on an ITO-coated glass slide in 0.5 M $Na_2SO_4 + H_2SO_4$ (pH 3) under open circuit (0V) and electrochemical reduction at the different applied potentials from -0.4 to -1.0 V for 30s.

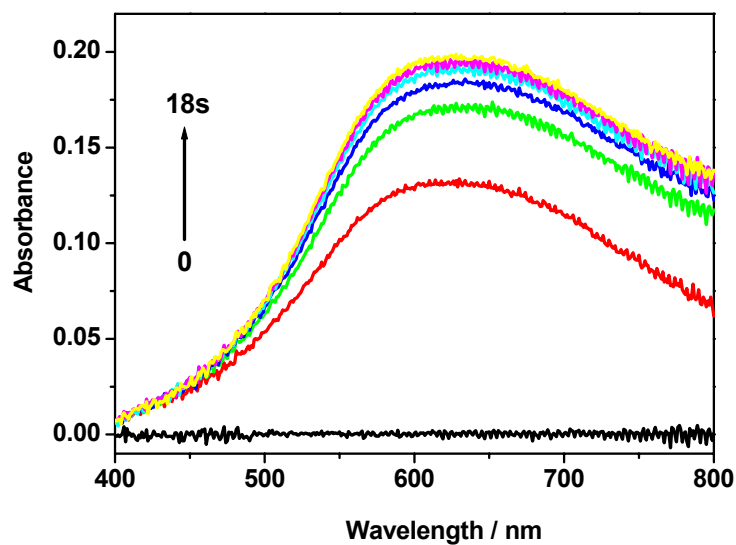


Fig. S4. UV-vis absorption spectra of the $\{(PEI/P_2W_{18})_8(PEI/P_2W_{18}/Rubpy/PSS)_5(PEI/P_2W_{18})_7\}$ thin-film on an ITO-coated glass slide in 0.5 M $Na_2SO_4 + H_2SO_4$ (pH 3) as a function of electrochemical reduction time. Black curve: open circuit; colored curves: the applied potential of -0.8 V.

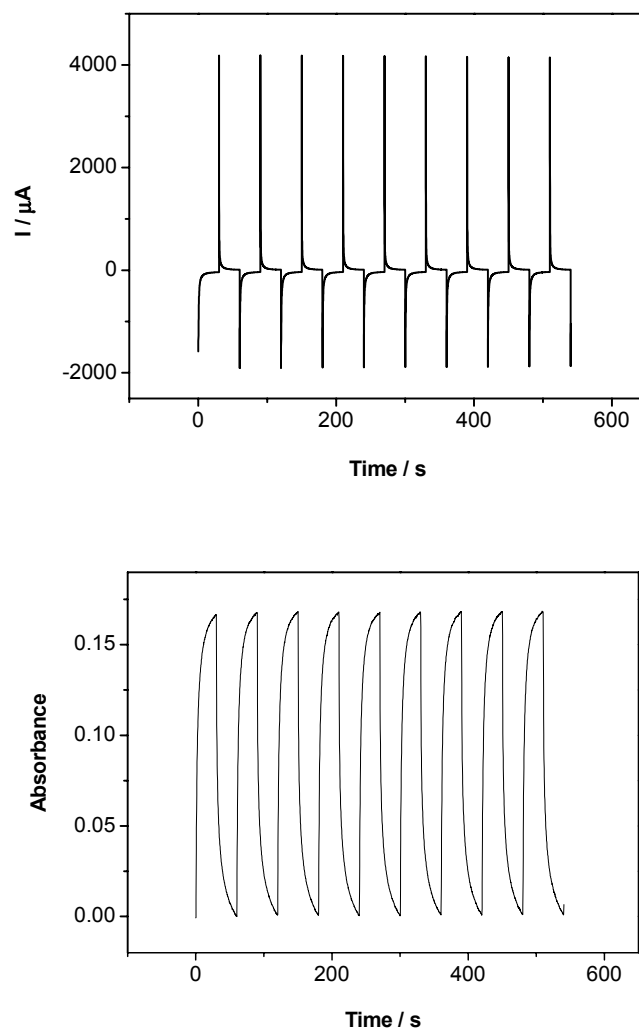


Fig. S5. Potential currents (top) and absorbances (bottom) at 627 nm of a $\{(PEI/P_2W_{18})_8(PEI/P_2W_{18}/Rubpy/PSS)_5(PEI/P_2W_{18})_7\}$ thin-film on an ITO-coated glass slide during subsequent double-potential steps from -0.8 to 0.8 V in 0.5 M $Na_2SO_4 + H_2SO_4$ solution (pH 3).