**Fig. S1.** UV-vis spectra of P$_2$W$_{18}$ (1.2×10$^{-5}$ M, black curve) and Rubpy (3.47×10$^{-5}$ M, red curve) in the solutions (top), \{PEI/P$_2$W$_{18}$\}_2(PEI/P$_2$W$_{18}$/Rubpy/PSS)$_2$(PEI/P$_2$W$_{18}$)$_2$ thin-film on quartz as a function of the number of layers (middle) and the relationship of the absorption 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$_2$W$_{18}$ (middle) and 
{(PEI/P$_2$W$_{18}$)$_8$(PEI/P$_2$W$_{18}$/Rubpy/PSS)$_5$(PEI/P$_2$W$_{18}$)$_7$} thin-film at different scan rates of 50, 80, 100, 120 and 150 mV·s$^{-1}$ (bottom) in 0.5 M H$_2$SO$_4$ + Na$_2$SO$_4$ at pH 3.
Fig. S3. UV-vis absorption spectra of a \{(\text{PEI/P}_2\text{W}_{18})_8(\text{PEI/P}_2\text{W}_{18}/\text{Rubpy/PSS})_5(\text{PEI/P}_2\text{W}_{18})_7\}\ thin-film on an ITO-coated glass slide in 0.5 M Na$_2$SO$_4$ + H$_2$SO$_4$ (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_{2}W_{18})_{8}(PEI/P_{2}W_{18}/Rubpy/PSS)_{5}(PEI/P_{2}W_{18})_{7}\} thin-film on an ITO-coated glass slide in 0.5 M Na_{2}SO_{4} + H_{2}SO_{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).