Supporting Information

Figure S1. (left) CVs of 0.1mM Mn16-Cs (top) and Mn16-Rb (bottom) in 0.5M NaAc+HAc (pH 7) solutions at scan rates of 50, 100, 150, 200, 250, 300, 350, 400, 450, 500 mV/s, ITO electrode. (right) The relationships of square root of scan rates vs the oxidation peak currents of Mn$^{4+}$. 
Figure S2. UV-vis spectrum of Mn16-Cs (8.33*10^{-6}M) in solution.

Figure S3. UV-vis spectrum of Mn16-Rb (8.33*10^{-6}M) in solution.
Figure S4. (left) CVs of the films [PDDA/Mn16-Cs]₆ (top) and [PDDA/Mn16-Rb]₆ (bottom) in 0.5M NaAc + HAc (pH 7) solutions at scan rates of 40, 60, 80, 100, 120, 140, 160, 180 mV/s on ITO surfaces. (right) The lines show the relationships of scan rates vs the oxidation peak currents of Mn⁴⁺.
Figure S5. CVs of the films [PDDA/Mn16-Cs]$_3$ (top) and [PDDA/Mn16-Rb]$_3$ (bottom) on GCE electrodes with different pH (5, 6, 7) at scan rate of 50 mV/s.
Figure S6. XPS spectra of the films [PDDA/Mn16-Cs]$_{10}$.
Figure S7. XPS spectra of the films [PDDA/Mn16-Rb]_{10}. 
Figure S8. UV-vis spectrum of Rubpy (2.14*10^{-5}M) in solution.
Figure S9. (left) CVs of the films [Mn16-Cs/Rubpy]_6 (top) and [Mn16-Rb/Rubpy]_6 (bottom) in 0.5M NaAc + HAc (pH 7) solutions at scan rates of 40, 60, 80, 100, 120, 140, 160, 180 mV/s on ITO surfaces. (right) The lines show the relationships of scan rates vs the oxidation peak currents.
Figure S10. XPS spectra of the films [Rubpy/Mn16-Cs]$_{10}$. 
Figure S11. XPS spectra of the films [Rubpy/Mn16-Rb]_{10}.
Figure S12. AFM top images of the film [PDDA/Mn16-Rb]$_2$ (a), [PDDA/Mn16-Cs]$_2$ (b), [Mn16-Rb/Rubpy]$_2$ (c) and [Mn16-Cs/Rubpy]$_2$ (d) on ITO substrates in the scanning range of 1.5 μm (a,b) and 3 μm (c,d).
Figure S13. (top) The CVs of the films (PDDA/Mn16-Cs)$_6$ (left) and (PDDA/Mn16-Rb)$_6$ (right); (bottom) the CV cycles of the films (Mn16-Cs/Rubpy)$_3$ (left) and (Mn16-Rb/Rubpy)$_3$ (right) in their original states and after three days in 0.5M NaAc + HAc solution (pH 7) recorded on ITO at a scan rate of 50 mV/s. The black lines show the CVs before three days and the red lines show the CVs after three days.
Figure S14. XPS spectra of the films [PDDA/Mn16-Cs]₁₀ after a long water oxidation process.
Figure S15. XPS spectra of the films [PDDA/Mn16-Rb]_{10} after a long water oxidation process.
Figure S16. XPS spectra of the films $[\text{Rubpy/Mn16-Cs}]_{10}$ after a long water oxidation process.
Figure S17. XPS spectra of the films [Rubpy/Mn16-Rb]_{10} after a long water oxidation process.