Supporting Information

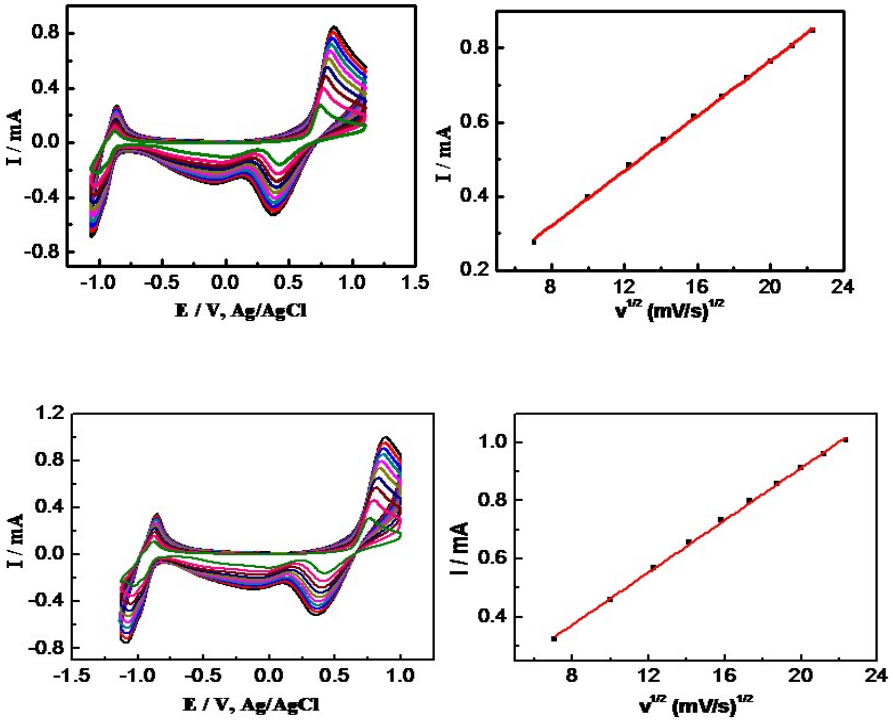

Figure S1. (left) CVs of 0.1mM Mn16-Cs (top) and Mn16-Rb (bottom) in 0.5M NaAc+HAc (pH 7) solutions at scan rates of 50, 100, 150, 200, 250, 300, 350，400，450，500 mV/s, ITO electrode. (right) The relationships of square root of scan rates *vs* the oxidation peak currents of Mn^{4+}.

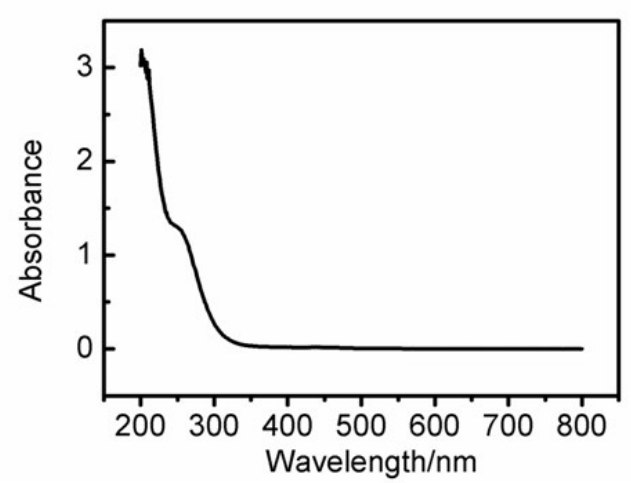

Figure S2. UV-vis spectrum of Mn16-Cs ($8.33*10^{-6}$M) in solution.

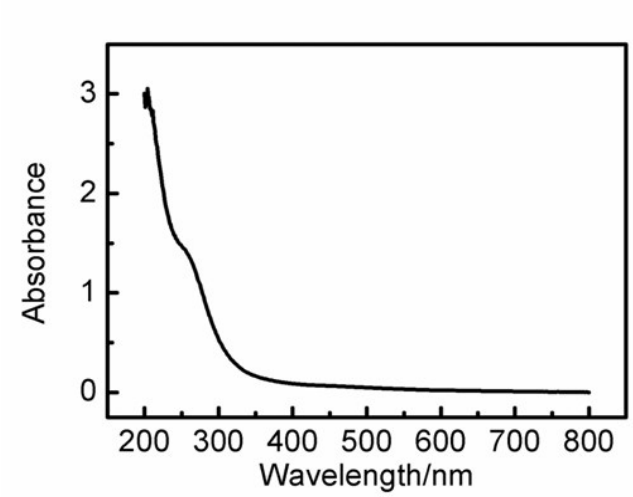

Figure S3. UV-vis spectrum of Mn16-Rb ($8.33*10^{-6}$M) in solution.

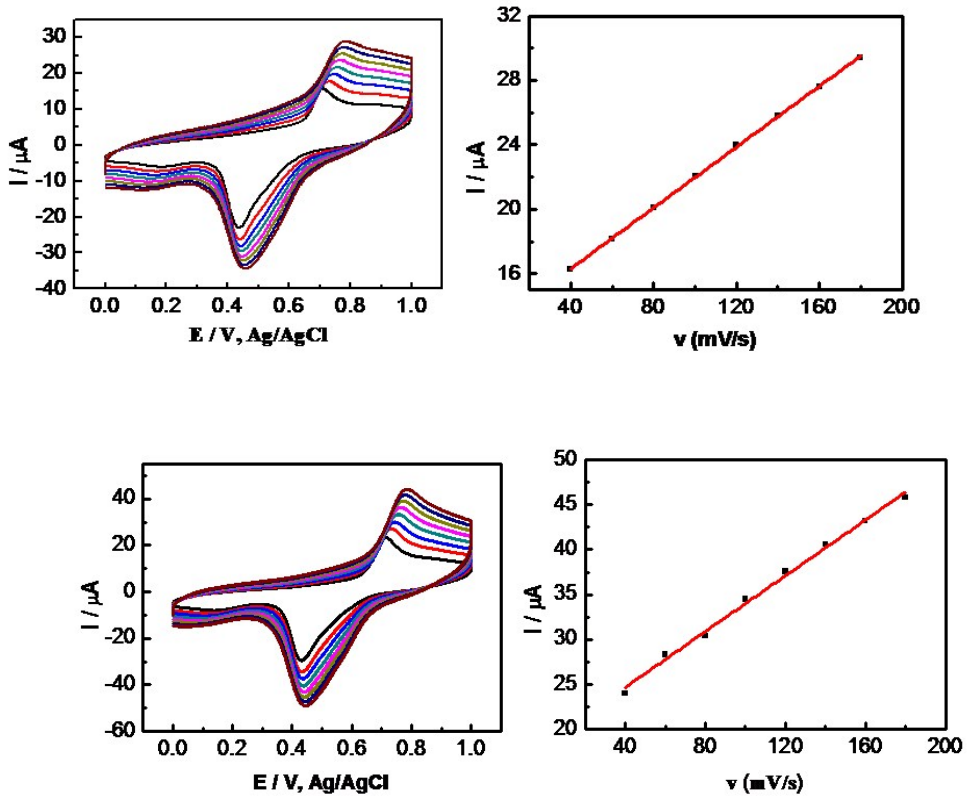

Figure S4. (left) CVs of the films $[PDDA/Mn16\text{-}Cs]_6$ (top) and $[PDDA/Mn16\text{-}Rb]_6$ (bottom) in 0.5M NaAc + HAc (pH 7) solutions at scan rates of 40, 60, 80, 100, 120, 140, 160, 180 mV/s on ITO surfaces. (right) The lines show the relationships of scan rates *vs* the oxidation peak currents of Mn^{4+}.

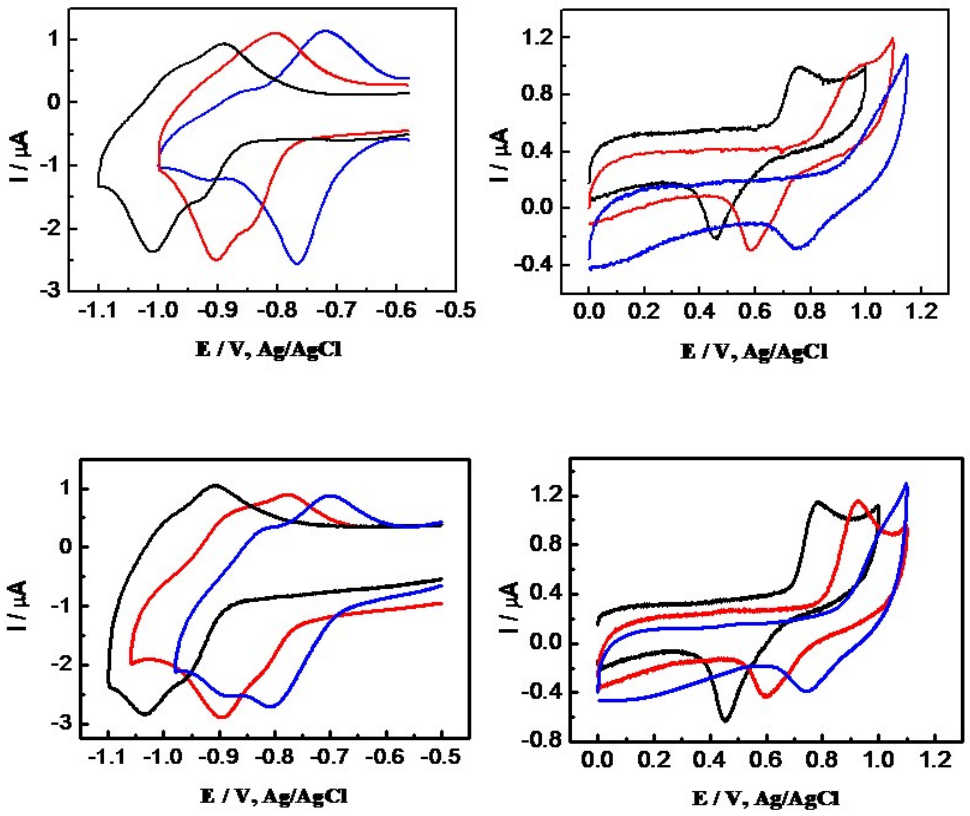

Figure S5. CVs of the films $[PDDA/Mn16\text{-}Cs]_3$ (top) and $[PDDA/Mn16\text{-}Rb]_3$ (bottom) on GCE electrodes with different pH (5, 6, 7) at scan rate of 50 mV/s.

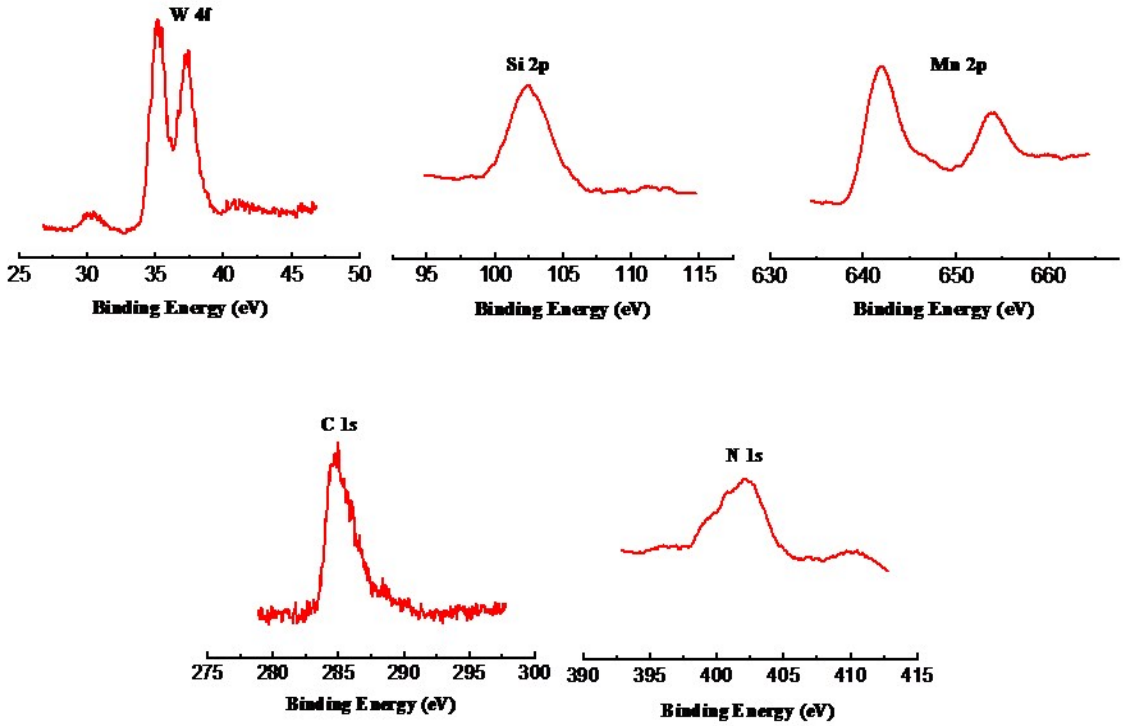

Figure S6. XPS spectra of the films $[PDDA/Mn16\text{-}Cs]_{10}$.

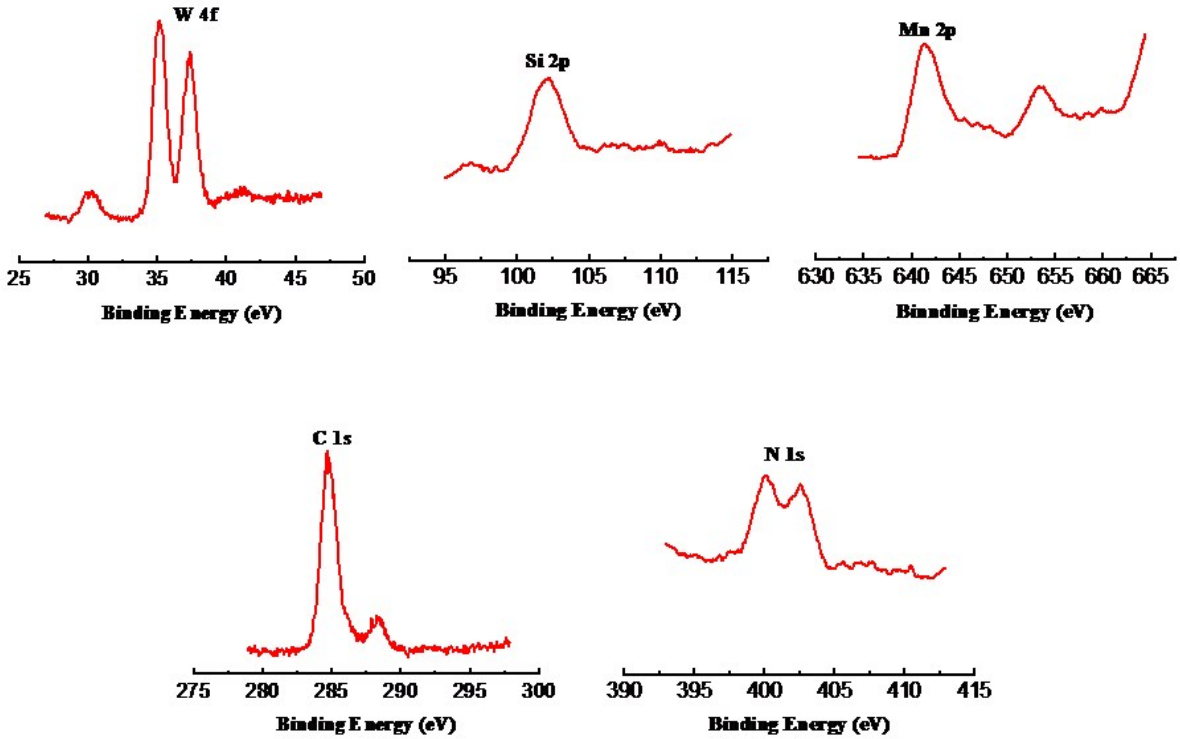

Figure S7. XPS spectra of the films $[PDDA/Mn16\text{-}Rb]_{10}$.

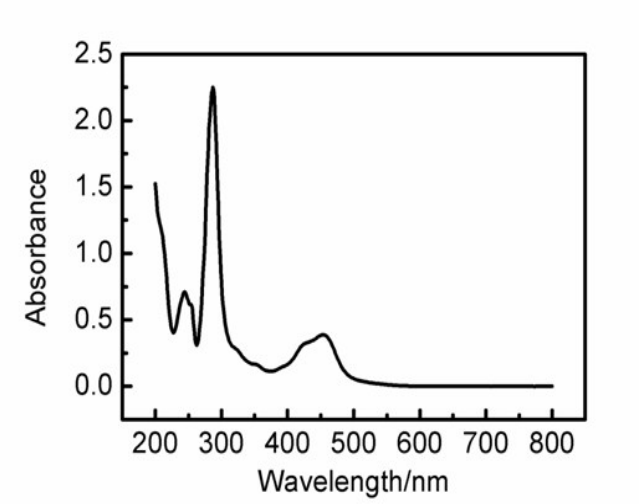

Figure S8. UV-vis spectrum of Rubpy ($2.14*10^{-5}$M) in solution.

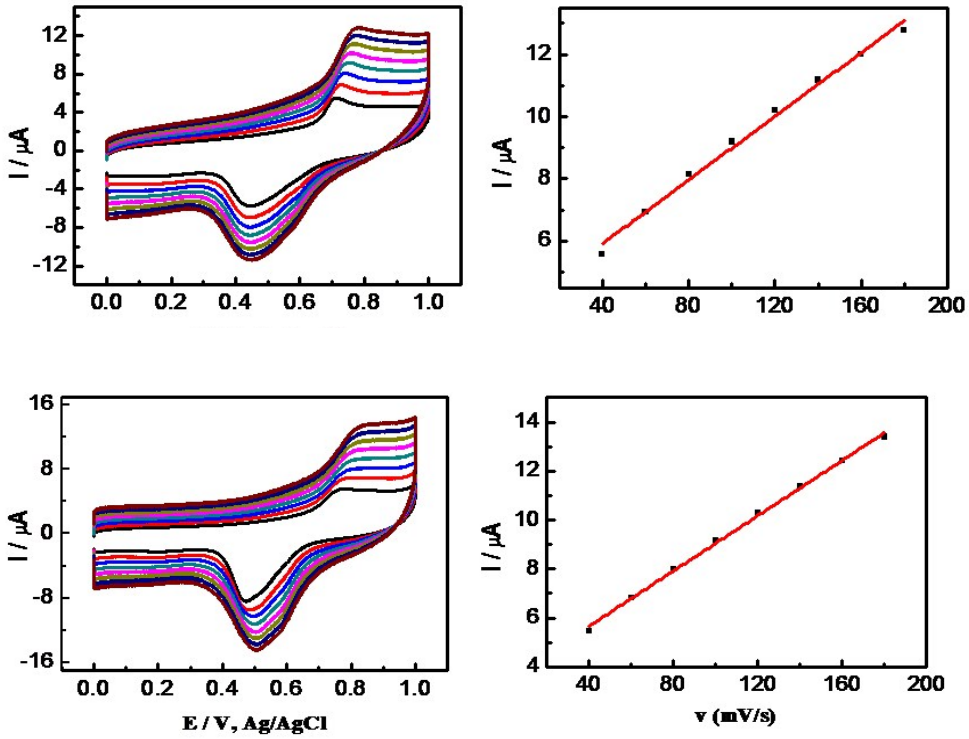

Figure S9. (left) CVs of the films $[Mn16\text{-}Cs/Rubpy]_6$ (top) and $[Mn16\text{-}Rb/Rubpy]_6$ (bottom) in 0.5M NaAc + HAc (pH 7) solutions at scan rates of 40, 60, 80, 100, 120, 140, 160, 180 mV/s on ITO surfaces. (right) The lines show the relationships of scan rates *vs* the oxidation peak currents.

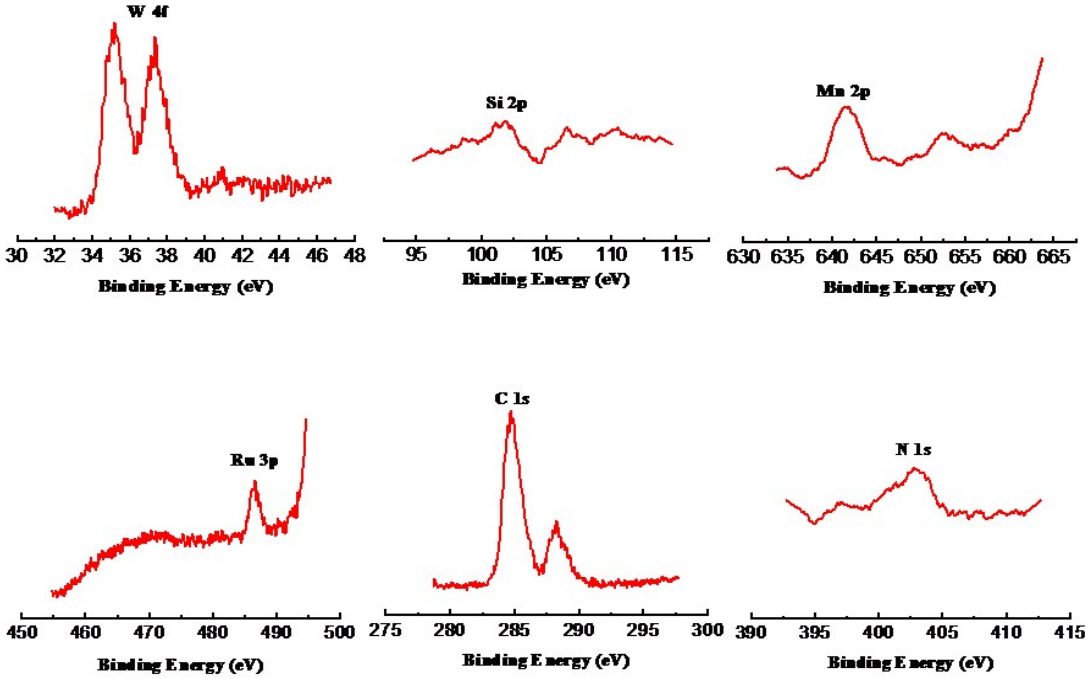

Figure S10. XPS spectra of the films $[Rubpy/Mn16\text{-}Cs]_{10}$.

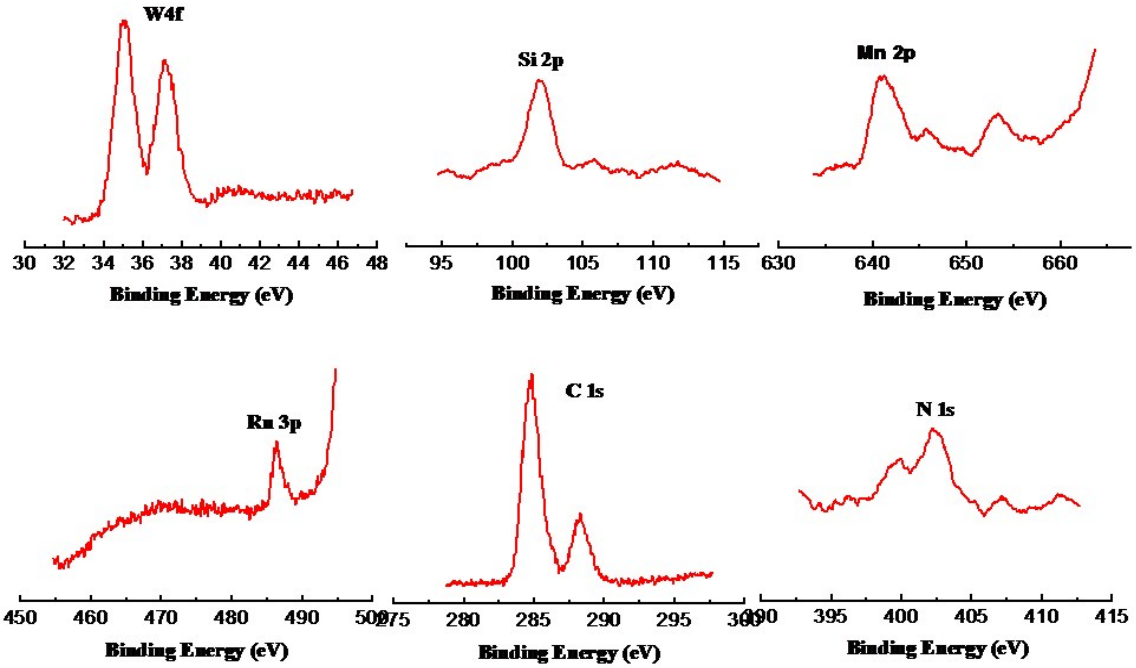

Figure S11. XPS spectra of the films $[Rubpy/Mn16\text{-}Rb]_{10}$.

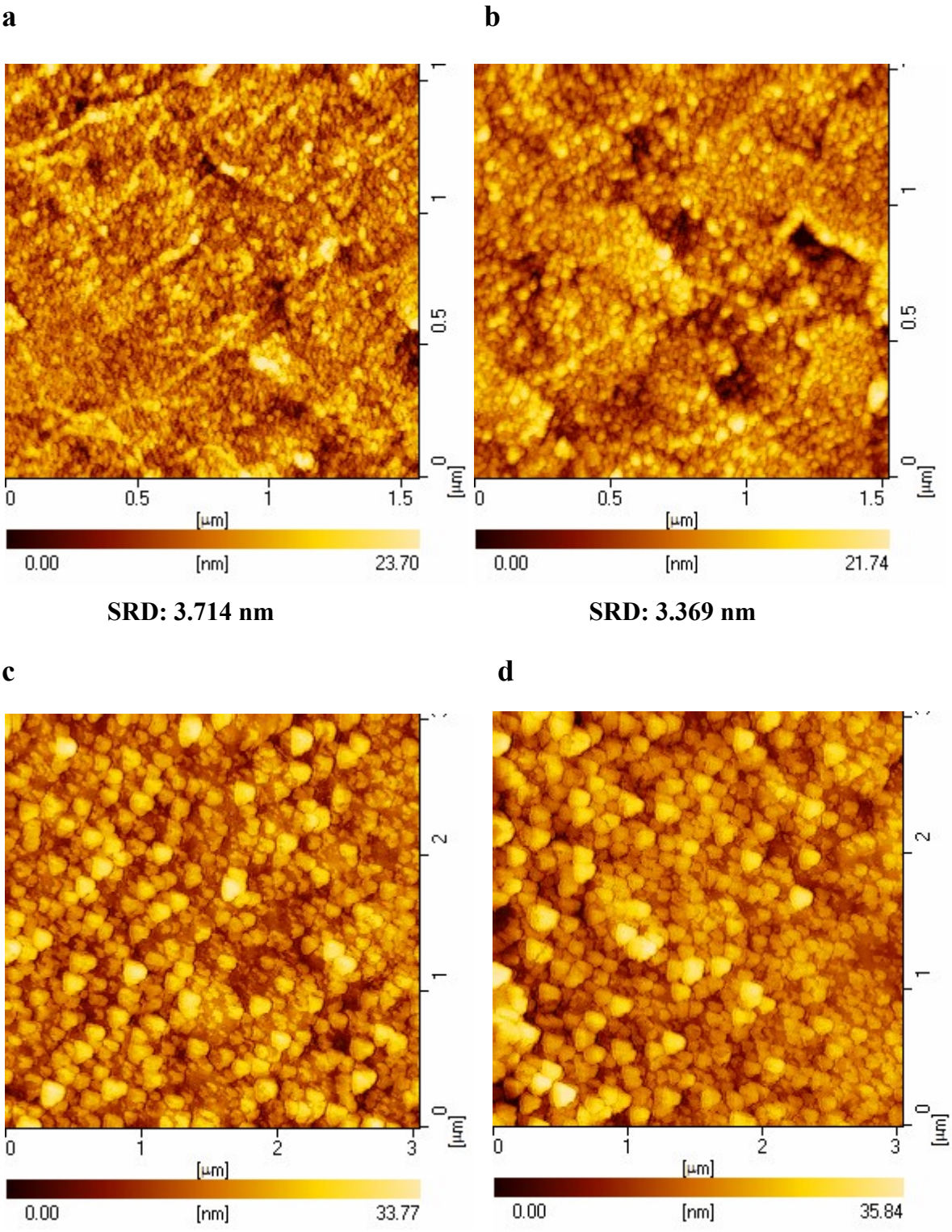

Figure S12. AFM top images of the film $[PDDA/Mn16\text{-}Rb]_2$ (a), $[PDDA/Mn16\text{-}Cs]_2$ (b), $[Mn16\text{-}Rb/Rubpy]_2$ (c) and $[Mn16\text{-}Cs/Rubpy]_2$ (d) on ITO substrates in the scanning range of 1.5 µm (a,b) and 3 µm (c,d).

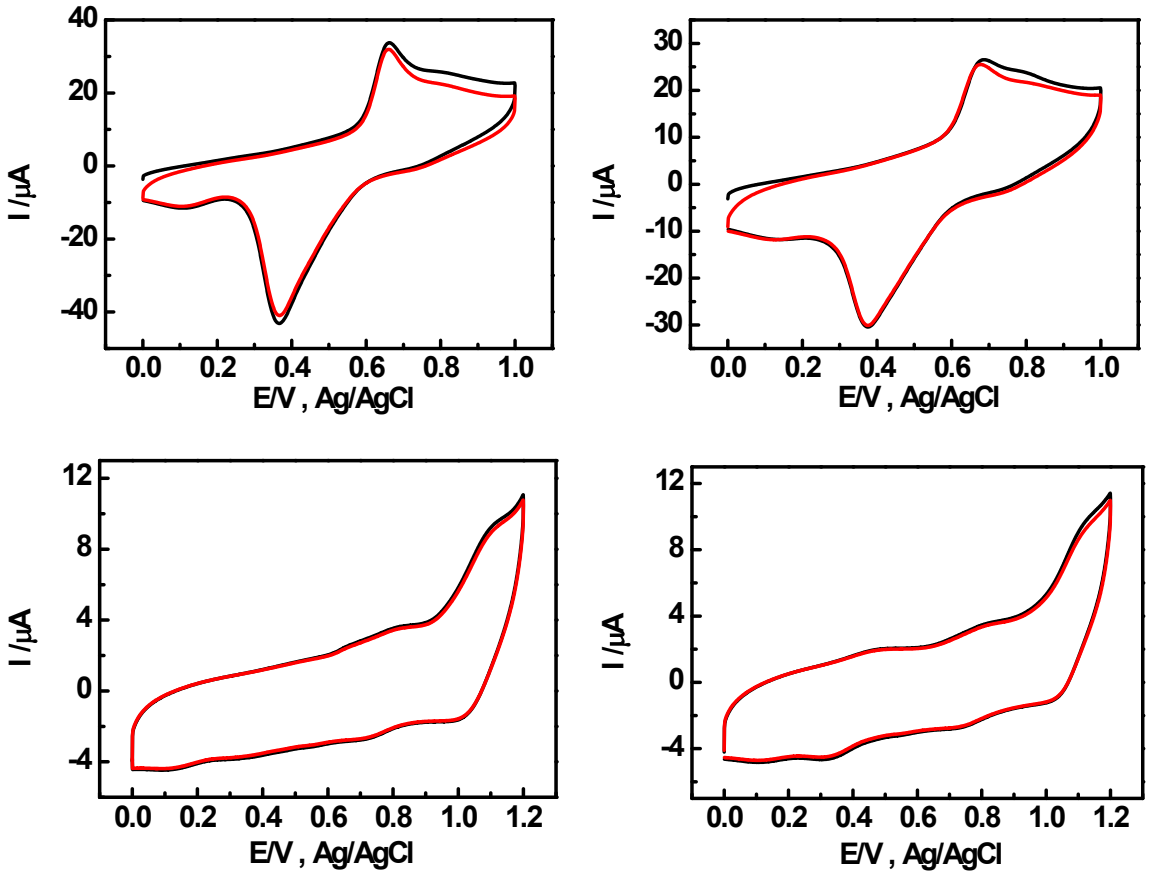

Figure S13. (top) The CVs of the films $(PDDA/Mn16\text{-}Cs)_6$ (left) and $(PDDA/Mn16\text{-}Rb)_6$ (right); (bottom) the CV cycles of the films $(Mn16\text{-}Cs/Rubpy)_3$ (left) and $(Mn16\text{-}Rb/Rubpy)_3$ (right) in their original states and after three days in 0.5M NaAc + HAc solution (pH 7) 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

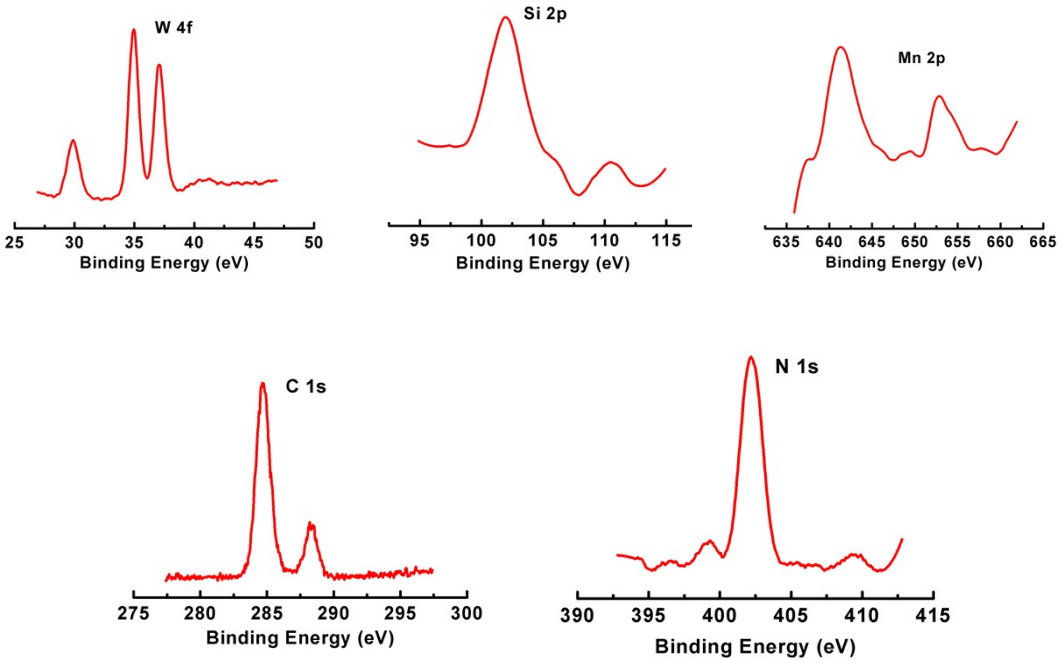

Figure S14. XPS spectra of the films $[PDDA/Mn16\text{-}Cs]_{10}$ after a long water oxidation process.

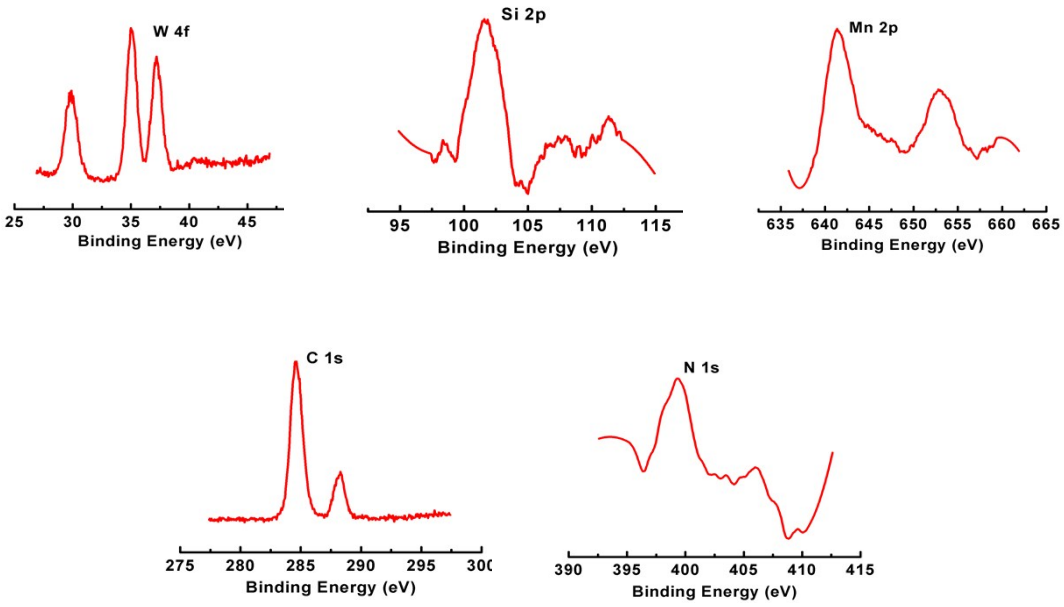

Figure S15. XPS spectra of the films $[PDDA/Mn16\text{-}Rb]_{10}$ after a long water oxidation process.

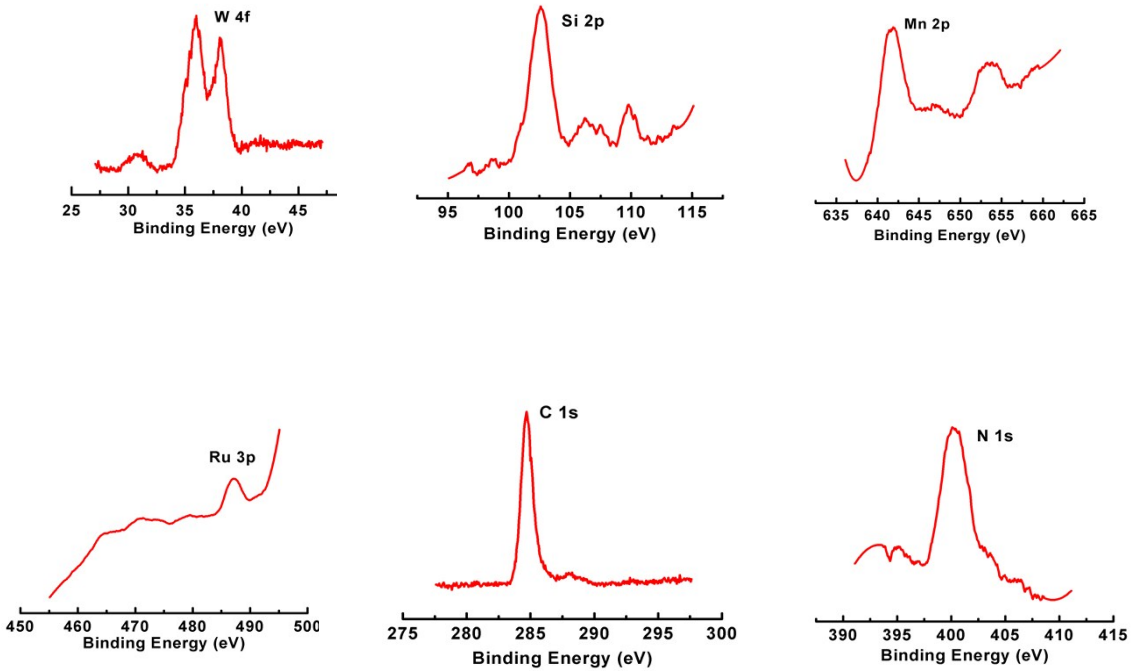

Figure S16. XPS spectra of the films $[Rubpy/Mn16\text{-}Cs]_{10}$ after a long water oxidation process.

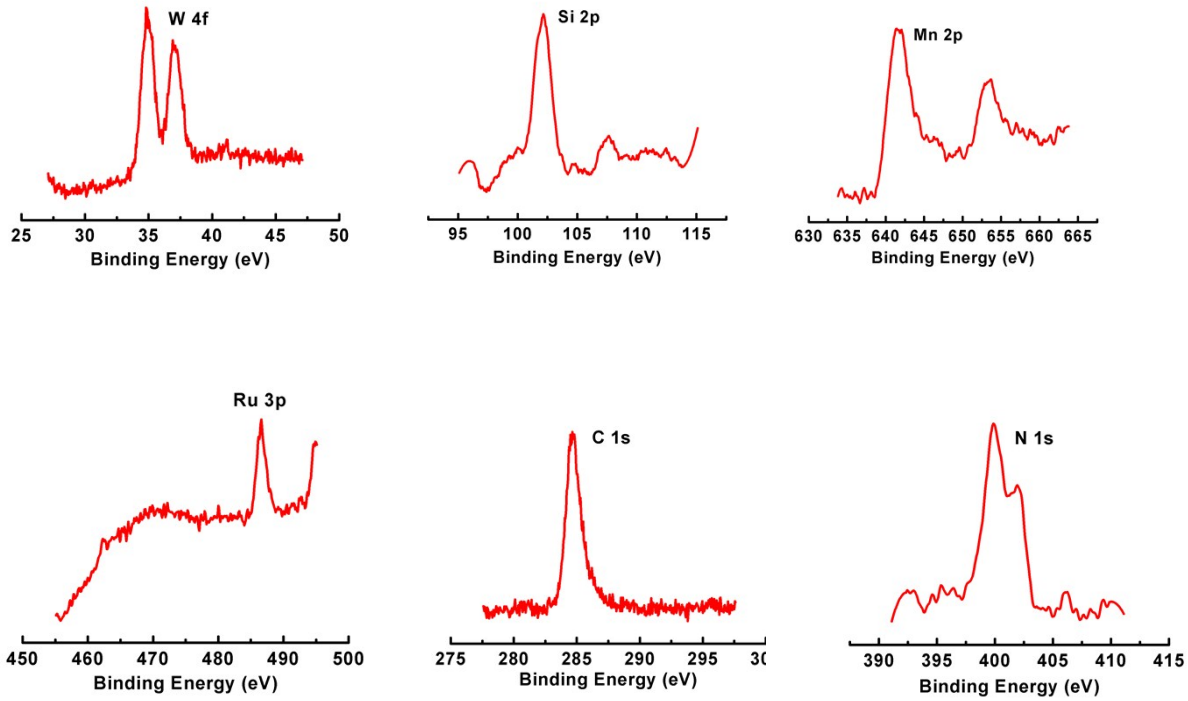

Figure S17. XPS spectra of the films $[Rubpy/Mn16\text{-}Rb]_{10}$ after a long water oxidation process.