Supporting Information

High Turnover Catalysis of Water Oxidation by Mn(II) complexes of Monoanionic Pentadentate Ligands

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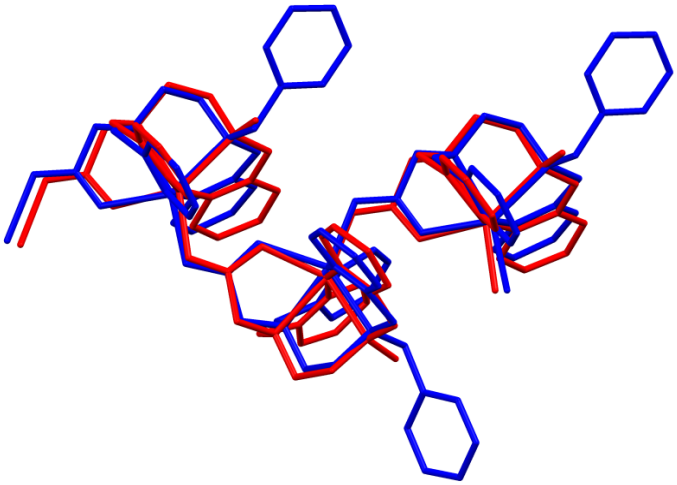

Figure S1. Overlay of the 1D polymeric chains in $[Mn(mebpena)]_n(ClO_4)_n{\cdot}nH_2O$ (red) and $[Mn(bzbpena)]_n(ClO_4)_n{\cdot}nCH_3OH$ (blue) showing the closely comparable geometry.

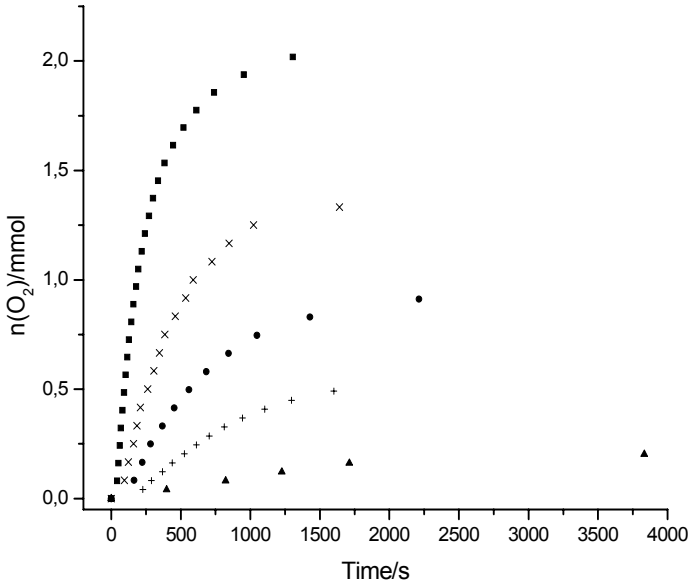

Figure S2. Amount of oxygen evolved as function of time and $[Mn(mcbpen)]_n(ClO_4)_n{\cdot}n(H_2O)$ in the presence of 6.4 mmol of TBHP. ▲, [Mn]= 0.025 µmol; +, [Mn]= 0.050 µmol; •, [Mn]= 0.10 µmol; ×, [Mn]= 0.20 µmol; ▪ , [Mn]= 0.50 µmol; The TON for each experiment is calculated by dividing the amount of oxygen evolved with the amount of catalyst giving TONs of 8000, 10000, 9000, 7000, and 4200 mole of O_2/mol of $[Mn(mcbpen)]_n(ClO_4)_n{\cdot}n(H_2O)_n$ (n=1).

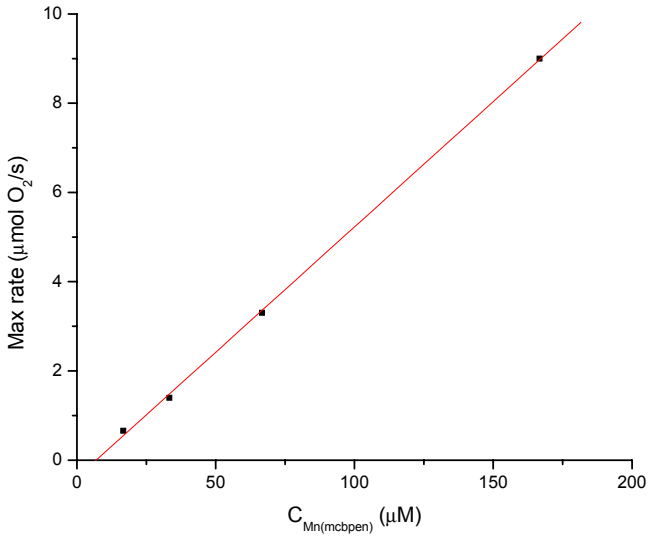

Figure S3 Maximum rate of oxygen evolution as function of the concentration of $[Mn(mcbpen)]_n(ClO_4)_n{\cdot}nH_2O$ in the presence of 2.13 M TBHP(■) and the best linear fit.

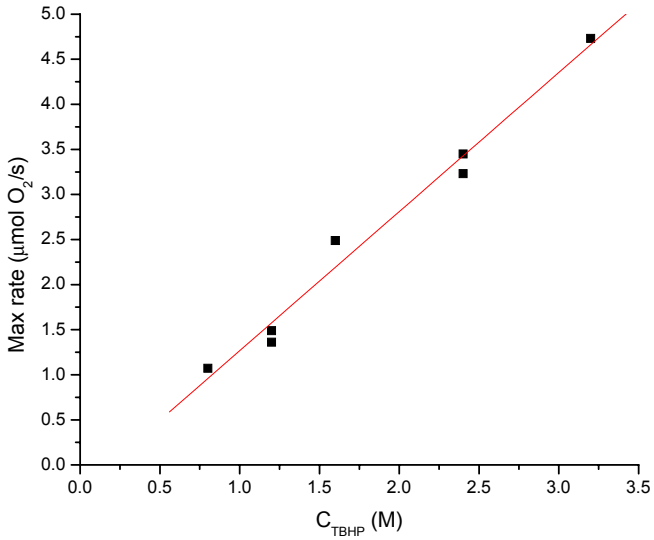

Figure S4 Maximum rate of oxygen evolution as function of the concentration of tbhp in the presence of 40 µM [Mn(mcbpen)] (■) and the best linear fit.

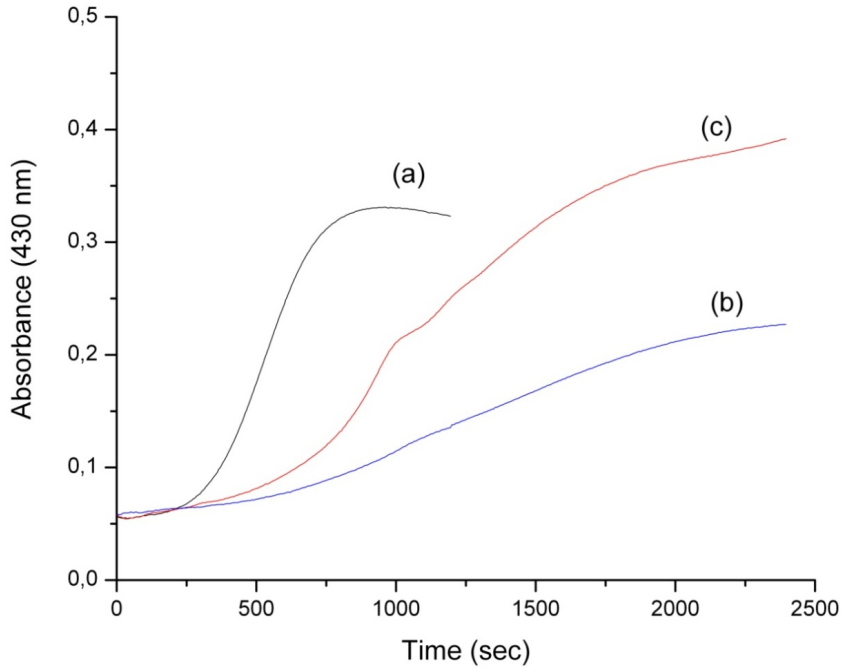

Figure S5. Time course of absorbance changes at 430 nm of the oxidation of $[Mn(mcbpen)]_n(ClO_4)_n \cdot nH_2O$ by TBHP ([Mn] = [TBHP] = 1 mM) in acetate buffer at pH (a) 4.5, (b) 5.5, (c) 6.5.

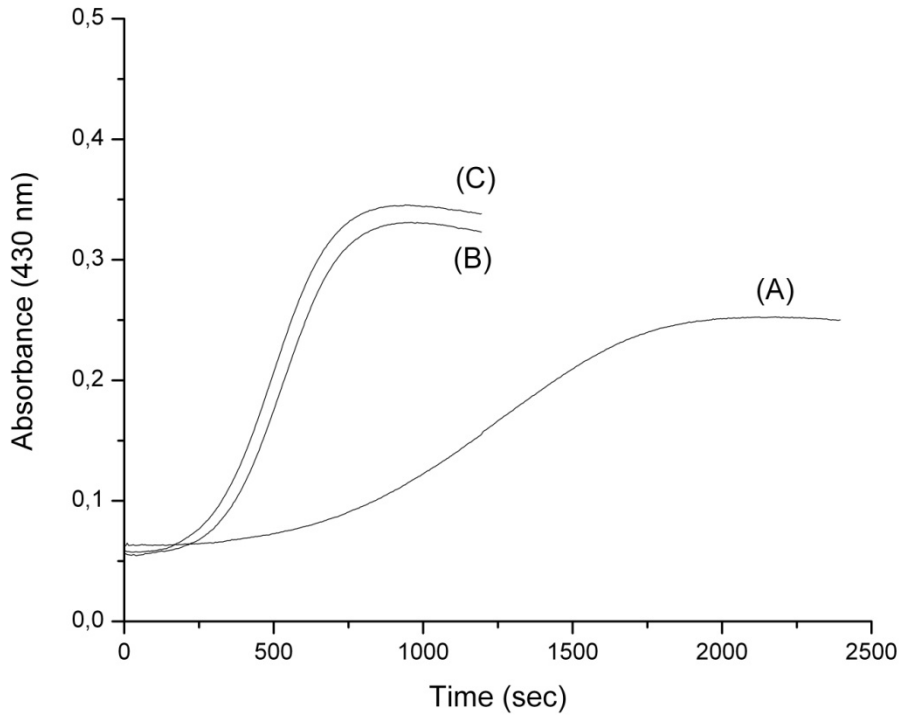

Figure S6. Time course of absorbance changes at 430 nm due to the reaction of $[Mn_n(mcbpen)_n(H_2O)_n]^{n+}$ (1 mM in [Mn]) in acetate buffer (pH 4.5) and (a) 0.5mmM TBHP, (b) 1mM TBHP and (c) 2mM TBHP.

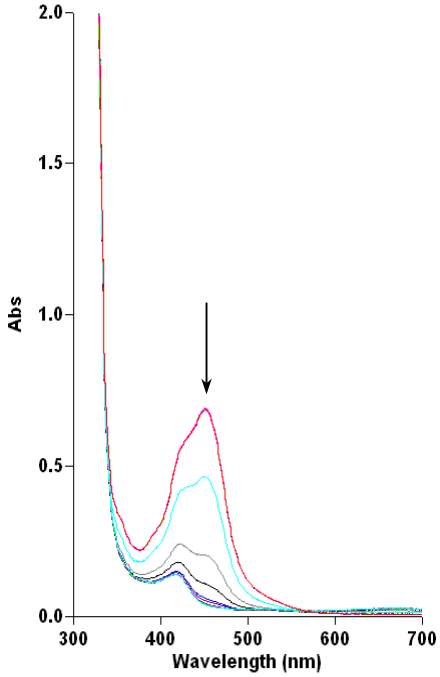

Figure S7: Spectral changes of $[Ru(bipy)_3]^{2+}$ (0.05 mM) and *p*-bromobenzenediazonium (4.0 mM)in a degassed acetonitrile solution. Light (λ > 400 nm) was switched on after 5 minutes. Absorption spectra of the solution taken with 1 minute intervals are shown. The change in the spectra corresponds to oxidation of $[Ru(bipy)_3]^{2+}$ to $[Ru(bipy)_3]^{3+}$.

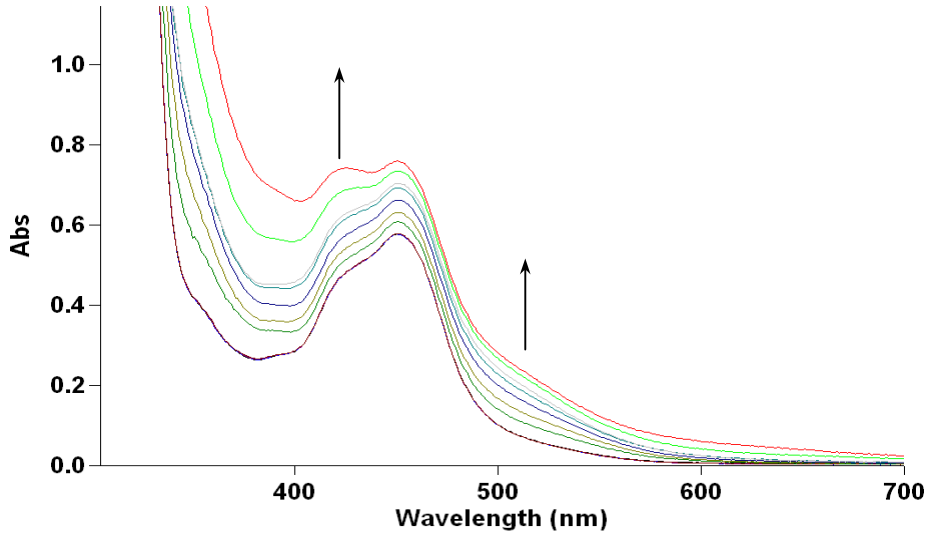

Figure S8: Changes in the absorption of a degassed solution of $[Ru(bipy)_3]^{2+}$ (0.04 mM), *p*-bromobenzenediazonium (4 mM) and $[Mn(mcbpen)]_n(ClO_4)_n{\cdot}nH_2O$ (0.5 mM) in acetonitrile 0 – 10 minutes. The spectra were taken with one minute intervals. The light (λ > 400 nm) was switched on after three minutes. (Spectra at 0, 1, 2, and 3 minutes are superimposed).