Supplementary Information

Detailed Mechanism of the Autoxidation of N-hydroxyurea Catalyzed by a Superoxide Dismutase Mimic Mn(III) Porphyrin: Formation of the Nitrosylated Mn(II) Porphyrin as an Intermediate

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The UV-vis titrations and the data evaluation were carried out according to:
T. Weitner et. al. *Dalton Trans.*, 2010, **39**, 11568-11576

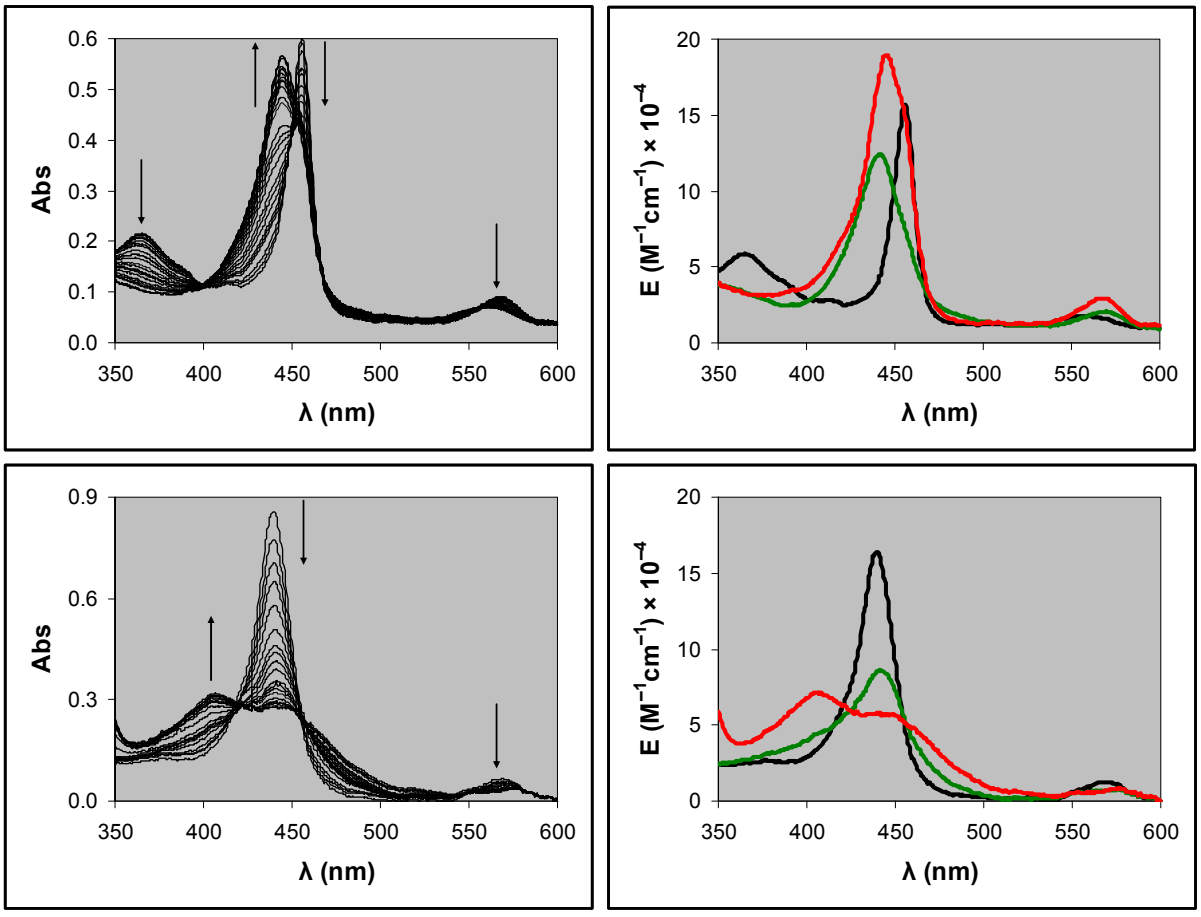

Figure S1 UV-vis titration of Mn(III)TTEG (up) and Mn(II)TTEG (down) from pH 9.3 to pH 12.6. Left: spectral change, the pH increases with the arrows. Right: calculated individual spectrum of the protonated (black), the singly deprotonated (green) and the duobly deprotonated (red) species. c(Mn(III)TTEG) = 3.80 μM or c(Mn(II)TTEG) = 5.23 μM, I = 1.0 M, T = 25.0 °C, unaerobic conditions

The ^{17}O-NMR measurements and the data evaluation were carried out according to:
A. Budimir et. al. *Dalton Trans.*, 2010, **39**, 4405–4410

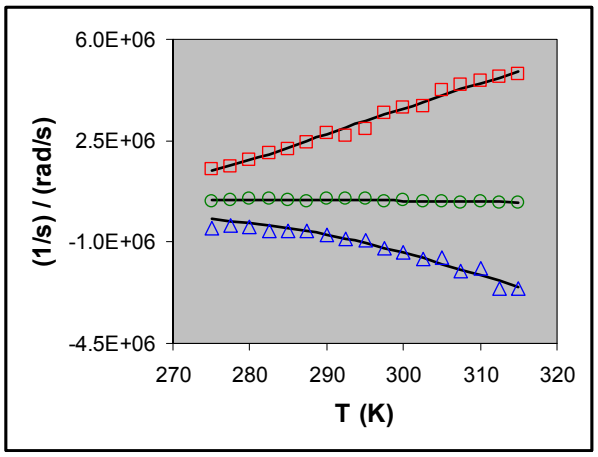

Figure S2 Reduced relaxation rates (circles: $1/T_{1r}$ and squares: $1/T_{2r}$ in s^{-1} units) and chemical shift (triangles: $\Delta\omega_r$ in s^{-1}rad units) of Mn(III)TTEG studied as a function of temperature at pH 6. Lines: result of fit according to the reference above.

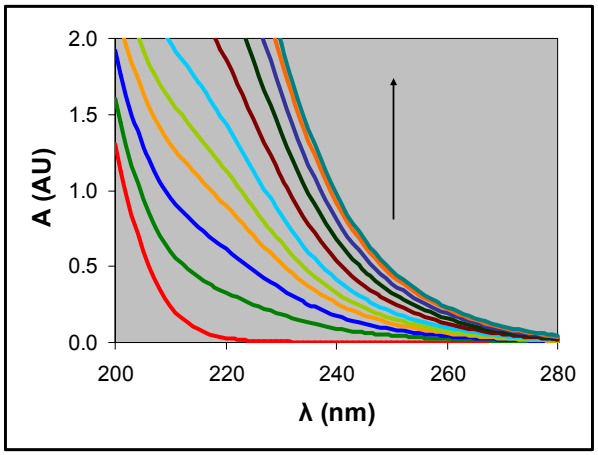

Figure S3 The UV-vis titration of HU from pH 5.8 to pH 11.7, the pH increases with the arrow. c(HU) = 1.00 mM, I = 1.0 M, T = 25.0 °C, unaerobic conditions.

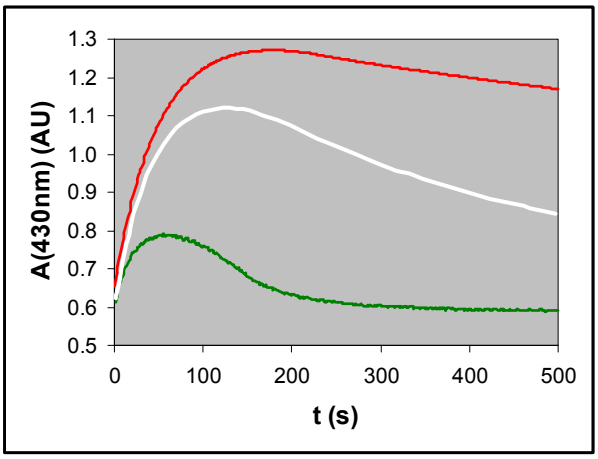

Figure S4 The effect of the conditions of illumination on the reaction of Mn(III)TTEG and HU. The green curve was recorded in a stopped-flow instrument with PMT detection, the white in a diode-array photometer and the red in a scanning photometer, under otherwise identical conditions. c_0(Mn(III)TTEG) = 7.50 μM, c_0(HU) = 15.0 μM, c(NaOH) = 5.0 mM, $c_0(O_2)$ = 254 μM, I = 1.0 M, T = 25.0 °C.

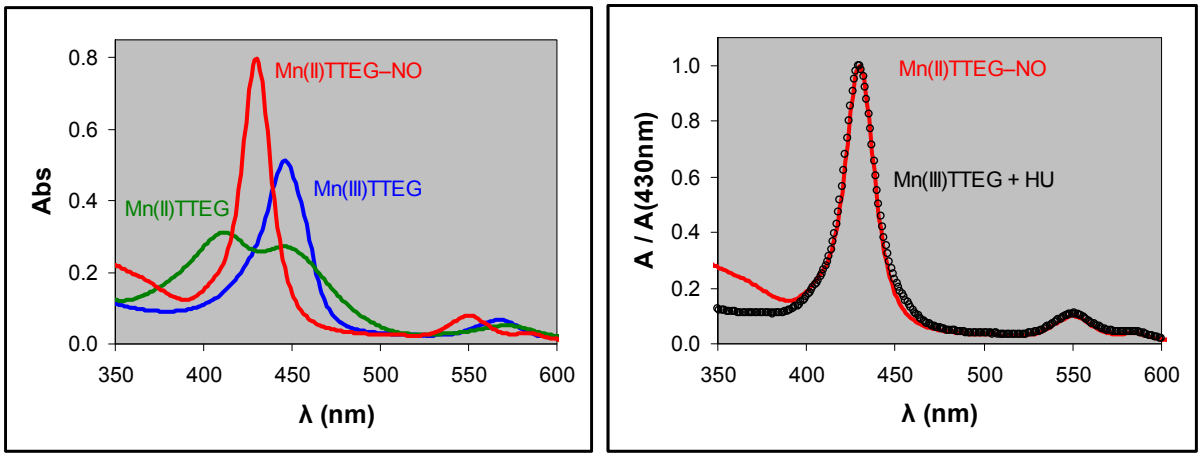

Figure S5 Left: The UV-vis spectra of Mn(III)TTEG, Mn(II)TTEG and Mn(II)TTEG–NO. c(Mn(III)TTEG) = c(Mn(II)TTEG) =c(Mn(II)TTEG–NO) = 3.54 μM, c(NaOH) =5.0 mM, unaerobic conditions. Right: The normalized UV-vis spectra of Mn(II)TTEG–NO and the intermediate of the reaction Mn(III)TTEG + HU recorded 150 s after mixing. c_0(Mn(III)TTEG) = 3.75 μM, c_0(HU) = 150 μM, c(NaOH) = 5.0 mM, $c_0(O_2)$ = 254 μM, I = 1.0 M, T = 25.0 °C.

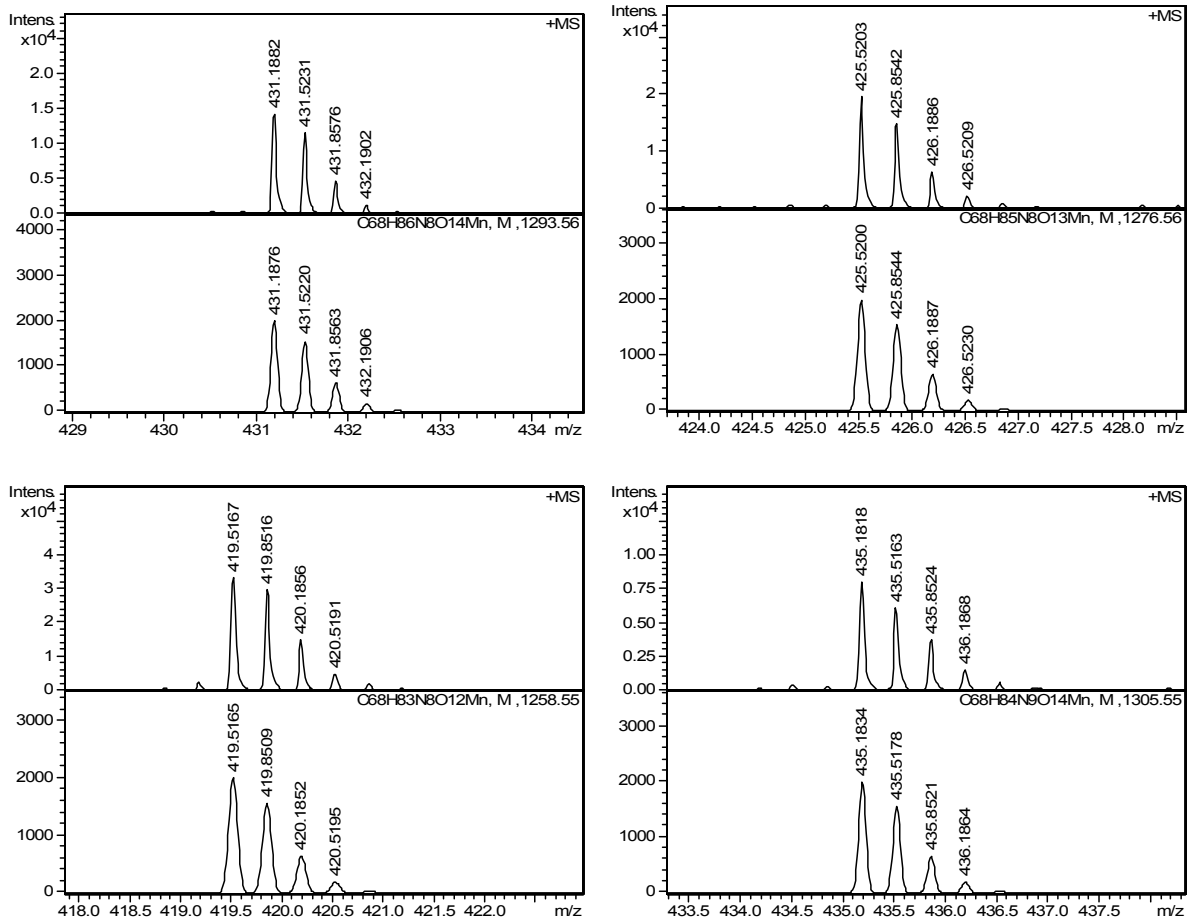

Figure S6 Measured (upper halves) and simulated (lower halves) isotopic distributions of species corresponding to Mn(III)TTEG (m/z 431.1882), Mn(II)TTEG (m/z 425.5203 and m/z 419.5167) and Mn(II)TTEG-NO (m/z 435.1818) as seen in Table 1.

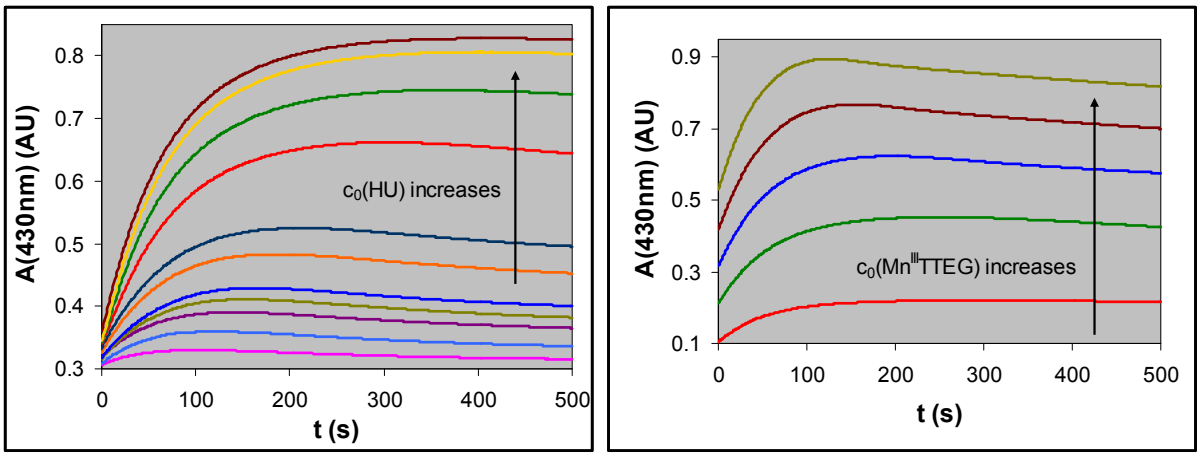

Figure S7 The series of kinetic curves recorded during the concentration dependence measurements. Left: The initial concentration of HU was varied while that of Mn(III)TTEG was constant. c_0(Mn(III)TTEG) = 3.75 μM, c_0(HU) = from 0.763 μM to 114 μM, c(NaOH) = 50mM, $c_0(O_2)$ = 254 μM, I = 1.0 M, T = 25.0 °C. Right: The initial concentration of Mn(III)TTEG was varied while that of HU was constant. c_0(Mn(III)TTEG) = from 1.25 μM to 6.25 μM, c_0(HU) = 6.35 μM, c(NaOH) = 5.0 mM, $c_0(O_2)$ = 254 μM, I = 1.0 M, T = 25.0 °C.

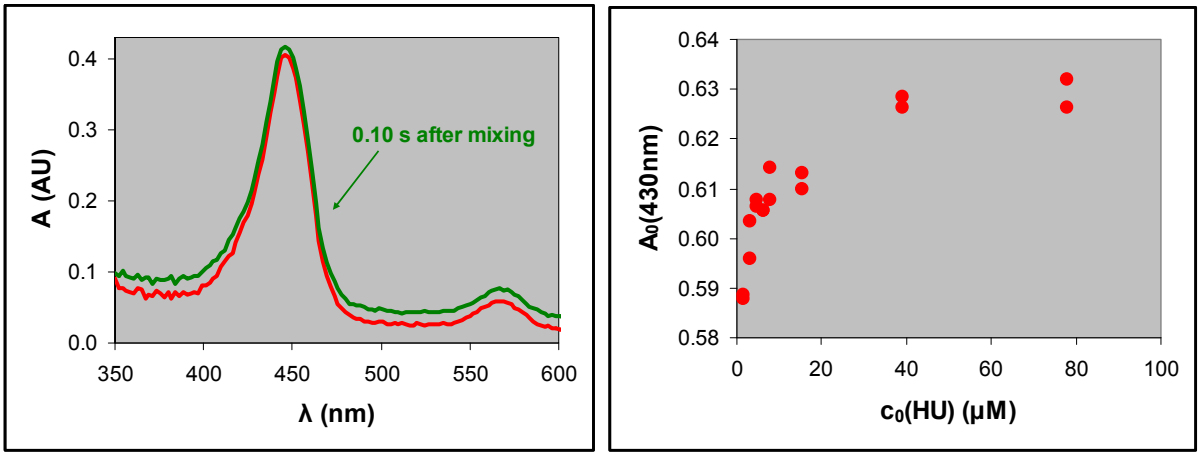

Figure S8 Left: The visible part of the spectrum of the 0.1 s old reaction mixture of Mn(III)TTEG + HU (green) compared to the spectrum of Mn(III)TTEG (red) recorded under identical conditions. c_0(Mn(III)TTEG) = 3.03 μM, c_0(HU) = 61.2 μM, c(NaOH) = 5.0 mM, $c_0(O_2)$ = 254 μM, I = 1.0 M, T = 25.0 °C. Right: Dependence of the absorbance (0.10 s after mixing) at 430 nm on the initial HU concentration with constant initial Mn(III)TTEG concentration. The kinetic curves were recorded by stopped-flow PMT. c_0(Mn(III)TTEG) = 7.52 μM, c_0(HU) = from 1.56 μM to 78.1 μM, c(NaOH) = 50mM, $c_0(O_2)$ = 254 μM, I = 1.0 M, T = 25.0 °C.

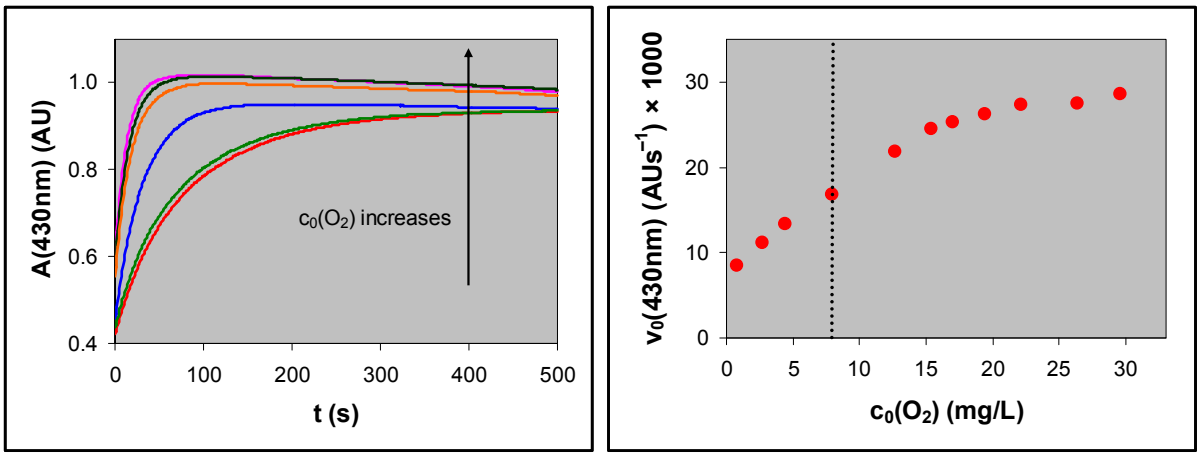

Figure S9 Left: Kinetic curves recorded with different initial concentrations of dissolved O_2. The initial concentrations of Mn(III)TTEG and HU were constant. Right: Dependence of the initial rate of reaction on the initial concentration of O_2. The dotted line indicates the solution saturated with air at atmospheric pressure. c_0(Mn(III)TTEG) = 4.98 μM, c_0(HU) = 101 μM c(NaOH) = 5.0 mM, $c_0(O_2)$ = from 0.81 mg/L to 7.99 mg/L, I = 1.0 M, T = 25.0 °C.