Electronic Supplementary Information for Dalton Transactions

Direct Evidence of Singlet Molecular Oxygen Generation from Peroxynitrate, a Decomposition Product of Peroxynitrite

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Supporting Information

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$$O_2NOOH + 2\,I^- + H^+ \rightarrow H_2O + NO_3^- + I_2 \quad (1)$$

$$H_2O_2 + 2\,I^- + H^+ \rightarrow 2\,H_2O + I_2 \quad (2)$$

$$I_2 + I^- \rightarrow I_3^- \quad (3)$$

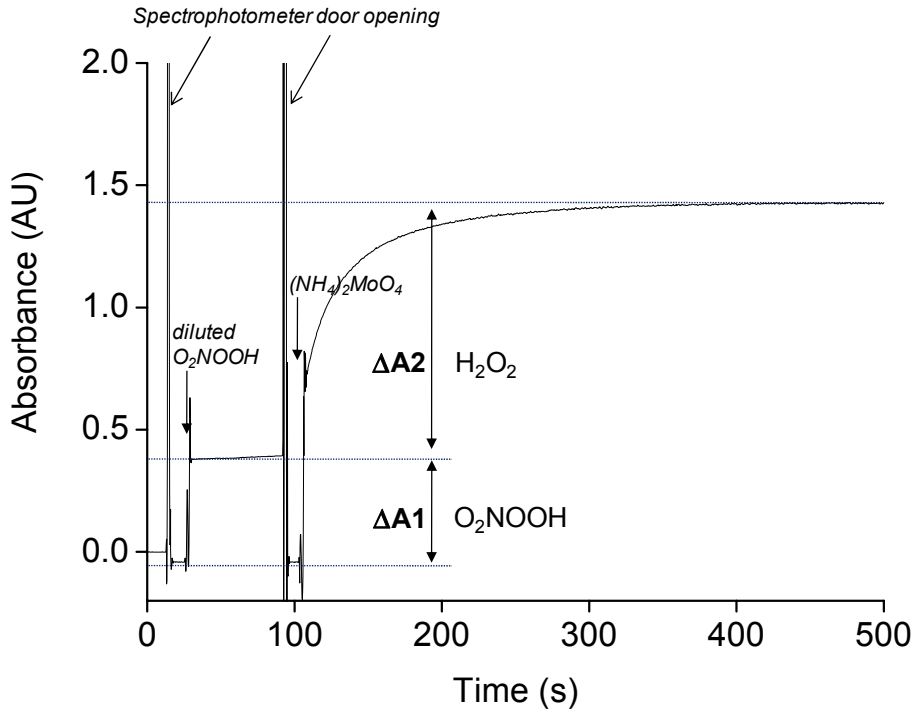

Figure S1. Quantification of O_2NOOH by spectro-iodometry. The quantification is based on the rapid reaction of O_2NOOH with iodide (eq. 1), which has an intense absorption at 352 nm (ε = 26400 $M^{-1}cm^{-1}$). The reaction of H_2O_2 with iodide (eq. 2) undergoes at an appreciable rate only after the addition of ammonium molybdate as a catalyst. For the experiment, 2 ml of 8 mM KI and 20 µl of 2.4 M HNO3 were pipetted into a cuvette. After recording the baseline, 20 µl of the diluted (1000 times) O_2NOOH solution in 2.4 M HNO_3 was added and the absorbance was measured for about 1 min. To determine the H_2O_2 concentration, 20 µl of 2% ammonium molybdate solution was added and the absorbance was recorded until a plateau was reached. I_3^- has a strong absorption at 352 nm and its concentration was determined by using its absorption coefficient of 26400 M^{-1} cm^{-1}.

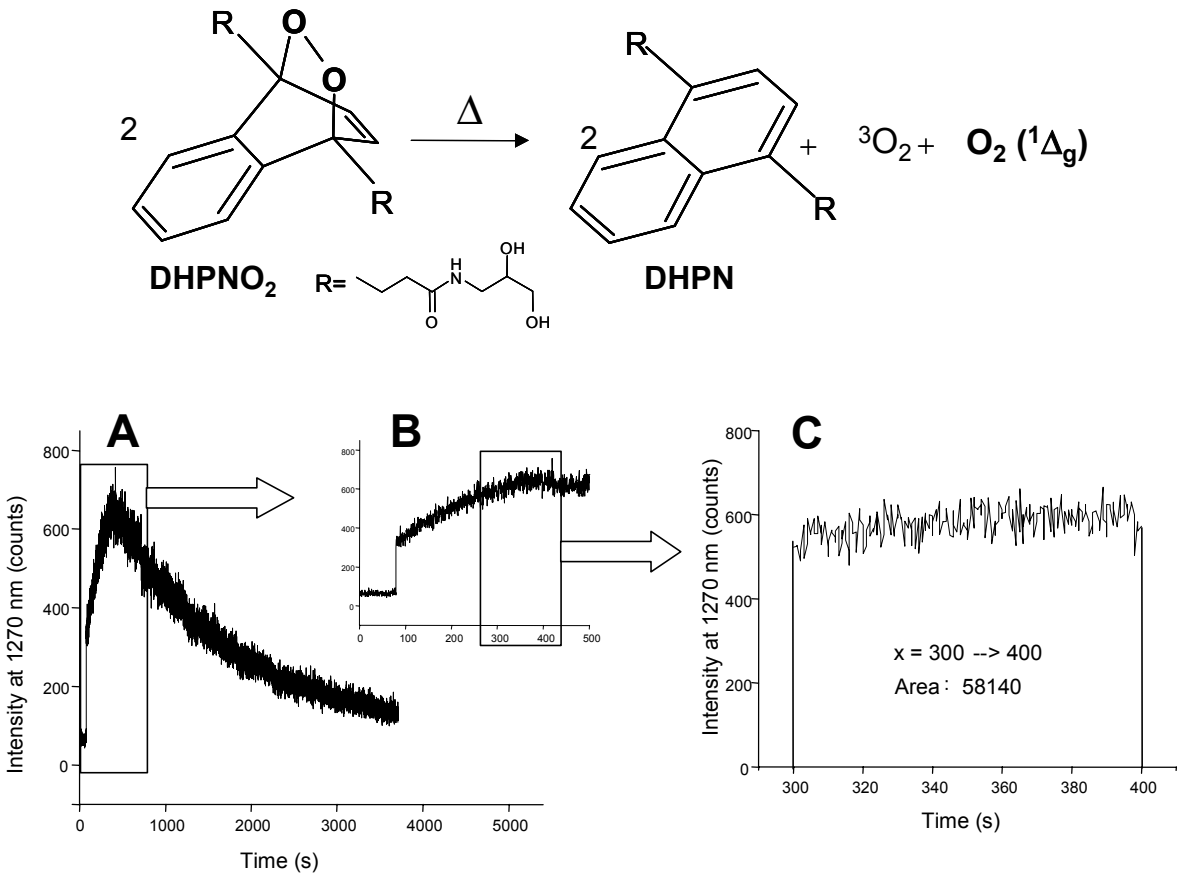

Figure S2. Kinetics of the decay of monomolecular light emission at 1270 nm due to O_2 ($^1\Delta_g$) generated during decomposition of 10 mM $DHPNO_2$ incubated in 0.1 M phosphate buffer pD 7.8: A) decay curve of data collected for 3810 s (63.5 min), B) expanded view of the Intensity – time curve in the first 500 s, which show the region selected for integration, and C), the area integrated from 300 – 400 s. Thermolysis of $DHPNO_2$ follows first-order kinetics [30]: based on the half-life of decomposition of $DHPNO_2$ at 37°C ($t_{½}$ = ln 2/k = 23 min), the calculated value for the first-order rate constant k is 5.02×10^{-4} s^{-1}. Taking into account that thermolysis of $DHPNO_2$ yields 59% O_2 ($^1\Delta_g$) [30], the estimated rate of O_2 ($^1\Delta_g$) production from 10 mM $DHPNO_2$ at 37°C is 2.96 μM.s^{-1}. The area obtained by integrating the light emission intensity over a

period of 100 s yielded a value of 58140 (arbitrary units), which corresponds to 296 μM of O_2 ($^1\Delta_g$). This value was used to convert integrated area to [O_2 ($^1\Delta_g$)].

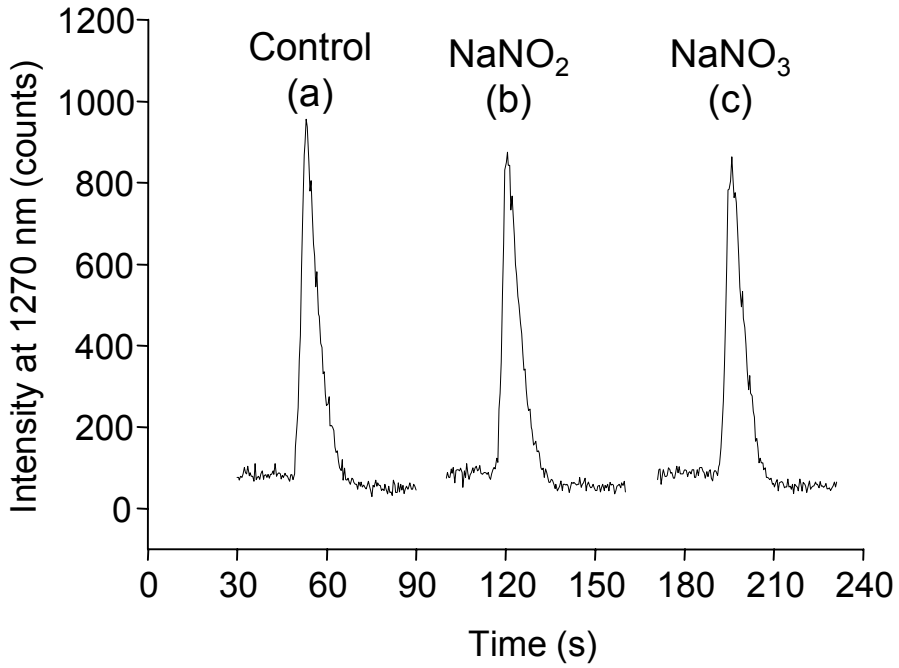

Figure S3. Time course for the emission of light from of O_2 ($^1\Delta_g$) generated during injection of 0.9 M phosphate buffer at pD 7.6 into 1.5 ml of 1 mM $ONOO^-$ in the absence of a) and in the presence of 10 mM b) $NaNO_2$ or c)$NaNO_3$.

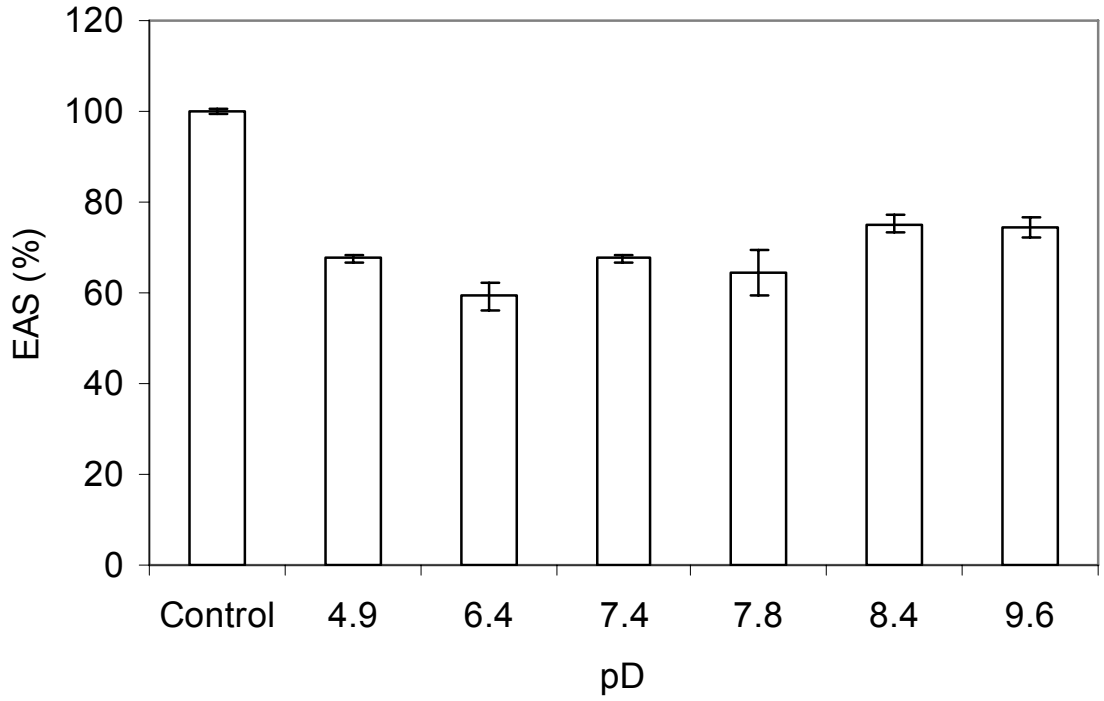

Figure S4. Influence of pD on the amount of EAS consumed during incubation with $ONOO^-$. Reaction conditions are the same as those described in Figure S3.